THE EFFECT OF BLENDING ON SELECTED PHYSICAL PROPERTIES OF CRUDE OILS AND THEIR PRODUCTS

by

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Doctor of Philosophy

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SUMMARY

A study was made of the effect of blending practice upon selected physical properties of crude oils, and of various base oils and petroleum products, using a range of binary mixtures. The crudes comprised light, medium and heavy Kuwait crude oils. The properties included kinematic viscosity, pour point, boiling point and Reid vapour pressure. The literature related to the prediction of these properties, and the changes reported to occur on blending, was critically reviewed as a preliminary to the study.

The kinematic viscosity of petroleum oils in general exhibited non-ideal behaviour upon blending. A mechanism was proposed for this behaviour which took into account the effect of asphaltenes content. A correlation was developed, as a modification of Grunberg's equation, to predict the viscosities of binary mixtures of petroleum oils. A correlation was also developed to predict the viscosities of ternary mixtures. This correlation showed better agreement with experimental data (<6% deviation for crude oils and ~2.0% for base oils) than currently-used methods, i.e. ASTM and Refutas methods.

An investigation was made of the effect of temperature on the viscosities of crude oils and petroleum products at atmospheric pressure. The effect of pressure on the viscosity of crude oil was also studied. A correlation was developed to predict the viscosity at high pressures (up to 8000 psi), which gave significantly better agreement with the experimental data than the current method due to Kouzel (≤ 5.2% and 6.0% deviation for the binary and ternary mixtures respectively). Eyring's theory of viscous flow was critically investigated, and a modification was proposed which extends its application to petroleum oils.

The effect of blending on the pour points of selected petroleum oils was studied together with the effect of wax formation and asphaltenes content. Depression of the pour point was always obtained with crude oil binary mixtures. A mechanism was proposed to explain the pour point behaviour of the different binary mixtures.

The effects of blending on the boiling point ranges and Reid vapour pressures of binary mixtures of petroleum oils were investigated. The boiling point range exhibited ideal behaviour but the R.V.P. showed negative deviations from it in all cases. Molecular weights of these mixtures were ideal, but the densities and molar volumes were not.

The stability of the various crude oil binary mixtures, in terms of viscosity, was studied over a temperature range of 1°C - 30°C for up to 12 weeks. Good stability was found in most cases.

KEY WORDS: Petroleum oil mixtures, Crude oil blends, Viscosity, Pour point.

To:

MY PARENTS
MY WIFE
AND MY CHILDREN

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

"Crude oil", "crude petroleum oil" or, simply, "crude", are the generic terms used in the petroleum industry to describe the vast number of, qualitatively different, petroleum deposits which have been discovered all over the world since Drake first struck "rock oil" in Pennsylvania in 1859 (1).

Crude oils are complex mixtures of thousands of chemical compounds which differ widely from each other (2, 3). Although crude oils have been known for about 130 years and many analysts have expended considerable effort to unravel the complexities of crude oil composition, the extent of current knowledge regarding the individual compounds rarely extends much beyond the gasoline/naphtha range (i.e. up to a boiling point of about 150°C). However, more emphasis is now being placed on the complex higher ranges, in an attempt to identify as many as possible of the chemical constituents. The objective is to predict the behaviour of these particular cuts of crude oil when subjected to conditions,such as changing temperature and pressure or mixing with other hydrocarbons, which may change some of the original physical or chemical properties. For example, attempts have been made to identify the major chemical constituents of some heavy oils and residues (4, 5, 6).

Crude oil is a naturally occurring, mobile liquid which has a specific gravity (~ density) in the range 0.700 - 1.00. A different gravity scale - the API (American Petroleum Institute) gravity - has been widely used, in addition to specific gravity. The relationship between them is given in the following equation (3):

$$\mathrm{API} = \left[\frac{141.5}{\mathrm{S.G.}}\right] - 131.5 \qquad 1.1$$

where:

API - API gravity, degrees

S.G. - Specific gravity (60°F/60°F)

It is very rare to find two crudes from different geological formations of identical composition, even if they are from the same field. However, the elementary composition of most crude oils falls within the following ranges (4):

Element	Weight %
carbon	83.0 - 87.0
hydrogen	10.0 - 14.0
sulphur	0.05 - 6.0
nitrogen	0.05 - 2.0
oxygen	0.05 - 1.5

Crude oils, generally, also contain trace amounts of other elements such as vanadium, nickel, and may be contaminated with chlorine, arsenic, lead, etc. These are, normally, only present in parts per million (ppm) or even parts per billion (ppb).

As this analysis indicates, crude oils consist mainly of complex hydrocarbon mixtures. Generally, they contain three types of hydrocarbon compounds : paraffins, naphthenes and aromatics. Whilst olefins and diolefins probably do not occur naturally in crude oil, they are formed during refinery processing.

Although the elementary composition of crude oils does not appear to vary widely, these differences, in conjunction with the differences in the distribution of the various types of hydrocarbon compounds, have a considerable effect upon the physical and chemical characteristics of crude oil. Hence each crude oil possesses a unique quality.

The traditional products which the petroleum industry provides by refining crude oils are, themselves complex mixtures. Their uses range from power generation (gasoline, aviation turbine kerosene (A.T.K.), diesel fuels), heating (gas oil, fuel oil), speciality purposes (lubricating oils, road asphalts) or to use as basestocks for chemicals (e.g. naphthas for ethylene manufacture).

Initially, crude oil is produced in association with natural gas (NGL) which consists, mainly, methane, ethane, propane and butane in different proportions. The crude oil is stabilised by separating the gases in stabilisers, usually located on-shore in the

Gathering Centres (G.C.), where the crude oils from different wells are collected by means of pipelines and stored in tanks. In North Sea, the stabilisers are located on the platforms. The crude oils are, then, desalted and dewatered as necessary.

Most producers require to blend two or more types of oil to produce crude oils which meet the required quality, termed specifications, for either exporting or refining purposes.

Recently, many refineries have been revamped and modernised with new technology being introduced, to produce more products to better specifications such as high Octane Number (unleaded) gasoline, low sulphur motor gasoline and low sulphur fuel oil. The tight specifications of the finished products are strongly affected by the properties of the feedstock crude oils. Therefore, the feedstocks properties need to be carefully controlled. This may be done by mixing low quality crude oil, usually heavy crude oil, with crude oil of higher quality, usually light crude oil, in proportions that maximise overall profitability. The objective is to use a mixed crude oil feedstock of the lowest cost, but best quality, which gives the least problems when subjected to the different refining processes. In most cases, these three conditions cannot be met simultaneously. The study of the effect of mixing on the properties of crude oils and petroleum products, as well as the effect of the changes imparted by one property on the others due to mixing, has therefore attracted more attention. It is common practice for two or more crudes or petroleum products to be mixed together in order to upgrade a certain property (e.g. density or API gravity) ; other important properties (e.g. viscosity, pour point, freezing point) may however be adversely affected. This may lead to off-specification mixtures, and/or create problems during processing. Clearly therefore a more scientific basis would be desirable for the blending of crude oils or petroleum mixtures.

1.2 ESTIMATION OF PROPERTIES:

Due to the complex nature of crude oils and petroleum products, they are sometimes termed "undefined mixtures", ie mixtures of unknown composition. Hence, the petroleum industry has learned to live with empirical, and semi-empirical, measurements and correlations for the estimation of the essential physical properties. However, there is a real need to be able to predict the properties of mixtures from a knowledge of the properties of components.

The majority of the better estimation methods involve equations based on the form of a theory, with empirical correlations of the constants. The introduction of empiricisms into minor parts of a theoretical relation is a powerful method of developing an excellent correlation(7). However, it is necessary to know what information is required, in addition to the corresponding property of the components and their concentrations, in order to make valid estimates of the property of the mixture. For example, the behaviour of the components upon mixing, with respect to the property under study is essential additional information. However, in most cases, so little theory is available that empirical methods must be used to evaluate these additional factors. Therefore, the proper type of equation must be selected for accurate estimation of any specific property.

Most crude oils are exported as blends and not as individual crudes. Hence, the reasonable prediction of the properties of crude oils blends, made from different types of crudes to meet the specifications of the international market demand, is a crucial consideration. Its importance is clear in terms of the "Net Back Value" in pricing the crude oil (discussed later in Chapter 2), which takes into consideration the amounts and prices of the different petroleum products that can be produced from a barrel of crude oil.

1.3 AIMS AND OBJECTIVES

The present study was concerned with the changes which occur in selected properties of crude oils and their products when subjected to mixing. It set out to examine the behaviour of mixtures under different conditions, e.g. temperature and pressure. The aim was to improve the understanding of the mechanisms of their behaviour, and to propose methods to estimate some important properties for industrial use. The intention was to extensively examine the following properties of binary mixtures of crude oils and their products : molecular weight, density, kinematic viscosity, pour point, T.B.P. and Reid vapour pressure. As the study progressed, the following objectives were defined:

a) To study the effect of mixing on selected physical properties of crude oils and their products, namely, molecular weight, density, kinematic viscosity, pour point, T.B.P. and Reid vapour pressure.

b) To study the mechanisms of the behaviour of these properties upon mixing.

c) To determine the effect of various operating conditions, i.e. temperature and pressure, on these properties.

d) To propose/develop new methods, or test available methods, for the prediction and estimation of some of the physical properties.

e) To study the stability of crude oil mixtures, to assist in the assessment of the validity of the estimation method developed.

The experimental investigation which enabled these objectives to be met is described in Chapter 8. The significance of the results obtained are discussed in Chapter 9, and future recommendations for other predictive methods and further continuation of the study of other properties are given in Chapter 10.

It is hoped that the insight gained into the behaviour of the selected physical properties of the petroleum oils upon mixing and the correlation methods proposed, will assist in a better scientific understanding of the mechanism of the changes that may occur in mixtures. This should help oil producers and refiners in a better utilisation of the existing oil resources, i.e. crude oils and petroleum products, and related processing units.

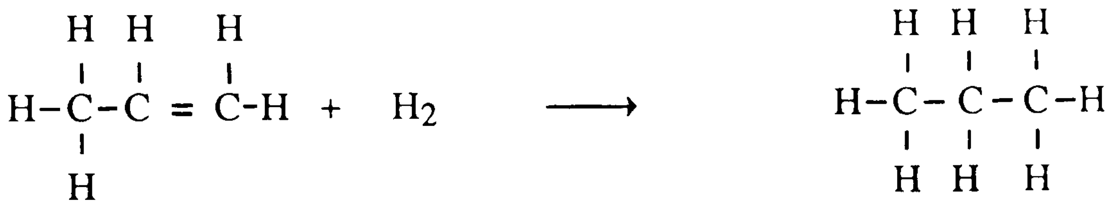
CHAPTER 2

CHARACTERISATION AND BLENDING OF CRUDE OILS

2.1 CHARACTERISATION OF CRUDE OIL

2.1.1 Chemistry

Since more than 95% of crude oil is generally composed of carbon and hydrogen, it is chemically termed "hydrocarbons". These two elements can be combined together to give an almost unlimited number of compounds. Each carbon atom has four valency bonds $(-\underset{|}{\overset{|}{C}}-)$ with which it can be attached to either another carbon atom, or hydrogen atoms each with one valency bond. If all four bonds of each carbon atom are linked to separate atoms (i.e. all bonds are single, C-C), the compound is saturated and relatively unreactive. Alternatively, if two or more bonds are linked to two carbon atoms (except in special cases of aromatics), the compound is unsaturated and more reactive, i.e. one or more of the multiple bonds can be broken, and the free ends then joined to other separate atoms to form a saturated compound, for example:



$$H-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-\overset{\displaystyle H}{\overset{|}{C}}=\overset{\displaystyle H}{\overset{|}{C}}-H + H_2 \longrightarrow H-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-H$$

C_3H_6, propylene

unsaturated

C_3H_8, propane

saturated

In general, crude oils consist of three main hydrocarbon groups : paraffins, naphthenes and aromatics.

Paraffins :

Paraffins are saturated compounds of a very long series of hydrocarbons starting at the light end with the petroleum gases : methane, ethane, propane, butane and pentane.

Compounds in the paraffin group with the general formula C_nH_{2n+2}, can be further subdivided into normal (straight chain, or linear) and iso - (branched, or with side chains) compounds. As the number of carbon atoms in the molecule increases, the number of different theoretically possible "structural isomers" increases very rapidly, e.g.:

carbon atoms	number of isomers
C_5	3
C_6	5
C_8	18
C_{12}	355
C_{15}	4347

Typical normal and iso-paraffins in crude oil are shown in Figure 2.1.

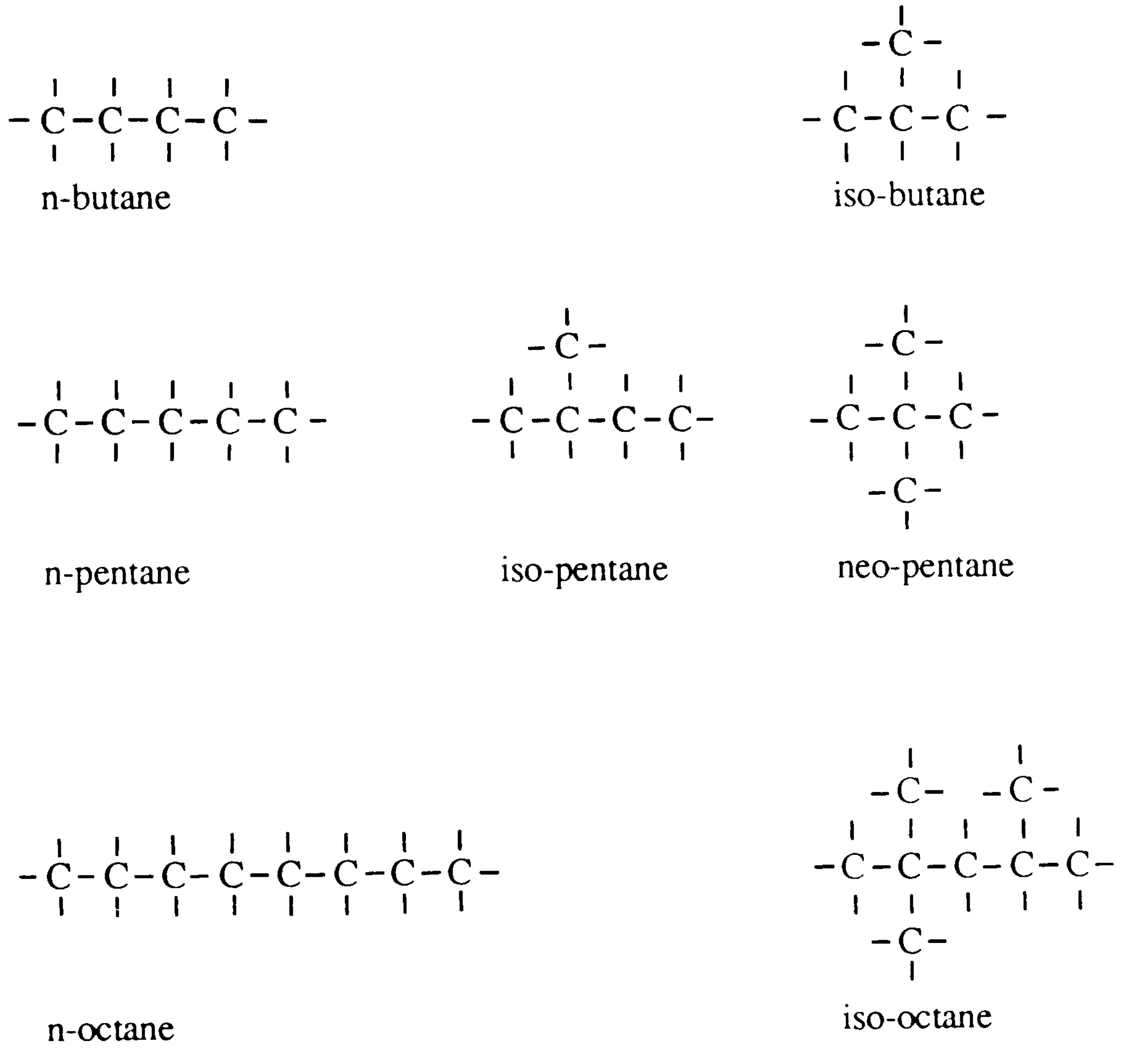


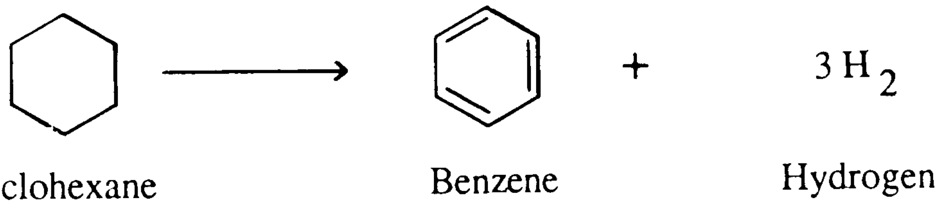
Figure 2.1 Paraffins in Crude Oil

The important differences between these two classes of paraffins, when crude oils are processed in a refinery, are that the straight chain normal paraffins are undesirable in the gasoline range since they have much lower Octane Numbers than the highly-branched paraffins. In the higher boiling ranges, e.g. with kerosene and diesel fuels, normal paraffins improve the burning qualities, smoke point and cetane number, but they have much higher melting points and hence their presence adversely affects the cloud point and pour point of heavier oils. However, the normal paraffins can be selectively isolated to a high degree of purity using molecular sieves; in this form they are valuable for detergents manufacture. Stocks rich in normal paraffins are also preferred for the bacteriological production of protein, i.e. single cell protein.

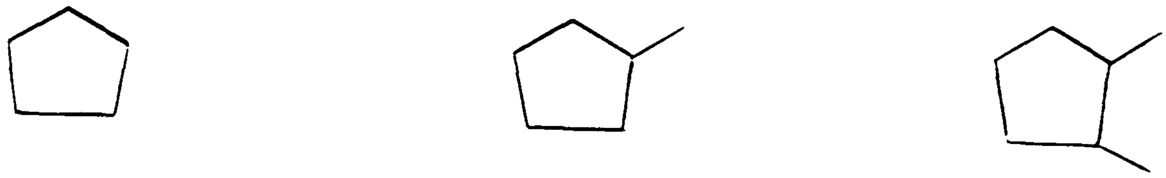
<u>Naphthenes:</u>

This group contains cycloparaffins in which all the available bonds of the carbon atoms are saturated with hydrogen. Many types of naphthenes are present in crude oil but, except for the lower molecular-weight compounds such as cyclopentane and cyclohexane, these are not usually separated as individual compounds.

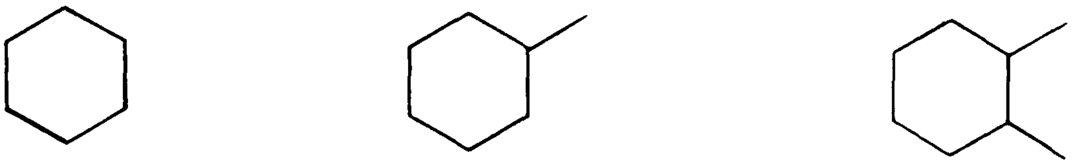
The important difference between these two classes of naphthenes is that the cyclohexanes can be readily dehydrogenated using a platinum or other metallic catalyst to yield aromatics, thereby resulting in a remarkable improvement in gasoline Octane Number:



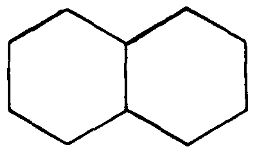
Straight, branched paraffinic side chains or other fused naphthene rings may be introduced to the cyclopentanes and cyclohexanes ; this introduces a considerable complexity into the molecules. Some typical naphthenic compounds are shown in Figure 2.2.



Cyclopentane Methylcyclopentane Dimethylcyclopentane



Cyclohexane Methylcyclohexane 1,2 Dimethylcyclohexane



Decalin

(Decalydronaphthalene)

Figure 2.2: Naphthenes in Crude Oil

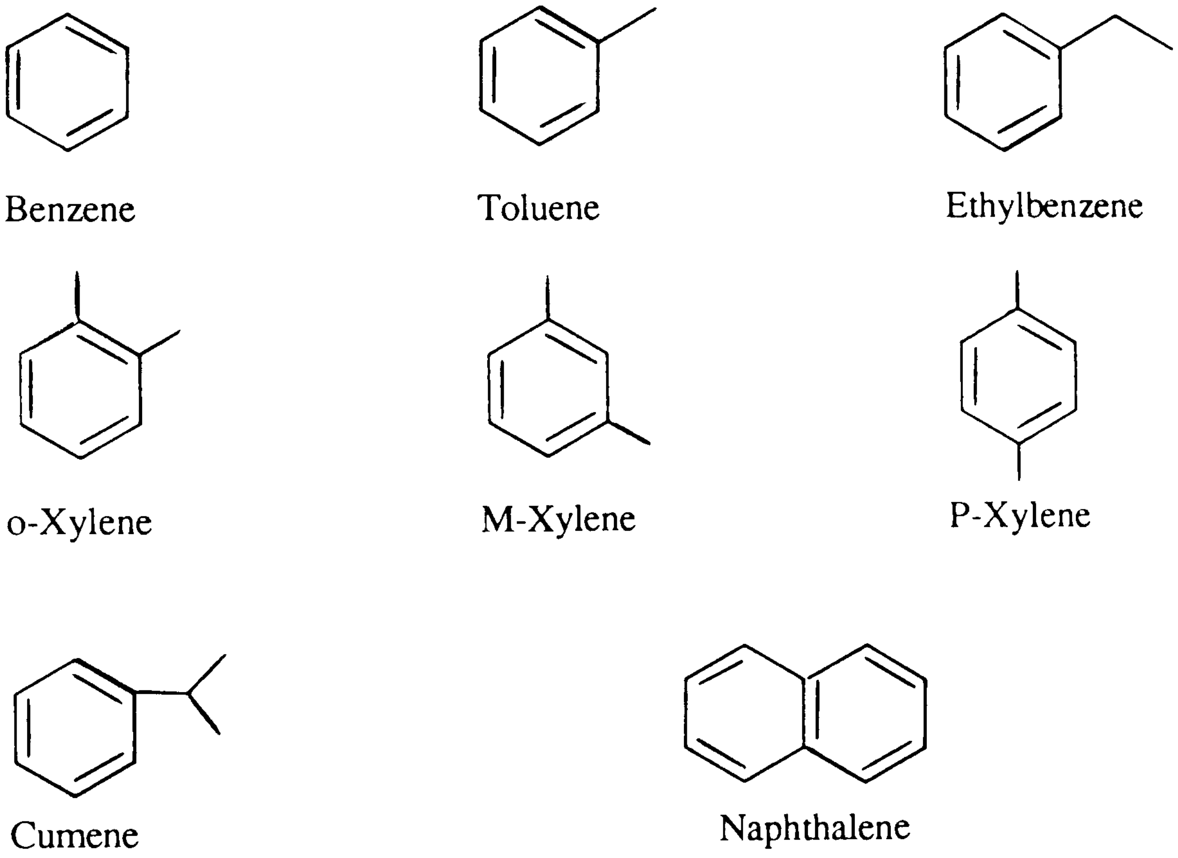
Aromatics:

The aromatics group of hydrocarbons is chemically and physically very different from the paraffins and naphthenes. Aromatic hydrocarbons contain a benzene ring which is unsaturated but very stable. Again a large number of isomers become possible as the number of carbon atoms in the side chains attached to the benzene ring is increased. Some typical aromatic compounds are shown in Figure 2.3.

Aromatics are desirable in the gasoline range (to improve Octane Number) but adversely affect the burning properties of kerosenes and gas oils. They are relatively easy to remove by solvent extraction (1). Benzene, toluene and xylenes have many applications in the chemical industry (1).

Olefins :

Olefins do not occur naturally in crude oils but are formed during processing. They are unsaturated hydrocarbons in which at least two of the carbon atoms are joined by double bonds.



Benzene Toluene Ethylbenzene

o-Xylene M-Xylene P-Xylene

Cumene Naphthalene

Figure 2.3: Aromatic Hydrocarbons in Crude Oil

$CH_2 = CH_2$

Ethylene

$CH_2 - CH = CH_2$

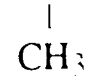
Propylene

$CH_2 = CH - CH_2 - CH_3$

Butene - 1

$CH_3 - CH = CH - CH_3$

Butene - 2



$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2$

Iso-Butylene

Figure 2.4: Olefinic Hydrocarbons in Crude Oil

The general formula is $C_n H_{2n}$. Generally, olefins are undesirable in finished, refined products due to the reactivity of the carbon-carbon double bonds. This results in instability of the products which may easily become oxidized and polymerized. However, olefinic gases such as ethylene, propylene and butenes are of commercial importance as raw materials for the polymer and petrochemicals industries. Typical olefins are shown in Figure 2.4.

Much of the higher boiling point portions of crude oils, i.e. > 250°C, consists of mixed molecules of high molecular weights of fused naphthene and aromatic rings with aliphatic side chains.

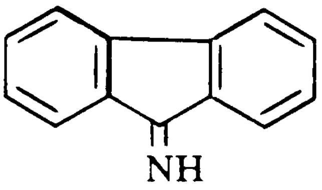
Other compounds :

Crude oils also contain non-hydrocarbon compounds generally comprising sulphur, nitrogen and oxygen combined with carbon and hydrogen.

Sulphur compounds form the largest group of non-hydrocarbon compounds, and are very important to refiners. Typical sulphur compounds likely to be present in crude oils are shown in Figure 2.5. Sulphur in crude oils is generally undesirable for a number of reasons namely corrosivity, odor, air pollution, poor burning or explosive characteristics, and the potential for catalyst poisoning.

Crude oils vary considerably in their sulphur content, ranging from some extremely low sulphur content crudes with <0.1% weight of sulphur up to high sulphur contents of 5 - 7% weight. The majority of the sulphur compounds are concentrated in the higher boiling range products during the distillation of crude oil. Sulphur removal during processing of crude oils is usually achieved by high pressure destructive hydrogenation, in which the sulphur atom is hydrogenated to H_2S gas and subsequently removed.

Nitrogen compounds are, also, present in some crude oils. The nitrogen is believed to be present in complex ring structures such as

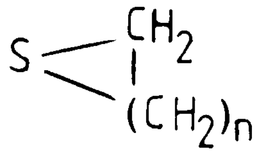
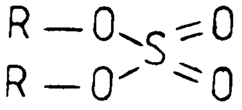
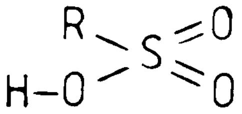
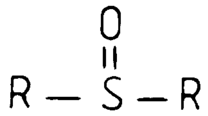
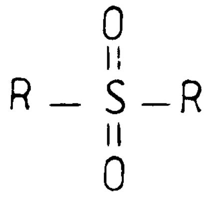
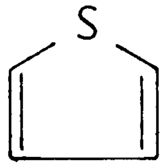
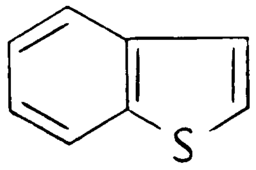


and depending upon their boiling points, they appear in the various distillates. They have an adverse effect on the catalyst performance of some of the refinery units such as hydrocrackers; therefore, some pretreatment for nitrogen removal is usually necessary.

Much less is known about oxygen compounds in crude oils, because it is difficult to determine the oxygen content of a crude oil directly. Some crude oils, particularly heavy naphthenic crudes, contain small amounts of organic acids (carboxylic acids), termed naphthenic acids. Some crudes also contain traces of phenols and cresols.

Traces of many other elements such as vanadium, nickel, lead, calcium, aluminium and silicon, can be found in most crude oils.

Vanadium and nickel are present in parts per million in most crude oils, usually as oil soluble organo-metallic compounds termed porphyrins. These have a chemical structure similar to that of the green chlorophyl in plants. There is increasing interest in V/Ni ratio as one of the criteria for crude oil finger printing (8).

Hydrogen sulphide	$H-S-H$
Mercaptans	$H-S-R$
Sulphides	$R-S-R$
Disulphides	$R-S-S-R$
Cyclic sulphides	
Alkyl sulphates	
Sulphonic acids	
Sulphoxides	 $R-\overset{O}{\overset{\|}{S}}-R$
Sulphones	 $R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-R$
Thiophene	
Benzothiophene	

* R refers to any aliphatic or aromatic group.

Figure 2.5 : Structural Formulae of Sulphur Compounds

2.1.2 Classification of Crude Oils :

Due to the vast number of crude oils produced all over the world, it was necessary to establish a reliable method for classification. The methods proposed initially did not provide a precise classification. Nevertheless, some of them are still widely used.

U.S.B.M. classification

Crude oils have been classified as paraffins, intermediate or mixed, and naphthene based according to a system developed by the United States Bureau of Mines (3, 9). Some crudes have also been classified as either asphalt-base or aromatic-base crudes, but these terms are not common. The U.S. Bureau of Mines System categorises crude oils by the API gravity of two key fractions obtained by a standardized Hempel distillation : No. 1 from 250 to 275°C at atmospheric pressure and No.2 from 275 to 300°C at 40 mm Hg pressure. These classifications are defined as follows:

Classification	API Gravity of Fraction	
	No. 1	No. 2
Paraffin	≥ 40	≥ 30
Paraffin, intermediate	≥ 40	20 - 30
Intermediate, paraffin	33 - 40	≥ 30
Intermediate	33 - 40	20 - 30
Intermediate, naphthene	33 - 40	≤ 20
Naphthene, intermediate	≤ 33	20 - 30
Naphthene	≤ 33	≤ 20

The first word of the name base applies to the gasoline or low boiling fractions and the second applies to the lubricant or high - boiling fractions of the crude.

Characterisation factors :

The two most widely used characterisation factors are the UOP or Watson Characterisation Factor (K) and the U.S. Bureau of Mines Correlation Index (CI).

Watson and Nelson (2, 3) introduced the characterisation factor as an index of the chemical character of pure hydrocarbons and petroleum oils. The Watson characterisation factor, K, is defined as,

$$K = \frac{(T_b)^{1/3}}{S} \qquad 2.1$$

where,

K = Watson characterisation factor

T_b = mean average boiling point, °R

S = specific gravity @ 60°F

This factor provides a useful parameter for correlating physical and thermal properties, since it can be applied to the entire range of a crude. It has been generally accepted by the petroleum refining industry.

Although the values of Watson characterisation factor for crude oils cover a narrow range (10.5 - 12.9), they can be classified as follows:

Classification	K - factor
Paraffin base	12.15 - 12.9
Intermediate base	11.5 - 12.1
Naphthene base	10.5 - 11.45

The U.S. Bureau of Mines Correlation Index (CI) is defined as (3):

$$CI = (87552/T_b) + 473.7S - 456.8 \qquad 2.2$$

where,

CI = correlation index

T_b = mean average boiling point, °F

S = specific gravity @ 60°F

The CI scale is based upon straight chain paraffins having a CI value of 0 and benzene having a CI value of 100. Generally, the lower the CI value, the greater the concentrations of paraffinic hydrocarbons in the oil, and the higher the CI value the greater the concentrations of naphthenes and aromatics (3).

Other criteria :

Other criteria have been used for approximate classifications of crude oils, e.g. API gravity, sulphur content and wax content.

API gravity has a strong historical association with the crude oil values, since it is frequently used to indicate the general quality of a crude oil and whether it is light (high API gravity) or heavy (low API gravity).

Generally, crude oils range from the ultra-heavy naphthenic crudes of 10 - 15° API, such as Boscan and Bachaquero from Venezuela, some of the heavy Californian crudes or Kuwaiti heavy crude, up to very light crudes of 42 - 47° API such as Qatar (Middle East), Hassi Messaoud (Algeria), Kimmeridge (UK), Cumarebo (Venezuela) (1). Lighter materials of 50 - 51° API are sometimes marketed, but these are really condensates and not true crude oils. Although the range from 10° to 47° API is wide, the bulk of crude oil produced probably lies within narrower ranges (1), namely intermediate of 20 - 30° API such as Khafji and South UmmGudair (Kuwait), and light of 30 - 40° API such as the majority of the Middle East crudes, and North Sea crude.

As mentioned previously, sulphur content has been used to classify crude oils generally as follows:

a) High sulphur crudes, > 3% wt, typified by Middle East crudes and some USA crudes.

b) Moderate sulphur crudes, 1.7 - 3% wt, typified by Venezuelan crudes.

c) Low sulphur crudes, 0.3 - 1.7% wt, typified by North African, Nigerian and most USA crudes.

Wax content has also been used as a measure to classify crude oils, generally, as follows:

Wax free	< 0.5% wt
Very low	0.5 - 3% wt
Low	3 - 5% wt
Moderate	5 - 10% wt
High	10 - 20% wt
Very high	20 - 35% wt

It is clear that there is no precise method for the classification of crude oils, and most of those in use are based upon general terms. However, these classifications are very useful, especially for marketing purposes. More than one method is often used to identify a certain group of crudes as illustrated in Table 2.1 (1).

Table 2.1: Classes of Crude Oils (1)

Classification	High					Intermediate			Low		
Hydrocarbon type	Paraffinic		Mixed base	Naphthenic		Intermediate			Naphthenic		
Source	Brazil	Libya	United Kingdom	Nigeria	Assam	Iraq	Venezuela	Iran	Australia	Nigeria	Canada
Gravity °API	39	35	38	35	31	34	31	31	36	20	15
Wax content % wt	28	15	14	11	22	7	8	6.5	0.7	1	1.5

2.1.3. Properties and International Marketing Specifications of Crude Oils

The crude oil international market is huge and accommodates different types of sellers and buyers with differing interests and motives. Therefore, it was essential to have a method by which the quality of the crude oils could be reliably assessed, and their prices can be estimated, accordingly. The physical and chemical properties were naturally the proper basis for such a method. Consequently, standard internationally-accepted, testing methods for measuring the physical and chemical properties of the crude oils and their products were established by international organisations such as the American Society for Testing and Materials (ASTM), Institute of Petroleum (IP) and others, in conjunction with the oil companies. These provide a means for the proper measurement and control of oil properties. These standard methods are, frequently, subjected to revision to cater for the changing specifications of crude oils and petroleum products in the international market resulting from the vast, sophisticated growth of petroleum technology in crude oil production, transportation and refining. For example, the International Air Transport Association (IATA) introduces new specifications for Aviation Turbine Kerosene (ATK) from time to time, and oil refiners therefore change the properties of this product in order to meet the IATA specifications.

Changes in the lubricating oil specifications usually introduced to market to meet new demands of vehicle or heavy machinery manufacturers, is another example. The refiners, consequently, may change the properties of the base oil stocks in order to meet these specifications.

There are many ways in which refiners can overcome the problem of changing the properties of the down-stream products. One of the most important and economical ways of doing so, is to alter the properties of the crude feedstock itself, usually by blending with other crudes with different properties. Therefore, most of the newly - built, or revamped, refineries have been designed so that they can accommodate a wide range of crude oil.

A list of the most important analyses of crude oils and petroleum products together with their definitions and significance, are give in Appendix A.

To assess the potential sales value of a new feedstock crude oil, or to plan for its most effective utilisation, it is essential to perform precise, detailed analyses on carefully - selected representative crude oil samples. This is termed a "Crude Oil Assay" and provides the refiners with a preliminary assessment of the main characteristics of the crude oil. Considerable additional information would, of course, be necessary to assess the suitability of the crude for manufacture of speciality products such as lubricating oils, road asphalt, solvents, normal paraffins or chemicals. However, the type of "standard assay" shown in Table 2.2 provides adequate information from which to assess the yields and qualities of their main products (gasoline, middle distillates and fuel oils). It also allows prediction of the behaviour of intermediate feedstocks in such processes as treatment of light gasolines, catalytic reforming of naphtha, hydrofining of diesel oil and catalytic cracking of heavy vacuum distillates.

For a precise analysis, it is necessary to fractionate the crude oil into fractions by distillation using a column equivalent to approximately 14 - 18 theoretical plates. In this way, a precise and repeatable boiling curve (total yield of distillate plotted against head temperature) can be obtained. This is termed a "true boiling point", "TBP", curve.

The fractions are then subjected to the required analyses which, when combined with the analyses of the crude oil, gives a full detailed assay.

Table 2.2: Typical Crude Oil Assay of Kuwait Export Crude (1)

	TOTAL ORIGINAL CRUDE OIL	ATMOSPHERIC DISTILLATION										VACUUM DISTILLATION		
		Distillates							Residues			Distillate		Residue
		GAS C_1-C_4	GASOLINES (debutanised)		NAPHTHA (Ref. feed)	KEROSINE	DIESEL OILS		FUEL OILS			WAX DISTILLATE		BITUMEN (feedstock)
												Orig.	Dewaxed	
TBP range °C	—	to 15	15–95	15–149	95–175	149–232	232–343	343–371	>343	>371		371–525		>525
TBP range °F	—	to 60	60–203	60–300	203–347	300–450	450–650	650–700	>650	>700		700–977		>977
Yield on crude % wt	100	1·77	6·05	13·55	11·6	12·25	17·0	4·15	55·45	51·3		21·0	18·7	30·3
Yield on crude % vol	100	2·52	7·85	16·65	13·4	13·55	17·5	4·1	49·8	45·75		19·85	17·5	25·9
Specific gravity 60 °F/60 °F	0·869	—	0·663	0·703	0·749	0·785	0·843	0·885	0·967	0·975		0·917	0·929	1·016
Total sulphur % wt	2·5	—	0·020	0·025	0·049	0·15	1·27	2·41	4·02	4·16		2·86	—	5·06
Mercaptan sulphur % wt	—	—	0·015	0·018	0·018	0·006	—	—	—	—		—	—	—
H_2S (dissolved) % wt	nil	—	nil	nil	nil	nil	—	—	—	—		—	—	—
Paraffins % wt	—	—	87·5	77	67·5	62	—	—	—	—		—	—	—
Naphthenes % wt	—	—	11	16	18·5	20	—	—	—	—		—	—	—
Aromatics % wt	—	—	1·5	7	14	18	—	—	—	—		—	—	—
Octane number (Research) clear	—	—	63·5	50	35	—	—	—	—	—		—	—	—
Octane number + 2 5 ml TEL/UK gal	—	—	79	67	54	—	—	—	—	—		—	—	—
Smoke point mm	—	—	—	—	—	28	—	—	—	—		—	—	—
Freezing point °C	—	—	—	—	—	−54·5	—	—	—	—		—	—	—
Aniline point °F	—	—	—	—	—	60	70	74	—	—		—	—	—
Diesel index	—	—	—	—	—	68	58	47	—	—		—	—	—

Table 2.2 Continued

		TOTAL ORIGINAL CRUDE OIL	ATMOSPHERIC DISTILLATION									VACUUM DISTILLATION		
			Distillates							Residues		Distillate		Residue
			GAS C_1-C_4	GASOLINES (debutanised)		NAPHTHA (Ref. feed)	KEROSINE	DIESEL OILS		FUEL OILS		WAX DISTILLATE		BITUMEN (feedstock)
												Orig.	Dewaxed	
Cloud point	°F	—	—	—	—	—	—	10	52	—	—	—	—	—
Pour point	°F	−25	—	—	—	—	—	5	50	60	70	80	0	—
Wax content (BP)	% wt	5·5	—	—	—	—	trace	*ca*5	12·8	9·1	8·7	10·8	—	7·6
Viscosity at 70 °F	cs	17·0	—	—	—	—	—	—	—	—	—	—	—	—
100 °F	cs	9·6	—	—	—	—	1·15	3·53	9·85	1,150	2,185	47	59·2	233,000
122 °F	cs	—	—	—	—	—	1·00	2·79	6·8	480	850	27	—	51,000
140 °F	cs	—	—	—	—	—	—	—	—	260	436	18·4	—	17,700
210 °F	cs	—	—	—	—	—	—	—	—	44·6	64·4	6·12	6·7	837
Viscosity index		—	—	—	—	—	—	—	—	—	—	—	62	—
Acidity	mg KOH/g	0·15	—	—	—	—	0·02	0·07	0·14	0·17	0·17	0·23	—	0·16
Total nitrogen	ppm	1,200	—	—	—	—	—	40	290	—	—	790	—	—
Total ash	% wt	0·006	—	—	—	—	—	—	—	0·011	0·012	—	—	0·02
Vanadium	ppm	27	—	—	—	—	—	—	—	49	53	1	—	88
Nickel	ppm	7	—	—	—	—	—	—	—	13	14	1	—	22
Carbon residue (Con)	% wt	5·2	—	—	—	—	—	—	—	9·3	10·1	—	—	17·4
Asphaltenes	% wt	1·4	—	—	—	—	—	—	—	2·5	2·7	—	—	5·0
Molecular weight	(av)	—	54	82	96	118	150	222	289	550	595	383	—	965
Water	% vol	trace	—	—	—	—	—	—	—	—	—	—	—	—
Salt	lb/1,000 bbl	4	—	—	—	—	—	—	—	—	—	—	—	—
Reid vapour pressure	lb	av8	—	8·8	4·9	0·6	—	—	—	—	—	—	—	—
Gas C_1-C_3	% wt	0·45	25	nil	nil	—	—	—	—	—	—	—	—	—
C_4	% wt	1·32	75	nil	nil	—	—	—	—	—	—	—	—	—
C_5	% wt	2·11	nil	35	15·6	—	—	—	—	—	—	—	—	—

2.2. CRUDE OIL UTILISATION

2.2.1 Refining of Crude Oil

At the beginning of the century, when the petroleum industry was in its early stages of development, a major portion of crude oil was used either directly or as a kerosene cut for domestic purposes. The picture, now, is totally different ; almost all of the crude oils produced in the world are refined, either in refineries in the producer - countries or those of the buyers.

The world refining capacity in 1987 was approximately 75 million barrel/day, with an average utilisation rate of approximately 70%, while the world oil production in the same year was 60.2 million barrel/day (10).

2.2.2 Blending of Crude Oils

As explained earlier, the blending of crude oils is a practice of a great importance, for both oil producers and buyers. The reasons for this include,

A - for producers :

1. It facilitates the improvement and upgrading of low quality, and hence low value, crude oils by blending with higher quality crudes.
2. It enables crude oil sales volume to be maintained at a higher price.
3. It ensures that a wide range of crude oil quality can be covered, which enables the producers to meet the differing customer's requirements in terms of availability and quality.
4. Moreover, blending of crude oils leads to a better utilisation of the oil reserves, particularly for those countries with high reserves of heavy crudes and less amounts of light crudes.

B - for buyers:

1. It provides the required quality of crude oil feedstocks to meet the configurations of their refining operation.

2. It provides the required distillate yields and properties which in turn ensures the optimum operating conditions for other refinery units (e.g. catalytic crackers, desulphurisers etc.) leading to finished products of competitive quality.
3. It provides a crude feedstock suitable for the production of speciality products, e.g. production of a high yield of wide range base oils for lubricating oil manufacturing.
4. A better utilisation of the capacity and operating capability of refineries with flexible configurations could be achieved by using the proper crude blend feedstocks. For example, the production of different grades of low sulphur fuel oils, which gives the refiner a better competitive marketing position, kerosene or gas oil of wide range specification together with residue must be ensured. This can be done by selecting the proper crude feedstock.

In general, studying the effect of blending on the physical and chemical properties of crude oils and their products has become increasingly important to the oil industry. This followed, in particular, the adoption by many oil producers of the "Net Back Value" for crude oil pricing, in which crude prices are set on the basis of product markets.

2.2.3 Net Back Value

Prior to the introduction of the "Net Back Value" concept to the oil market in the first quarter of this decade, crudes were priced upon a "spot price". On this system, the prices of world crudes are calculated on the basis of, the fluctuating prices of three market - leading standard crudes namely U.S. West Texas Intermediate 40° API, North Sea Brent blend 38° API and Middle East Abu Dhabi 39° API. These fluctuations arise from market speculation. Prices of other crudes are calculated with respect to them ; crudes of better quality (e.g. higher API, lower sulphur, etc.) have a higher price, conversely crudes of less quality have a lower price. Prices of some selected world crude oils are shown in Table 2.3.

However, there are many factors involved in determining crude oil prices which fluctuate strongly from time to time. For example, Figure 2.6 illustrates the fluctuation of the price of North Sea Crude oil Brent blend 38° API since 1985.

Table 2.3: Average Prices of Selected Crude Oils as at the First Week of August 1988(11)

SOURCE	API gravity	$/bbl.
USA West Texas Intermediate	40°	15.50
United Kingdom Brent blend	38°	15.75
Abu Dhabi - Murban	39°	14.50
USA California heavy	13°	10.00
Saudi Arabia-Arabian light	34°	14.15
Iran - Iranian light	34°	14.10
Iraq - Kirkuk blend	36°	14.80
Nigeria - Bonny light	37°	16.05
Libya - Es Sider	37°	15.30
Kuwait - Export blend	31°	13.40
Indonesia - Minas	34°	15.05
Venezuela - Tia Juana light	31°	17.62
Gabon - Mandji	30°	13.90
Egypt - Suez blend	33°	14.35
Mexico - Isthmus	33°	14.40
USSR - Export blend	32°	14.95

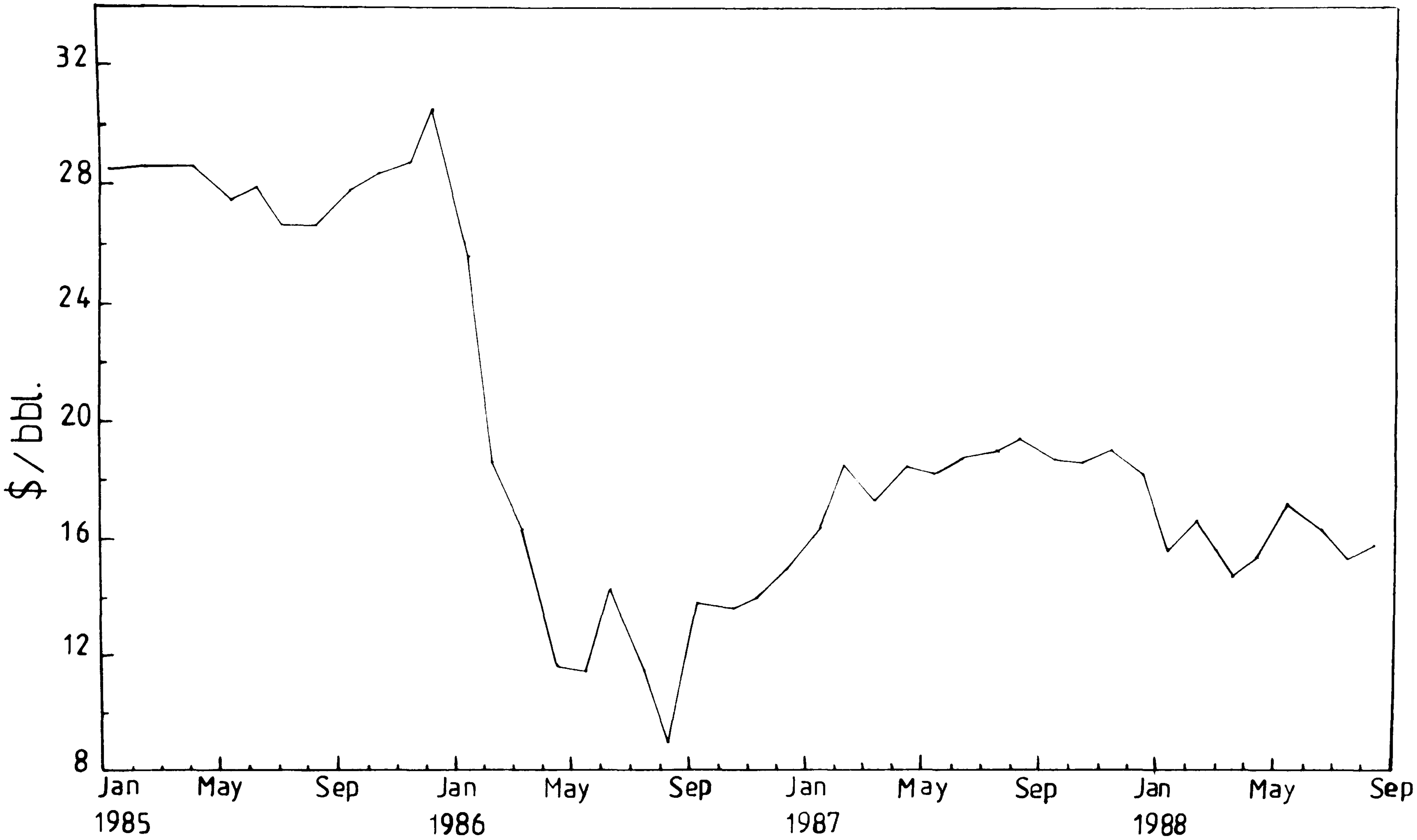


Figure 2.6: Brent Blend Crude Oil Spot Prices

In 1985 most of the crude oil sales were done on the basis of the net back principle. Now, both systems (spot price and net back) are used in pricing crude oil, depending on the specific agreement between the seller and the buyer (12).

There are four basic components of any netback deal : yield of products from a barrel of crude oil, product prices, fees and timing.

The yield is the portion of each individual refined product, which when combined with the other products, adds up to a whole barrel of refined crude. A specific spot product price reference point is selected for each portion of the yield to determine the total value of the crude. The products monitored usually include gasoline, kerosene, gas oil and residual fuel, and sometimes LPG's and natural gas.

In almost all cases the product pricing base used is the intended destination refining center. The only exception is the case of Saudi netback sales to the Far East, which are tied to Rotterdam prices (12).

Hence, the yield is the most important contributory factor in calculating the net back price. From the seller's point of view, the larger share of high-value light products (gasoline and kerosene), the higher the total price of the crude oil ; and the larger the share of low-value fuel oil (30% - 50% of yield, depending on the crude), the lower the total price of the crude oil. The formulae for calculating the yield vary from deal to deal depending on the agreement between the seller and the buyer. This may be attributed to the wide variety of regional and individual refinery configurations.

Due to the important role which yield and product types play in determining the crude price, obtaining crude oil blends of less spot price (i.e. increasing the percentages of low-value crude such as heavy crudes leading to slightly lower °API) producing higher yield and quality products is becoming of increasing interest to many oil producers (13).

This could be achieved by monitoring the changes which may occur in a certain crude blend when the properties and percentages of each crude component are changed.

The fees include many items, but the most important one is the processing or refining cost. The industry estimates of marginal refining costs range from approximately 65 ¢ a barrel in the USA, to 30 ¢ a barrel in Europe, and 20 ¢ elsewhere (12). The cost of refinery fuel is excluded and it is deducted from the yield. The larger the fees allowed, the better it is, of course, for the buyer. Fees also include freight costs in most netback deals. These can be significant and are deducted from the yield.

Other costs such as insurance, financing and import duties are sometimes included in netback deals, but they are relatively small factors.

Timing is an important factor in any netback deal. This item is again vague, and there is no fixed rule that determines at what day the price is calculated since the crude has been lifted from the refinery and it depends only on the agreement between the seller and the buyer. Generally, it may be up to 60 days.

The netback price of a particular crude depends on a combination of all of the four variable factors, which makes it very difficult to set a fixed rule governing netback deals. However, the basic method of calculating a netback is that the product prices, for the indicated time period, are multiplied by the yield according to set percentages for each product, on either a weight or volume basis. The sum total of these calculations gives the overall crude price. The fees are then subtracted from this total value, giving the netback value or price of the crude oil. An example of a basic netback calculation is given in Table 2.4.

Finally, the application of the netback principle to the pricing of crude oil is very complicated and many factors are involved in any deal. These factors may vary from time to time or from deal to deal for the same crude. An example of such deals is given in Table 2.5.

Table 2.4: A Sample Calculation of Netback Price of a Barrel of Arabian Light Crude Refined in Rotterdam with its Product Yield Sold at Spot Market Prices, Assuming May, 1986 Prices and a "Summer" Yield (12)

PRODUCT TYPE	ROTTERDAM SPOT PRICE		PRODUCT YIELD (Volume %)	VALUE OF YIELD
Naphtha	$ 14.85	x	7.0%	$1.04
Premium Gasoline	22.44	x	15.5%	3.48
Regular Gasoline	19.53	x	5.6%	1.09
Gas Oil	19.95	x	33.0%	6.58
Fuel Oil:				
1% Sulphur	10.89			
3.5% Sulphur	8.86			
Adjusted Fuel Price*	8.96	x	33.4%	2.99
Total Value of Arabian Light's Product Yield				$15.18
deducted : Incremental Refining Cost				-0.30
Spot Freight Cost (At world scale 28)				-0.93
Implied Value of Refined Arabian Light Crude				$13.95

* Adjusted to reflect value of 3.46% sulphur-fuel oil yield of Arabian Light Crude.

Table 2.5: Sample of Netback Terms for Saudi Arabian Crudes (12)

	ARAB. LIGHT								Arab.Heavy
	North west Europe				Mediterranean	US Gulf		Japan	US Gulf
NETBACK PRICE ($/BBL)	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
Mid-May 1986	$14.25	13.34	15.19	14.97	12.7	14.62	13.84	14.58	12.48
Mid-March 1986	17.30	16.81	17.59	17.66	15.88	14.07	12.71	17.86	12.79
YIELD %									
Natural Gas	0	0	0	0	0	5.9%	0	0	4.0%
Propane	0	0	0.7%	1.0%	1.4%	6.5	1.5%	1.9%	6.0
Butane	0	0	-3.3	1.0	2.6	5.8	0	0.8	4.5
Premium Gasoline	19.1%	15.0%	32.3	28.0	19.7	45.6	48.0	3.5	35.0
Regular Gasoline	0	6.0	0	0	0	0	0	18.0	0
Naphtha	4.1	0	0	0	0	0	0	5.2	0
Jet Kerosene	3.8	9.0	13.7	8.0	14.0	0	0	16.5	0
Gas Oil	41.0	32.0	22.6	34.0	27.5	13.6	25.0	24.0	8.0
Fuel Oil	24.5	33.0	29.5	23.0	30.9	29.4	24.5	26.0	45.0
Fuel & Loss	7.5	5.0	4.4	6.0	3.9	6.5	1.0	4.0	2.3
Basis	weight	weight	weight	weigh	weight	volume	volum	wt	volume
FEES ($/BBL.)									
Processing	$-1.63	-2.00	-2.25	-2.10	-1.71	-2.04	-2.00	-1.95	-2.04
Freight	Spot	Spot	Spot	Spot	Spot	Spot	Spot	Spot	Spot
Insurance & Loss	-0.10	-0.19	-0.11	-0.11	0.10	-0.13	-	-0.11	-0.13
Financing	0	0	-0.31	0	-0.25	-0.41	-	0	-0.41
Other Adjustments	0	0	+0.33	0	+0.68	+1.03	-	+0.60	+1.66
PRICING BASIS									
MARKET	Rott.	Rott.	Rott.	Rott.	Med.	US Gulf		Rott.	US Gulf
TIMING									
Days after loading	41-50	41-50	50	-	21-30	65	50	-	65

CHAPTER 3

CHARACTERISATION AND BLENDING OF PETROLEUM PRODUCTS

3.1 CLASSIFICATION OF PETROLEUM PRODUCTS

The oil refining business is a very complicated one, and many factors need to be considered carefully to ensure economical operational conditions for a certain refinery. These include:

(i) The type of feedstock crudes.
(ii) The type of marketable products to be produced.
(iii) The degree of flexibility of the refinery, which is often provided by cracking processes which permit heavier fractions to be broken-down into lighter and usually more valuable materials such as motor gasoline.
(iv) The location of the refinery (eg. how far it is from the international spot markets).
(v) Type of utilities and services available.
(vi) The interests of the end-users of the various products.
(vii) Other factors, eg. political and environmental considerations.

Petroleum products are sometimes considered as consisting of a few well-known items such as motor gasoline, jet fuel, kerosene, etc. However, a survey conducted by the American Petroleum Institute (API), and covering all petroleum refineries and petrochemical plants revealed over 2000 products made to individual specifications(3). The number of individual products produced in the United States(3) are shown in Table 3.1. However, the bulk-tonnage products such as gasoline, jet fuel, gas oils, fuel oils and residues are those which dictate refinery design, configuration and economics.

Table 3.1 - Products Made by the US Petroleum Industry (3)

Class	Number of types
Fuel gas	1
Liquefield gases	13
Gasolines	40
Motor	19
Aviation	9
Other (tractor, marine etc)	12
Jet fuels	5
Kerosenes	10
Distillates (diesel fuels, gas oils, light fuel oils)	27
Residual fuel oils	16
Lubricating oils	1156
White oils	100
Rust preventives	65
Transformer and cable oils	12
Greases	271
Waxes	113
Asphalts	209
Cokes	4
Carbon blacks	5
Chemicals, solvents, misc	300
	2347

In the early days of the oil industry, simple straight run fractions were used directly as saleable products. Nowadays, however, almost all petroleum products have to be specially manufactured, to meet the market demand, in terms of properties and freedom from impurities. In a modern refinery, it is the exception rather than the rule to use individual straight-run fractions as finished products.

A typical overall refinery flow diagram, with the main typical products, is shown in Figure 3.1.

The different petroleum products may be classified into major groups as discussed below.

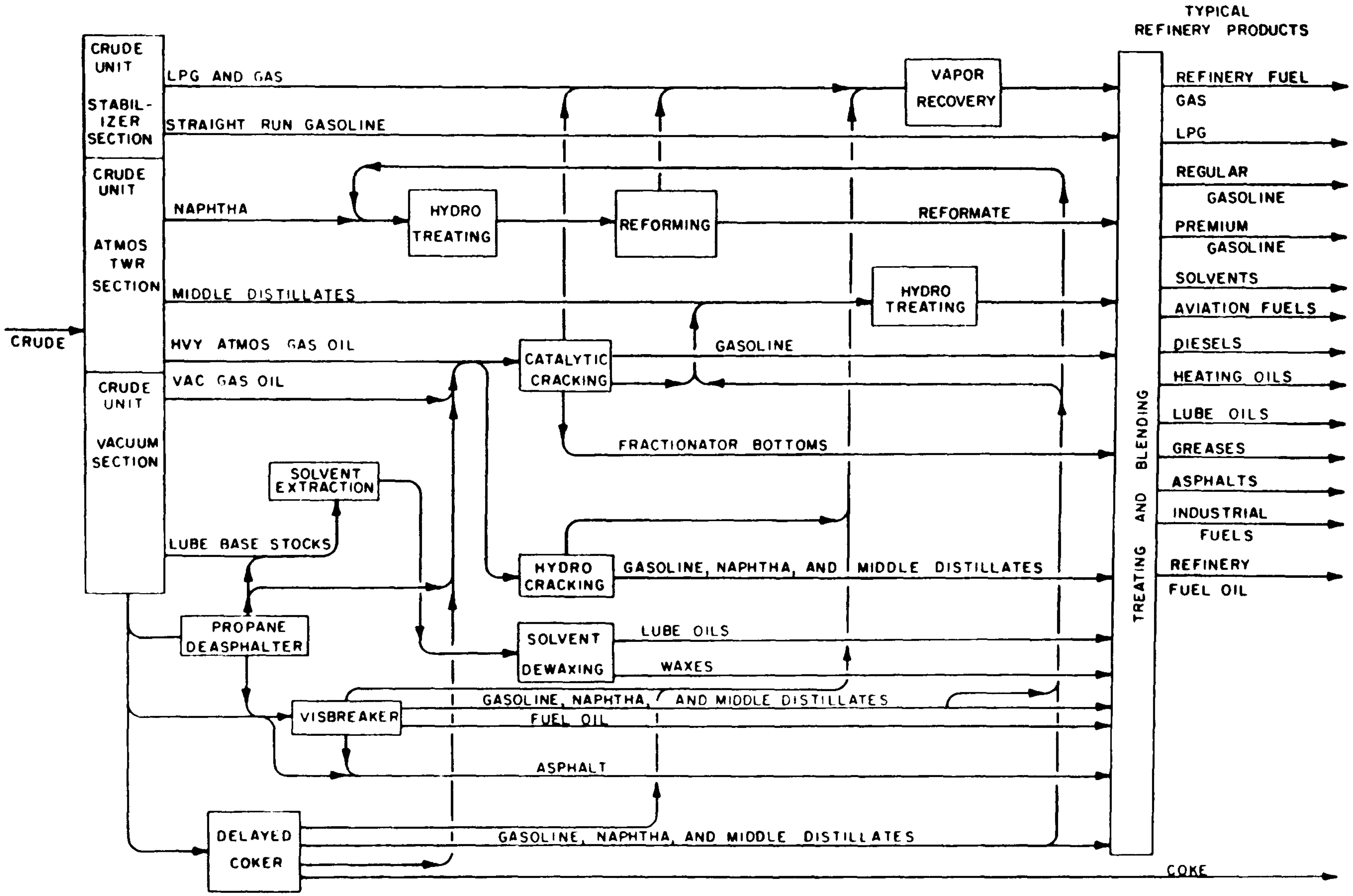


Figure 3.1: Refinery Flow Diagram

3.1.1 Low-Boiling Products

The main individual products of this class are the light gases, methane (C_1), ethane (C_2), propane (C_3), butane (C_4) and the corresponding olefin fractions.

C_1, C_2 and C_3 fractions are usually used as a refinery fuel. C_1 and C_2 can also be used as feedstock for hydrogen or ethylene production by thermal cracking, which are widely used for petrochemical industries. C_3 is also sold as liquifield petroleum gas (LPG).

Normal butane (n-C_4) is usually blended into gasoline to regulate its vapour pressure and to promote better starting in cold weather. Normal butane is also used as a feedstock to isomerization units for iso-butane production.

Iso-butane, which is originally present in crude oil, and is produced from hydrocracking units, is an important feedstock to alkylation units in which it is reacted with unsaturated materials such as propenes, butenes and pentenes to produce compounds of high-Octane Number in the gasoline boiling range.

Butanes can also be used in LPG, either alone or mixed with propane.

The properties of commercial propane and butane are given in Table 3.2.

Table 3.2 - Average Properties of Commercial Propane and Butane(3)

Property	Propane	Butane
Vapour pressure, psig:		
70°F	124	31
100°F	192	59
130°F	286	97
Specific gravity of liquid 60/60°F	0.509	0.582
Initial boiling point at 14.7 psia, °F	-51	15
Dew point at 14.7 psia, °F	-46	24
Specific heat of liquid at 60°F, Btu/(lb)(°F)	0.588	0.549
Specific heat of gas at 60°F, Btu/(lb)(°F)	0.404	0.382
Limits of flammability, % gas in air		
Lower limit	2.4	1.9
Upper limit	9.6	8.6
Latent heat of vaporization at boiling pt, Btu/lb	185	165
Gross heating values:		
Btu/lb of liquid	21550	21170
Btu/ft^3 of gas (60°F, 14.7 psia)	2560	3350

3.1.2 Gasolines

Gasolines include different grades of motor gasoline such as unleaded and leaded gasoline (premium and regular). They also include aviation gasoline, but in relatively small amounts, ie. approximately 3% of the total gasoline market(3).

Since the 1940's, motor gasolines have been the principal products of refineries, and in the 1960's, gasoline production was the largest tonnage of any of the basic industries in the United States and West Europe(3).

Down-stream gasolines consist of blends of many hydrocarbons(9) with a boiling range of 40-200°C, depending on the configuration of the refinery. The blend components are light straight-run gasoline (produced from the crude distillation unit), catalytic reformate, catalytically-cracked gasoline, hydrocracked gasoline, polymerized gasoline, alkylate and n-butane. Small percentages of other additives such as antioxidants, metal deactivators and Octane Number boosters (eg. TEL, TML. MEK, MIBK) are, also, usually incorporated into the blend.

Straight-run gasoline, which occurs naturally in crude oil, consists of the C_5 to approximately 88°C fraction of the naphtha cuts from the crude distillation unit. It is usually subjected to caustic washing or mild hydrotreating, separately from the heavier straight-run gasoline to produce a gasoline blending stock.

The composition of straight-run gasoline is influenced by the nature of the crude oil from which the gasoline is obtained, ie. paraffinic crudes such as Pennsylvania, Michigan and Mexican crudes produce lower Octane Number straight-run gasoline when distilled, whilst the naphthenic crudes may produce higher Octane Number straight-run gasolines. The higher the aromatic and naphthenic content in the straight-run gasoline, the higher the Octane Number, and hence the better for gasoline blending.

The American Petroleum Institute Project 6 provided a thorough analysis of paraffins, cyclopentanes and cyclohexanes for the fraction below 132°C, and of aromatics for the fraction below 180°C of Oklahoma (mid continent) crude(9). It was reported that although the gasoline is of relatively low boiling point range, it is a complex mixture of a vast number of hydrocarbons. However, gasolines produced from other crudes would not necessarily have the same composition.

The catalytic reformer fed by heavy straight-run gasoline produces the catalytic reformate (C_5^+ gasoline) of high Octane Number (90 to 100 RON clear).

The catalytic cracker and hydrocracker gasolines are generally used as gasoline blending stocks and sometimes require upgrading, by catalytic reforming, to improve their Octane Number prior to blending into motor gasoline.

Polymer gasoline is manufactured by polymerization of olefins to produce paraffins in the gasoline boiling range. However, due to the higher Octane Number products produced by the alkylation of light olefins, this process is preferred to isomerization.

Normal butane is blended into gasoline to achieve the desired vapour pressure in the finished product. The vapour pressure of gasoline is a compromise between a relatively high value to improve starting characteristics and a relatively low one to prevent vapour-lock and to reduce evaporation losses. Because of its high blending Octane Number, butane is a very desirable component of gasoline; refiners therefore add as much to their gasolines as vapour pressure limitations permit.

3.1.3 Naphthas

Naphtha is a fraction with a boiling point range that may overlap with gasolines and kerosene, and which varies from one refinery to another. It is a very important source of intermediates for speciality materials. Table 3.3 summarizes the average properties and uses for some typical naphthas$^{(14)}$.

Originally, straight-run naphthas do not possess high aromatic contents and hence are not good solvents for some materials. Therefore, further treatment is necessary to increase the aromaticity if high solvency is needed.

Table 3.3 - Approximate Properties and uses of Representative Solvents and Naphthas(14)

Property	Key Number Solvent 1	2	3	4	5	6
API gravity	75.1	75.5	64	59.5	58	48
Initial boiling point, °F	95	145	195	200	220	325
Final boiling point, °F	186	160	215	285	300	400
Flash point, °F	-73	-	-	25	45	115
Use of Solvent						
1 Castor oil or fat extraction	-	-	x	x	x	-
2 Seed extraction	-	-	-	x	x	-
3 Rubber cements, tire manufacture	x	x	x	x	x	-
4 Lacquers, art leather, rotogravure ink, adhesive tape	x	x	x	x	x	-
5 Brake linings, leather degreasing, bone degreasing	-	-	x	x	x	x
6 Paints and varnishes, thinners	-	-	-	x	x	x
7 Textile printing and proofing	-	-	x	x	x	x
8 Floor coverings, wax, polish, wash for printing plates or rolls	-	-	-	x	x	x
9 Dry cleaning, metal and machinery cleaning	-	-	-	x	x	x
10 Flat finishes, rust proof compounds	-	-	-	-	-	x

3.1.4 Jet Fuels

The majority of the fuels now used for aviation purposes are those in the kerosene boiling range. The exception is aviation gasoline which has limited uses, as discussed in Section 3.1.3.

Aviation Turbine Kerosene (ATK) has a boiling range of approximately 180 to 275°C; it is composed mainly of C_{11}-C_{16} hydrocarbons.

Very strict requirements for jet fuel have to be met by the refiners, in order to ensure reliable operation in flight, and to minimize risk of engine failure. Excellent pumpability of the fuel must be ensured at low temperatures. It must also comply with definite limits in terms of specific gravity and calorific value, and must also burn clearly, ie. without smoke formation, which reflects incomplete combustion. Therefore, the percentage which can be incorporated of cracked products high in aromatics is limited. The specification limit of the aromatic content is generally 20% by volume. The specified freezing point is very low; the maximum limit is usually -50°C. This may be achieved by isomerization of paraffins by hydrocracking, which lowers the freezing point considerably. Hence, well-controlled operating conditions in a hydrocracker could produce low smoke-point, and low freezing point (Appendix A) jet fuel. This can be achieved by the presence of a small amount of hydrogen sulphide(3).

The vapour pressure of the fuel must also be maintained relatively low (2.0 - 3.0 psi). It must also remain stable when heated to high temperatures; this requirement is very important, particularly for supersonic speed aircrafts where the fuel temperature may well achieve 200°C, as a result of the kinetic heating of the aircraft body. Any tendency towards instability under such severe conditions could therefore lead to deposition of gum and varnish in the heat exchangers or at the burner jets with potentially serious consequences(1). Special tests have therefore been devised to ensure high quality fuel resulting in safe operating conditions for aircraft(1).

Jet fuels are usually blended from the various components, ie. naphtha, gasoline and kerosene in order to yield the lowest-cost blend that meets specifications. Several commercial grades of jet fuels, such as JP-4, JP-5, Jet-50, ASTM Type A and A-1, are available with the requisite freezing point and distillation characteristics. Characteristics of a typical commercial aircraft turbine fuel are shown in Table 3.4.

Table 3.4 - Typical Characteristics of Aircraft Turbine Fuels

Property	Specification
Gravity, °API	
Max	57
Min	45
Specific gravity	
Max	0.7507
Min	0.8017
Distillation temperature, °F	
10% evaporated, max	
20% evaporated, max	290
50% evaporated, max	370
90% evaporated, max	470
FBP, max	
Flash point, °F, min	100
Freezing point, °F, max	-58
Sulphur %wt, max	0.3
Aromatics, % vol, max	20

3.1.5 Diesel Fuels

High-speed diesel engines fuels are widely used for automotive purposes, eg. in buses and lorries. Generally, the main component of this fuel is a gas oil distillate of Cetane Number (defined in Appendix A) above 50, and a boiling range 200-350°C; it thus overlaps to some extent with kerosene. Another grade of automotive diesel is of wider boiling range, 175-350°C. It usually contains some cracked stocks and may be blended from naphtha, kerosene and gas oils. Important specifications of the diesel fuel, eg. flash point (min 50-55°C), sulphur content (max 0.5% wt), distillation range, cetane number (min 52), viscosity, and pour point (max -25 to -10°C) can be achieved by controlling the proportions of the blend components. However, these specifications are not fixed, but are subjected to changes according to the interests of the manufacturers, where viscosity and cetane number are the main key properties in blending diesel oil components. Consequently paraffinic fuels are of better ignition quality (higher cetane number) than aromatic fuels. For this reason, the highly-paraffinic, Middle East crudes yield particularly good diesel fuel.

Stationary and marine diesel engines fuels are usually termed fuel oils. These are widely used in ships or for electricity generation. They often consist of a blend of gas oil, kerosene and some residual (asphaltic) material. Critical specifications are viscosity and sulphur content (low sulphur 1.0% wt and high sulphur, 3.5% wt).

Because the main components of fuel oil blends are of different chemical and physical natures, instability is a common problem, particularly when the residue used in blending is of coke form, eg. H-oil cracker residues. This may be attributed to the incompatibility of the blend components leading, after a certain period of time, to precipitation of residues and, subsequently engine failure.

Railroad diesel fuels are similar to the automotive diesel fuels but have higher boiling ranges up to approximately 370°C (700°F) end point and lower Cetane Numbers (40 to 45).

In general, the low-temperature characteristics of gas oils, diesel oil or other fuel oil depend strongly upon the wax content. At low temperatures, the wax separates in the form of crystals, and if these aggregate on fine filters or block fuel lines, engine failure may occur. Hence, a pour point test, (described in Chapter 6), which chracterises the temperature at which a fuel will no longer flow, is necessary to ensure good cold flow characteristics.

3.1.6 Lubricating Oils

This term covers a very wide range of products, specially blended to meet the requirements of all types of machinery, and under different conditions of temperature, loading, operating speed and materials of construction. Different grades and types of lubricating oils are produced by blending a small number of lubricating oil base stocks and additives. The lubricating base oil stocks are prepared from selected crude oils by distillation and special processing to meet the desired specifications.

The most critical properties of lubricating oils are viscosity, viscosity change with temperature (Viscosity Index), pour point and oxidation resistance.

The higher the viscosity of the oil, the thicker the film that clings to the metal surfaces during use. Clearly, the required thickness depends upon the specific service. The viscosity of the base oil blending stocks can be selected by the distillation boiling range of the straight-run fraction from the crude distillation unit, where from a given crude oil, the higher the boiling point range of a fraction the greater the viscosity of the fraction.

The viscosity index (VI) of the oil is an empirical measure of the rate of change of viscosity with temperature. A high value of VI, is indicative of a small change in viscosity for a given change in temperature, and is hence a desirable feature. Motor oils must be sufficiently thin at low temperatures to permit easy-starting but viscous enough at engine operating temperatures (80 to 120°C) to reduce friction and wear by providing a continuous liquid film between metal surfaces.

For motor oils, a low pour point is also very important to obtain ease of starting and proper start-up lubrication in cold weather.

The oxidation of motor oils is promoted by high temperature operation in the internal combustion engine, in which the temperature may reach 350°C at the piston heads(3). As a result, coke and asphaltic materials form from paraffin-base oils, and sludge from naphthenic-base oils(15). Consequently antioxidant additives, such as phenolic compounds, are usually added to the oil blends to inhibit the oxidation.

Other important properties such as flash point, boiling temperature, acidity and foaming characteristics should also be carefully considered during manufacture of the base oils or in blending them to produce the finished lubricating oils.

However, the desired specifications of the lubricating oils cannot usually be achieved without using different types of polymeric additives, such as VI improvers, pour point depressants and antioxidants.

Lubricating Oil Processing

In lubricating oil processing, the proper individual fractions are first selected from the crude distillation units according to their viscosity and boiling range specifications. A high proportion of the heavy base oils are usually included in the vacuum residues together with the asphaltenes, resins and other undesirable materials. The fractions are therefore subjected to four main processes to improve their properties;

1 Removing the asphaltenes and resins by solvent-extraction using propane as solvent.

2 Improving viscosity index by solvent extraction to remove aromatics from the base oil stocks. The solvents used are furfural, phenol and N-methyl-2-pyrrolidone (NMP). This also improves the oxidation resistance and colour of the oil, and reduces the coke and sludge-forming tendencies of the lubricating oils by separating the aromatics from the naphthenic and paraffinic portion of the base oil stocks.

3 Lowering pour points by solvent dewaxing using propane, dichloroethane, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK) toluene, or mixtures of them, at low temperatures.

Selective hydrocracking of the base oils is usually performed using zeolites with cavities $\simeq$ 6Å in diameter.

4 Improving colour and oxygen stability, and lowering organic acidity by hydrotreating (hydrofinishing) using cobalt-molybdate catalysts.

For economic and process reasons, the sequence is usually in the order of deasphalting, solvent extracting, dewaxing and hydrotreating.

3.1.7 Bitumen

The residue obtained after distillation of crude oil up to the gas oil range (about 350°C), can be further distilled, under vacuum, to give heavy distillates for the preparation of lubricating oils, or to feed units such as a catalytic cracker. The remaining vacuum residue is termed bitumen. By controlling the temperature to which the distillation is continued, the hardness and other properties of the residual bitumen can be varied. However, such properties are also very dependent upon the crude oil used. Bitumen is a dark viscous material, usually solid at normal ambient temperatures, and is widely used for road-making.

The degree of hardness is controlled by blowing air through molten bitumen, to promote chemical reactions which change the nature of the molecules. This increases the hardness of the bitumen. The hardness of bitumen is usually expressed in terms of a "softening-point" test which measures the temperature at which the bitumen reaches a standard degree of fluidity(16). Actual hardness, at a given temperature, is determined by another criterion, the penetration test, which measures the depth to which a standard needle will sink into a bitumen, when a specified load is applied to the needle for a fixed time(17).

3.1.8 Miscellaneous Products

Many products, other than those mentioned above, are produced from crude oils but in relatively smaller quantities. Such products are mainly in the form of solvents or raw materials to other industries. Petroleum solvents which are often of narrow distillation range are produced in many grades for different uses. A well-known example is white spirit, used as a paint thinner and in the dry-cleaning industry. Solvents also play an essential part in the manufacture of printing inks, polishes, adhesives, insecticides etc.

Aromatic hydrocarbons, such as benzene, toluene and xylenes (BTX) are also used as solvents, and as intermediates for conversion to many types of plastics, synthetic fibres, and plasticisers and as extenders for PVC and synthetic rubber manufacture.

Olefinic gases such as ethylene, propylene and butenes are widely used as starting materials for a vast range of petroleum chemicals and polymers.

3.2 BLENDING OF PRODUCTS

As has been discussed, the production of finished products in a refinery is essentially a matter of selective blending of available components in order to meet the many, often conflicting, quality requirements of the various grades of products. Therefore, increased operating flexibility and profitability result when refinery operations produce basic intermediate streams that can be blended to produce a variety of on-specification finished products. The objective of product blending is to allocate the available blending components in such a way as to meet product demands and specifications at the least cost, and to produce incremental products which maximize overall profit. Because of the vast quantities of products marketed, savings of a fraction of a cent per gallon will produce a substantial increase in profit over a year. For example, an average size refinery produces one billion gallons of gasoline per year; then, a saving of 0.01 of a cent per gallon results in an additional profit of $100000 per year. This could be achieved by:

1 Improving the properties of the finished product, thus commanding a higher price.

2 Using the least proportion of the high price individual blending stocks, and the highest proportion of low price blending stocks or unsaleable material, eg. some vacuum residues.

3 Using reliable models and mathematical correlations to accurately predict blended proportions of individual components which yield the best quality, finished products. This would minimise the amount of additives (either blending components or property improvers) usually used to compensate for the difference between the actual and assumed values of a particular property of the product (usually termed the "give away value"). It may also reduce the severity of processing the intermediate products; this would reduce the operational costs and extend the life times of the process catalysts and of the units themselves.

4 Using, initially, the proper crude oil feedstock that will produce intermediate products of the requisite properties for blending, and which requires the minimum amount of processing.

Almost all modern refineries use computer-controlled, in-line blending for blending high-volume products such as gasolines, kerosenes and fuel oils. The computer is fed with the specification data and the correlations to predict the different blend properties. A linear programming model hence optimizes the blending operations to select the blending components to produce the required volume of the specified product at the lowest cost.

Some properties such as viscosity, Octane Number and pour point are not additive, ie. they do not blend linearly. Therefore, one of the most widely-used methods to estimate the property of the blend is the blending index number which is fed into the LP model of the refinery. Chevron Research Company have compiled such index numbers for viscosity, flash point, aniline point and vapour pressure(3).

3.3 QUALITY GIVE-AWAY

As discussed earlier, almost all the marketable down-streams of a refinery comprise blends of two or more straight-run or intermediate products. Some selected properties are usually considered as controlling factors to which the product is referred. For example, Reid vapour pressure (RVP) and Octane Number (ON) are frequently considered as the controlling key properties of gasolines. Cloud point, pour point and viscosity are the controlling factors for gas oils. Viscosity and sulphur content are usually used for fuel oils.

However, the finished blend of a certain product is frequently off-specification, ie. its properties do not meet the required specifications, mainly the controlling key properties. Consequently, the refiner tends to upgrade the quality of the product in question by adding calculated amounts of one or more of the components (usually of higher quality) to compensate for the divergence from the target specification. This up-grading is usually expressed in terms of quantities of certain equivalent saleable products, eg. kerosene and gas oil, and the corresponding value in US Dollars.

The main causes for such 'quality give-aways' may be summarized as follows:

1 Non-availability of suitable components at the time of the product cargo preparation.

2 Availability of certain components in excess, either because they are unsaleable or cannot be stored for an extended period.

3 Due to operating difficulties, such as wide variations in the key properties of the different specifications, grades etc, which make it difficult to exercise tight control on the quality of the controlling key factors of the product. This is very common in the case of unleaded motor gasolines.

4 Constraints on blending. This arises when blending for one key property may affect another key property. For example, the Octane Number of a gasoline cannot, sometimes, be lowered to the required overall value by adding lower Octane Number material (eg. FCC light gasoline), because increasing its proportion in the blend beyond 50% increases the RVP above the maximum limit.

5 Lack of information of the intermolecular interactions between different components in a blend which may lead to unexpected behaviour of some properties, mainly those which do not blend linearly.

6 The use of correlations with high % deviations to estimate the required properties.

Table 3.5 shows typical quality give-away values for exported gas oil and fuel oil produced from a typical refinery during 1987.

Table 3.5 Typical Quality Give-Away Values for Gas Oil and Fuel Oil Cargoes of a Typical Refinery During 1987

Gas Oil	1st Qt	2nd Qt	3rd Qt	4th Qt	Whole of 1987
1 Total export quantity, MT	1468397	1499454	1632446	1626235	6226532
2 Total export quantity for which quality give-away occurred, MT	728909	839954	740374	467531	2776768
3 Quality give-away in terms of equivalent:					
(a) Saleable kerosene, MT	288972	364450	224994	202988	1081404
(b) Delta price ($/MT)†	13.21	11.60	19.96	18.71	
(c) Corresponding US dollars	3817320	4227620	4490880	3797905	16333726

Delta of mean average price for gas oil and jet kerosene, in US dollars during each quarter of 1987.

Fuel Oil	1st Qt	2nd Qt	3rd Qt	4th Qt	Whole of 1987
1 Total export quality, MT	2784056	3153448	2415746	3126178	11479428
2 Total export quantity for which quality give-away occurred, MT	475009	335081	82482	279695	1172267
3 Quality give-away in terms of equivalent:					
(a) Saleable gas oil, MT	8096	7227	3576	6301	25200
(b) Delta price ($/MT)†	54.10	43.07	56.26	75.03	
(c) Corresponding US dollars	437994	311267	201186	472764	1423210

† Delta of mean average price for oil and fuel oil, in US dollars during each quarter of 1987.

CHAPTER 4

PREDICTION OF THE PROPERTIES OF CRUDE OILS AND PETROLEUM PRODUCTS

4.1 INTRODUCTION

A knowledge of reasonably accurate physical property data for petroleum oils is important in crude oil production, transportation, petroleum refining and related processes. Density is, for example, a characteristic property of a liquid which is frequently used to predict other properties, e.g. viscosity. Reliable values of viscosity are required to accurately predict pressure drop in pipe lines. The critical properties of a liquid are required, in the corresponding states principle (CSP), in order to predict thermal and physical properties. Hence, predictive calculations are widely used in the petroleum industry, mainly for design and operating purposes.

It is impracticable to determine and tabulate physical, chemical and thermal properties data for every crude and petroleum fraction that may be encountered. The need for accurate and reliable prediction methods for these properties is, therefore, self-evident. The most extensive, recent survey of methods for predicting physical and thermodynamic properties is that conducted by the American Petroleum Institute (18).

However, although prediction of the physical properties of pure substances appears to be straight forward, these properties depend directly on the nature of the constituent molecules of each substance. Thus, the ultimate generalisation of physical properties of fluids requires a complete understanding of molecular behaviour, which in most cases is simply not available.

Even in the simplest case of gases, and in spite of the impressive developments of the molecular theory, there is still a need to predict values of physical properties, e.g. some constants in the equations of state, which have not been measured and which cannot be calculated from existing theory (7).

Most of the preferred estimation methods use equations based upon a theory, together with an empirical correlation of the constants. Reid, Prausnitz and Sherwood (7) reported that the introduction of empiricisms into minor parts of a theoretical relation is a powerful method of developing an acceptable correlation. For example, the Van der Waals equation of state is a modification of the simple PV = n RT,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad 4.1$$

Although the constants a and b are believed to have some theoretical basis, they are better considered as empirical. It has also proved useful to correlate a and b empirically with other properties of a substance.

An ideal model for the prediction of the properties of pure substances and mixtures would:

(i) Provide reliable physical and thermodynamic data, for pure substances and for mixtures, at any temperature and pressure.
(ii) Require a minimum of input data.
(iii) Select the least error route.
(iv) Indicate the probable error.
(v) Minimise computation time.

However, few published models and methods approach this ideal case. In many cases, especially in the oil industry, the most accurate model or method may not be most applicable for the purpose. Sometimes, for engineering purposes, a simple, quick and approximate estimation method, requiring a minimum of input data, is preferred over a complex but more accurate correlation (7).

Two well-known techniques for the prediction of physical properties of substances represent this approach:

A - Molecular Structure (Group Contribution) Method:

The basic principle of this method is that all properties are related to molecular structure which in turn determine the magnitude and type of the intermolecular forces. In this method, weighted characteristics of a certain property are determined algebrically in terms of the atoms, atomic groups, bond type, etc. The weighted characteristics are usually added, sometimes with a correction factor, to obtain the property in question.

Many workers have used this approach to estimate different properties of pure hydrocarbons. Lydersen(ref.7) proposed a method to estimate the critical properties of hydrocarbons T_c, P_c and V_c by structural contributions.

$$T_c = T_b\left[0.567 + \Sigma\,\Delta_T - (\Sigma\,\Delta_T)^2\right]^{-1} \qquad 4.2$$

$$P_c = M\,(0.34 + \Sigma\,\Delta_p)^{-2} \qquad 4.3$$

$$V_c = 40 + \Sigma\,\Delta_V \qquad 4.4$$

where,

T_c = critical temperature, °K

P_c = critical pressure, atm.

V_c = critical volume, $cm^3/gmol$

M = molecular weight

T_b = normal boiling point, °K

The Δ quantities are evaluated by summing contributions for different atoms or groups of atoms as shown in Table 4.1. The reported errors when using this method were 2-5%. Spencer and Daubert (19) found Lyderson's method the most accurate among those which they investigated.

Table 4.1 Example of Lydersen's Critical - Property Increments

GROUP	Δ_T	Δ_P	Δ_V
Non-Ring Increments:			
$-CH_3$	0.020	0.227	55
$>CH_2$	0.020	0.227	55
$-\overset{\vert}{\underset{\vert}{C}}H$	0.012	0.210	51
$-\overset{\vert}{\underset{\vert}{C}}-$	0.00	0.210	41
$=CH_2$	0.018	0.198	45
$=\underset{\vert}{C}H$	0.018	0.198	45
$=\underset{\vert}{C}-$	0.00	0.198	36
$=C=$	0.00	1.198	36
$\equiv CH$	0.005	0.153	36
$\equiv C-$	0.005	0.153	36
Ring Increments:			
$-CH_2-$	0.013	0.184	44.5
$-\overset{\vert}{\underset{\vert}{C}}H$	0.012	0.192	46
$-\overset{\vert}{\underset{\vert}{C}}-$	-0.007	0.154	31
$=\underset{\vert}{C}H$	0.011	0.154	37
$=\underset{\vert}{C}-$	0.011	0.154	36
$=C=$	0.011	0.154	36

A similar approach has been followed by many other workers, including Benson et. al. (20), Anderson(ref. 21) , and Rihani and Doraiswamy (22), to estimate the various thermodynamic properties (e.g. enthalpy, entropy, Gibbs energy and heat capacity) for gases and light liquids.

Thomas (23), Orrick and Erbar(ref.7),Van Velzen et. al. (24), and Diab and Maddox (25) also used the group contribution principle to estimate the viscosity of liquids. The % errors varied widely, covering a range from 0 to -89%.

However, whilst this approach is very useful for pure liquids of defined chemical structure, it is of little use for liquids of undefined chemical structure, i.e. petroleum liquids. It is also believed to be difficult to use this method for defined multi-component mixtures. This is due to multi-interactions between the various molecules, leading to high error.

B - The Corresponding States Principle (CSP):

This principle is one of the most important bases for the development of correlations and estimation methods. Basically, the properties which depend on intermolecular forces are related to the critical properties in the same way for all compounds. Hence, if pressure, volume and temperature are related to the corresponding critical properties, the function connecting the reduced properties becomes the same for each substance (7). The reduced property is commonly expressed as a fraction of the critical property:

$$P_r = P/P_c \, , V_r = V/V_c, \qquad T_r = T/T_c$$

The introduction of the compressibility factor, $Z = PV/nRT$, into the corresponding states principle in the correlation of P-V-T data was an important application, since Z_c is almost constant for many non polar substances and $\simeq 0.27$. This played a very important role in the impressive development of the equations of state (EOS).

Reid, Prausnitz and Sherwood (7) stated that successful application of the law of corresponding states in the correlation of P-V-T data encouraged many similar correlations for other properties which depend primarily on intermolecular forces. Equations describing various properties, including transport properties, are derived, such as the correlations of high pressure gas viscosity, by expressing η/η_c as a function of P_r and T_r. As in the case of the law of corresponding states, deviations from the resulting equations may be handled empirically.

Riazi and Daubert (26) stated that from the relationship of equations of state constants to critical properties of pure hydrocarbons, a generalisation can be made, that a critical property such as critical volume, V_c, is a power function of A and B which are constants in the equation of state.

$$V_c = a\ A^b\ B^c \qquad 4.5$$

where a, b and c are correlation constants. A and B in equation 4.5 can be any two parameters capable of characterising the molecular forces such as boiling point (T_b) and specific gravity (S). The equation can be generalised to the following form:

$$\theta = a\ T_b^b\ S^c \qquad 4.6$$

where θ is a physical property to be predicted. The maximum percent error reported was 19.6.

They also recommended this equation to predict the following properties of petroleum products with boiling-ranges of 100-850°F; molecular weight, liquid density, liquid molar volume, critical temperature, critical pressure, critical volume, refractive index, heat of vaporisation and ideal gas heat capacity.

4.2 PROPERTIES OF MIXTURES:

Many publications have discussed the prediction of properties of hydrocarbon mixtures and petroleum products. The most extensive publication is the API Technical Data Book, mentioned earlier in this chapter. However, few publications have discussed the prediction of crude oil mixture properties.

Some methods proposed in the literature require a knowledge of certain parameters such as the critical properties; this may complicate the calculation. In addition, these parameters may not be readily available in the literature, particularly, in the case of very complex systems like crude oil blends and petroleum products. Blends of petroleum products, especially the middle distillates and those of similar nature, such as kerosenes, gas oils, and lubricating oils, present less difficulty in the prediction of properties than crude oil. Blends of these products are stable and homogeneous in nature, i.e. the degree of similarity between the individual components is much higher than in crude oil blends, although each individual component is a complex mixture by itself. It is for this reason that published correlations have to date been limited to these products.

4.2.1 Classes of Mixtures:

In general, mixtures include both one-phase and two-phase systems. However, binary mixtures can be grouped into three general classes (27):

1. One-phase miscible mixtures; In this case the constituents are mutually soluble and the interactions between the molecules, and how they pack, are important in determining the properties of the mixture. There is always an entropy of mixing which tends to make the two substances miscible in one another. The entropy may arise from changes in how molecules pack due to preferred orientations. It is believed that any kind of interaction between the molecules may lead to an energy of mixing, depending on the degree and type of the interactions. In most cases, such interaction terms are determined empirically from experimental data.

The class of one-phase mixtures includes most of the liquid mixtures, of which crude oil and petroleum products mixtures are typical. The correlations that are used in predicting the properties of this class of mixtures are reviewed in the next section.

2. Two-phase systems with one continuous phase and one dispersed phase; These systems include most composite materials, suspensions, emulsions, foams and filled polymers.

   Interaction between the constituents occurs at the interface between the two phases. Thus, the nature of the interface can be very important. Depending on the physical and chemical composition of the two phases, if the interaction is small at the interface, the adhesion between the phases is usually poor. Conversely, if the interaction is strong, or if there is a slight solubility of one phase in the another, the adhesion between the two phases is strong. The degree of such adhesion may strongly affect the properties of the mixture (28).

   The shape of the particles of the dispersed phase, also has an important effect on the properties of the two-phase mixtures (29, 30).

3 Two-phase systems with two continuous phases; This type of mixture is far less common, but for example, includes froths with gases or liquids, crystalline polymers and various other kinds of interpenetrating networks. In addition to the concentration and the properties of the constituents, the nature of the interface and the morphology or shape and orientation of the two phases are important factors in determining the mixture properties.

4.2.2. Predictive Correlations of Mixtures Properties:

There are general mixture rules or equations to predict the properties of each of the three classes of mixture described in Section 4.2.1 (27). However, only correlations for predicting the properties of one-phase miscible mixtures are reviewed here, since they generally represent petroleum oil mixtures.

For accurate estimation of any given property of a mixture, the objective is to select the proper type of equation that best represents the behaviour of that property when subjected to blending. Nielsen (27) stated that publications very often describe attempts to calculate properties based upon some theory, but little effort has been expended on how to best estimate empirically the properties of all types of mixtures, in general. To make valid estimates of the property of the mixture, it is necessary to know, in addition to the corresponding property of the components and their concentration, the type of interactions between the constituents which determine their behaviour upon blending.

The correlations generally used to predict the properties of mixtures are described as "mixing rules" or "mixture-combination rules". The majority of the mixture-combination rules are empirical and have developed following numerous trials and comparisons of calculated mixture properties with experimental data. Many such rules have been proposed, e.g. Kay's rule (30) to predict the pseudocritical temperature of a mixture T_{cm},

$$T_{cm} = \sum_{i=1} y_i \, T_{ci} \qquad 4.7$$

where,

T_{ci} is the pseudocritical temperature of component i and $y_i$is the mole fraction of component i.

No binary or higher interaction parameters are included here; therefore these rules cannot reflect the real mixture properties. However, good results are often obtained when these simple pseudomixture parameters are used in corresponding states calculations to determine mixture properties (7). Less satisfactory results are obtained for mixtures of dissimilar components, especially if one or more of the components is polar or shows any tendency to associate into dimers, etc. Though, many options are open, one which has often proved successful is to change the previous equation from a linear to a quadratic form:

$$T_{cm} = \sum_{i} \sum_{j} y_i \, y_j \, T_{cij} \qquad 4.8$$

where

$$T_{cii} = T_{ci} \; , \; T_{cij} = K^{*}_{ij} \left(\frac{T_{ci} + T_{cj}}{2} \right)$$, and K^{*}_{ij} is a constant.

As mentioned earlier in this Chapter, an energy of mixing can greatly influence the solubility behaviour and also, thereby, many other properties (27). This energy is due to an interaction effect, and in most cases, the interaction terms for insertion into mixture rules must be determined from experimental data.

The general equation for one-phase binary mixtures is (27):

$$P = P_1 \, \phi_1 + P_2 \, \phi_2 + I \, \phi_1 \, \phi_2 \qquad 4.9$$

where

P is the value of property
ϕ is concentration (e.g. mole fraction)
I is the interaction term

Another mixture equation is,

$$P = P_1 \, \phi_1^2 + P_2 \, \phi_2^2 \qquad 4.10$$

which is a special case of a more general equation:

$$P = P_1 \, \phi_1^m + P_2 \, \phi_2^m \qquad 4.11$$

where, m is a constant.

If m = +1, then this equation gives the usual "rule of mixtures".

Interaction produces either positive or negative deviations from the "rule of mixtures" value. The greater the ratio P_2/P_1, the larger I must be to produce a given relative change in P/P_1 (27).

Another equation is that of Gordon and Taylor (31)

$$K_1 \phi_1 (P-P_1) + K_2 \phi_2 (P-P_2) = 0 \qquad 4.12$$

where K_1 and K_2 are constants. This can be rearranged to give,

$$P = \frac{K_1 \phi_1 P_1 + K_2 \phi_2 P_2}{K_1 \phi_1 + K_2 \phi_2} \qquad 4.13$$

Nielsen (27) reported that the effect of the interaction term I on property P can best be illustrated by graphs based upon equation 4.9. These graphs are shown in Figures 4.1, 4.2, and 4.3. Similar graphs are derived from equation 4.11, and presented in Figures 4.4 and 4.5.

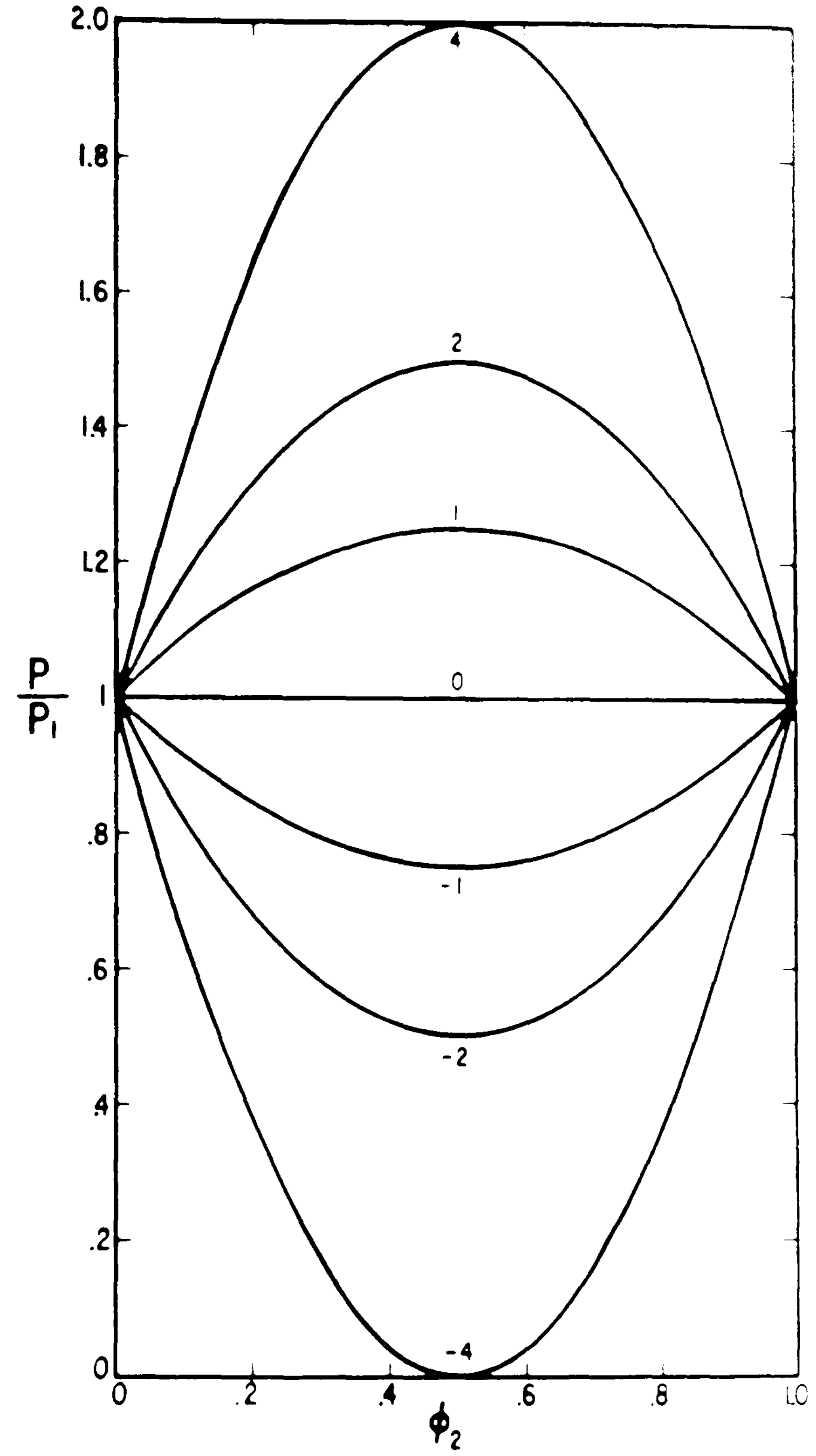


Figure 4.1: Plots of Equation 4.9 with $P_1 = P_2$. Numbers on the Curves Refer to the Value of I. (27)

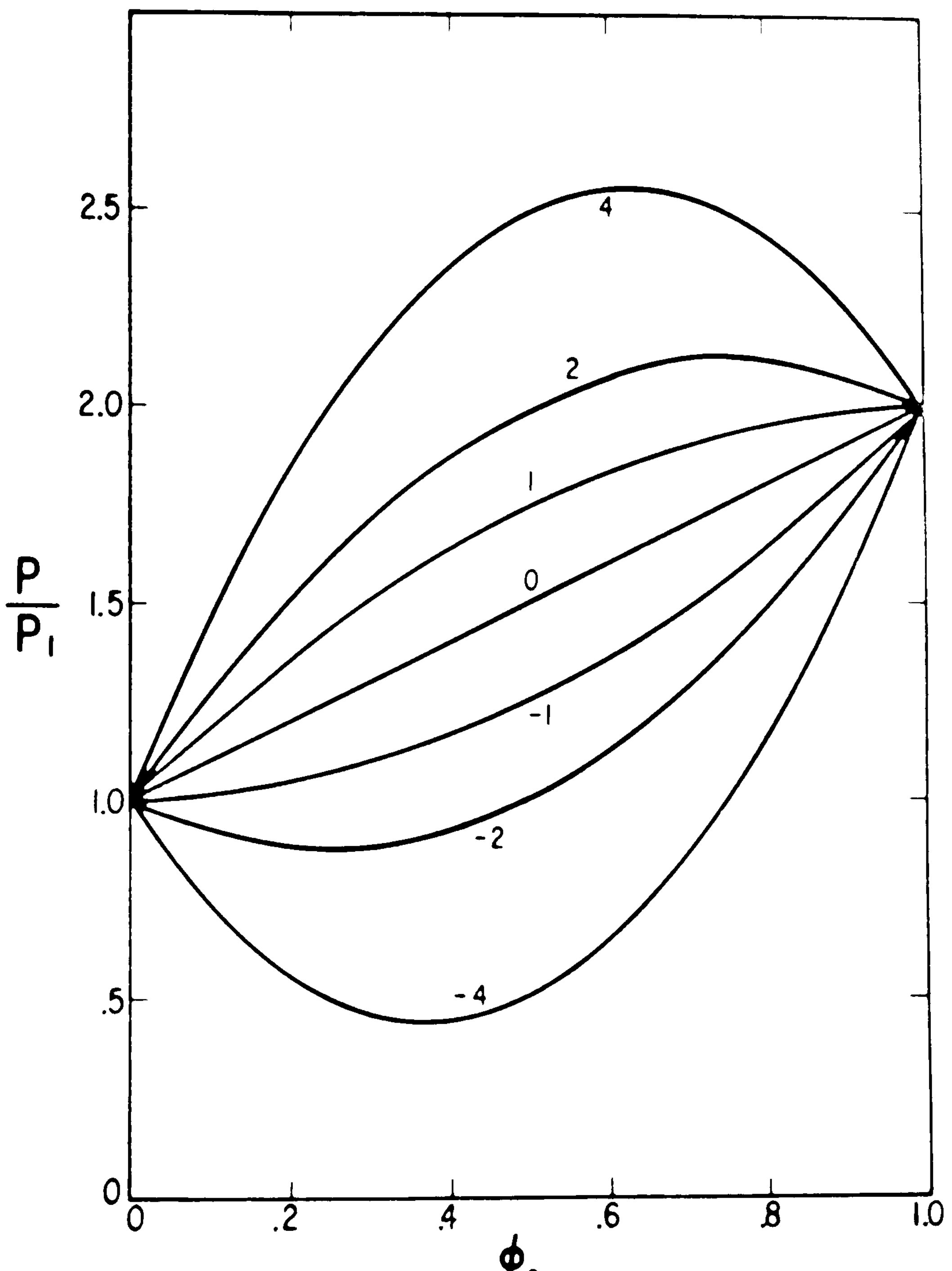


Figure 4.2: Plots of Equation 4.9 with $P_2/P_1 = 2$. Numbers on the Curves Refer to the Value of I [27].

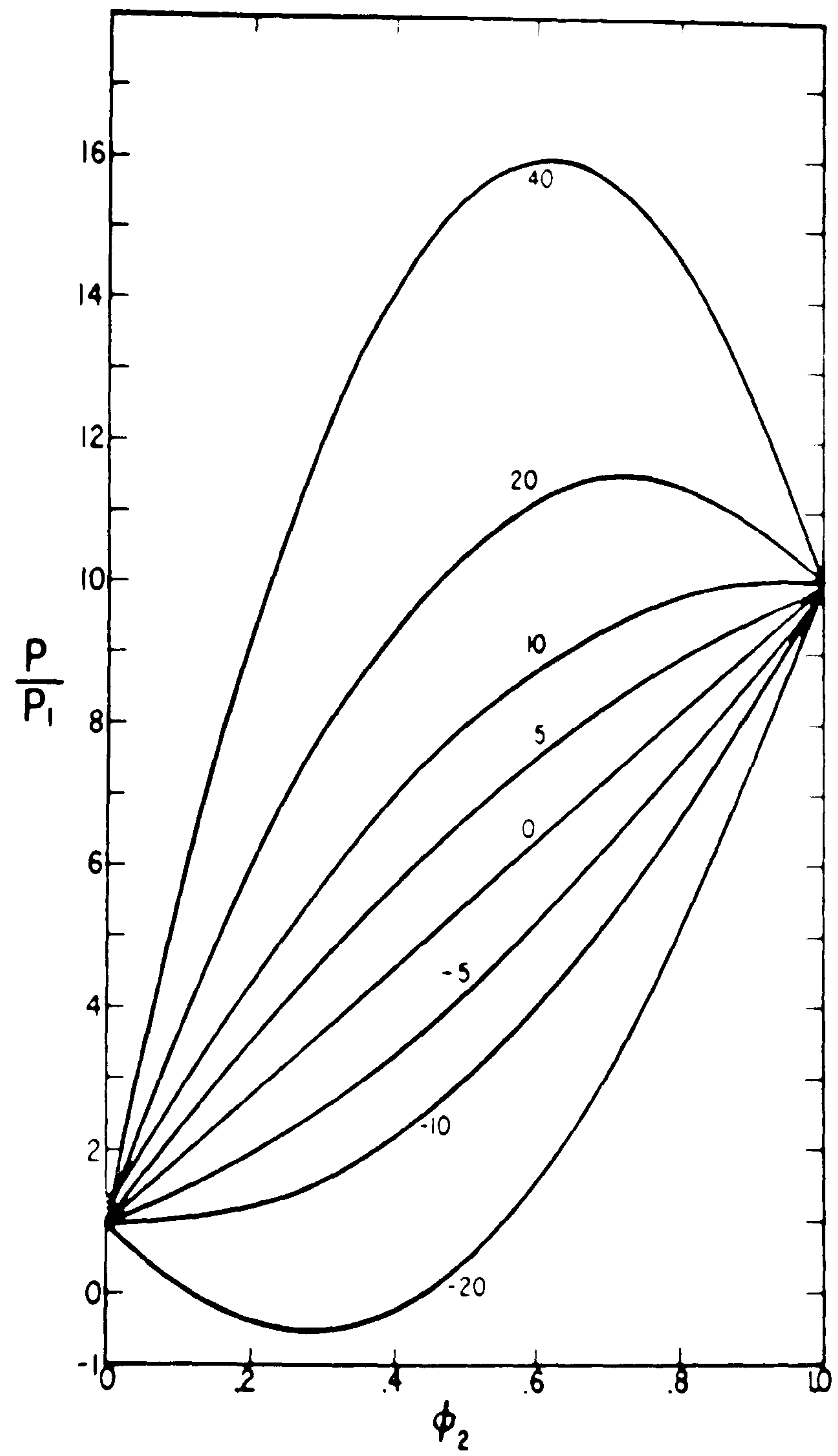


Figure 4.3: Plots of Equation 4.9 with $P_2/P_1 = 10$. Numbers Refer to the Value of I(27).

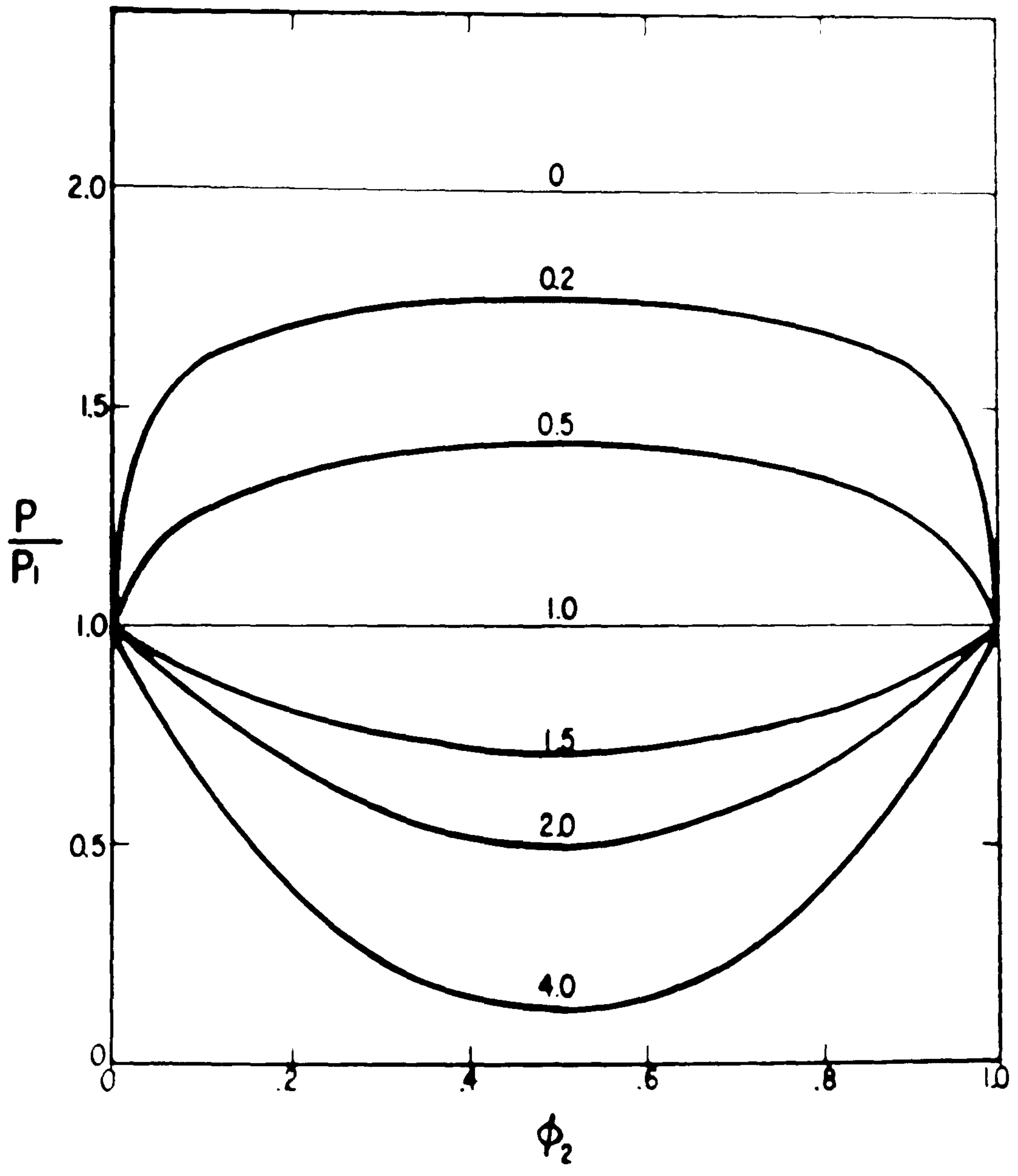


Figure 4.4: Equation 4.11 Plotted for Different Positive Values of m when $P_1 = P_2$ (27).

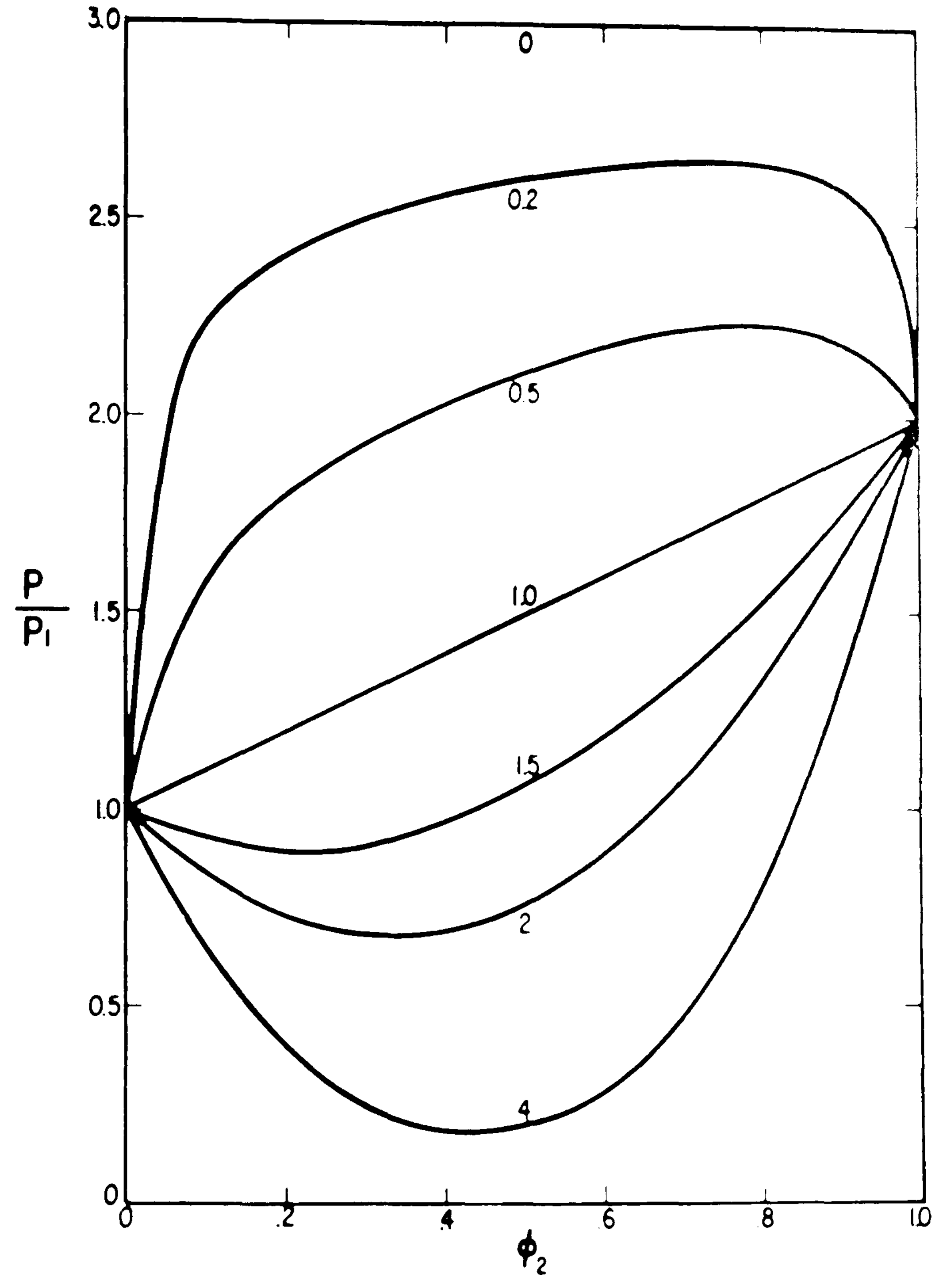


Figure 4.5: Equation 4.11 plotted for different values of m When $P_2/P_1 = 2$ (27).

Since the 1930's, the Watson characterisation factor K (32, 33) has been used to characterise petroleum mixtures using boiling point and specific gravity data as given by,

$$K \equiv \frac{T_b^{\ 1/3}}{S} \qquad 4.14$$

where T_b is the normal or cubic-average boiling point in degrees Rankine and S is the specific gravity at 290 K (60°F).

A useful relation between K, molecular weight and specific gravity can be developed by using the Riazi-Daubert relation for molecular weight (34),

$$M = 4.5673 \times 10^{-5} \; T_b^{2.1962} \; S^{-1.0164} \qquad 4.15$$

which, when combined with the definition of K, yields,

$$K = 4.5579 \; M^{0.15178} \; S^{-0.8457} \qquad 4.16$$

The values of the constants were obtained by non-linear regression. As mentioned earlier, many researchers have investigated the prediction of physical and chemical properties of pure hydrocarbons, mixtures of hydrocarbons, petroleum products (either straight-run or finished products) and mixtures of petroleum products (7, 20-33). However, little was found in the literature relating to crude oils and their mixtures. This is probably due to difficulty in obtaining general rules applicable to different crude oils all over the world. Therefore, an alternative approach which may be useful to predict the properties of crude oil mixtures would be to apply, with empirical modifications, the rules for mixtures of non-ideal hydrocarbons or petroleum products.

In an attempt to predict the properties of undefined mixtures such as petroleum products, Daubert (35) claimed that if X is the physical property to be predicted, and the molecular type fractions (paraffins, naphthenes, aromatics) are known, a pseudo-compound, i.e. a compound having the same boiling and specific gravity as the fraction, can be defined for each molecular type. The value of the property for each pseudo-compound can then be calculated. The properties can be combined by:

$$X = PX_p + NX_N + AX_A \qquad 4.17$$

where P, N and A are the fraction of paraffins, naphthenes and aromatics present in the fraction.

Clearly, from the above review, the prediction of the properties of low boiling point petroleum products, i.e. fractions up to light gas oils, and their mixtures can be achieved with acceptable accuracy, since most of the methods in the literature have, originally, been developed for pure hydrocarbons and petroleum products of low boiling points. However, the prediction of the properties of crude oils, high boiling point petroleum products and their mixtures, requires more investigations and consideration.

CHAPTER 5

VISCOSITY OF CRUDE OILS AND PETROLEUM PRODUCTS

5.1 INTRODUCTION

Viscosity is the most important characteristic controlling the motion of crude oils and their products. It is a measure of the internal resistance to motion of a fluid by reason of the forces of cohesion between molecules or molecular groupings. In general, a knowledge of the viscosity of liquids and of liquid mixtures is required for the solution of many problems concerning heat transfer and fluid flow. Viscosity measurements of crude oils and petroleum products are essential for reservoir studies, process design or the solution of transportation problems.

According to Newton's law (36), the viscosity of a liquid is a property sensitive to the force between individual molecules (which may be similar or different, and spherical or non-spherical) and also to the presence of internal molecular degrees of freedom, ie whether a molecule is rigid or rotates around an axis.

The absolute viscosity may be defined as the shear stress at a point divided by the velocity gradient at that point. Newton's law of viscosity presented this relationship as follows (36):

$$\tau_{yx} = -\mu \frac{dvx}{dy} \qquad 5.1$$

where,

τ_{yx} = the shear stress

μ = the viscosity

$\frac{dvx}{dy}$ = the velocity gradient

The unit of absolute viscosity is the poise, equal to "1g/(cm) (sec)" or 100 centipoises.

Kinematic viscosity, ν, is the ratio of the absolute viscosity, μ, to the density, ρ, both at the same temperature and pressure, ($\nu = \mu/\rho$). The unit of kinematic viscosity is the Stoke (cm^2/sec) or 100 centiStoke (cSt.). Kinematic viscosity is measured according to two standard test methods:

ASTM - D445 - 74 / IP 71 - 80 - Kinematic viscosity of transparent and opaque liquids and the calculation of dynamic viscosity.

ASTM - D2170 - 74 / IP 319 - 75 - Kinematic viscosity of asphalts (bitumens).

5.2 THEORIES OF VISCOSITY

Although the theories of gas and liquid viscosity have been considered by many workers (37 - 53), a complete theory of viscosity is still in its early stages (41).

The most important theories may be classified as (42, 43)

1. Rigorous Statistical Mechanical Theories.
2. Corresponding States Theory.
3. Model Theories.

5.2.1 General Formal Statistical Mechanical Theory of Viscosity (42)

This theory of momentum transfer in dense fluids is based on molecular theory. An expression for viscosity is derived by equating the averaged microscopic momentum conservation equation, to give the corresponding macroscopic equation (5.2), to the one derived by using continuum mechanics (equation 5.3) in which the viscosity is an empirical transport coefficient.

$$\bar{\bar{P}} = \left(\sum_{j=1}^{N} M \left[\frac{\bar{P}_j}{M} - \bar{U}\right]\left[\frac{\bar{P}_j}{M} - \bar{U}\right] \delta(\bar{r}_j - \bar{r}) - \frac{1}{2}\sum_{j \neq k}\sum \bar{r}_{jk}\left[\frac{\partial\varphi(r_{jk})}{\partial \bar{r}_{jk}}\right]\delta(\bar{r}_j - \bar{r}) \right) \qquad 5.2$$

where,

$\bar{\bar{P}}$ = pressure tensor
M = molecular mass
$\delta(x)$ = delta function
$\bar{P}_j$ = momentum of molecule j
$\bar{U}$ = mass velocity
$\bar{r}_j$ = position of molecule j
$\bar{r}$ = position considered in system
$\bar{r}_{kj}$ = $\bar{r}_j - \bar{r}_k$
$\phi\,(r_{jk})$ = pair potential

$$\bar{\bar{P}} = \left[P - \left[\mu_v - \frac{2}{3}\mu\right](\bar{\nabla}.\bar{U})\right]\bar{\bar{1}} - 2\mu\bar{\bar{E}} \tag{5.3}$$

with

$$E_{ij} = \frac{1}{2}\left[\frac{\partial U_i}{\partial X_j} + \frac{\partial U_j}{\partial X_i}\right] - \frac{1}{3}\,(\bar{\nabla}.\bar{U})\,\delta_{ij} \tag{5.4}$$

where

μ_v = bulk viscosity of fluid
P = equilibrium pressure
$\bar{\bar{1}}$ = unit tensor
$\bar{\bar{E}}$ = symetric traceless part of velocity gradient $\bar{\nabla}.\bar{U}$
δ_{ij} = kronecker delta
X = coordinate axis

For the case of dense gases and liquids, use is made of Kirkwoods Brownian Motion Theory which gives a "Fokker-Planck-type equation" for the time smoothed first order and second order non-equilibrium distribution functions (54, 55). The equation developed for the viscosity of a dense fluid is (42):

$$\mu = \frac{nMkT}{2\zeta} + \frac{\pi\zeta}{15\,kT} n^2 \int_0^\infty R^3 \left[\frac{d\phi}{dR}\right] g\,(R)\ \Psi_2\,(R)\ dR \qquad 5.5$$

where,

ζ = friction coefficient related to intermolecular force field for which different theoretical expression exist but none is completely satisfactory.

ϕ = pair potential

$g\,(R)$ = equilibrium radial distribution function

$\Psi_2\,(R)$ = a function for which a differential equation along with boundary conditions has been given

A comparison of the results predicted by equation 5.5 with those obtained experimentally showed deviations from one to several hundred percent, depending on the values of g, and ζ, (42). This, and the complicated numerical evaluation, renders this equation unsuitable for practical use.

The Enskog-Theory (42)

Enskog proposed a method for extending the Boltzman equation (5.6) which is derived for the lower order non-equilibrium functions, based on the assumption of pairwise additivity of intermolecular forces of simple fluid. Thus the total potential energy of the intermolecular forces can be replaced by the sum of the potential energy of molecular pairs.

$$\frac{\partial f_1}{\partial t} + \frac{\bar{P}_1}{M}\frac{\partial f_1}{\partial \bar{r}_1} = -\int (F_{12} \left(\frac{\partial f_2}{\partial \bar{P}_1}\right) d\bar{r}_2\ d\bar{P}_2 \qquad 5.6$$

where

f_i = distribution function; index i indicates its order

F_{12} = is the force exerted on molecule 1 due to its interaction with molecule 2

Using the assumption of a fluid consisting of hard spherical molecules, and with ternary and higher order collisions neglected, the following equation was obtained.

$$\frac{\mu}{\mu_o} = \frac{1}{g\,(d)} + 0.800\,l\,n + 0.761\,l^2\,n^2\,g\,(d) \qquad 5.7$$

where,

μ_o = viscosity of 'hard sphere molecular' gas at very low density

g (d) = equilibrium radial distribution function evaluated at a distance d, the hard sphere diameter

l = $(\frac{2}{3})\,\pi\,d^3$

n = number density

Stephans and Lucas (42) reported that, predictions from the Enskog formula for hard spheres,equation 5.7, had an error within 20% when tested against experimental data.

However, the prediction of the viscosity of liquids using statistical mechanical theories is very complex and involves many tedious computations. Furthermore, these theories have to date only been applied to simple and pure fluids, e.g. liquid argon. A similar conclusion has been reported by Khan (41), who reported that the statistical mechanical themes cannot, as yet, be applied even to simple liquid mixtures and that even for pure simple liquids, the complex computations involved render the equations for viscosity unsuitable for engineering application.

5.2.2. Theory of Corresponding States:

Generally, the law of corresponding states expresses the generalisation that the properties dependent on intermolecular forces are related to the critical properties in a similar way for all compounds (7).

The derivation of the theory of corresponding states for the transport properties starts from the time-correlation function equation for viscosity of pure fluids (42):

$$\mu = \frac{1}{VkT} \int_0^\infty \langle J^{xy}(o)\, J^{xy}(\tau) \rangle d\tau \qquad 5.8$$

where

$$J^{xy} = \sum_{i=1}^{N} \left(\frac{P_{ix} P_{iy}}{M} - \frac{1}{2} \sum_{j \neq 1}^{N} r_{ij}^{y} \frac{d\phi}{dr_{ij}^{x}} \right) \qquad 5.9$$

where

P_{ix} = momentum of molecule i in x - direction

τ = time coordinate

$\int_0^\infty \langle J^{xy}(o)\, J^{xy}(\tau) \rangle d\tau$ = time correlation function, and measures the extent to which the value of a dynamical variable at a given time is affected by its value at an earlier time, and is therefore a function of time.

$\langle\ \rangle$ = angular brackets indicate averaging over an equilibrium ensemble.

The main assumption in the theory of corresponding states is that the intermolecular potential energy is of the form:

$$U = f\,(r_{R1}, r_{R2}, \ldots\ldots r_{RN}) \qquad 5.10$$

where

U = intermolecular potential

r_R = $r\,i/\sigma$

σ = molecular parameters with dimensions of distance

f = a universal function for all fluids considered.

Equation 5.10 implies that the total potential energy may be characterised by two parameters only, and that it is independent of molecular orientations. It is also assumed that intramolecular energy and quantum effects can be neglected.

Using the time correlation function formula for viscosity, i.e. equation 5.8, and writing all terms in dimensionless form, the resulting equation for viscosity is (42, 43)

$$\mu_R = \mu_R\,(T_R, V_R) \qquad 5.11$$

where

$$\mu_R = \frac{\mu\sigma^2}{(M\varepsilon)^{1/2}} \qquad 5.12$$

$$T_R = \frac{kT}{\varepsilon} \qquad 5.13$$

$$V_R = \frac{V}{N\sigma^3} \qquad 5.14$$

N = number of molecules

ε = molecular parameter with dimensions of energy

M = molecular mass

k = Boltzmann constant

This simple formula (equation 5.11) is known as the corresponding states principle for viscosity. Khan (43) reported that it is applicable for the heavy noble gases in all fluid states. However, deviations are obtained even for simple polyatomic fluids like O_2, CH_4 in the liquid state.

For practical use, it is extremely difficult to accurately predict the characteristic molecular parameters ε and σ. Since the critical point is a corresponding point at which the temperature, pressure and volume must assume fixed reduced values, the critical point properties are often used for scale factors (56). The reduced variables formed using the critical properties are:

$$V_r = \frac{V}{V_c} \qquad 5.15$$

$$T_r = \frac{T}{T_c} \qquad 5.16$$

$$P_r = \frac{P}{P_c} \qquad 5.17$$

The equation of state with the reduced variables in terms of the compressibility factor, Z, is thus:

$$Z = f\left(\frac{T}{T_c}, \frac{P}{P_c}\right) = f(T_r, P_r) \qquad 5.18$$

leading to the following formulation of the corresponding states principle for viscosity (42):

$$\mu \xi = f(T_r, P_r) \qquad 5.19$$

with

$$\xi = \frac{(T_c R)^{1/6} N_L^{1/3}}{M^{1/2} P_c^{2/3}} \qquad 5.20$$

where

T_c, P_c, V_c = the critical temperature, pressure and volume, respectively.

T_r, P_r, V_r = the reduced temperature, pressure and volume, respectively.

M = the molecular weight

N_L = Loschmidt - constant

It was reported that this expression is capable of predicting gas viscosities with an error of about 6%, except for those gases with strong dipole moments (42).

For mixtures of defined composition Kay's mixing rules are usually used (57).

$$T_c' = \sum_i x_i T_{ci} \qquad 5.21$$

$$P_c' = \sum_i x_i P_{ci} \qquad 5.22$$

$$V_c' = \sum_i x_i V_{ci} \qquad 5.23$$

where,

T_c', P_c' and V_c' = the critical temperature, pressure and volume of the mixture

T_{ci}, P_{ci} and V_{ci} = the critical temperature, pressure and volume of the components

x_i = mole, volume or weight fraction of component i

However, several correlations for extensions of the law of corresponding states have been proposed. Jossi et al.(ref.58) proposed a correlation in which the viscosity, μ, is related to a fourth degree polynomial of the reduced density, $\rho_r = \rho/\rho_c$:

$$[(\mu - \mu^*) \zeta + 10^{-4}]^{1/4} = a_1 + a_2 \cdot \rho_r + a_3 \rho_r^2 + a_4 \rho_r^3 + a_5 \rho_r^4 \qquad 5.24$$

where

a_1 = 0.10230

a_2 = 0.023364

a_3 = 0.058533

a_4 = -0.040758

a_5 = 0.0093324

ρ_r = reduced density

ρ_c = critical density

μ^* - is the low pressure gas mixture viscosity

$$\zeta = \frac{\left[\sum_{i=1}^{n}(X_i \cdot T_{ci})\right]^{1/6}}{\left[\sum_{i=1}^{n}(X_i \cdot M_i)\right]^{1/2}\left[\sum_{i=1}^{n}(X_i \cdot P_{ci})\right]^{2/3}} \qquad 5.25$$

n = is the number of components in the mixture

M_i = molecular weight of component i

For pure components, ρ_c is well defined and can easily be calculated, but Jossi did not elucidate which ρ_c to use for a complex hydrocarbon mixture.

Lohrenz et. al.(ref. 60) proposed a method to calculate the critical density of a complex mixture of hydrocarbons, which is a petroleum fluid, as follows:

$$\rho_c = \frac{1}{V_c} = \frac{1}{\sum_{\substack{i=1 \\ i \neq C_{7+}}}^{n}(x_i V_{ci}) + x_{c7+} \cdot V_{c7+}} \qquad 5.26$$

where the critical molar volume (ft^3/lb mole) of the C_{7+} fraction is found from the expression:

$$Vc_{C7+} = 21.573 + 0.015122\, M_{C7+} - 27.656\, SG_{C7+} + 0.070615\, M_{C7+} \, . \, SG_{C7+} \qquad 5.27$$

where,

SG = specific gravity

M = molecular weight

x = mole fraction

Ely and Hanley (53) have proposed a corresponding states model for prediction of viscosities. They started from the assumption that a group of substances obey the corresponding states principle if the functional dependence of μ_r on ρ_r and T_r shown in equation 5.28, is similar for all substances within the group.

$$\mu_r(\rho, T) = f\,(\rho_r, T_r) \qquad 5.28$$

Therefore, comprehensive viscosity data are needed only for one conformable component of the group. That component is then used as reference substance (o), and the viscosity of another component (x) within the group can be calculated as follows:

$$\mu_x(\rho, T) = \left(\frac{T_{cx}}{T_{co}}\right)^{1/2} \cdot \left(\frac{V_{cx}}{V_{co}}\right)^{-2/3} \cdot \left(\frac{M_x}{M_o}\right)^{1/2} \cdot \mu_o\left[\frac{\rho \cdot \rho_{co}}{\rho_{cx}}, \frac{T \cdot T_{co}}{T_{cx}}\right] \qquad 5.29$$

Ely and Hanley introduced two new terms, the shape factors θ and ϕ, which are functions of the reduced volume, V_r and reduced temperature, T_r and enter equation 5.29 as follows:

$$\mu_x(\rho, T) = \left(\frac{\theta T_{cx}}{T_{co}}\right)^{1/2} \cdot \left(\frac{\phi V_{cx}}{V_{co}}\right)^{-2/3} \cdot \left(\frac{M_x}{M_o}\right)^{1/2} \cdot$$

$$\mu_o\left[\frac{\rho_x \cdot \rho_{co} \cdot \phi}{\rho_{cx}}, \frac{T \,.\, T_{co}}{T_{cx} \,.\, \theta}\right] \qquad 5.30$$

where,

T_{co}, V_{co}, ρ_{co}, M_o, μ_o are the critical temperature, critical volume, critical density, molecular weight and viscosity of the reference substance.

The determination of θ and ϕ involve an interactive procedure. Ely and Hanley used methane as a reference substance, and Baltatu (58) extended the correlation to cover petroleum fractions. He reported absolute average deviations of 5.7% and 6.0% for pure hydrocarbons and some crude oils, respectively.

Tham and Gubbins (59) proposed an equation for the viscosity of liquids, similar to equation 5.29 with a rotational coupling coefficient, α_{TG}.

$$\eta_x(P, T) = \left(\frac{T_{cx}}{T_{co}}\right)^{-1/6} \cdot \left(\frac{P_{cx}}{P_{co}}\right)^{2/3} \cdot \left(\frac{M_x}{M_o}\right)^{1/2} \frac{\alpha_{TG,x}}{\alpha_{TG,o}}$$

$$\cdot\, \eta_o\left[\frac{P \,.\, P_{co}\, \alpha_{TG,o}}{P_{cx}\, \alpha_{TG,x}}, \frac{T \,.\, T_{co}\, \alpha_{TG,o}}{T_{cx}\, \alpha_{TG,x}}\right] \qquad 5.31$$

The coefficient α_{TG} is treated as an adjustable parameter, and for a number of pure fluids it is determined by fitting to experimental liquid viscosities.

Pedersen et. al. (60) also proposed a method to predict the viscosity of a hydrocarbon mixture at a given pressure P and temperature T, which is similar to Ely and Hanley's equation

$$n_{mix}(P, T) = \left(\frac{T_{C,mix}}{T_{Co}}\right)^{-1/6} \cdot \left(\frac{P_{C,mix}}{P_{Co}}\right)^{2/3} \cdot \left(\frac{M_{mix}}{M_o}\right)^{1/2} \frac{\alpha_{mix}}{\alpha_o}$$

$$x\, n_o \left[\frac{P \cdot P_{Co}\, \alpha_o}{P_{C,mix}\, \alpha_{mix}}, \frac{T \cdot T_{Co} \cdot \alpha_o}{P_{C,mix}\, \alpha_{mix}}\right] \qquad 5.32$$

where,

$$T_{C,mix} = \frac{\sum_i \sum_j x_i x_j \left[\left(\frac{T_{ci}}{P_{ci}}\right)^{1/3} + \left(\frac{T_{cj}}{P_{cj}}\right)^{1/3}\right]^3 \left[T_{ci}\, T_{cj}\right]^{1/2}}{\sum_i \sum_j x_i x_j \left[\left(\frac{T_{ci}}{P_{ci}}\right)^{1/3} + \left(\frac{T_{cj}}{P_{cj}}\right)^{1/3}\right]^3} \qquad 5.33$$

$$P_{C,mix} = \frac{8 \sum_i \sum_j x_i x_j \left[\left(\frac{T_{ci}}{P_{ci}}\right)^{1/3} + \left(\frac{T_{cj}}{P_{cj}}\right)^{1/3}\right]^3 \left[T_{ci}\, T_{cj}\right]^{1/2}}{\left(\sum_i \sum_j x_i x_j \left[\left(\frac{T_{ci}}{P_{ci}}\right)^{1/3} + \left(\frac{T_{cj}}{P_{cj}}\right)^{1/3}\right]^3\right)^2} \qquad 5.34$$

$$M_{mix} = \overline{M}_n + 0.291\,(\overline{M}_w - \overline{M}_n) \qquad 5.35$$

$$\overline{M}_n = \sum_i x_i M_i \qquad 5.36$$

$$\overline{M}_w = \frac{\sum_i x_i M_i^2}{\sum_i x_i M_i} \qquad 5.37$$

$$\alpha_{mix} = 1 + 7.747 \times 10^{-5}\, \rho_r^{4.265}\, M_{mix}^{0.8579} \qquad 5.38$$

$$\alpha_o = 1 + 8.374 \times 10^{-4}\, \rho_r^{4.265} \qquad 5.39$$

$$\rho_r = \frac{\rho_o \left(\dfrac{T \,.\, T_{co}}{T_{c,mix}} , \dfrac{P \,.\, P_{co}}{P_{c,mix}} \right)}{\rho_{Co}} \qquad 5.40$$

The reported deviations of the viscosity from experimental values were 3.9% - 6.5% for petroleum oils and 4.0% - 29.8% for some pure fluids.

In recent work, Hwang and Whiting (61) extended Ely and Hanley's viscosity model for the prediction of fluid viscosities to 90 substances including non polar, polar and hydrogen bonding chemical compounds.

In conclusion, although the corresponding states principle for prediction of the viscosity of liquids is gaining increased importance, its application to predict the viscosity of heavy hydrocarbon mixtures, e.g. heavy oils and bitumen, needs more investigation (41, 62).

5.2.3 Model Theories

The most important model theories based on the principle of momentum transport in liquids are:

A - The activated state theory (Eyring's Theory).
B - The free - volume theory (Hildebrand's Theory).
C - The combined model theory.

These theories do not provide a rigorous statistical description of the molecular transport and are highly simplified. However, such semi-theoretical approaches are very useful for predicting the viscosity of complex liquids.

A - Activated State Theory of Liquid Viscosity

Eyring et. al., (44, 45, 46, 47) developed an approximate theory which illustrates the mechanisms involved in the phenomena of liquid viscosity. They considered viscous flow as a chemical reaction in which the elementary process is the passage of a single molecule from one equilibrium position to another over a potential energy barrier.

Figure 5.1 representes a schematic diagram of the proposed mechanism for viscous flow. Eyring et. al. considered two layers of molecules in a liquid, at a distance λ, apart, when one layer slides past the other under the influence of an applied force. This results in successive passage of individual molecules from one equilibrium position to another as indicated in Figure 5.1. Such passage requires either a vacant hole or site to be available. The production of such a site requires the expenditure of energy to push-back other molecules. The movement of the molecule may be regarded as the passage of the system over a potential - energy barrier related to the so-called viscous flow activation energy (63).

Starting from the early equation which relates the absolute viscosity of a liquid to temperature,

$$\mu = A\,e^{B/T} \qquad 5.41$$

Eyring presented the following equation,

$$\mu = \frac{\lambda_1\, h}{\lambda_2\, \lambda_3\, \lambda^2}\; e^{\Delta F/R} \qquad 5.42$$

where,

μ = absolute viscosity

ΔF = the activation energy of viscous flow

R = gas constant

T = absolute temperature

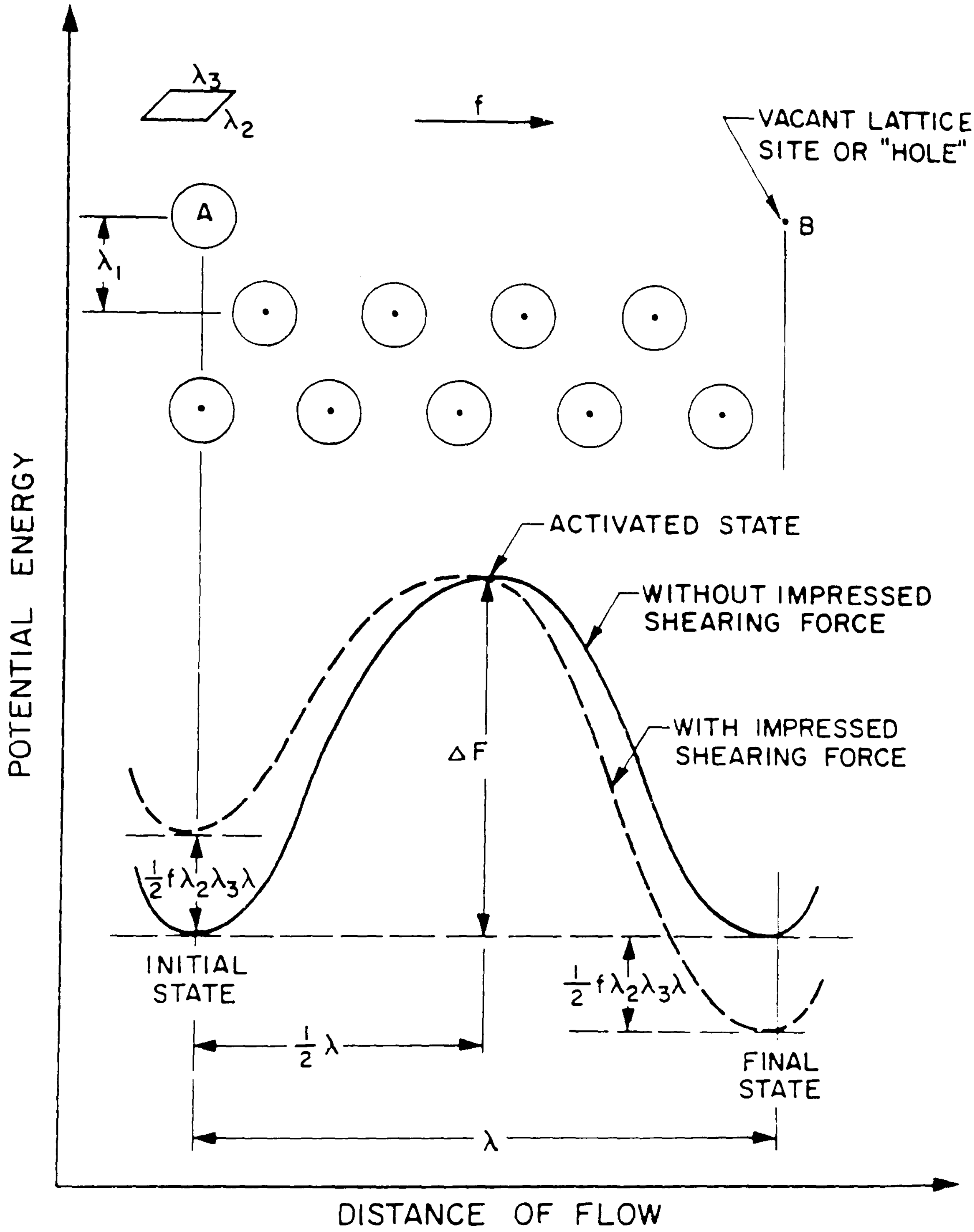


Figure 5.1 Schematic Diagram of the Fundamental Rate Process Involved in Viscous Flow for Liquids

and with reference to Figure 5.1,

λ = Distance between equilibrium position in the direction of flow.

λ_1 = Perpendicular distance between adjacent layers of molecules.

λ_2 = Distance between adjacent molecules in the direction of flow.

λ_3 = Distance between molecules in the plane of flow and normal to the direction of flow.

If λ is assumed equal to λ_1 and λ_1, λ_2, λ_3 are identified with the molecular volume of a single molecule in the liquid state, then:

$$\frac{\lambda_1}{\lambda_2 \lambda_3 \lambda^2} = \frac{N}{V} \qquad 5.43$$

where,

V = molar volume, cm^3/g-mole

N = Avogadro number

Thus, equation 5.42 becomes:

$$\mu = \frac{h\,N}{V}\, e^{\Delta F/RT} \qquad 5.44$$

or

$$\nu = \mu/\rho = \frac{h\,N}{M}\, e^{\Delta F/RT} \qquad 5.45$$

Therefore, equations 5.44 or 5.45 could be used to calculate the absolute, or kinematic, viscosity of a liquid from its molar volume and energy of activation. However, the latter is not easy to obtain for most liquids.

Eyring reported a relationship between the energy of activation of viscous flow (ΔF) and the internal energy of vaporisation (ΔE_{vap}) for many liquids,

$$\frac{\Delta E_{vap}}{\Delta F} = 2.45 \qquad 5.46$$

Substituting equation 5.46 in equation 5.44 results in,

$$\mu = \frac{h N}{V} e^{\Delta E_{vap}/2.45 RT} \qquad 5.47$$

Further simplification of equation 5.47 in terms of the normal boiling point of a liquid, T_b yields

$$= \frac{h N}{V} e^{3.8 T_b / T} \qquad 5.48$$

As a result, Eyring's theory can be considered as an approximate one. More details on the significance and application of this theory are presented in Section 9.3.

B - Free Volume Theory (Hildebrand's Theory)

Hildebrand (49) proposed a theory of liquid viscosity based upon Batschinski's proposal, which states that flow is proportional to the difference between the specific volume of the liquid, V, and a certain constant, ω, similar to the Van der Waals constant b. Batschinski's relationship was $n = C/(V-\omega)$, where C is another constant.

After examining the viscosity-molar volume relationship of many pure simple liquids, Hildebrand arrived at a similar conclusion and obtained the equation

$$\frac{1}{\mu} = \phi = \frac{B (V-V_o)}{V_o} \qquad 5.49$$

where,

ϕ = Fluidity of the liquid.

V = Specific or molar volume.

$B = V_0/C$ = A measure of the extent to which the external momentum, that produces viscous flow, is absorbed by the molecules of the liquid (43).

V_0 = The molar or specific volume of the liquid at which fluidity is zero (49). It is a fraction of the critical volume, defined as the volume at which molecules are so closely packed as to prevent viscous flow, but still retaine rotational freedom. At a volume $<V_0$, only plastic flow is possible (43). V_0 is known as the "limiting specific volume", which is constant.

C = Constant.

Hildebrand also reported that, for the simple and pure liquids he examined, the limiting specific volumes $\simeq \frac{V_c}{3}$.

He also reported that the relationship between fluidity ($1/\mu$) and molar volume of a liquid is linear.

The theory of viscosity based on the free-volume law has been investigated by numerous workers including Brule et. al. (64), Kottler (50) and Irving (51). However, Irving (51) reported that the derived equations have several disadvantages:

(i) They can only be applied when the specific volume of the liquid is known.

(ii) They require a knowledge of the constants of liquids which may not be easily obtained.

(iii) The free volume law of viscous flow holds only at temperatures above the freezing point.

(iv) They are restricted to pure, non-associated, liquids at atmospheric pressure.

The free-volume theory has also been extensively investigated by Khan et. al., (41). They reported that the Hildebrand fluidity molar volume relationship equation 5.49 did not provide a satisfactory fit for the viscosity of gas - free Athabasca bitumen. They concluded that it holds only for pure and simple structured liquids with no branching in the molecular structure and when no strong dipole moments exist in the liquid molecules. Therefore, they sought a new empirical equation for the viscosity of Athabasca bitumen. The following polynomial yielded the best results,

$$\ln\left(\frac{1}{\mu}\right) = B_o + B_1 \sinh \beta + B_2 \sinh^2 \beta + B_3 \sinh^3 \beta \qquad 5.50$$

where,

$$\beta = \frac{V - V_o}{V_o}$$

B_0 = -0.323709

B_1 = 103.750

B_2 = 219.723

B_3 = 15096.3

The reported absolute average deviation was 7.5%

C - Combined Model Theory (65)

Macedo and Litovitz (65) derived a hybrid equation for viscosity in which both mechanisms, the effect of activation energy and that of redistribution of the free volume, are assumed to be present simultaneously. Their equation is:

$$\mu = A\, e^{\left[\gamma\left(\frac{V_o}{V - V_o}\right) + \frac{E_o}{RT}\right]} \qquad 5.51$$

where

γ = Factor which takes into account overlap of free volume.

A, E_o, V_o are empirical parameters.

5.3 EMPIRICAL ESTIMATIONS AND CORRELATIONS FOR VISCOSITY

This section contains a summary of those methods which are, basically, empirical or semi-empirical in origin and correlate viscosity data in terms of molecular structures and in terms of different fluid properties.

Many equations are available in the literature to predict the viscosity as a function of temperature. The commonly accepted method of predicting viscosities of hydrocarbons is the modified ASTM D-341(66) method. This method was modified by Wright(67,68) to predict the viscosity of petroleum liquids.

$$\log \log Z = A - B \log T \qquad 5.52$$

where,

Z = $(v + 0.7 + C - D + E - F + G - H)$

log = logarithm to base 10

v = kinematic viscosity, cSt

T = temperature in degree Rankine

A&B = constants

C = $\exp(-1.14883 - 2.65868\, v)$

D = $\exp(-0.0038138 - 12.5645\, v)$

E = $\exp(5.46491 - 37.6289\, v)$

F = $\exp(13.0458 - 74.6851\, v)$

G = $\exp(37.4619 - 192.643\, v)$

H = $\exp(80.4945 - 400.468\, v)$

The terms C through H are exponentials on the natural base e, while the remainder of the equation is expressed in logarithms base 10. The limits of applicability are listed below:

$Z = (v + 0.7)$	2×10^7 to 2.00 cSt
$Z = (v + 0.7 + C)$	2×10^7 to 1.65 cSt
$Z = (v + 0.7 + C - D)$	2×10^7 to 0.90 cSt

$Z = (\nu + 0.7 + C\text{-}D + E)$	2×10^7 to 0.30 cSt
$Z = (\nu + 0.7 + C\text{-}D + E\text{-}F + G)$	2×10^7 to 0.24 cSt
$Z = (\nu + 0.7 + C\text{-}D + E\text{-}F + G\text{-}H)$	2×10^7 to 0.21 cSt

A hand-held calculator program is now available to replace the tedious graphical manipulation of this log equation(69).

Blok(70) reviewed the different approaches used to describe the viscosity-temperature-pressure relationship of lubricating oils in terms of empirical formulae, and their prediction from correlations based on properties that are easily accessible at atmospheric pressure. The aim was to study the effect of any increase or decrease, in viscosity of lubricating oils on the hydrodynamic load-carrying capacity of machine parts. An approach was proposed in which the viscosity-temperature-pressure relationship is first studied individually for "similar groups" of natural lubricating oils originating from a similar source and refined in a similar way. Data on Pennsylvania oils, as a typical "similar group", were used to examine several correlations. Block presented a formula first proposed by Skinner(71) to calculate the viscosity of liquids at high pressure.

$$\eta_{(P)} = [\,(1 + \varepsilon) \,.\, e^{AP} - \varepsilon\,] \,.\, \eta_a \qquad 5.53$$

where

$\eta_{(P)}$ = viscosity at the required pressure

$\eta_{(a)}$ = viscosity at atmospheric pressure

A and ε are constants

P = the required pressure.

It was proposed that viscosity could be a function of specific volume only. This implies that, given knowledge of the effects of temperature and pressure on density (equation of state), an equivalence could be established between their effects on viscosity.

Whilst this may serve as a reasonable approximation for simple liquids, lubricating oils and crude oils comprise complex mixtures of heterogeneous compounds.

Sanderson(72) presented a formula to calculate the kinematic viscosity ν.

$$\log \log [\nu_{(P)} + 0.6] = C.P^{1/2} + D \qquad 5.54$$

where

C and D are constants

P = pressure

$\nu_{(P)}$ = kinematic viscosity at required pressure

The left hand side of equation 5.54 essentially represents the ASTM viscosity scale(66).

Mehrotra and Svrcek(73) presented new data on the effect of temperature and pressure on the viscosity of Marguerite Lake bitumen in Canada. They observed that the viscosity of the dead bitumen decreased with an increase in temperature, but the reduction in viscosity was less steep in the high temperature region compared with at lower temperatures. Similar behaviour was observed for Athabasca bitumen(74). They also reported that the viscosity of CO_2-saturated bitumen reduced with an increase in pressure at all temperatures, due to the solubility of CO_2 in the bitumen which increased at high pressure and low temperature.

Khan et al(41) proposed two correlations for the viscosity of Athabasca bitumen as functions of temperature using the data of Jacobs et al(75), and Svrcek and Mehrotra(76), namely:

$$\text{Model (1): } \ln \ln (\mu_d) = e^{-a(1)T} [1 + a(1)T + a(2) \{a(1)T\}^2] \qquad 5.55$$

$$\text{Model (2): } \ln \ln (\mu_d) = A(1) \ln (T) + A(2) \qquad 5.56$$

where

μ_d = dead bitumen viscosity, m.Pa.s

T = absolute temperature, ^oK

a(1), a(2), A(1), A(2) = constants

Different forms of correlation were proposed based on the double logarithmic function to fit the same data.

$$\ln \ln (\mu_g) = b(1) [\ln \ln (\mu_d) + b(2) \frac{P}{T}]^{b(3)} \qquad 5.57$$

and the equation of Mehrotra and Svrcek (1982).

$$\log \log (\mu_g) = B(1) + B(2)\, t + B(3)\, P + B(4) \frac{P}{(273.16 + t)} \qquad 5.58$$

where

μ_g = live bitumen viscosity, m.Pa.s.

μ_d = dead bitumen viscosity at T, m.Pa.s.

T = temperature ^oK

t = temperature, ^oC

P = pressure, MPa

b(1) - b(3), B(1) - B(4) = constants

The average deviations obtained for Marguerita Lake bitumen when using equation 5.57 were 15.1% ($T \leq 40^oC$) and 7.4% ($T > 40^oC$). For Athabasca bitumen, the average deviations were 7.4% ($T \leq 40^oC$) and 4.2% ($T > 40^oC$). Equation 5.58 by comparison gave average deviations of 8.4% and 6.5% for Marguerita Lake bitumen and Athabasca bitumen respectively.

Mehrotra and Svrcek(77), subsequently, presented new data for the effect of pressure and temperature on a gas-free Athabasca bitumen viscosity covering a temperature range of 43-120°C and pressure up to 10 MPa. The compression of bitumen was found to result in a significant increase in viscosity but only a small increase in density. Two correlations were developed that include the effect of pressure and temperature on the viscosity of the bitumen.

Model (1): $\ln(\mu) = \exp . [a_1 + a_2 \ln T] + a_3 P$ 5.59

Model (2): $\ln \ln(\mu) = [a_1 + a_2 \ln T] + a_3 P$ 5.60

where μ is in (M Pa.S.), T is in (°K), and pressure P is in M Pa.

The average absolute deviation with model 2 was 1.8% compared to 2.8% with model 1. An increase in pressure to 10 MPa resulted in a 49% increase in the bitumen viscosity at 43°C compared with a 33% increase at 120°C. Thus the effect of pressure was more significant at lower temperatures, at which the viscosity of the bitumen was high. Graphical representation of the increase of viscosity with pressure demonstrated a non-linear relationship, but a linear relationship with ln μ over the whole range of temperature.

Kouzel(78) presented an equation to calculate the effect of pressure on the viscosity of high-molecular weight hydrocarbons.

$$\log \frac{\mu}{\mu_o} = \frac{P}{1000} [0.0239 + 0.01638 \, \mu_o^{0.278}] \qquad 5.61$$

where,

μ = viscosity at T and p, in cP

μ_o = viscosity at T and 1 atm, in cP

P = pressure, in psi

This equation has been adopted by the American Petroleum Institute(18). The deviations between calculated and experimental viscosities of high molecular weight hydrocarbons were reported as approximately 5% for pressure <5000 psi and approximately 8% for pressures up to 10000 psi.

Recently, Ahrabi et al(79) measured the viscosities of a crude oil and natural gas liquid (NGL), from a North Sea Oil reservoir, within a temperature range of 303°K to 375°K and pressure range of 1 bar to 445 bar. Measured viscosities for NGL increased with a decrease in pressure, while in the case of liquid phase crude oil, the viscosity increased with an increase in pressure, with a pronounced break at the bubble point at all temperatures. The method of Lohrenz et al was applied for the prediction of the liquid phase viscosities, for which purpose the molar volumes were calculated from the various equations of state. The agreement between calculated and experimental results was generally rather poor. The Lohrenz method together with the Soave-Redlich-Kwong (SRK) equation of state gave the best results for NGL (average absolute deviation from all experimental points of 20%), but the viscosities were all underestimated. The predictive method for crude oil yielded even poorer results, but it was apparent that the method was extremely sensitive to the equation of state. The Zudkevitch-Joffe-Redlich-Kwong (ZJRK) equation of state/Cavett correlations gave the best results, the average absolute deviation being 34%. The predictions were all consistently low, but the variation with pressure was of the correct order. Because of this poor performance, this method may only be applied to crude oils with considerable caution.

Ahrabi et al also reported that the viscosity of the North Sea crude oil decreased with an increase in pressure until about 65 bar; it then increased linearly with increase in pressure at 4 different temperatures. This behaviour is unusual, since the log (viscosity) of liquids generally exhibits a linear relationship with pressure.

5.4 VISCOSITY OF MIXTURES

The shape of a viscosity-composition curve at a fixed temperature and pressure is widely used to determine whether a homogeneous liquid mixture is ideal or non-ideal. This criterion is then used in the prediction of the viscosity of mixtures. The shape of this curve depends strongly upon the liquids comprising the mixture. Usually, so-called ideal mixtures exhibit an approximately linear shape, whereas non-ideal mixtures are non-linear and may exhibit a maximum or a minimum and sometimes both. Thus the viscosity of a binary liquid mixture can be greater, or smaller, than that of either of its components. The situation with multicomponent mixtures is even more complex.

An ideal mixture is commonly defined as one that undergoes no change of volume. In the case of viscosity, an ideal mixture is, also defined as one that obeys the simple mixing rule equation.

$$\eta_{mix} = \Sigma x_i \eta_i \qquad 5.62$$

where

x_i is mole, volume or weight fraction

η_{mix} is the viscosity of the mixture

η_i is the viscosity of components.

Hence, the deviation from equation 5.62 is considered as the degree of non-ideality of the mixture. Numerous equations have therefore been proposed to describe the behaviour of liquid mixture viscosity when it departs from ideality. Introduction of empirical constants is commonly used to compensate for the deviations from ideality. Although, numerous hydrocarbons have been used to develop the proposed equations, no one equation is claimed to be of general application. Some equations were constructed to predict the viscosity of pure hydrocarbon mixtures (defined mixtures), where pure hydrocarbons were used to develop the equations themselves(80-86). Their application is therefore limited to the pure hydrocarbons. Conversely, equations constructed for petroleum mixtures (undefined mixtures) have limited application to petroleum mixtures(87-91).

In terms of internal forces, viscosity may be considered a form of friction. Very few molecules are in such perfect equilibrium that no attractions would be active between them. These forces are chemical or physical by nature and cause an interference with motion and mobility of the molecules which is observable as viscosity. Deviations from ideality can be attributed to the interactions between the molecules of the components. Hence, a mixture of similar molecules will usually exhibit less non-ideality.

The earliest equation proposed to predict the viscosity of binary mixtures was the Arrhenius equation,

$$\ln \eta = V_1 \ln \eta_1 + V_2 \ln \eta_2 \qquad 5.63$$

This equation is in many cases inadequate and many modifications have been proposed.

Kendall and Monroe(80) examined the viscosity - composition curves of the binary liquid systems: benzene-benzylbenzoate, benzene-ethylbenzoate, toluene-ethylbenzoate, toluene-benzylbenzoate, benzene-naphthalene, benzene-diphenyl, toluene-naphthalene, and toluene-diphenyl. Although the viscosity curves for these binary systems were slightly concave upwards and not straight lines, especially those for the system benzene-benzylbenzoate, Kendall and Monroe considered them as ideal mixtures, with the assumption that no change in volume would occur in mixing the two components in the liquid state. Following examination of several equations to predict the viscosity of these binary mixtures, they proposed the well-known "cube-root equation".

$$\eta^{1/3} = x_1 \eta_1^{1/3} + (1-x_1) \eta_2^{1/3} \qquad 5.64$$

The experimental data were used to test the proposed equation and very good accuracy was obtained with a maximum % deviation of 2.5. API(18) recommended Kendall and Monroe's equation for pure hydrocarbons only.

Kendall and Wright(81) subsequently examined the viscosity curves for the liquid-liquid systems: ethyl ether-phenetol, ethyl ether-diphenyl ether, phenetol-diphenyl ether, ethyl acetate-enthylbenzoate, ethyl acetate-benzylbenzoate, and ethyl benzoatebenzylbenzoate. Although these mixtures were reported to be very nearly ideal, the experimental data were not correlated satisfactorily by any simple formula. The logarithmic viscosity equation of Arrhenius gave values uniformly a little low (1-18%), and the cube root viscosity equation of Kendall and Monroe gave values uniformly a little high (2-25%). All other proposed formulae failed to correlate the experimental data. The logarithmic viscosity equation and cube root equation gave average deviations of 68% and 17.6% respectively, and maximum deviations of 10.6% and 26.0% respectively, when used for diethyl ether-diphenyl ether binary mixtures.

Kottler(50) proposed a new equation based on the theory of free-volume for binary mixtures of pure hydrocarbons.

$$\varphi = \frac{1}{MC} \left(x_1 \varphi_1 M_1 C_1 + x_2 \varphi_2 M_2 C_2 + M \Delta V \right) \qquad 5.65$$

It was assumed that limiting specific volumes are additive and that the logarithms of the specific moduli of viscosity are additive. $M = x_1 M_1 + x_1 M_2$ and C is defined by

$$\ln MC = x_1 \ln M_1 C_1 + x_2 \ln M_2 C_2 + x_1 x_2 \ln MC_{12} \qquad 5.66$$

The conditions for ideality are that both ΔV and $\ln MC_{12}$ are zero. These conditions correspond to a plot of fluidity against mole fraction which curves below a straight line relation.

Irany(92,93) reported that paraffinic hydrocarbons constitute the best choice for substances to form ideal mixtures and may be accepted as standards. A new scale was proposed for the viscosity-composition curves, where any single standard curve was plotted not in absolute viscosity units, but on a scale which compensates for the curvature in such a manner that a straight line results. Hence, there is a general function of viscosity which is additive in ideal mixtures. Irany stated that, on a diagram in which the scale of viscosity is adjusted to make any one ideal mixture appear as a straight line, all other ideal mixtures also appear as straight lines. Consequently, any deviations from those straight lines should be attributed to the non-ideality of the mixture.

Grunberg and Nissan(94,95) proposed a modification of the Arrhenius equation to predict the viscosity of liquid binary mixtures,

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + 2x_1 x_2 G \qquad 5.67$$

with x defined as mole fraction.

Irving(51) tested this equation and reported that, for binary liquid mixtures, it is the best descriptive equation, which is comparatively simple but has the widest applicability. The equation requires a knowledge of the parent liquid viscosities, η_1 and η_2, and the value of the empirical parameter G. The units of concentration depend upon the type of liquids comprising the mixture. Irving, also, reported that no method was found for predicting the parameter G, which varies smoothly with temperature for a given mixture.

The commonly accepted method for predicting the kinematic viscosities of hydrocarbons is the modified ASTM D-341 method(66), originally, proposed by Wright(67). This method uses the ASTM special charts, where the procedure is to plot the viscosity-temperature lines of the oils, and then to blend by linear proportioning along the log T axis. Wright, also developed a mathematical relationship based upon these charts to predict the viscosity of petroleum liquids on blending, using values of the kinematic viscosities at 40°C and 100°C for both components. API(18) recommended the ASTM-D341 method for mixtures of petroleum liquids.

The REFUTAS viscosity blending function, proposed by British Petroleum(96), has been widely used to predict the viscosity of petroleum products mixtures. This method was developed to predict blend viscosities of all petroleum components from gasoline to vacuum residue. The REFUTAS function, or blending index, is given by the following equation:

$$I = f(v) = 23.097 + 33.468 \log \log (v+0.8) \qquad 5.68$$

where I is the REFUTAS index and v is the kinematic viscosity.

To determine the viscosity of a mixture by this method, the REFUTAS index of each component is determined based upon known viscosities. The REFUTAS index of the mixture is then calculated, based on the weight fraction of each component:

$$I_{\beta} = \sum_{i}^{n} I_i W_i \qquad 5.69$$

where I_{β} is the REFUTAS index of the mixture and W_i is the weight fraction of component i. The viscosity of the mixture is then read directly from a corresponding table or deduced from equation 5.68.

In conclusion, the behaviour of liquid viscosity upon blending differs from one liquid to another. However, there is no general theoretical method that describes the mechanism of the changes that occur during blending, from the molecular point of view, particularly for complex liquids such as the petroleum oils which are considered as undefined mixtures.

CHAPTER 6

POUR POINT

6.1 INTRODUCTION

The pour point is one of the main indications of flow properties and low temperature characteristics of crude oils and petroleum products. It is particularly relevant to areas where cold weather is experienced, e.g. in Europe, where the refineries are generally supplied with crude oils having a low sulphur content, but which tend to be waxy and yield products of high pour point. In this context, 'cold' would apply to ambient temperatures in the range approximately 20°C to -20°C depending upon the specific crude or product.

The pour point of an oil is defined as the lowest temperature at which the oil will pour, or flow, when it is chilled without disturbance under specified conditions. The pour points of petroleum oils are measured by the standard ASTM-D79 (66) and IP-15 (16) methods.

The pour point indicates the lowest temperature at which an oil can be stored and still flow under very low applied forces, e.g. gravity. Therefore, in oil transportation or pumping, it is necessary to indicate the process conditions for which a high pour point oil is permissible given heated storage and piping.

6.2 LITERATURE SURVEY

6.2.1 Physics of Pour Point

Under low temperature conditions, the paraffin contents of an oil or fuel tend to precipitate and coagulate as a wax. The temperature at which precipitation occurs depends upon the origin, type and boiling range of the fuel (97, 98, 99, 100, 101). The higher the paraffin content of the oil or the fuel, the higher the precipitation temperature,and the less suitable it is for low-temperature operation. Thus, pour point or freezing point are relative measures of the wax content in an oil or fuel.

Any oil subjected to low temperature may undergo changes in its physical properties due to (102):

1. Solidification due to high viscosity of the bulk (e.g. > 2000 cSt @ 20°C). This phenomenon is not associated with wax precipitation. It is common with high molecular weight / viscous mineral oils, and bright stock base oils.
2. Solidification due to wax precipitation. This may include either complete solidification by forming a total network of crystalline wax, or partial formation of a network of wax which tends to cage the hydrocarbon matrix, and hence hinders its motion, rendering the liquid completely immobile (103). Most of the petroleum products are of these two families.

Pour Point Reversion

Some oils exhibit an increase in pour point if stored for long periods (depending upon the nature of the oil and the storage conditions) at a temperature near to that of their freezing or pour point, or when they are subjected to cyclic temperature variations during storage (104). These pour point temperature elevations may be of the order of 20°C to 30°C (102). This phenomenon is referred to as "Pour Point Reversion". An oil which has been sufficiently dewaxed has a more stable pour point, i.e. it will vary very little with storage conditions. Schilling (102) reported that the phenomenon varies with the type of solid phase, i.e. wax crystals, present in the oil, its concentration, and the thermal history of the oil. It was considered difficult to provide a complete explanation of the phenomenon as the composition of the solid phase is too variable, in that it may be composed of macrocrystals, microcrystals or both.

6.2.2. Predictive Correlations for Pour Point

The fact that pour point is a measure of a physical change which occurs in the liquid at low temperature, i.e. the separation of wax crystals, and its relation to other properties such as paraffins content, boiling point and viscosity, have been used to develop correlations to predict the pour point of petroleum products. Most attention has been directed to the middle distillates, fuel oils and lubricating oils.

Nelson (99) developed a method for estimating the pour points of jet fuels, diesel or distillate fuels and lubricating oils, as a function of the mid boiling point and the characterisation factor (Section 2.1.2) using Figure 6.1. However, the accuracy of this method was variable with deviations in the following ranges:

	Average Deviation
jet fuels	± 20°F
diesel or distillate fuels	± 10°F
lubricating oils	± 25°F

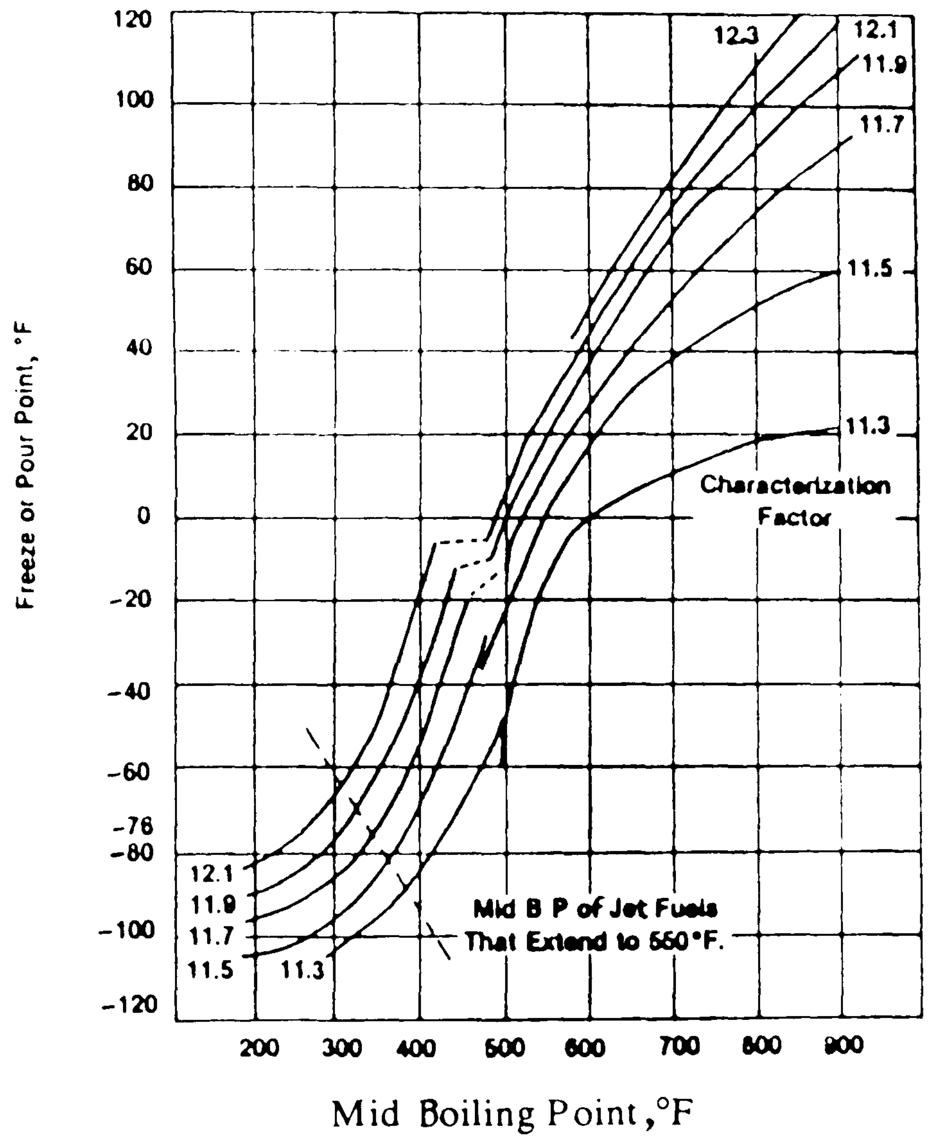


Figure 6.1: Nelson Pour Point Correlation

Nelson and O'Donnell (105) proposed a second method of predicting the pour points of wide-boiling fractions. This was based on the observation that the pour points of wide-boiling (> 60°F) fractions, when plotted against the 65% temperatures (TBP) of the fractions, constitute a substantially smooth curve regardless of the widths of the fractions. This method is shown in Figure 6.2. It is also applicable to the estimation of narrow fractions' pour point using mid % points (50% temperatures). Nelson and O'Donnell considered this method very convenient for predicting pour points, but did not report the limits of accuracy.

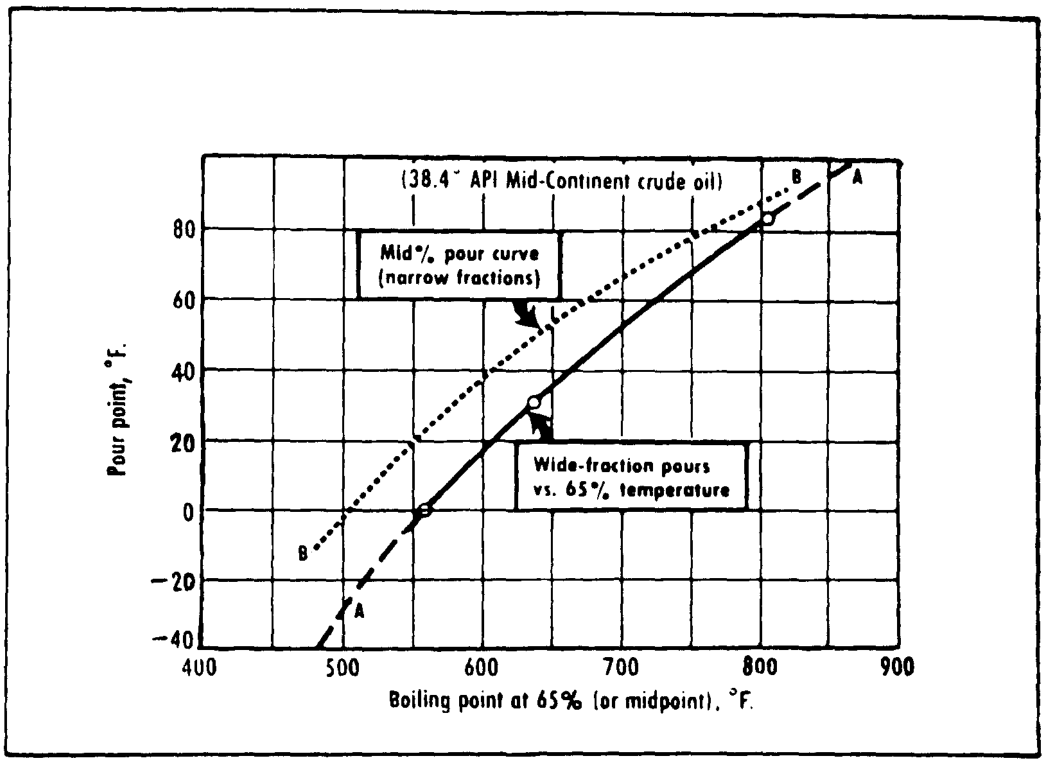


Figure 6.2: Nelson and O'Donnell Method of Pour Point Correlation

Clandy et al (103) presented a method to estimate the pour points of diesel fuels using a differential scanning calorimetry (d.s.c.) technique to determine the amount of crystallised paraffins and the temperature at which crystals appear, T_c, in a diesel fuel containing no additive and submitted to slow cooling (0.5°C/min). They proposed the following correlation:

$$T_c = 1.0696\ T_p - 0.0415 \qquad 6.1$$

where:

T_c = crystallisation temperature, °C.

T_p = pour point.

Reproducibility was stated to be < 3°C.

Recently, Riazi and Daubert (106) developed a correlation for prediction of pour points of undefined petroleum fractions. Based on experimental data for pour points of more than 300 fractions, the following equation was determined:

$$T_p = 234.85 \times S^{2.970566} \times M^{(0.61235 - 0.473575\ S)} \times V_{100}^{(0.310331\ -\ 0.32834\ S)} \qquad 6.2$$

where,

T_p = pour point of petroleum fraction, °R

v_{100} = kinematic viscosity at 100°F, cSt

S = specific gravity, 60/60°F

M = molecular weight

This equation was reported to be applicable to fractions with molecular weights ranging from 140 to 800. The reported average absolute deviation was 7.0% with a maximum deviation of 28%. Clearly therefore the exponents which imply an improbable degree of accuracy of measurement should have been rounded up, e.g. to result in:

$$T_p = 234.85 \times S^{2.971} \times M^{(0.612 - 0.474S)} \times v^{(0.310 - 0.328S)} \qquad 6.2a$$

6.2.3 Pour Point of Binary Mixtures of Petroleum Products:

It is frequently necessary in refinery operations, stock forcasting and crude oil blending to estimate the pour points of blended stocks from a knowledge of the pour points of the component stocks. However, unlike with viscosity, how this may be achieved has received little attention in the literature.

Pour and freezing points of petroleum oils do not blend linearly, and thus, for binary mixtures the pour point - composition curves are in general not straight lines. Most binary mixtures of petroleum oils exhibit a higher pour point than the ideal case (i.e. from a linear pour point - composition curve) (107). The blend composition and pour points of the components, alone, do not entirely define the blend curve. The problem of estimating pour points is thus one of predicting the shape of the curve. Therefore, blending indices or numbers are commonly used in oil blending calculations.

Reid and Allen (107) developed a method to calculate the pour points of mixtures of middle distillate fuels using blending indices. The blending number, or index, for each component of the blend stock is determined from special tables and a blending chart using the mid-boiling point and pour point of the stock. The blending index of the final blend is then calculated from the equation.

$$T_b = \sum V_i T_i \qquad 6.3$$

where,

T_b = blending index of final blend

T_i = blending index of component i

V_i = volume fraction of component i

The same tables are then used to back-calculate the pour point of the final blend from the blending index. Reid and Allen reported that in this way the pour point was predicted within ± 5°F (± 3°C) in over 90% of the cases.

Hu and Burns (108, 109) published a similar method based on the equation:

$$T_b^{1/X} = \sum_{i=1}^{n} V_i \, T_i^{1/X} \qquad 6.4$$

where,

T_b = pour point of the blend, °R

T_i = pour point of component i, °R

V_i = volume fraction of component i

x = constant

This equation is the general form to calculate the pour point of a blend (T_b) from the corresponding property of its components (T_i). The optimum values for the constant (x) were determined by trial and error. The index curve (Figure 6.3) relates pour point for components and blends to an appropriate index value. Using these curves, indices are obtained for the components. Component's indices were volumetrically averaged to calculate indices for the blends. Then the calculated blend indices are read back through the curve to estimate the pour point. On log-log paper, a family of straight lines was obtained with slopes equal to 1/x.

Hu and Burns reported that 94% of the predicted pour points were within ± 5°F of the experimental data.

They also reported that (108)

1. There was a correlation between the pour point of a blend and the concentration of the component with the highest pour point in the blend.
2. Components with the greatest effect on blend properties should form the basis for prediction.
3. The equation for a parabola would be a good starting point.

However, this method was tested only for distillate fuel blends and not for crude oil blends.

The advantage of this method is that it only requires a knowledge of the pour points of the componets of the blend, whereas the Reid-Allen method also requires the mid-boiling points of the components of the blend and of the final blend.

British Petroleum (96) devised a blending index for blending most middle distillate components. The index system needs slight modification to handle hydrocracked materials and rerun bottoms from the catalytic cracker. Two regression equations have been evaluated. One equation gives blending index from pour point and the other gives pour point from the index.

For blending index (=I) in terms of pour point °F (=T).

$$I = 22.499 + 25.445 \left(\frac{T}{100}\right) + 44.442 \left(\frac{T}{100}\right)^2 + 89.356 \left(\frac{T}{100}\right)^3 - 62.214 \left(\frac{T}{100}\right)^4 - 104.83 \left(\frac{T}{100}\right)^5 + 161.19 \left(\frac{T}{100}\right)^6 \qquad 6.5$$

for pour point °F (=T) in terms of index (=I).

$$T = 161.68 + 0.12464 \left(\frac{I}{100}\right) - 3307.2 \left(\frac{I}{100}\right)^2 + 4976.4 \left(\frac{I}{100}\right)^3 - 4170.9 \left(\frac{I}{100}\right)^4 + 1816.8 \left(\frac{I}{100}\right)^5 - 321.02 \left(\frac{I}{100}\right)^6 \qquad 6.6$$

The components indices are blended on a weight basis. The blending indices are given in a special table at 1.0°F intervals.

Clearly, very little attention has been devoted to either studying the effect of mixing on the pour point of petroleum oils in general, or proposing a probable mechanism, from a molecular point of view, to describe the behaviour of the pour point of blends. This would, also, facilitate the estimation of the pour points of different blends of petroleum oils.

Furthermore, the international trend, nowadays, is towards constructing highly flexible refineries which depend strongly on blending processes, for both feedstocks and straight run products, to produce various grades of gas oils, fuel oils and lubricating oils, of which the pour point is a property of essential marketing specifications that must be met. Therefore, a reliable mechanism of pour point behaviour under blending could contribute strongly to solving the problems that may arise due to blending processes, such as off specification products, and severe processing conditions.

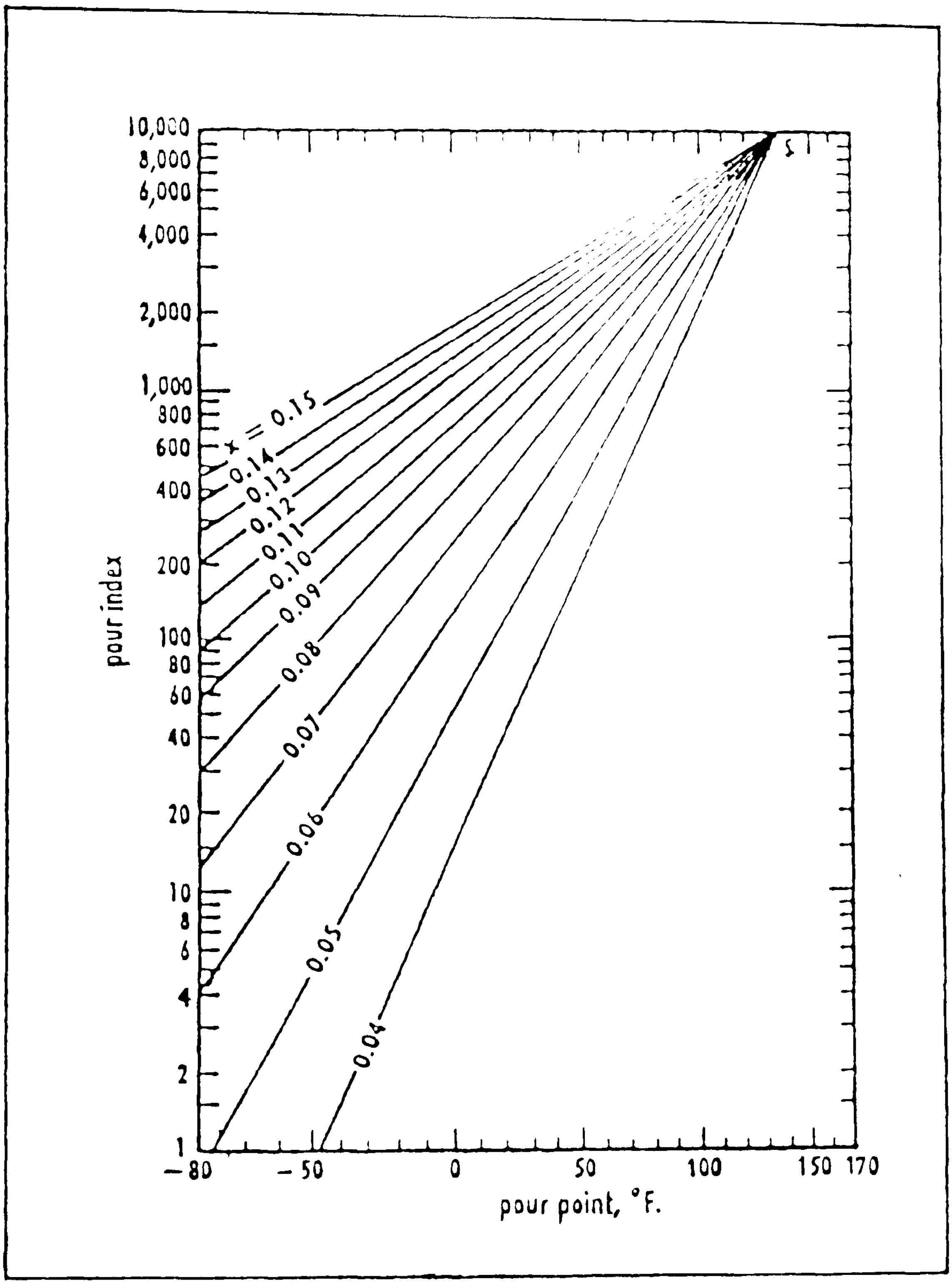


Figure 6.3: Pour Point Index Curves

CHAPTER 7

DISTILLATION AND VAPOUR PRESSURE CHARACTERISTICS OF CRUDE OILS AND PETROLEUM PRODUCTS

7.1 DISTILLATION

In any homologous series of hydrocarbons, the boiling point of each member increases with molecular weight (4). Structure also has a marked influence; generally, the branched paraffin isomers have lower boiling points than the corresponding normal alkane (Table 7.1).

Table 7.1: Boiling Points of Some Hydrocarbons

Hydrocarbon	Boiling Point °C	Boiling Point °F
n-Butane	-0.5	18
n-Pentane	36	97
n-Hexane	68	154
n-Heptane	98	208
n-Octane	126	259
2-Methylheptane	117	243
2, 4-Dimethylhexane	109	228
2, 2, 4-Trimethylpentane	99	210
n-Nonane	151	304
n-Decane	174	345
n-Pentadecane	271	520

The boiling points of petroleum fractions are not distinct temperatures. Hence, it is more correct to refer to the boiling ranges of the various fractions. In order to determine these ranges, the petroleum oil is tested by various standard methods of distillation - either at atmospheric pressure or at reduced pressure.

7.1.1 Definitions

Distillation is usually used to indicate the yield of straight run products from crude oils. The distillation curve may also be used to define the volatility characteristics of crudes, petroleum products and hydrocarbon mixtures. The most widely used laboratory distillation procedures are the true boiling point (TBP) method and the ASTM (American

Society for Testing and Materials) methods. Other common methods include the Hempel method used by the U.S. Bureau of Mines for crude oil, and the equilibrium or flash vaporisation method, which is used in the design of crude distillation units.

The TBP and ASTM distillations are of a batch type but differ from one another mainly in the degree of fractionation (2). The true boiling point distillation is carried out using a packed column at a relatively high reflux ratio, i.e. 5-10:1, to ensure a high degree of fractionation. The ASTM distillations are performed using an Engler flask without a packed section in most cases, so that the only reflux results from heat losses through the neck of the flask. The ASTM distillations are more widely used because they are simpler and less expensive to run, require less sample, and consume less time than the TBP distillation.

The ASTM distillation procedures currently in use are (2):

ASTM D86/IP 123 - Standard Method for Distillation of Petroleum Products.
ASTM D216/IP 191 - Standard Method for Distillation of Natural Gasoline.
ASTM D285 - Standard Method for Distillation of Crude Petroleum.
ASTM D1160 - Standard Method for Distillation of Petroleum Products at Reduced Pressures.

Of these, the D86 and D1160 methods are the most widely used.

The ASTM D86/IP 123 procedure is used for motor aviation gasolines, aviation turbine fuels, naphthas, kerosenes, gas oils, distillate fuel oils and similar products. It is carried out at atmospheric pressure, therefore at temperatures above 475°F (~ 245°C) thermal decomposition produces some discrepancy in the results.

The ASTM D216/IP 191 method is used for natural gasoline and is also performed at atmospheric pressure. The ASTM D285 method is similar to the D86 method except that it is for crude oils.

The ASTM D1160 method is used for characterising heavy petroleum oils which can be vaporised completely, or partially, at a maximum liquid temperature of 750°F (~ 400°C) at absolute pressures down to 1 mm Hg, and condensed as liquids at the pressure of the test. It is carried out at absolute pressures between 1 and 760 mm Hg, and the temperatures are measured with a thermocouple.

In these distillations there is no fractionation. Accordingly, the vapour temperature does not represent the true or actual boiling point of the liquid in question, because adjacent cuts from the ASTM distillation overlap considerably and contain many hydrocarbons in common (110). In contrast the TBP distillation is precise and separates individual compounds in order of increasing boiling point. There is, practically, very little overlapping of adjacent cuts.

In 1971, the first standard method for TBP distillation was published by the ASTM D2892 - Standard Method for Distillation of Crude Oil (15 - theoretical plate column). TBP distillations are usually performed in packed columns with 15 to 20 theoretical plates at a relatively high reflux ratio, e.g. 5 to 1 or greater. The high degree of fractionation in these distillations gives relatively accurate component distributions for mixtures. TBP distillations are carried out at atmospheric and reduced pressures.

The Hempel distillation of the U.S. Bureau of Mines (2) is considered semifractional distillation, in which a mild degree of fractionation is attained by the use of a section of packed column between the flask and the condenser.

Another method is the "flash vaporisation", in which the feed flows continuously into the unit. This method is usually used to obtain data for use in the design of crude distillation units.

Gas chromatographic methods have also been developed (111, 112) to obtain boiling point distribution data equivalent to that obtained by the TBP distillation procedure. Their advantage is that, whereas the time for analysis is similar to that for the conventional ASTM methods, the precision is better and the data obtained agree closely with TBP distillations. In 1973 the ASTM published a method for a gas chromatographic procedure applicable to all petroleum fractions with a final boiling point of 1000°F (538°C) or less (ASTM D2887 Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography). This method is limited to samples having a boiling range of at least 100°F (55°C).

In reporting distillation data for petroleum oils, the following convention is used,

Initial Boiling Point: This is the reading of the thermometer, or the thermocouple, in the neck of the distillation flask when the first drop of distillate leaves the tip of the condenser tube. In a TBP distillation apparatus, it is the overhead temperature read by the thermocouple, fitted in the reflux section of the fractionation column, when the first drop of the distillate appears.

Distillation Temperatures: These are, usually, the overhead temperatures (when the vapour/liquid equilibrium is maintained) at which each portion of distillate is cumulatively recovered (usually at 10% increments, with the temperatures for the 5% and 95% recovery often included as appropriate).

End Point or Maximum Temperature: This is the highest temperature observed during the distillation. In most cases, it is reached when all of the sample has been vaporised. If a liquid residue remains in the flask after the maximum permissible adjustments are made in heating rate and pressure, the fact is recorded as indicative of the presence of very high boiling compounds.

7.1.2 Distillation Curves

The distillation data obtained are used to construct the distillation curves, when the ASTM method is used, or TBP curves, which are very important characteristics and properties for petroleum liquids.

The distillation curves obtained from ASTM methods differ slightly from the TBP curves particularly with lower - boiling fractions, e.g. naphtha, gasoline and kerosene. These differences are (113):

1. The ASTM initial point is higher than the initial point shown by the TBP curve.
2. The ASTM curve crosses the TBP curve at some point in the middle range of the distillation.
3. The ASTM end point is usually lower than the TBP end point.

Conversion is possible between the ASTM and TBP distillation curves. Nelson (2), Geddes (114), Gandhir (115), Henderson (113), and Wilckens and Perez (116) have proposed a number of methods for computing the various distillation curves from each other. However, the most widely accepted method for interconverting ASTM D86 and atmospheric TBP distillation data was developed by Edmister et. al. (117, 118). When using this method to estimate the atmospheric distillation curve of a petroleum fraction from its ASTM D86 distillation curve, the ASTM D86 temperatures above 475°F (~245°C) must first be corrected for thermal cracking using the equation:

$$\log D = -1.587 + 0.00473\,T \qquad 7.1$$

The correction factor D (°F) should be added to the observed D86 temperature T (°F). Next, the atmospheric TBP 50% temperature is determined from the ASTM D86 50% temperature using a special chart. Finally, the temperature differences for each segment of the TBP curve are estimated from the temperature differences of the corresponding segments of the ASTM D86 curve using another special chart. To convert TBP data to ASTM D86 data, this procedure is simply reversed.

Edmister (118) also developed a procedure for inter converting ASTM D1160 and TBP distillation data. In this method the ASTM D1160 distillation temperatures at, and above, the 50% point are assumed to be equal. For points below the 50% point, a special chart is used to estimate the temperature difference for each segment of the TBP curve from the temperature difference from the corresponding segments of the ASTM D1160 curve.

A number of methods have been proposed to estimate crude oil TBP curves (113, 116). However, they do not generally offer a way to extrapolate the TBP data into the vacuum residue range. Nelson (2) proposed a technique to extrapolate TBP data by estimating the percentage distilled at 1100°F (593°C) using the equation:

$$Y = 100.0 - 3.0\ CCR \qquad 7.2$$

where

Y = cumulative yield at 1100°F, vol. %

CCR = Conradson carbon residue of crude oil, wt. %.

The most important feature of the distillation curves of petroleum liquids is the temperature of 50% recovery (sometimes referred to as Mean Average Boiling Point) which has been correlated with many other physical properties. The UOP or Watson characterisation factor, K , and the U.S. Bureau of Mines correlation index, CI discussed in Section 2.1.2 and represented in equation 2.1 and 2.2, are very good examples of utilising the 50% temperature.

Many correlations have, consequently, taken into account the characterisation factor and established either mathematical or graphical relationships with many other properties of petroleum products or crude oils, such as the chemical composition, molecular weight, critical temperature, pseudo critical pressure, viscosity, refractive index, aniline point, gross heat of combustion, latent heat of vaporisation, flash point and other such properties of oils (119 - 122). Figure 7.1 demonstrates how the characterisation factor and the mean average boiling point relate to several physical properties of petroleum fractions (18).

Alder and Hall (123) have also correlated the mean average boiling points of petroleum fractions with gross heat of combustion, molecular weight, hydrogen to carbon ratio, latent heat of vaporisation, API gravity and refractive index.

Riazi (124), Daubert (35), and Riazi and Daubert (26, 125) used the mean average boiling point, T_b, of petroleum products together with the specific gravity, S, in their equation (equation 4.6 in section 4.1) to estimate many other properties such as molecular weight, viscosity, critical volume, critical pressure, critical temperature and other thermophysical properties. The petroleum products used in developing this method were of average boiling points from 80 to 650°F.

7.1.3 Distillation Blending Values

The distillation blending behaviour of a component is affected by several factors which include:

1. Difference between the average boiling point temperature of the component and the distillation temperature of the blend that is of interest.
2. Boiling range of the component.
3. Hydrocarbon composition of the component.
4. Properties and composition of the blend in which the component appears.

Unzelman and Forster (110) stated that distillation characteristics of blends can be determined from respective distillation data for component stocks. They also reported that boiling points of fuels taken from a TBP curve are additive.

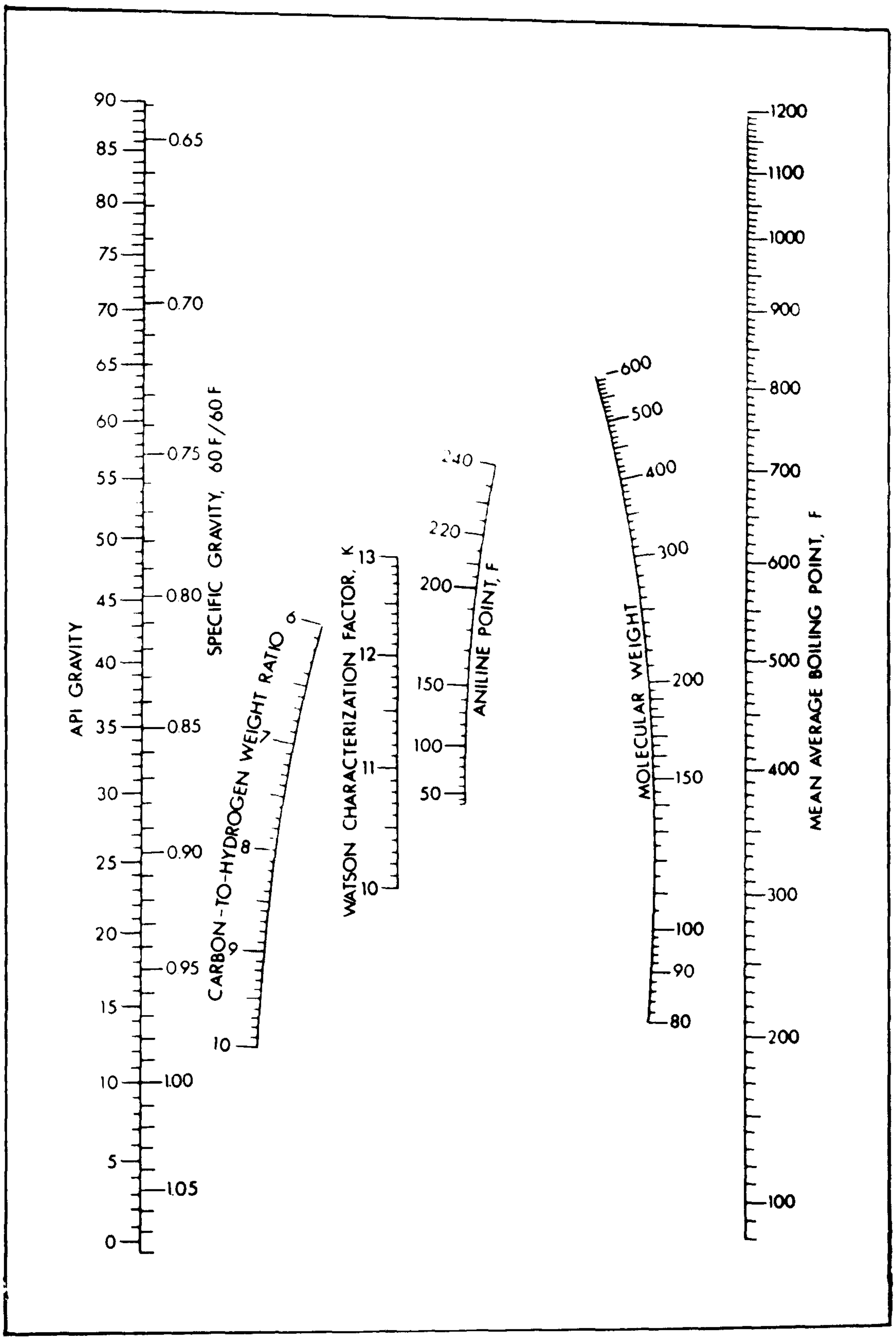


Figure 7.1: Watson Characterisation Factor and Other Physical Properties of Petroleum Fractions

This is not necessarily correct for ASTM curves, because ASTM distillations are non-fractionating and adjacent cuts overlap. However, a composite TBP curve is obtained by averaging the percent distilled at selected temperatures for the components according to their volume fractions in a blend.

Unzelman and Forster also reported that one convenient method of handling distillation calculations is by the use of blending numbers. This approach is applicable only to a component in a specific refinery arrangement, since the values change for different blending schemes. They have presented the distillation blending values for n-butane and isopentane, in a number of different light base stocks, on a special chart.

7.2 VAPOUR PRESSURE

7.2.1 Definitions

Vapour pressure is the pressure at which the vapour phase of a substance is in equilibrium with the liquid phase of that substance at a specified temperature (18). The composition of the vapour and liquid phases of a mixture of hydrocarbons influences this equilibrium pressure.

The Reid vapour pressure (RVP) test is a widely used a criterion for blending crudes, gasolines and other fuels. The RVP is the absolute pressure exerted by a mixture, in pounds per square inch, determined at 100°F and at a vapour - to - liquid volume ratio of 4. The apparatus and procedures are standardised, defined and specified in ASTM method D323. Details of this method are presented in Section 8.8.

Although the RVP provides a convenient approximation of the absolute vapour pressure of a partly vaporised sample at 100°F, it is not equivalent to the true vapour pressure. In general, true vapour pressures are higher than RVP's (110). Figures 7.2 and 7.3 (18) can be used to relate RVP and ASTM D86 boiling characteristics to true vapour pressure over a wide range of temperatures for crude oils and for gasoline and other finished petroleum products. At any temperature, extrapolation through the Reid vapour pressure gives the true vapour pressure.

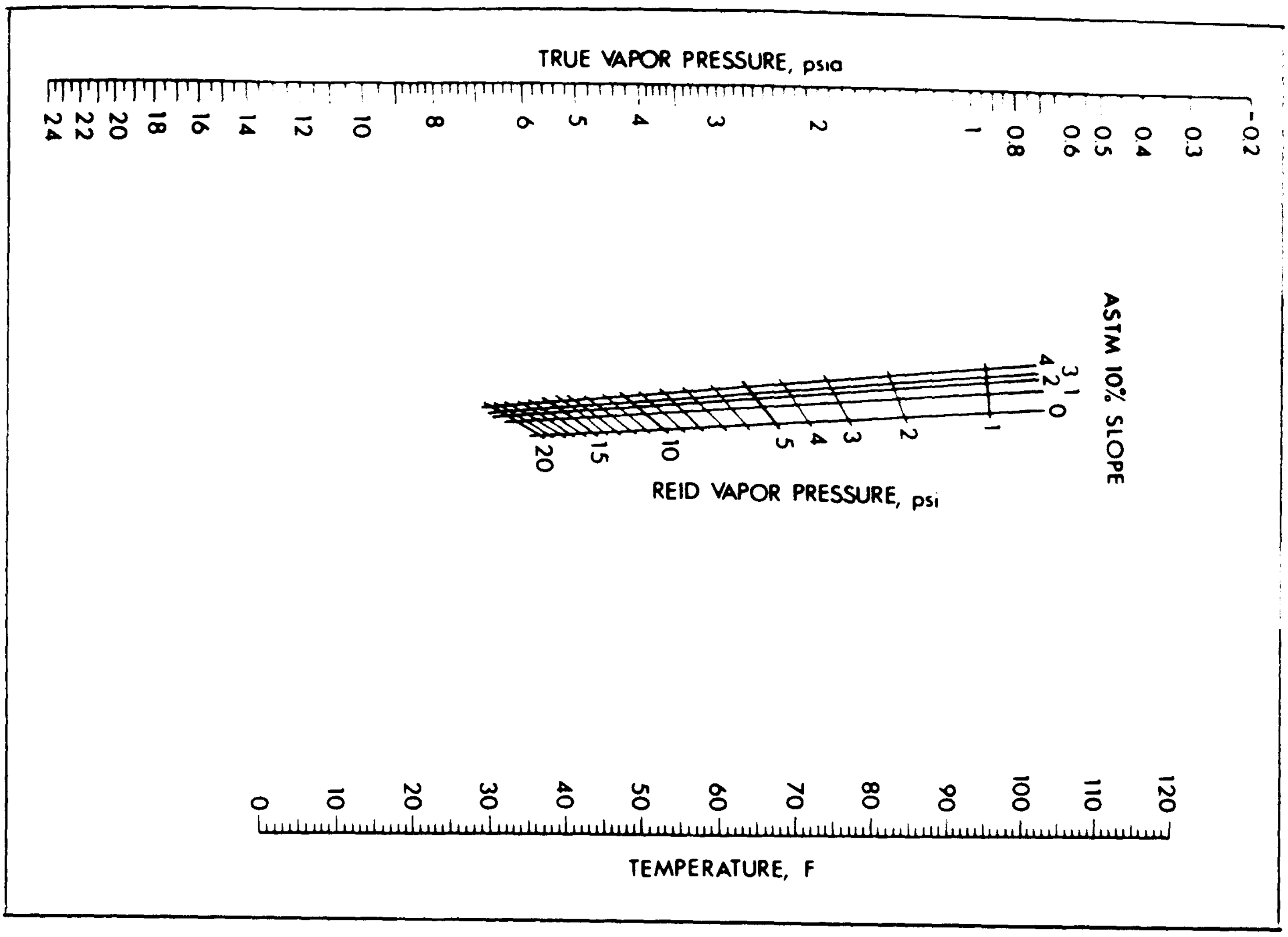


Figure 7.2: True Vapour Pressure and Reid Vapour Pressure of Gasolines and Finished Petroleum Products. (18)

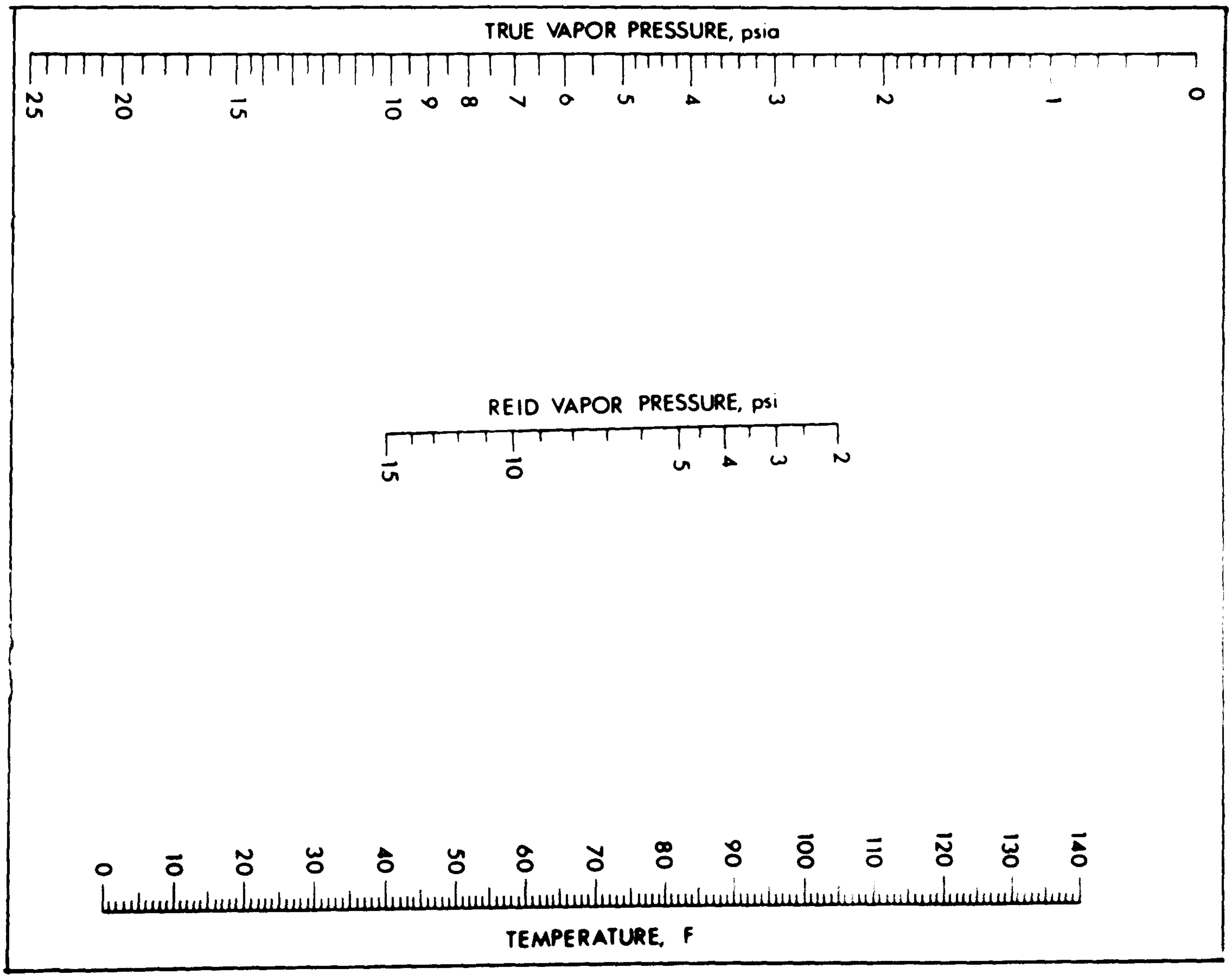


Figure 7.3: True Vapour Pressure and Reid Vapour Pressure of Crude Oils (18)

7.2.2 Predictive Correlations

There are a number of methods for estimating vapour pressures of pure hydrocarbons, narrow cut petroleum fractions, and simple mixtures of light hydrocarbons or condensates, such as the Maxwell-Bonnell correlations and charts (126). In this method, if the vapour pressure of the hydrocarbon or hydrocarbon mixture is known at one temperature, then the vapour pressure at any other temperature can be estimated using special charts or via the equation:

$$\log P = \sum_{i=o}^{6} A_i \, (x)^i \tag{7.3}$$

where,

$$X = \frac{(T_b'/T) - 0.0002867\,(T_b)}{748.1 - 0.2145\,(T_b)} \tag{7.4}$$

$$T_b = T_b' + 2.5\,(f)\,(K - 12.0)\,\log\left[\frac{P}{14.7}\right] \tag{7.5}$$

$$f = \frac{T_b - 659.7}{200.0} \tag{7.6}$$

P = Vapour pressure, psi

T_b' = boiling point corrected to K = 12, °R

T_b = normal boiling point, °R

T = temperature, °R

K = Watson characterisation factor

f = correction factor

A_o = 5.32159

A_1 = -4615.5003

$A_2 = 2.6174539 \times 10^6$

$A_3 = -1.6013485 \times 10^9$

$A_4 = 4.3264211 \times 10^{11}$

$A_5 = -5.257646 \times 10^{13}$

$A_6 = 2.2744129 \times 10^{15}$

Nelson (127) reported a method to estimate the Reid vapour pressure of gasoline from ASTM distillation temperatures of 5% and 20% volume recovery, using special charts for this purpose.

A set of equations for the calculation of the Reid vapour pressure of motor gasolines and aviation fuels from distillation data (ASTM D86) was published by Jenkins and White (128). These equations are:

$$\begin{aligned} R.V.P. = {} & 29.3 - 0.76\,(T_5) + 0.16\,(T_{10}) + 7.0\,(10^{-3})\,(T_5)^2 \\ & -2.46\,(10^{-5})\,(T_5)^3 - 1.3\,(10^{-3})\,(T_{10})^2 + 6.5\,(10^{-4})\,(T_{50})^2 \\ & -1.79\,(10^{-6})\,(T_{50})^3 - 2.3\,(10^{-3})\,(T_{10})\,(T_{50}) \\ & +1.48\,(10^{-5})\,(T_{10})^2\,(T_{50}) \end{aligned} \tag{7.7}$$

$$\begin{aligned} R.V.P. = {} & 30.0 - 0.31\,(T_{IBP}) - 0.33\,(T_{10}) + 3.2\,(10^{-3})\,(T_{IBP})^2 \\ & +1.4\,(10^{-3})\,(T_{10})^2 + 5.23\,(10^{-4})\,(T_{IBP})\,(T_{20}) - 2.34\,(10^{-4}) \\ & (T_{IBP})\,(T_{50}) - 1.3\,(10^{-5})\,(T_{IBP})^3 \end{aligned} \tag{7.8}$$

$$\begin{aligned} R.V.P. = {} & 49.2 - 0.368\,(T_5) - 1.026\,(T_{10}) + 0.133\,(T_{30}) \\ & - 0.57\,(T_{50}) + 0.0099\,(T_{10})^2 \end{aligned} \tag{7.9}$$

where,

R.V.P = Reid vapour pressure

T_{IBP} = Initial boiling point

T_5 = temperature of 5% volume recovery, °C

T_{10} = temperature of 10% volume recovery, °C

T_{20} = temperature of 20% volume recovery, °C

T_{30} = temperature of 30% volume recovery, °C

T_{50} = temperature of 50% volume recovery, °C

The limits reported on the use of these equations are:

	eq. 7.7		eq. 7.8		eq 7.9	
	min	max	min	max	min	max
RVP, psi	-	11.0	-	11.0	8.0	-
T_{IBP}, °C	30.0	-	30.0	165.0	-	40.0
T_5, °C	40.0	180.0	40.0	-	-	50.0
T_{10}, °C	45.0	184.0	45.0	180.0	-	55.0
T_{20}, °C	-	-	-	190.0	-	-
T_{50}, °C	-	-	-	205.0	-	-
$T_{10} - T_5$, °C	40	-	-	-	-	-

The reported standard deviations from the experimental values for equations 7.7, 7.8 and 7.9 are 0.7, 0.7 and 0.65 respectively.

7.2.3 Blending for Vapour Pressure

The Reid vapour pressure test is widely used as a criterion for blending of gasolines and other petroleum products. Ideally, accurate prediction of fuel compositions having a specified Reid vapour pressure is therefore necessary for estimating the RVP of the different fuel blends for the purpose of refinery scheduling and economic studies. In practice however, this cannot be achieved, because it is very difficult to analyse all the components of the different petroleum products.

However, a number of methods were developed for estimating the Reid vapour pressures of finished petroleum products and petroleum products blends. Bird and

Kimball (112) have published a model for predicting the Reid vapour pressure of gasolines from a low resolution gas chromatographic analysis. The gasoline is divided into 28 fractions characterised by their average boiling point. A blending RVP of each cut is then calculated via the equation:

$$Bi = \left[\frac{110.83}{e^{0.0189\, T_{bi}}} \right] \qquad 7.10$$

where,

Bi = RVP blending number for fraction i

T_{bi} = Normal boiling point of fraction i, °F

The RVP of the gasoline is computed by summing the blending RVP's of the fractions and applying a correction factor for the average boiling point.

$$P = \sum_{i=1}^{i=28} B_i \, V_i \qquad 7.11$$

$$f = 1.0 + 0.00208\,(ABP - 200) \qquad 7.12$$

$$RVP = fP \qquad 7.13$$

where,

P = uncorrected RVP of the gasoline

B_i = blending RVP of fraction i

V_i = volume fraction of fraction i

f = correction factor

ABP = average boiling point, °F

RVP = Reid vapour pressure, psi

Stewart (129, 130) has developed a method to predict the Reid vapour pressure of a gasoline blend as a function of the activity coefficient. In this method the RVP is correlated to the composition for a variety of multicomponent blends. This method is based on the equations:

$$RVP = \frac{\sum X_i (K\pi)_i \gamma_i}{\sum X_i} \qquad 7.14$$

where,

$$(K\pi)_i = P_i^o e^{0.0021\ RVP_i} \qquad 7.15$$

therefore,

$$RVP = \frac{\sum X_i \gamma_i P_i^o e^{0.0021\ RVP_i}}{\sum X_i} \qquad 7.16$$

$$P^o = \frac{\sum X_i \gamma_i P_i}{\sum X_i} \qquad 7.17$$

$$X_i = \frac{F_i}{F + H \gamma_i P_i^o} \qquad 7.18$$

where,

P_i^o and H are given in special tables

F = Density of blend as liquid at 60°F and 1 atm, lb moles/bbl.

F_i = Pound-moles of component i per barrel of liquid blend at 60°F and 1 atm $= V_i \, \rho M_i$

H = coefficient dependent on the ratio of gas chamber volume to liquid chamber volume in the RVP test of the blend.

P_i^o = reference value of vaporisation equilibrium constant, for component i at zero blend RVP given in special tables.

P^o = reference vaporisation equilibrium constant for the total blend (given in tables)

X_i = estimated equilibrium mole fraction of component i in the liquid phase in the RVP bomb, if the RVP of the blend were actually measured.

γ_i = activity coefficient for component i (dimensionless)

V_i = volume fraction of component i in blend at 1 atm. and 60°F

ρM_i = molar density of component i (pound - moles per barrel as liquid at 1 atm. and 60°F).

Stewart has reported that this approach is applicable to mixtures of more than two components.

CHAPTER 8

EXPERIMENTAL INVESTIGATION

8.1 SELECTION OF CRUDE OILS AND SAMPLING:

Three types of Kuwait crude oils were used in this study. These were selected to cover a wide range of density or °API gravity (i.e. 35.96 - 14.79 °API), in order to typify Kuwait produced crudes and other crudes in the world. As discussed in Chapter 2 the density @ 15°C of crude oils generally range from ~0.780 g/ml (50°API) to ~1.00 g/ml (10°°API).

The crudes were as follows (Figure 8.1):

1. Light crude oil, with relative density = 0.8445 g/ml (35.96°API), produced from Sabriya crude oil field, North Kuwait.
2. Medium crude oil, with relative density = 0.9059 g/ml (24.62°API), produced from Wafra - Ratawi crude oil field, South Kuwait.
3. Heavy crude oil, with relative density = 0.9667 g/ml (14.79°API), produced from North Kuwait field.

The characteristics of these crude oils are summarised in Table 8.1

TABLE 8.1 Inspection Data for Light, Medium and Heavy Crude Oil

Test	Units	Light Crude	Medium Crude	Heavy Crude
Density @ 15°C	g/ml	0.8445	0.9059	0.9667
API gravity	°API	35.96	24.62	14.79
Kinematic Viscosity				
@ 10°C	cSt.	14.22	163.4	2193
@ 20°C	cSt.	9.512	81.46	887.9
@ 30°C	cSt.	7.1410 ←	51.81	426.4
@ 40°C	cSt.	5.960	34.63	223.5
@ 50°C	cSt.	4.850	24.98	130.0
Pour Point	°C	-18	-14	-23
Asphaltenes Content	%wt.	0.89	4.4	6.75
Sulphur Content	%wt.	2.15	3.75	4.66
Conradson Carbon Residue	%wt.	4.74	7.840	11.37
Metals on Ash by				
ASTM -D3327 Ni	μg/g	3.4	20.0	26.7
V	μg/g	13.8	44.3	100.9

All the crude oil samples were taken either directly from the well head or from the mixing manifold in the gathering centres at the oil fields. A special sampling system was constructed (Figure 8.2) to ensure that the samples taken were representative samples and un-weathered, i.e. the loss of volatile materials was kept to the minimum. It consisted of three barrels each of 200 litres capacity, and coupled together by metal tubing and fittings and provided with pressure gauges and valve. The system worked by displacement of crude oil from one barrel to another. The system was connected to the crude pipeline or the well head so that the crude oil flowed into barrel No.1, then No.2, and finally No.3 which was vented to air. When barrel No.3 was half full, the system was disconnected from the pipeline, and the barrels were disconnected from each other one by one, such that no exposure to air occurred. Barrel No.3 was then, discarded and barrels No.1 & 2 were taken as, un-weathered, representative crude oil samples.

Figure 8.1. The Crude Oil Fields in the State of Kuwait

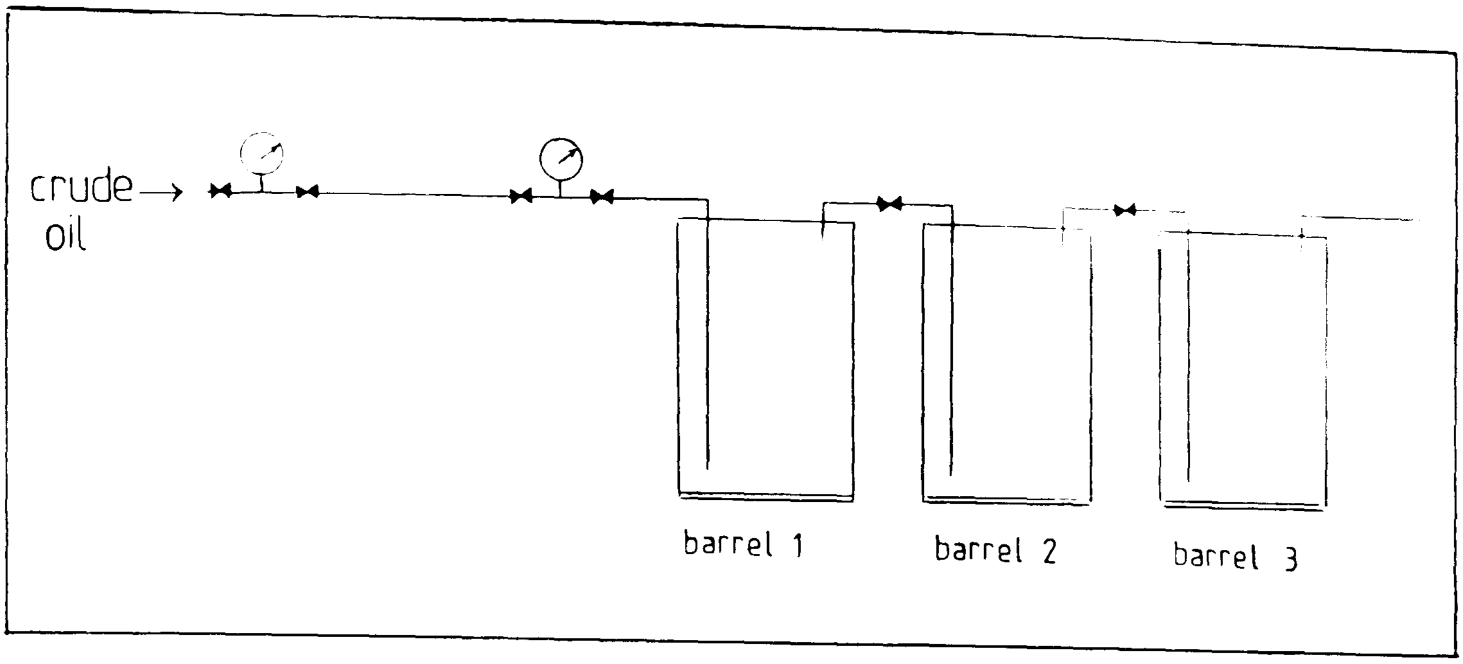


Figure 8.2. System Used for Crude Oil Sampling

8.2 SELECTION OF PETROLEUM PRODUCTS:

Three types of straight-run petroleum products (produced by distilling the crude oils using a 14 - 18 theoretical plates fractional distillation unit) were selected for study. These petroleum products differed in nature, and varied widely in their densities (i.e. a high Δ API).

1. Light straight-run products:

   Kerosene (boiling point range 240-290°C); wax-free and asphaltenes-free.

2. Heavy straight-run products:

   Heavy gas oil (boiling point 230-554°C); moderate wax and asphaltenes-bearing product.

3. Straight-run residue of boiling point >360°C; wax-bearing and asphaltenes-rich products.

The characteristics of these petroleum products are shown in Table 8.2.

TABLE 8.2 Inspection Data for Kerosene, Heavy Gas Oil and Residue >360°C.

Test	Units	Kerosene	Heavy Gas Oil	Residue >360°C
Density @ 15°C	g/ml	0.8190	0.9177	0.9940
API Gravity	°API	41.2	22.6	10.6
Boiling Point	°C	190-240	238-554	>360
Sulphur Content	%wt	0.21	3.08	3.85
Pour Point	°C	-	4	-
Refractive Index at 20°C	-	1.4541	1.5087	-
Asphaltene Content	%wt	Nil	0.05	4.8
Flash Point	°C	70.0	127.0	204.0

8.3 SELECTION OF BASE OILS:

Four additives - free base oils were chosen for study. These were supplied by the Lubricating Oil unit in Kuwait National Petroleum Company. The base oils (light base oil, medium base oil, heavy base oil and bright stock) were asphaltenes - free and similar, but not identical, in nature. The characteristics of these base oils are shown in Table 8.3.

TABLE 8.3 Inspection Data for light, Medium and Heavy Base Oils and Bright Stock

Test	Units	Light Base Oil	Medium Base Oil	Heavy Base Oil	Bright Base Oil
Density @ 15°C.	g/ml	0.8624	0.8782	0.8842	0.8938
API Gravity		32.50	29.55	28.45	26.70
Flash Point, COC	°C	216	241	269	302
Sulphur Conntent	%wt.	0.03	0.09	0.10	0.28
Pour Point	°C	-21	-17	-15	-14
Kinematic Viscosity cSt.					
@ 20°C	cSt.	45.34	177.7	424.7	1756
@ 40°C	cSt.	19.31	60.21	125.9	425.5
@ 100°C	cSt.	4.002	8.025	13.17	29.93

8.4 BLENDING OF CRUDE OILS, PETROLEUM PRODUCTS AND BASE OILS

In order to study the effect of the mixing of crude oils or the other petroleum products and base oils on selected physical properties, binary and ternary mixtures were prepared.

All the binary and ternary mixtures studied in this project were prepared on weight bases. Prior to mixing any sample with another, vigorous shaking was applied to ensure homogenity of the sample and to avoid any layering, or stratification, that could occur, mainly with crude and heavy petroleum products (e.g. heavy gas oil). The crude oils were shaken in closed containers at ambient temperature and then cooled at ~0°C., in order to ensure that no volatile materials were lost. The intermixing of the crude oils was carried out at ~5°C.

The preparation of petroleum products or base oils mixtures was carried out at ambient temperature. However, when straight-run residue >360°C. and bright stock base oil were used, the application of some heat (using an electrical oven of maximum heating temperature 250°C) was necessary to increase the fluidity of the liquid sample to facilitate mixing and to ensure homogeneous mixtures.

The compositions of the binary and ternary crude oil mixtures are shown in Tables 8.4 and 8.5, respectively.

TABLE 8.4 Compositions of Crude Oil Binary Mixtures Comprising Light, Medium and Heavy Crude Oils.

Mixture No.	Weight % of		
	Light Crude Oil	Medium Crude Oil	Heavy Crude Oil
1	90	10	-
2	60	40	-
3	40	60	-
4	10	90	-
5	90	-	10
6	60	-	40
7	40	-	60
8	10	-	90
9	-	90	10
10	-	60	40
11	-	40	60
12	-	10	90

TABLE 8.5 Compositions of Ternary Crude Oil Mixtures

Mixture No.	Weight % of		
	Light Crude Oil	Medium Crude Oil	Heavy Crude Oil
1	30	30	40
2	30	50	20
3	40	50	10
4	55	40	5
5	20	30	50
6	10	70	20
7	70	10	20
8	10	20	70

The compositions of the prepared binary mixtures of petroleum products are shown in Table 8.6.

TABLE 8.6 Compositions of Binary Mixtures of Petroleum Products Comprising Kerosene, Heavy Gas Oil and Residue >360°C.

Mixture No.	Weight % of		
	Kerosene	Heavy Gas Oil	Residue >360°C.
1	10	90	-
2	40	60	-
3	60	40	-
4	90	10	-
5	10	-	90
6	40	-	60
7	60	-	40
8	90	-	10
9	-	10	90
10	-	40	60
11	-	60	40
12	-	90	10

Finally, the composition of the prepared base oil binary mixtures are shown in Table 8. 7.

TABLE 8.7 Compositions of Base Oils Binary Mixtures Comprising Light, Medium and Heavy Base Oils and Bright Stock.

Mixture No.	% Weight of			
	Light Base Oil	Medium Base Oil	Heavy Base Oil	Bright Stock
1	10	90		
2	30	70		
3	60	40		
4	90	10		
5	10		90	
6	30		70	
7	60		40	
8	90		10	
9	10			90
10	30			70
11	60			40
12	90			10
13		10		90
14		30		70
15		60		40
16		90		10
17			10	90
18			30	70
19			60	40
20			90	10

8.5 MEASUREMENT OF KINEMATIC VISCOSITY:

8.5.1 Kinematic Viscosity at Atmospheric Pressure:

Calibrated glass capillary type viscometers were used for the determination of the kinematic viscosity at atmospheric pressure over a range of temperatures. A miniature suspended level viscometers, type BS/IP/MSL were used (Figure 8.3) for the determination of the kinematic viscosity of transparent petroleum liquids. A BS/IP-RF-U tube viscometers were used (Figure 8.4) for the determination of the kinematic viscosity of opaque and black liquids.

The viscometer was placed in a water or oil bath capable of maintaining the temperature within ± 0.01°C (±0.02°F) of the selected temperature (Figure 8.5). The kinematic viscosity was determined by the standard method of test IP71/ASTM D445 (16,66) for the measurement of kinematic viscosity of transparent and opaque liquids. The kinematic viscosity ν was calculated from the measured flow time t, of a fixed volume of liquid under gravity, and the viscometer calibration constant using the following equation.

$$\nu = Ct \qquad 8.1$$

where,

ν = kinematic viscosity, cSt.

C = calibration constant of the viscometer, cSt./sec

t = flow time, seconds

Duplicate measurements did not deviate more than 0.35% about their mean. This was considered an acceptable level of accuracy since the standard method of test states that reproducible measurements should not deviate more than 0.7% about their mean.

Tube	1- Filling tube 2- Timing tube 3- Air tube 4- Connecting tube 5- Capillary tube 6- Overflow tube
Bulb	A- Reservoir B- Suspended level bulb C- Timing bulb D- Subsidiary bulb
Marks	E & F- Timing marks G & H- Filling marks

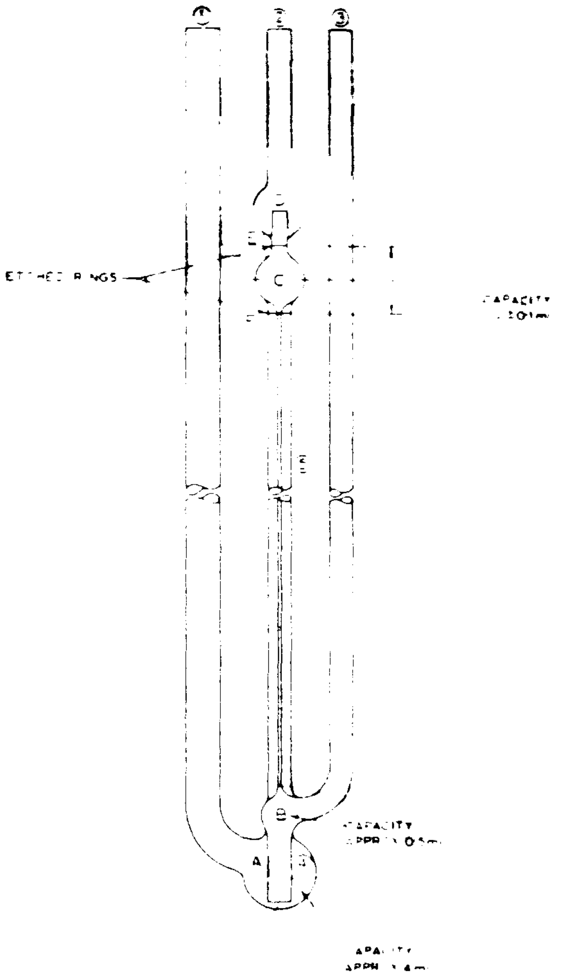


Figure 8.3 Miniature Suspended Level Viscometer, Type BS/IP/MSL

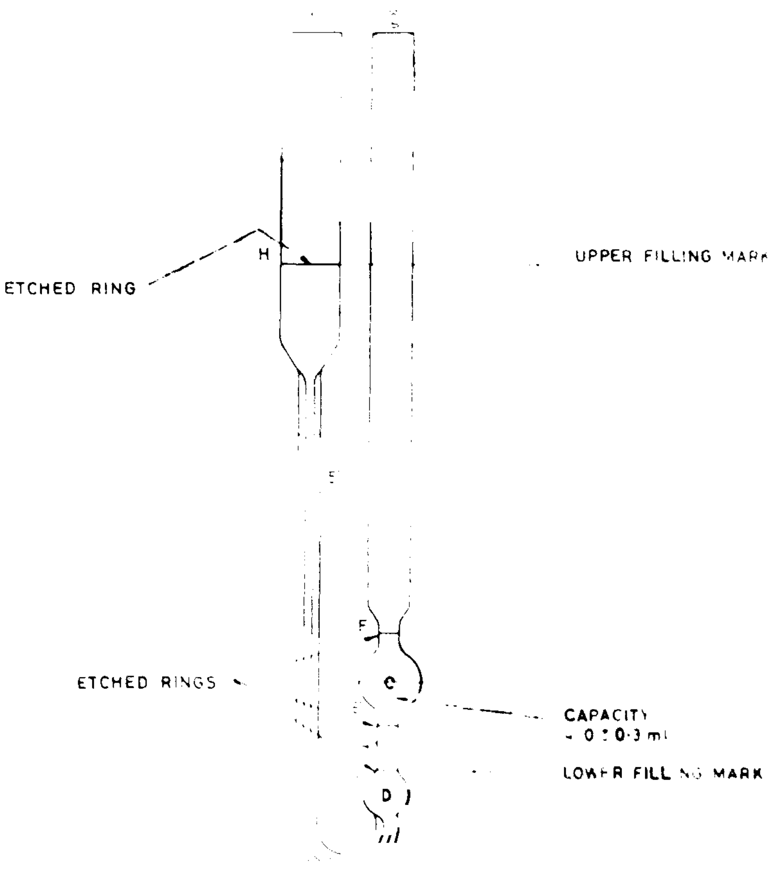


Figure 8.4 U-Tube Viscometer for Opaque Liquids.

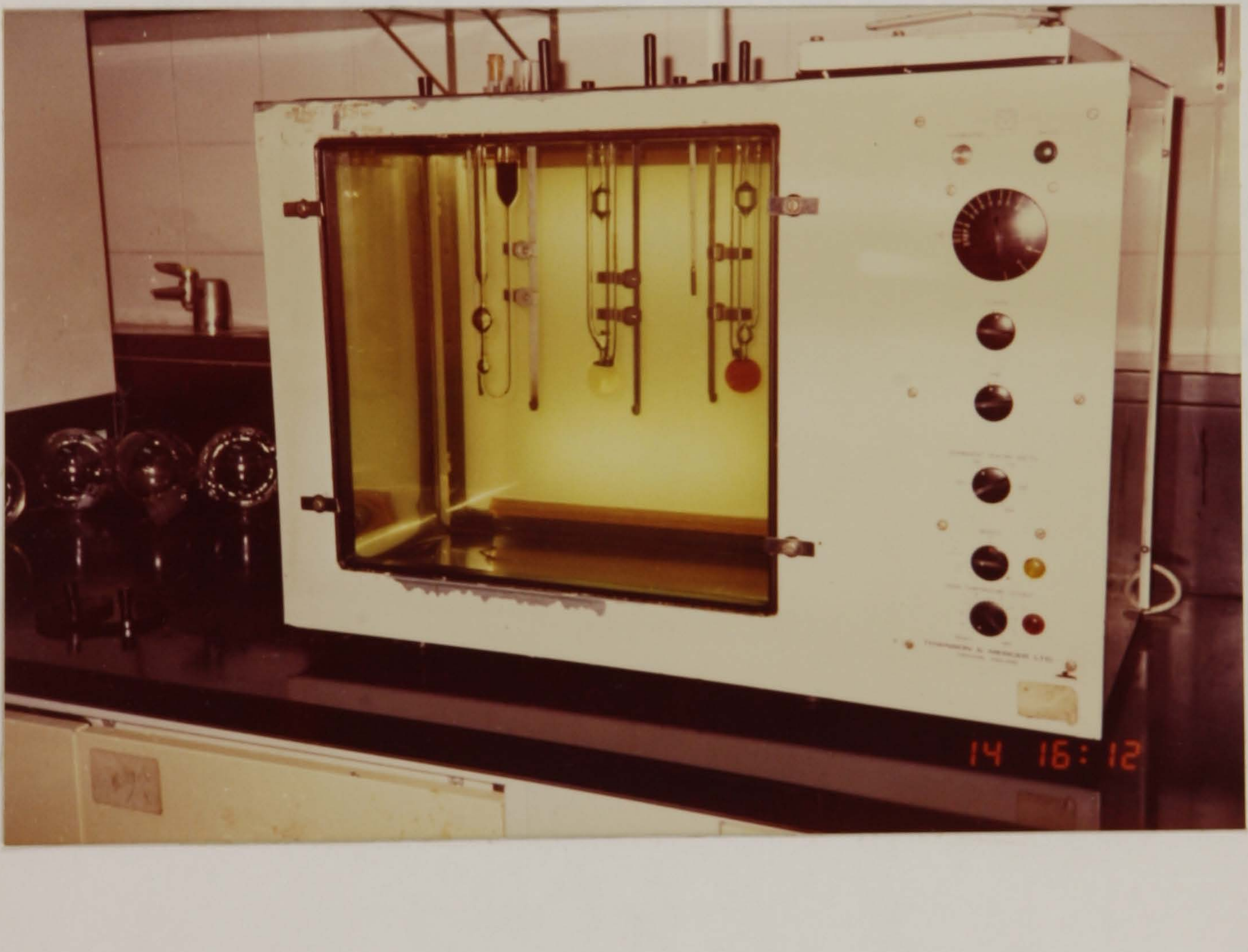


Figure 8.5 Kinematic Viscometers in the Viscosity Bath.

8.5.2 Kinematic Viscosity at Pressures of 14.7 to 8000 psi:

Viscosity measurements at high pressure were performed using the Ruska rolling ball viscometer (type 1602) which is part of the Ruska P.V.T system (Figures 8.6, 8.7 and 8.8). The viscometer was heated electrically by a jacket control system, which facilitated temperature control up to 150°C, and connected to a digital time clock for measurements with a repeatability of 0.1%.

This apparatus consisted of a manually operated mercury pump connected to a stainless steel reservoir cell of about 600 cm^3 capacity. The cell was connected to the viscometer, which contained a bleed valve, and could be adjusted at angles of 23°, 45° or 70° to promote free fall of a stainless steel ball of specific diameter. The instrument was calibrated at each temperature using Dow Corning Dc and Brookfield standard fluids covering the range 5 - 5000 cP. at 25°C, and three different balls with densities of 7.6781, and 7.7096 and 7.7641 gm/cm^3 respectively.

The reservoir and the viscometer were evacuated and then filled with crude oil such that no air bubbles could enter the system. The appropriate ball was then, allowed automatically to fall freely in the barrel inside the viscometer full of crude oil at the required temperature and pressure. The fall time in seconds was recorded for each combination of temperature and pressure at the three roll angles (23°, 45° and 70°). The viscosity (in c.Poise) was subsequently calculated and converted to the kinematic viscosity. Repeatable viscosity measurements were considered acceptable if they did not deviate more than 0.1% about the mean value

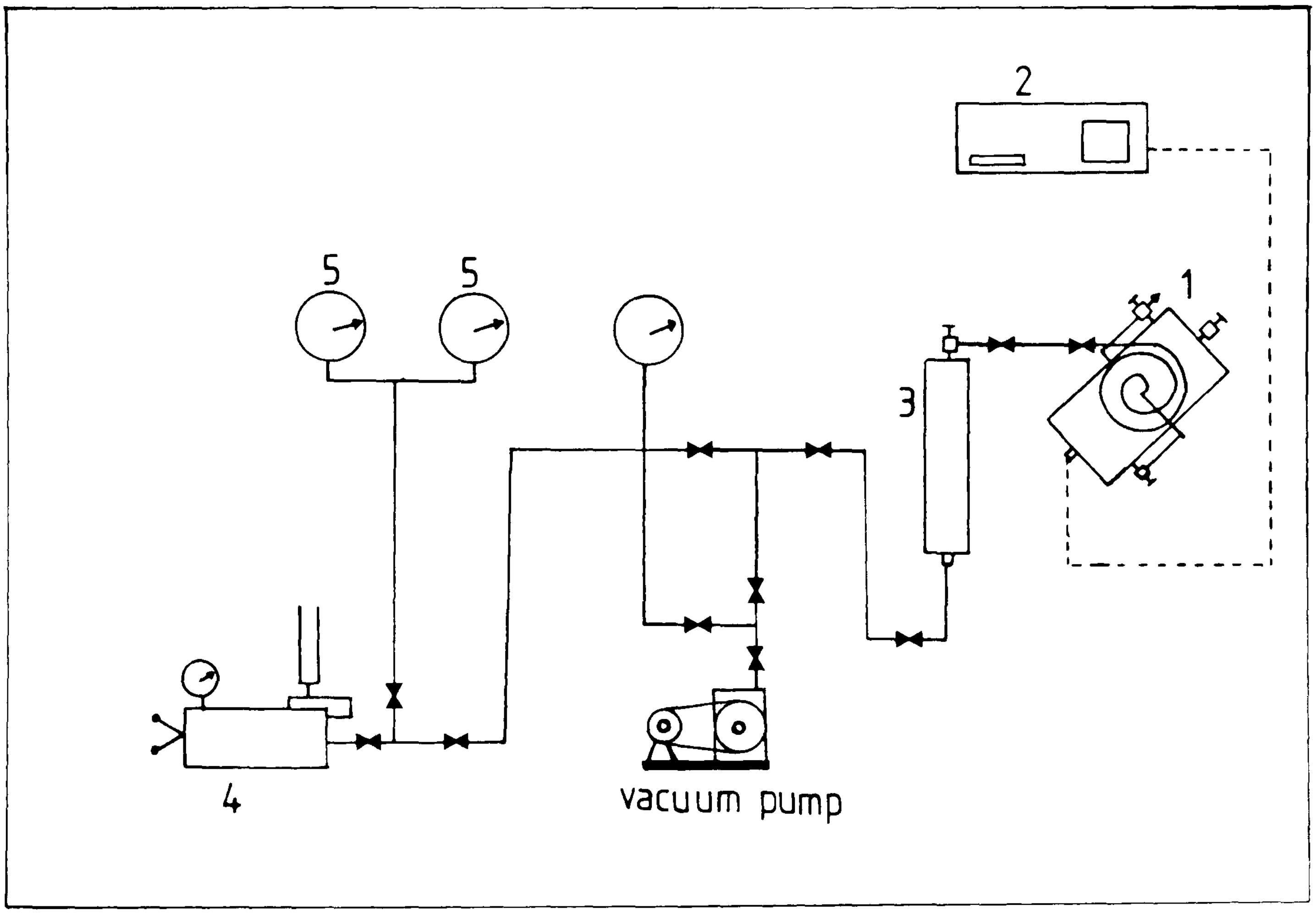


Figure 8.6. Diagram of Ruska P.V.T. System

1.	Viscometer	2.	Timer and temperature controller
3.	Reservoir cell	4.	Mercury pump

5. Pressure gauges

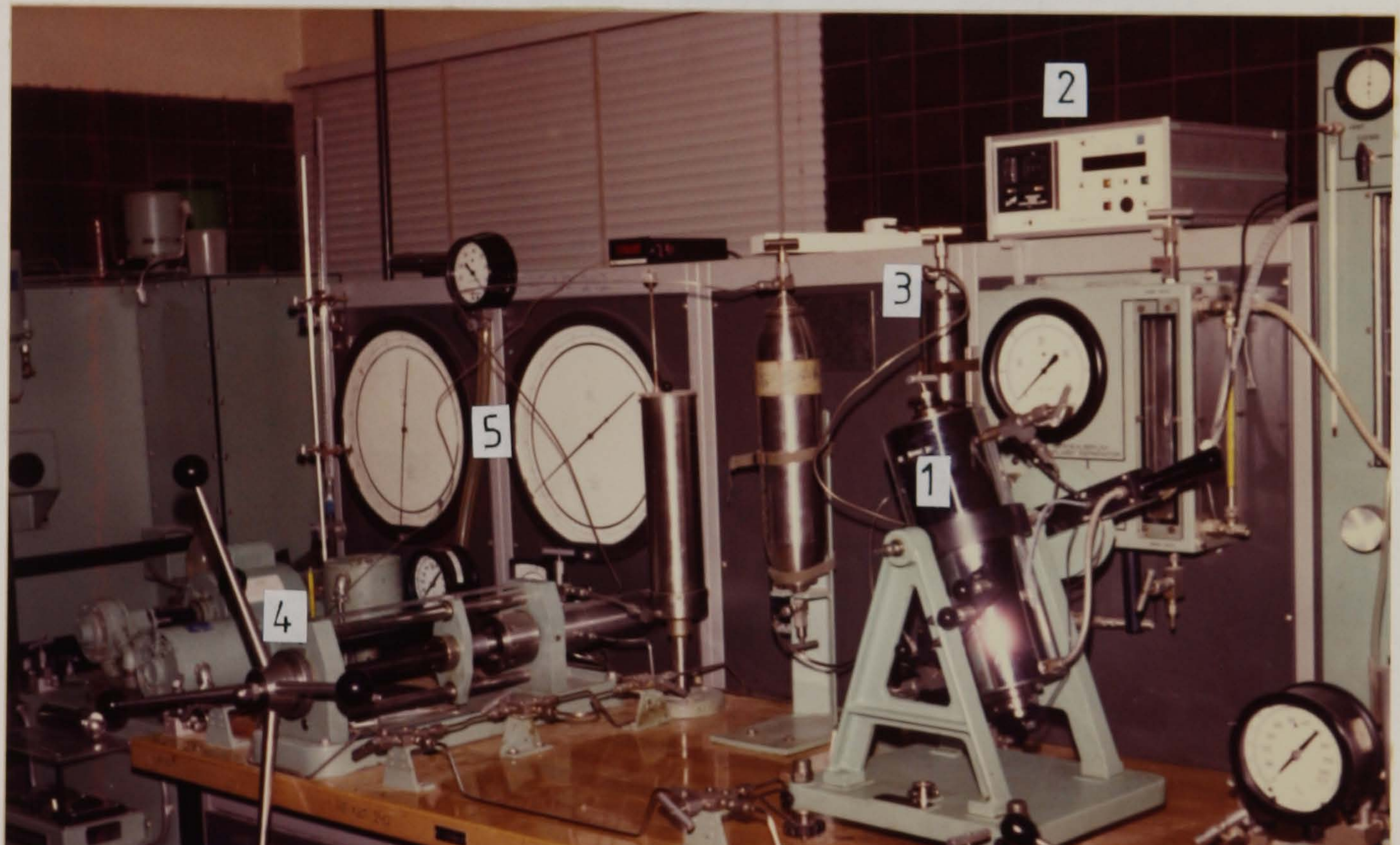


Figure 8.7 The Ruska P.V.T. System

1.	Viscometer	2.	Timer and temperature controller
3.	Reservoir cell	4.	Mercury pump

5. Pressure gauges

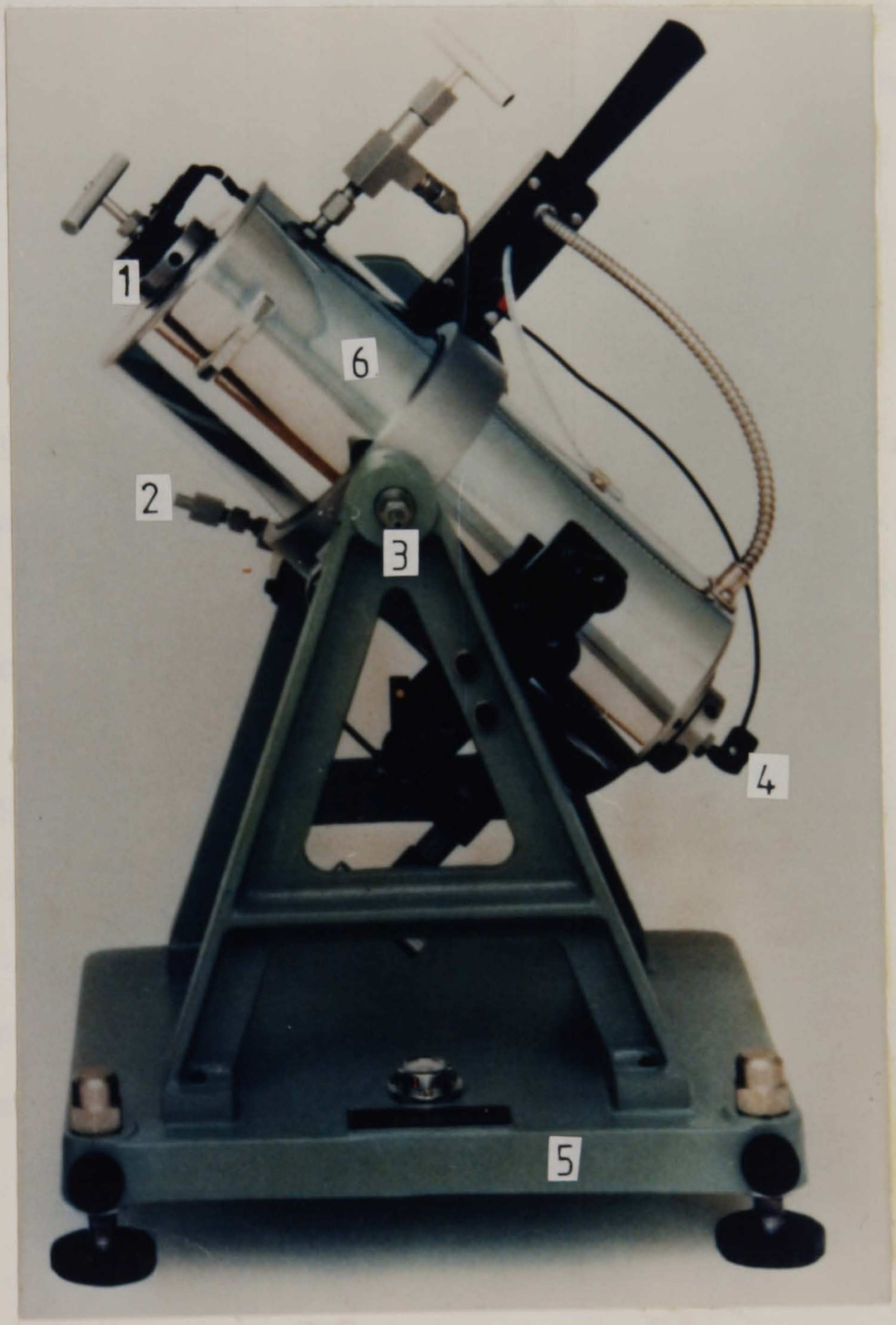


Figure 8.8. High Pressure Rolling Ball Viscometer

1. Solenoid 2. Inlet 3. Outlet 4. Contact assembly

5. Viscometer base 6. Insulated jacket

8.6 MEASUREMENT OF POUR POINT:

The pour points of crude oils and the petroleum products were determined using the standard method IP 15 / D97 (16, 66). The oil sample was placed in a cylindrical test jar of clear glass; this had a flat bottom and was approximately 30 to 33.5 mm internal diameter, and 115 to 125 mm in height. The sample height was indicated by a marked line 54 ± 3mm above the bottom. A thermometer type IP/2C, with a suitable sized cork, was immersed in the liquid such that the thermometer bulb was just covered by the liquid. The jar was, then, placed in the bath containing coolant (methylated spirit). The bath was connected to a refrigerant circulating pump capable of producing a reduction in temperature down to -60°C. (Figures 8.9 and 8.10). The jar was then tilted periodically as cooling continued.

The pour point was recorded as the lowest temperature (in °C) at which the liquid was observed to flow when cooled. This was determined precisely as the temperature at which the liquid in the test jar showed no movement when the test jar was held in a horizontal position for exactly 5 seconds.

Heavy petroleum liquids such as straight-run residue >360°C, heavy gas oil, heavy base oil and bright stock base oil were pre-heated up to 46°C. This was to disperse any wax which had separated out prior to the test, which would otherwise result in a pour point measurement less than the correct value. Duplicate measurements of the pour point were considered acceptable if they did not differ by more than 1°C.

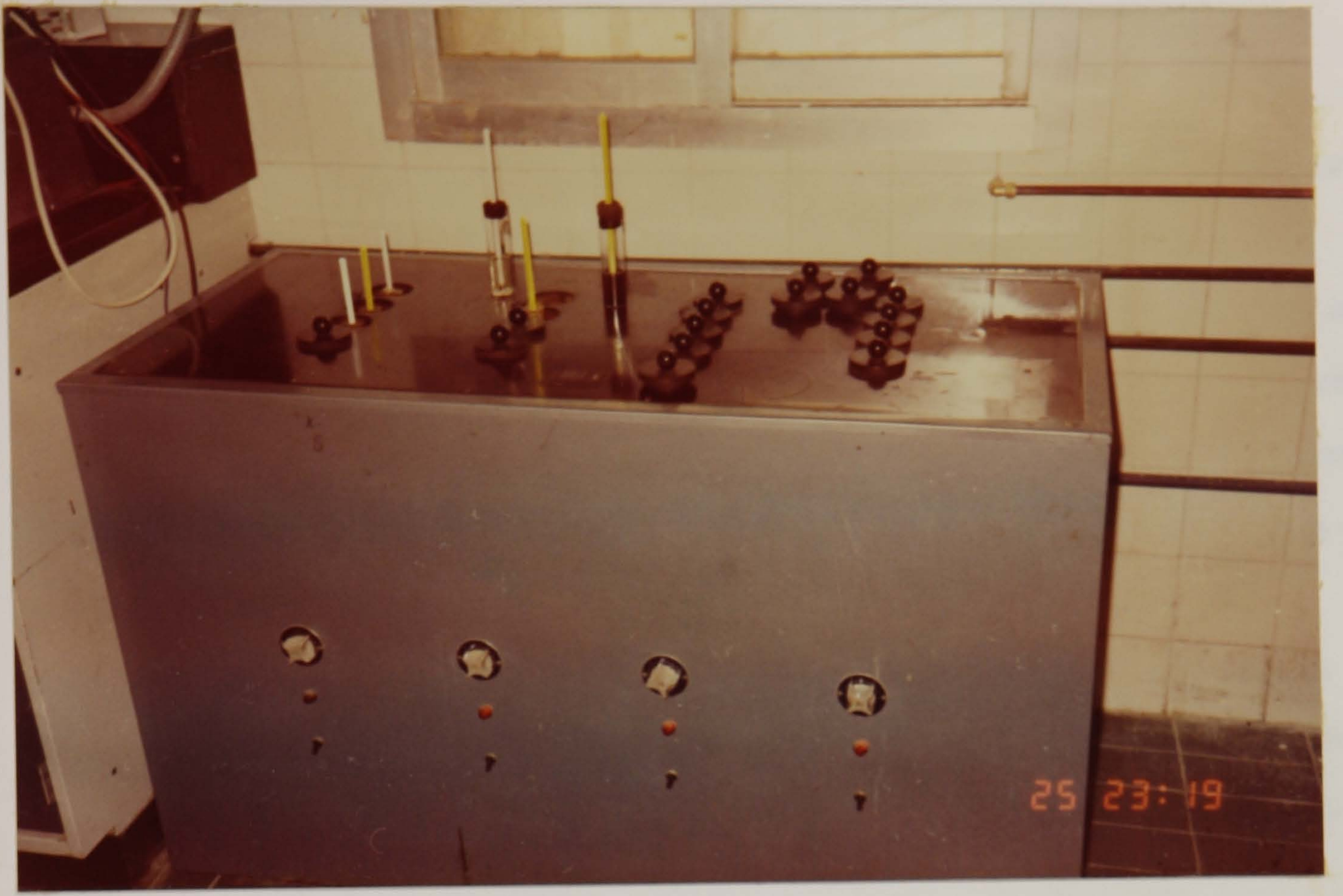


Figure 8.9. Apparatus for Pour Point Test

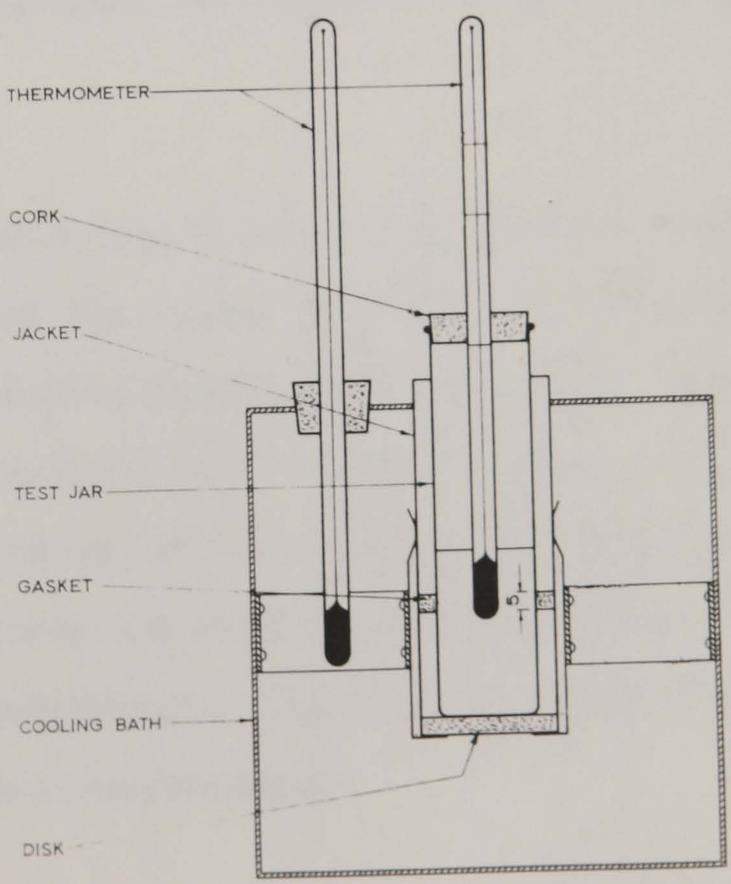


Figure 8.10. Pour Point Apparatus

8.7 DETERMINATION OF TRUE BOILING POINT DISTILLATION:

8.7.1 T.B.P. Distillation of Crude Oils:

The ASTM-D 2892$^{(66)}$ standard method was followed for the determination of the True Boiling Point (T.B.P.) of the crude oils. A Normschliff Geratebau Wertheim electronically-controlled batch, semi-pilot unit was used for this purpose (Figures 8.11 and 8.12). The distillation system contained a six litres capacity glass still with an automatically controlled heater and was connected to a control unit. It contained a fractionation column of 70mm internal diameter and 91cm height. The column was packed with Propak fillings of size 6mm, and surrounded with an electronically-regulated, heating jacket. It was connected to a magnetically-controlled head with a magnetic solenoid-valve. The reflux ratio was controlled by means of the solenoid-valve at the column-head, the required value being pre-selected at the control unit. The reflux ratio during the distillation process was 5:1.

The unit could operate at atmospheric pressure or under vacuum, for which purpose a high vacuum pump was connected to the system to produce vacuum down to 0.1 m bar.

To distil a crude oil, the feed was charged into the distilling flask via aside branch using a funnel. The volume of the feed was calculated from measured weight and density. The flask was then heated gradually, at atmospheric pressure, and the distillates collected at the observed head 10°C temperature intervals. The weight and volume of each collected fraction were reported for each head temperature at which it was collected. The distillation was continued until the temperature of the distillation flask reached about 320°C. Then, in order to avoid thermal cracking of the feed, the heater was switched off and the system cooled down to room temperature.

The distillation was then continued under vacuum following a similar procedure to that described above. The pressure (in m bar), at which each fraction was collected, was reported as well as the head temperature. The temperature was then converted to the equivalent atmospheric temperature (E.A.T.). The distillation was subsequently continued until the flask temperature reached about 320°C., under the minimum possible pressure. At this the system was switched off and the distillation considered to be complete.

The boiling point curve was, then, drawn (temperature vs. % volume recovery), and consequently, the temperature at 50% volume recovery ($T_{50\%}$) was determined.

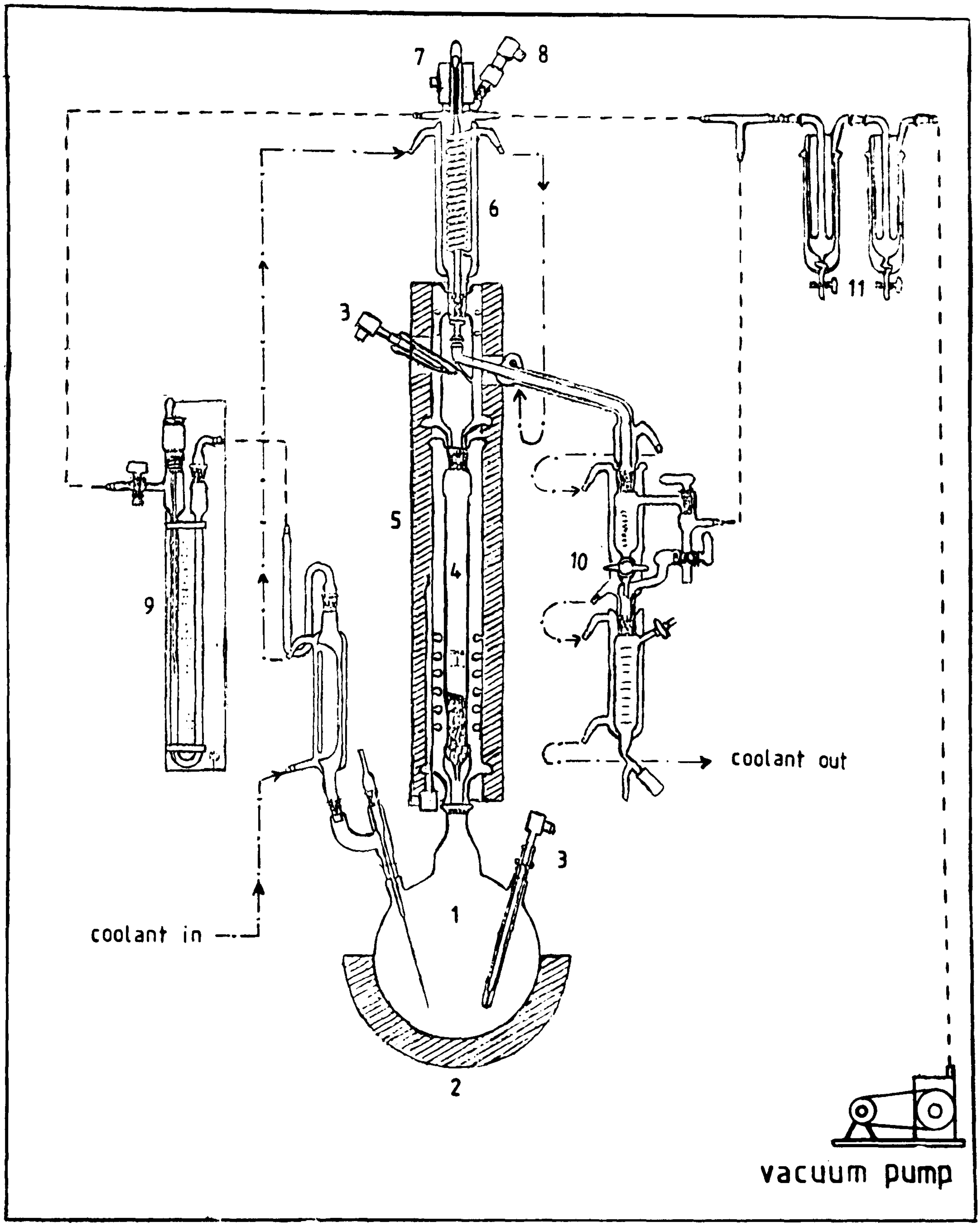


Figure 8.11. A Diagram of Fractional Distillation Apparatus (T.B.P.)

1. Still
2. Electrical heater
3. Thermocouple
4. Fractionation column
5. Heating jacket
6. Condenser
7. Magnetic solenoid valve
8. Pressure sensor
9. Manometer
10. Receiver
11. Trap

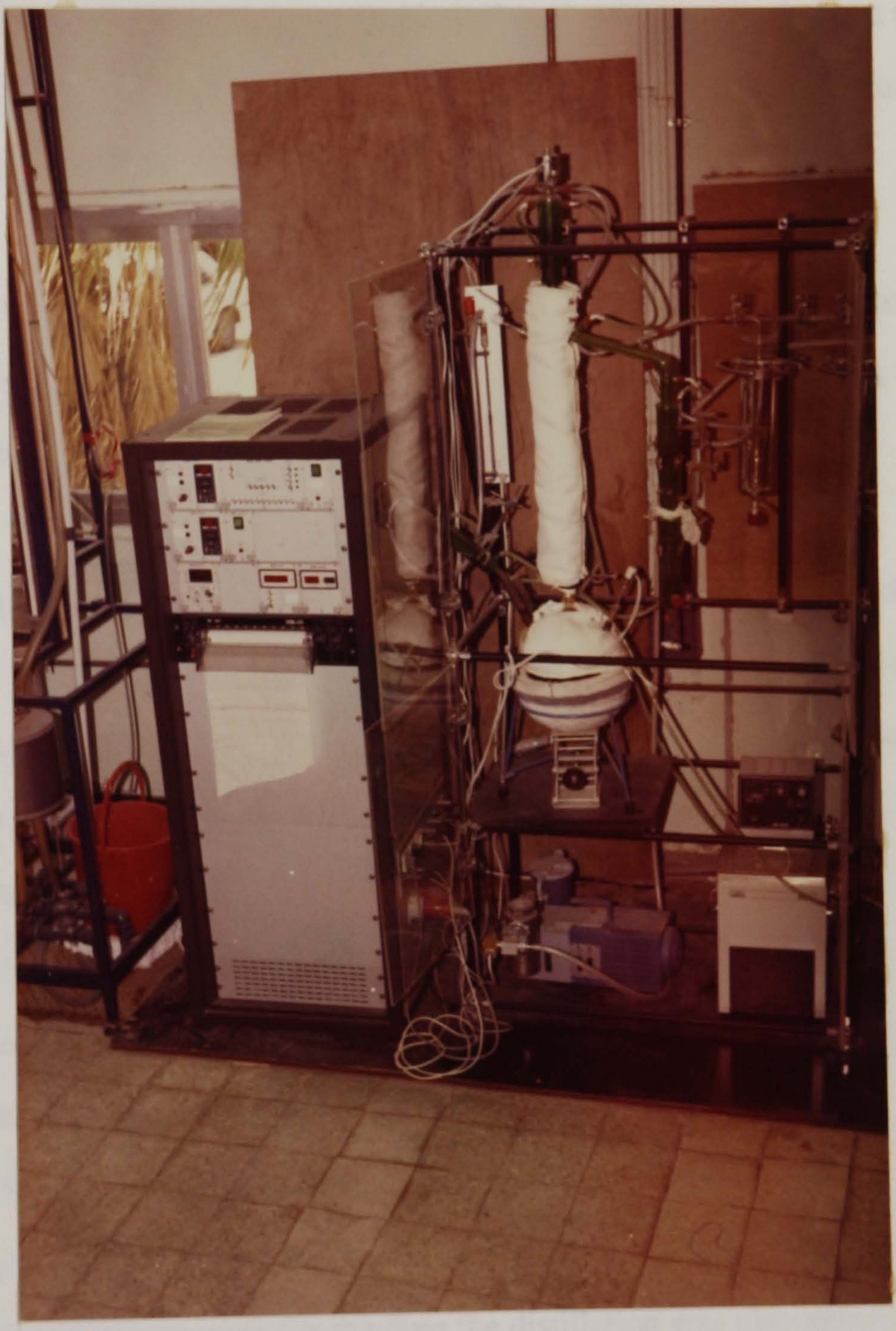


Figure 8.12 Fractional Distillation Apparatus (T.B.P.)
(ASTM-D 2892)

8.7.2 Distillation of Petroleum Products and Base Oils:

Distillation boiling point curves of petroleum products and base oils were determined using the standard method for distillation of petroleum products ASTM-D1160(66) (Figure 8.14). This distillation apparatus comprised a 1 litre capacity distillation flask, and a double-jacketed glass distillation column (260mm height and 28mm i.d.) of approximately 3-5 theoretical plates. A thermocouple was provided to measure the head temperature of the distillation column where vapor - liquid equilibrium occurred. The overhead condenser was connected to a double-jacketed side arm coupled to a cooling system. The distillate was collected in a 200ml capacity double-jacketed graduated receiver connected to the cooling system.

The apparatus was connected to a vacuum pump which facilitated vaporization of the liquid, either partially or completely, at absolute pressures down to 1mm Hg, and their condensation as liquids at the pressure of the tests.

A known weight of 200ml of the sample were placed in the distillation flask and the desired vacuum level for distillation was then applied. The flask was then heated gradually by means of an electrical heater. As soon as vapour or refluxing liquid appeared at the joint between the flask and the column, the rate of heating was adjusted so that the distillate was recovered at 4 to 8 ml/min. The distillation was continued until either a liquid temperature of300°C or the maximum vapour temperature was reached. The head temperature measured by the thermo-couple was recorded when each of the following volume percentage fractions of charge has been collected in the receiver: 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95 and at the end point. If the liquid temperature reached 300°C. or if the vapour reached a maximum temperature before the distillation end point was observed, the head temperature was recorded at the time the distillation was discontinued. The total volume percent recovered was then recorded.

The recorded temperatures were then converted to Equivalent Atmospheric Temperatures (E.A.T.). The boiling point curve was then drawn and $T_{50\%}$ determined as described previously in section 8.7.1.

The ASTM-D1160 boiling point curve can be converted to T.B.P. using the Edmister method (117, 118) adapted and recommended by American Petroleum Institute(18) For the purpose of this method the ASTM-D 1160 distillation temperatures at and above the 50 - percent point are assumed to be equal (18). Therefore, the 50 - percent point (T 50%) determined for the crude oils or petroleum products by either ASTM-D2898 (T.B.P.) or ASTM-D 1160 were considered in this work to be analogous to each other.

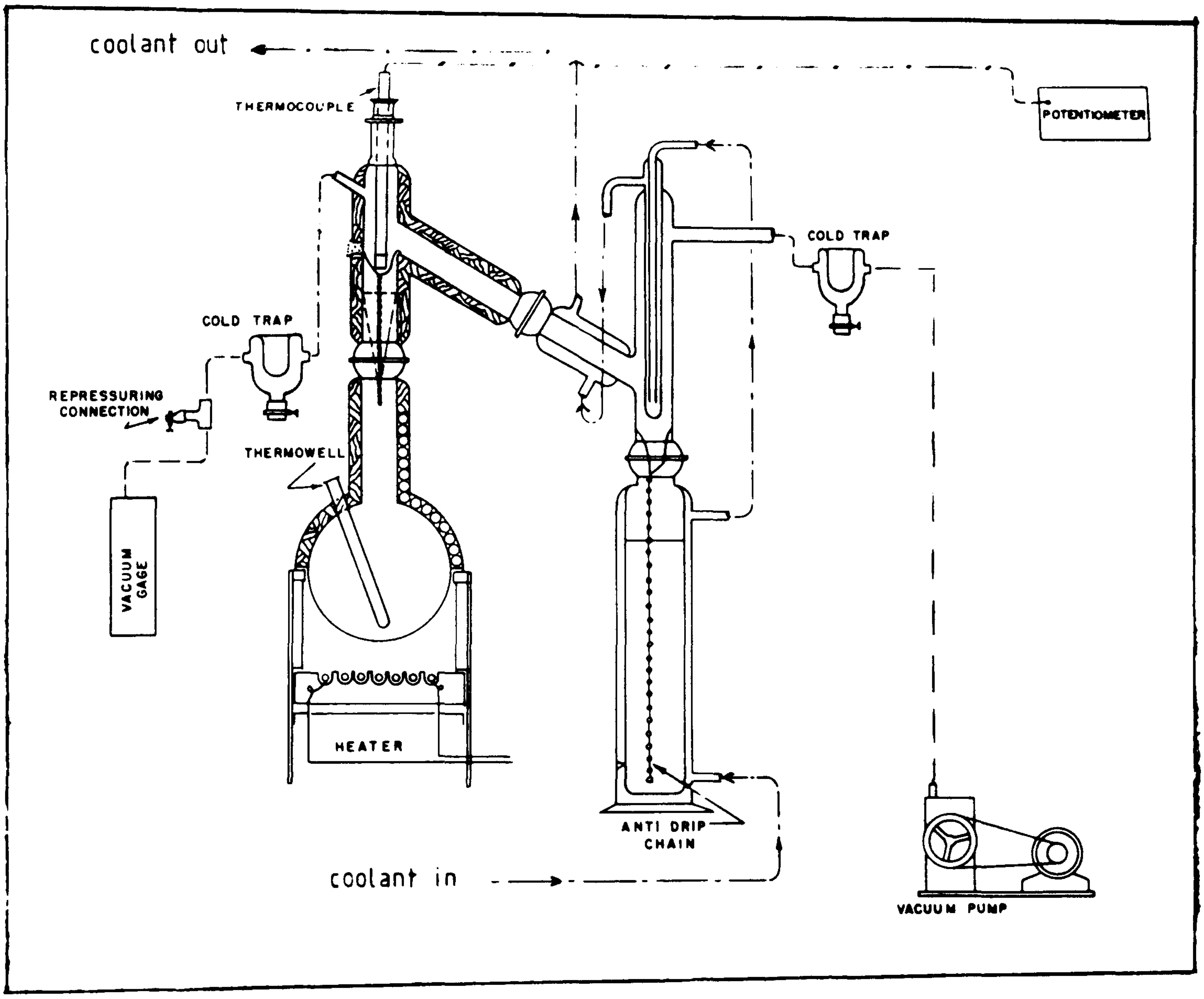


Figure 8.13 ASTM-D 1160 Distillation Apparatus

8.8 MEASUREMENT OF REID VAPOUR PRESSURE

The Reid vapour pressure (R.V.P.) is the absolute pressure exerted by a mixture (in pounds per square inch) determined at 37.8°C. (100°F) and at a vapour - to - liquid volume ratio of 4.

The apparatus used for the determination of R.V.P., and procedures are standardized, defined and specified in ASTM method D323 (66) or IP69(16). In this method the un-weathered chilled sample ($T \approx 0°C.$) was placed in the liquid chamber of the apparatus which was connected to an air chamber (Figure 8.15). The apparatus was then immersed in a constant-temperature bath at 37.8 ±0.1°C. and shaken periodically until equilibrium was reached. The equilibrium pressure was measured by a gauge fitted into the air chamber and checked against a manometer (Figure 8.16).

Gross errors can be obtained in vapour pressure measurements if the sample to be tested is exposed to air for a significant time or is not kept cool, since this may result in loss of volatile materials and a change in composition of the sample. It is also necessary for the apparatus to be checked before and during each test for liquid and vapour leaks. This can be done by immersing the apparatus into a clean water bath at the same temperature (37.8°C). The appearance of gas bubbles or liquid droplets indicates vapour or liquid leaks. Duplicate results should be considered suspect if they differ by more than

$0.014 + 0.014\,A$ (16, 66)

where, A represents the mean of two results, in bar.

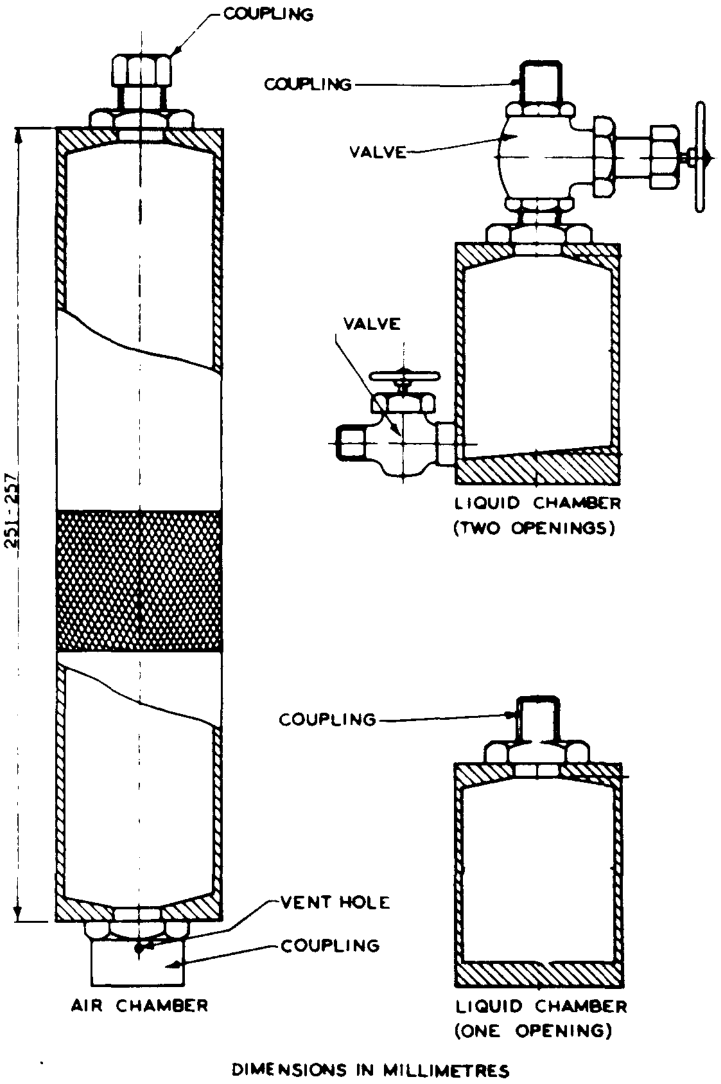


Figure 8.14. Vapour Pressure Apparatus

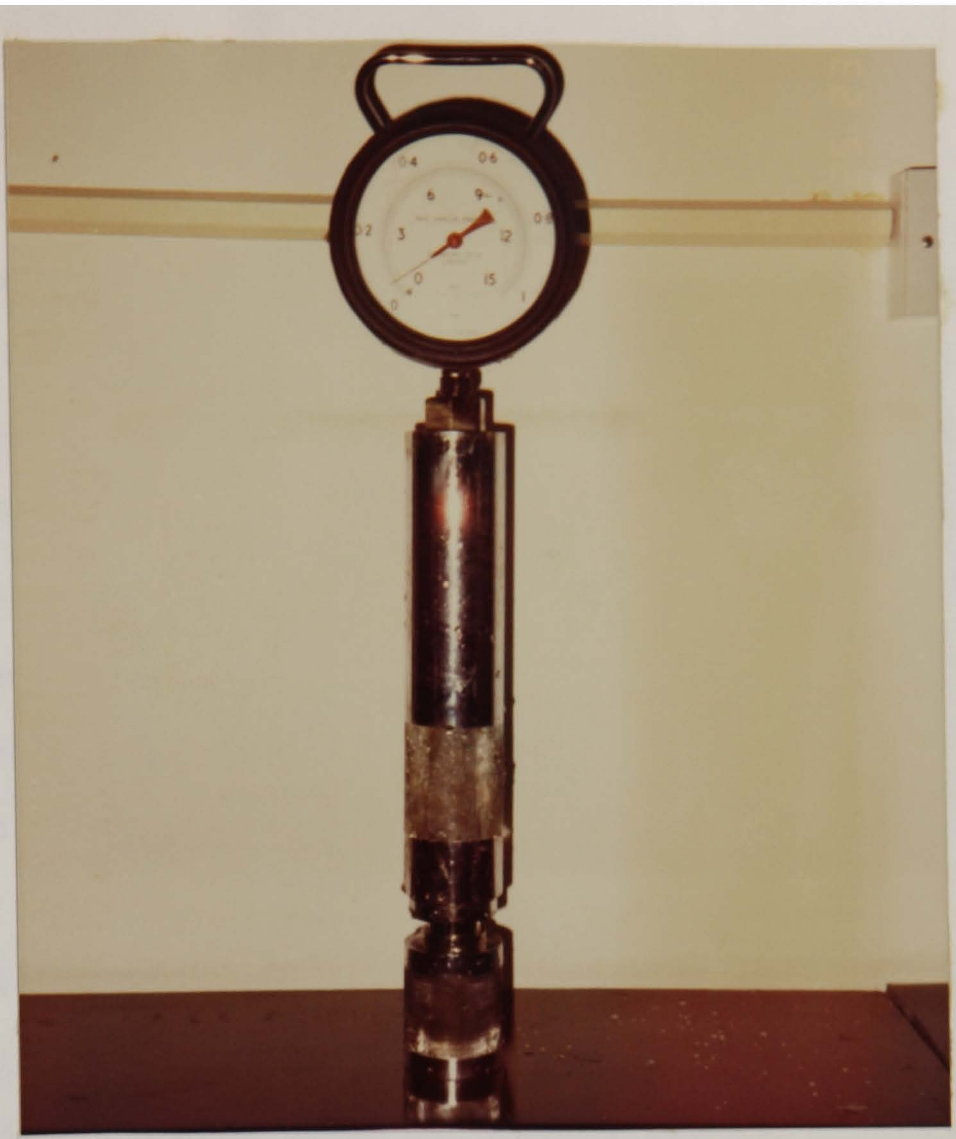


Figure 8.15. Assembly of Reid Vapour Pressure Apparatus

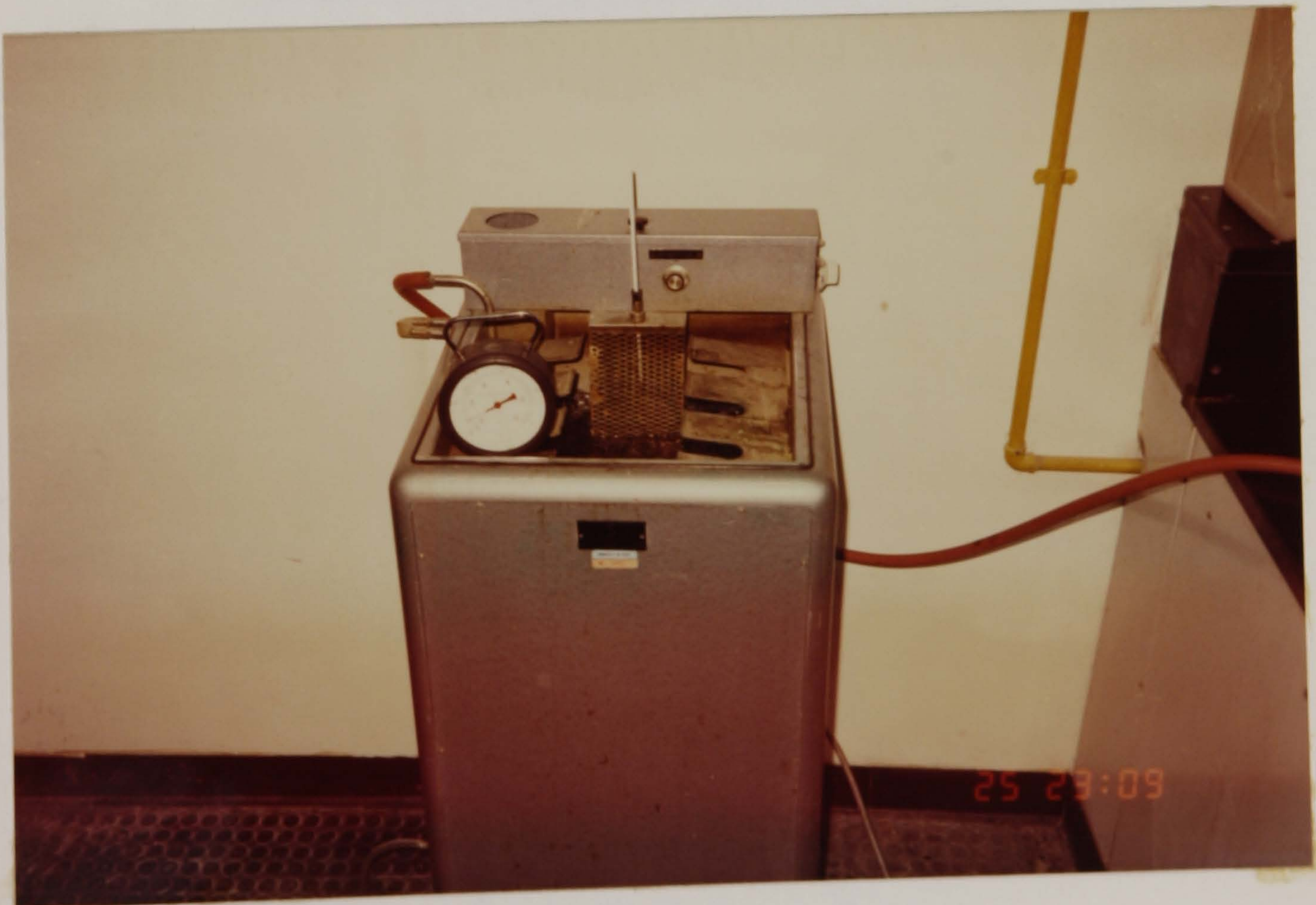


Figure 8.16. Reid Vapour Pressure Apparatus and Temperature Controlled Water Bath

8.9 DETERMINATION OF DENSITIES:

The densities of the crude oils, petroleum products and base oils, were determined by means of capillary-stoppered pyknometers, by which the weights of equal volumes of the liquid samples and of pure distilled water were compared. Equal volumes were ensured by placing the filled pyknometers of known volume (25ml) in a water bath at 15 ± 0.05°C (when crude oils or light petroleum products were tested) or at 65 ± 0.05°C (when residues, heavy petroleum products, or heavy base oils were tested) until equilibrium was reached. Different types of pyknometers were used during the course of this project; narrow neck pyknometers were used for the light liquids, while those of wide neck were used for the heavy liquids (Figure 8.17).

The pyknometers were first calibrated using deionized, pure water of known density. The procedure of the test is fully described in the Institute of Petroleum method IP 190/86 (16). The density measurements were reported as g/ml.

Duplicate measurements should not differ by more than 0.0006 g/ml (16), and in this work did not in fact vary by more than 0.0004 g/ml.

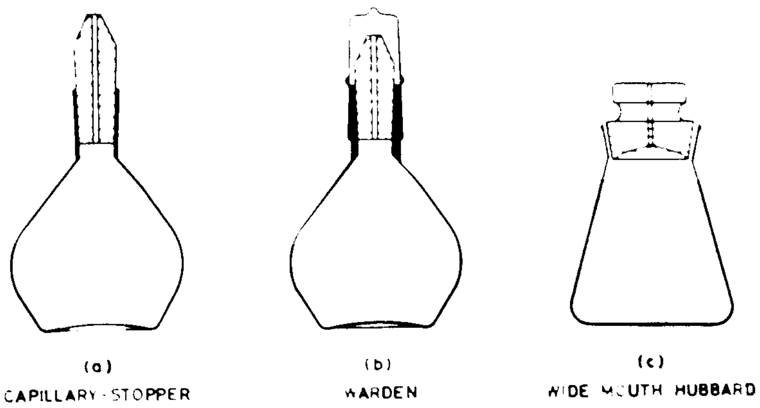


Figure 8.17. Pyknometer Forms

8.10 DETERMINATION OF MOLECULAR WEIGHTS:

The determination of the molecular weight of an undefined mixture, such as crude oil or a petroleum product, is a tedious procedure with many limitations. Therefore, many workers prefer not to determine it experimentally, but to calculate or estimate it from other properties which can be easily measured, e.g. viscosity and boiling point. A major limitation of the practical determination of molecular weight arises from the nature of the liquid sample itself, particularly if it contains a wide variety of hydrocarbons of different natures (e.g. as with crude oils, which contain very light hydrocarbons up to very heavy compounds of very complex nature such as asphaltenes and resins).

During the course of this project, the molecular weights of crude oils, petroleum products and base oils were determined by the vapour pressure osmometry (V.P.O.) method or Gel Permeation Chromatography (G.P.C.) method, or both. Each of these methods has its own limitations and draw backs, mainly with crude oils. High molecular weight asphaltic materials present in crude oils may not dissolve in the solvent used in the V.P.O. method, and hence lead to spurious results. G.P.C. is the most appropriate and suitable method for molecular weight determinations of high molecular weight asphaltic materials in crude oils, but the R.I. detector used in the system cannot detect the fractions of boiling point less than about 250°C. This is due to the R.I's of those fractions <250°C being lower than the R.I. of the solvent used (tetrahydrofurane, T.H.F.).

Therefore, the best way to deal with such a case was to split the crude oil into two fractions by distillation (distillate <250°C and residue >250°C). Consequently, the molecular weights of distillates <250°C were determined by the V.P.O. method, and those of residues >250°C by the G.P.C. method. The total molecular weights of both fractions of each crude sample were combined, based on the percent weight of the fractions.

8.10.1 Molecular Weight by Vapour Pressure Osmometry:

A KNAUER apparatus was used for the determination of molecular weight by vapour pressure osmometry. This apparatus consisted of two main parts: a vapour pressure osmometer and a universal temperature measuring instrument. In the former, the temperature variation could be measured by the resistance change of a sensor or by the change in E.M.F. generated by a thermo-couple. The instrument consisted of a modified Wheatstone Bridge with precision manganin resistors, a highly stable transistor amplifier and a measuring instrument with mirror backed scale. Measurements were normally made by reading meter deflection.

For measurement of very small temperature changes and for temperature differential work, thermistors were generally used. Highest resolving power was achieved by the use of thermistors. The temperature measuring instrument was capable of resolving a 0.0005% change in resistance. The zero point could be optionally suppressed by use of the Wheatstone Bridge.

The vapour pressure osmometer contained a measuring cell (Figure 8.18) held very accurately at a constant temperature and containing a little solvent (drops of carbon tetrachloride). At the set temperature the solvent vapour pressure in the cell stabilized at a constant valve. Two thermistors located in a probe in the vapour space of the cell acted as temperature sensors. By means of syringes, a drop of solvent was placed on each of the two thermistors. Since the surroundings were saturated with vapour, the two drops on the thermistors adjusted to the temperature of the cell. If one of the solvent drops was replaced with a drop of solution, this latter would adjust to a higher temperature. Initially, the solution drop has a lower vapour pressure (due to a reduction in vapour pressure according to Raoult's Law) than the solvent drop on the other thermistor. Sufficient solvent now condenses out of the vapour space until the heat of condensation raises the temperature of the solution drop to such an extent that its vapour pressure corresponds to the pressure in the cell. This results in a temperature difference ΔT between the two thermistors which is proportional to the vapour pressure difference of the two drops; i.e. the concentration of the solution.

Before the start of the measurement, the instrument was set at zero. This was done by applying solvent to both thermistors. The instrument was adjusted until the meter read zero. Solutions containing different concentrations of a calibrating substance were next placed on one thermistor. Solutions of the liquid sample dissolved in CCl_4 were between 0.005 and 0.05 molal. A calibration curve was prepared using a known substance (benzil, i.e. diphenyl ethane dione). The measurement in scale divisions (as read on the meter) was plotted against molality.

The solution of the unknown substance (for which the weight in a certain volume of solvent was known) then gave a reading "DIVISION". The concentration corresponding to this value was read on the calibration curve. The molecular weight was calculated as follows:

$$\text{Molecular weight} = \frac{\text{sample weight in mg}}{\text{solvent volume in ml x molality found}}$$

8.10.2 Molecular Weight by Gel Permeation Chromatography:

Gel Permeation Chromatography (G.P.C.) is one of the most advance techniques, and works on the principle of non-destructive separation of the molecules of a mixture based on the size of the molecules in solution. To use G.P.C., the sample must first be dissolved in an appropriate solvent. The separation of sample molecules is based upon difference in their "effective size" in solution, which is very closely related to molecular weight. Separation is accomplished by a column containing closely-controlled pore sizes. Molecules with small effective sizes (low molecular weight) will penetrate more pores than molecules of higher molecular weight and therefore take longer to emerge from the column than the larger molecules. If the column packing material covers the appropriate range of molecular sizes, the result will be a size separation with the largest molecules coming out first (Figure 8.19).

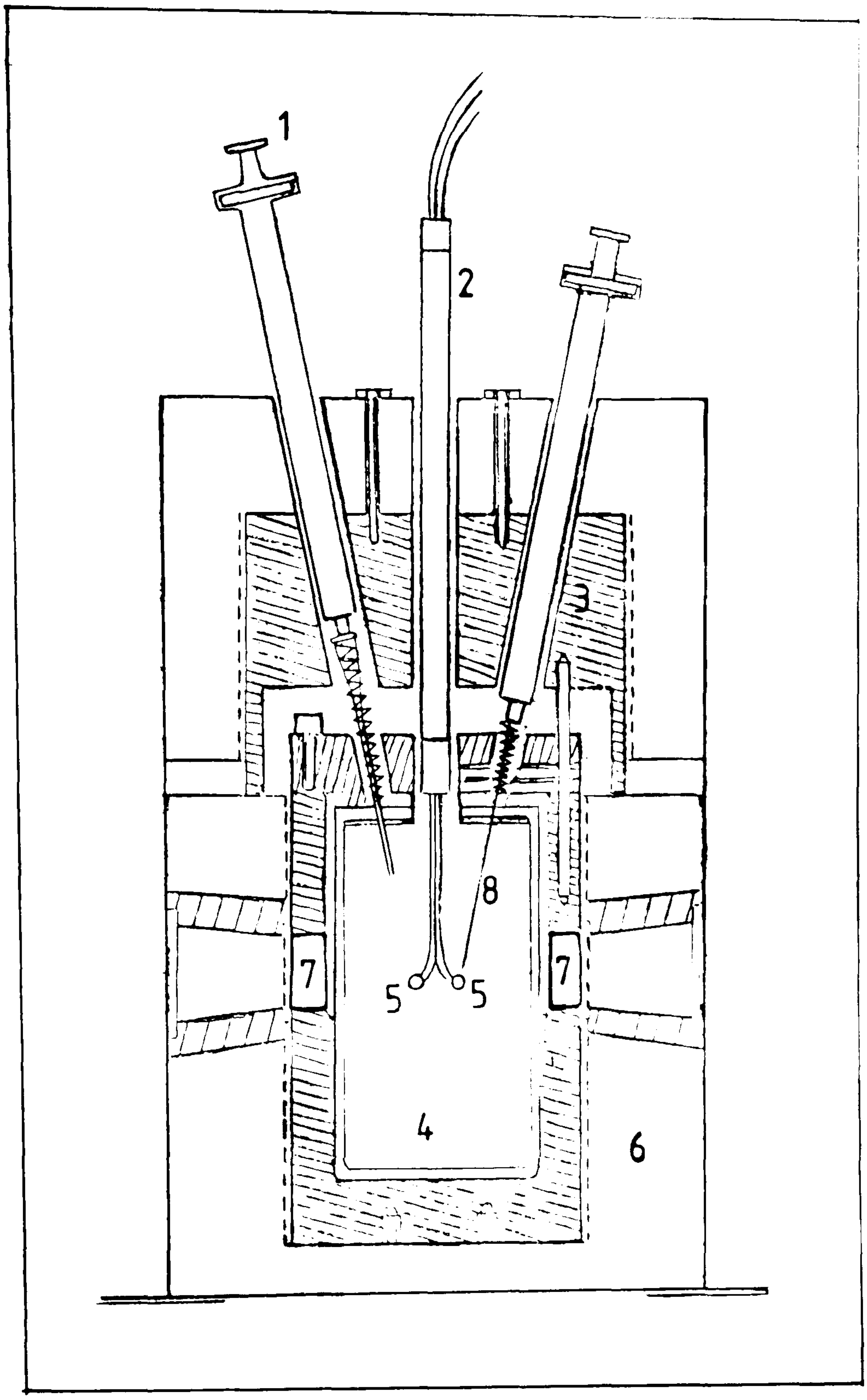


Figure 8.18 Diagram of Vapour Pressure Osmometry Cell

1. Syringe	2. Thermistor probe	3. Metal-block for syringe heating
4. Measuring cell	5. Thermistor	6. Glass wool insulation
7. Inner glass window		8. Needle

A Waters G.P.C. apparatus was used for the determination of molecular weights of crude oils residues >250°C, heavy petroleum products and base oils. The apparatus (ref: Millipore Waters HPLC Catalog) consisted of (Figure 8.20.):

a - Waters Intelligent Sample Processor, WISP Model 710B:
A fully automatic sample injection module capable of continuously variable injection volumes, automatic needle wash and individual sample programming.

b - Solvent Delivery Systems Model 6000 A:
A high-precision, versatile solvent delivery system with full range of flow rates from 0.1 to 9.9 ml/min. up to 6000 psi.

c - Discrete Multi-wavelength Absorbance Detector, Model 441 UV/VIS:
A Low UV to visible discrete multi-wavelength absorbance detector with eleven available wavelengths from from 214nm. to 658nm. Standard wavelength is 214nm or 229nm.

d - Differential Refractive Index Detectors - 400 Series:
A Differential Refractometer could be used throughout the entire RI range from 1.00 to 1.75 for detecting changes in refractive index as small as 10^{-7} RI units.

e - Data Module - Model 730:
A Printer, plotter and integrator that calculated and reported chromatographic data. It featured a choice of calculation method, base line corrections, and individual sample calculations with 10 calibration files.

f - Automated Gradient Controller - Model 680:
A CRT - interactive pump controller which automates set -up and control of up to 3 Waters solvent delivery systems for microprocessor - controlled automatic gradient and/or flow programming operations.

g - G.P.C. Columns:
ULTRASTYRAGEL Columns represent state-of -the-art technology for Gel Permeation Chromatogrphy.

The packing materials are manufactured by crosslinking styrene divinyl benzene to form small, rigid, gel particles with carefully controlled pore sizes. In the present work, three stainless steel columns, of dimensions 7.8mm x 30 cm each,were connected together in series. The pore sizes of the packing material were 1000 Å, 500 Å and 100 Å, respectively.

Polystyrenes and petroleum products of known molecular weights were used to prepare a calibration curve, of molecular weights plotted against the retention times.

An exact weight of the sample was dissolved in tetrahydrofurane (T.H.F.), approximately 0.02 mg/2 ml. The sample was then filtered using the special, highly inert filter. The sample was then placed in the sample processor WISP for automatic injection.

Operational Conditions:

column: Ultrastyragel 1000 Å - 500 Å - 100 Å

solvent: T H F, HPLC grade

flow rate: 0.8 ml/min.

Injection volume: 10μl.

Detector: R.I.

calibration standards: polystyrene and petroleum products

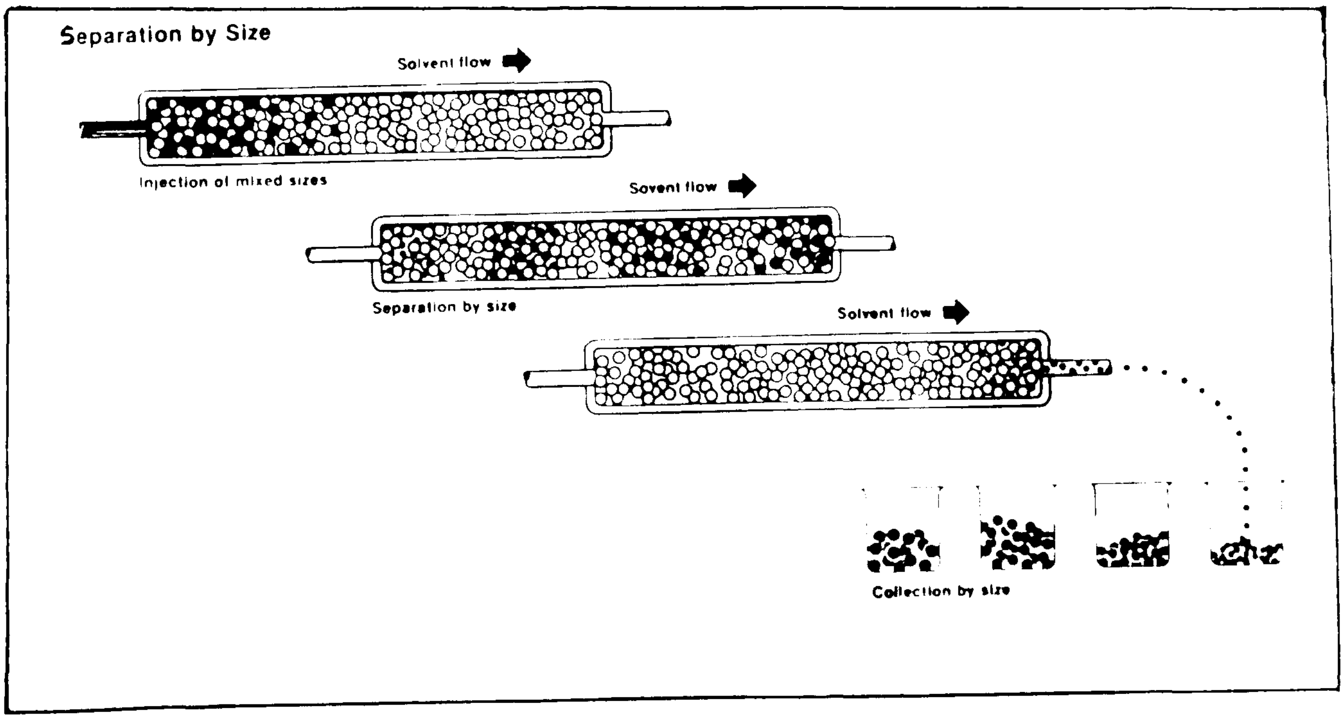


Figure 8.19. The Principle of Separation by Size in G.P.C. Columns

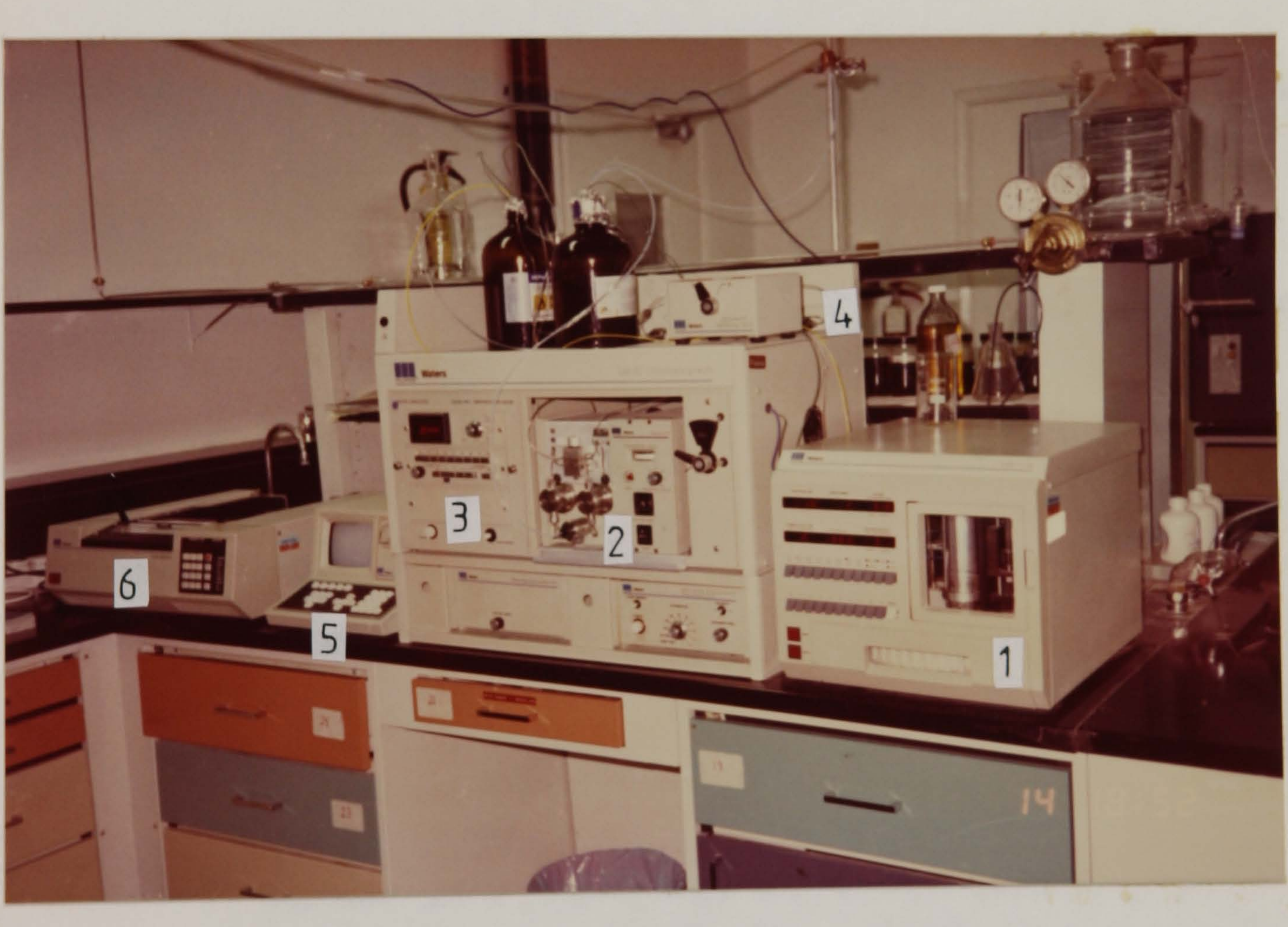


Figure 8.20. "Waters" Gel Permeation Chromatography Apparatus.

1. Automatic sample injection module
2. Solvent delivery system
3. Detector
4. Columns
5. System controller
6. Data module

8.11 DETERMINATION OF ASPHALTENES CONTENT:

The asphaltenes content of a petroleum liquid is the percentage by weight of wax-free material insoluble in n-heptane but soluble in hot benzene. In the present work, the IP 143/84 standard method (16) was followed for the determination of asphaltenes precipitation of base oils, petroleum products and of crude oils topped to 260°C, by normal heptane.

A known quantity of the sample was dissolved in n-heptane and the insoluble material, consisting of asphaltenes and waxy substances, was separated under the hot reflux with n-heptane. The asphaltenes were isolated by extraction with toluene. The solvent was then evaporated at a temperature of 110°C. The weight of dry asphaltenes was measured and the percent weight was then determined.

Crude oil samples were, initially, distilled up to 260°C and the residues were then extracted by normal heptane as described above.

Duplicate results should not differ by more than 5% (16); in this study they were in fact within 3.5%.

8.12 DETERMINATION OF WAX CONTENT:

Wax content was determined by its separation from crude oils and other hydrocarbon oils containing asphaltenes.

Initially, 5 gm of sample was dissolved in 10 ml of petroleum spirit (60-80°C boiling range) and then de-asphalted by adding it on top of a glass column containing activated alumina (50 g). Elution was then performed with about 250 ml of petroleum spirit. The eluant was then collected and the solvent evaporated in a pre-weighed flask (Figure 8.21).

The contents of the flask were dissolved in hot dichloromethane. The volume of dichloromethane required was normally 10 ml for each gram of sample. The solution in the flask was then cooled to -32°C, and the precipitated wax was separated by filtration, through a specially-designed sintered glass filter funnel, using suction. The filtrate contained the solvent and the dissolved coloured oily materials, while a white pure wax was retained in the funnel. If the wax separated was of oily appearance or coloured, then the addition of dichloromethane and filtration was be repeated.

The separated wax was, then, dissolved in hot petroleum spirit. The solvent was then evaporated and the weight of wax measured. The percentage by weight of wax was calculated as follows:

$$\text{wax \% (@ -32°C)} = \frac{A}{B} \times 100$$

where,

A = weight (g) of wax separated

B = weight (g) of original sample

The asphaltenes - free petroleum products or base oils did not require de-asphalting, and de-waxing was performed directly.

8.13. MEASUREMENT OF CRUDE OIL STABILITY

This experiment was carried out for the determination of the stability of crude oils against stratification and layering, which may occur on long-term storage. No standard test method exists for this; therefore a simple technique was developed.

A crude oil sample (1500ml) was placed in a transparent glass measuring graduated cylinder. Two metal syringe needles were fitted into the measuring cylinder via a cork, shown in Figure 8.22. One of the needles was long enough to reach the bottom of

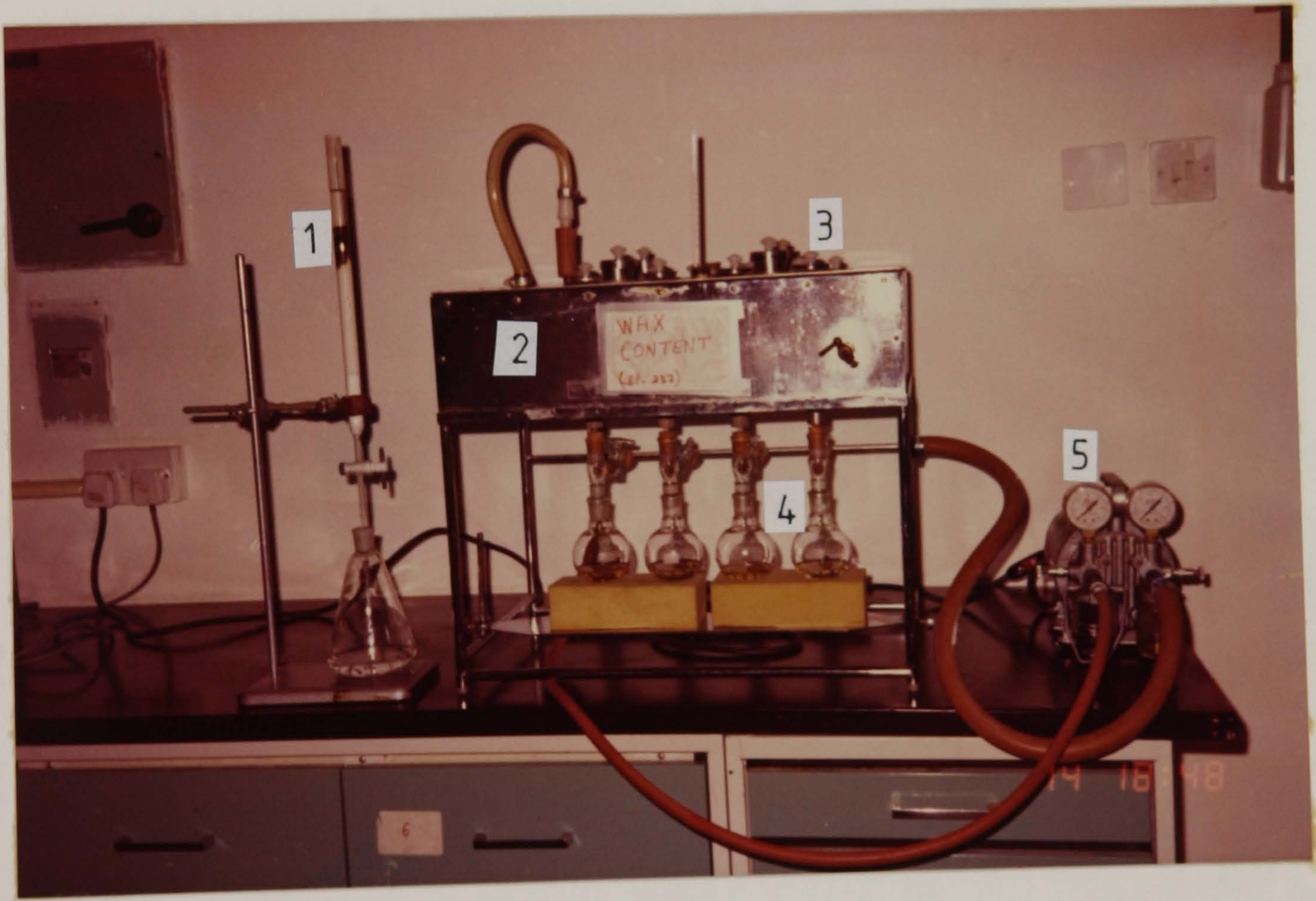


Figure 8.21 De-asphalting Column Chromatography and Wax Content Separation Apparatus

1. De-asphalting column chromatography	2. Coolant container
3. Sintered glass filter funnel	4. Flasks containing filtrates
5. Vaccum pump	

the cylinder, for the withdrawal of bottom samples; the other extended about 3 cm below the level of the crude oil in the cylinder, for top samples withdrawal.

50 ml capacity syringes were used to withdraw crude samples.

Three different measuring cylinders containing each particular crude oil were maintained at three different temperatures, i.e. 1°C ± 1, 16°C ± 1 and 30°C ± 1, for the duration of the test (12 weeks). Care was taken not to expose the cylinders to any shaking or weathering of the crudes, particularly during withdrawal samples.

Top and bottom samples (30 ml) were withdrawn from each cylinder, by the means of the syringes, for kinematic viscosity determinations, initially and after time periods of 2, 4, 8 and 12 weeks. Details of the calculations are given in Section 9.7.

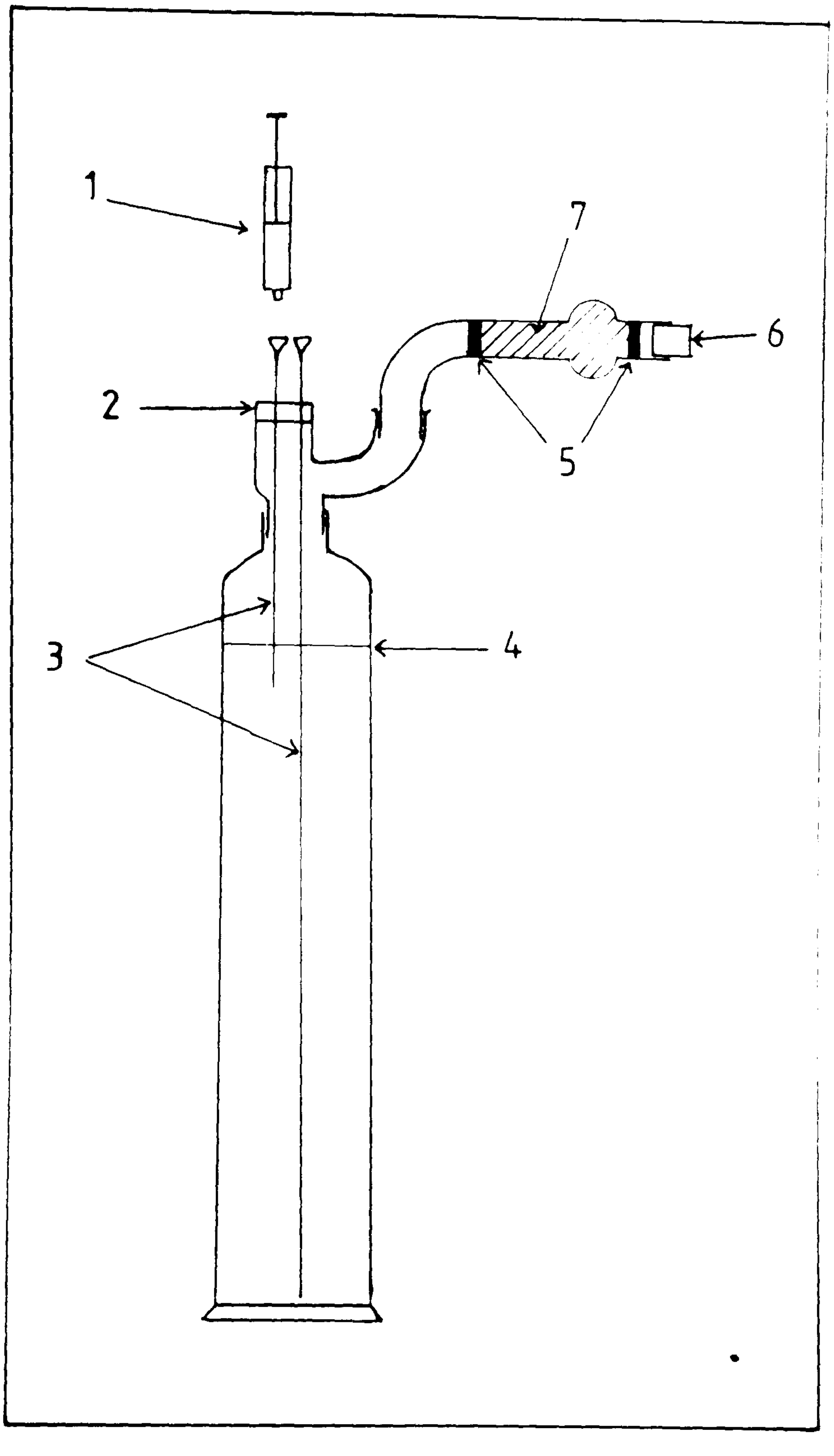


Figure 8.22 Apparatus for the Determination of Crude Oil Stability

1. Syringe 2. Cork 3. Syringe needles 4. Crude oil level

5. Glass wool 6. Stopper 7. Drying agent ($CaCl_2$)

CHAPTER 9

RESULTS AND DISCUSSION

9.1 MOLECULAR WEIGHT

The molecular weights of crude oils, base oils and petroleum products and their binary mixtures, measured as described in Section 8.10, are summarised in Tables 9.1, 9.2 and 9.3, and presented graphically in Figures 9.1, 9.2 and 9.3.

The molecular weight of liquid mixtures is an additive property, ie. the molecular weight composition diagrams of binary mixtures exhibit a linear relationship. Hence,

$$M_{mix} = \Sigma x_i M_i \qquad (9.1)$$

where,

M_{mix} = molecular weight of the mixtures
M_i = molecular weight of each components
x_i = mole, volume or weight fraction of component

However, the measured molecular weight-composition diagrams of the petroleum oils tested in this study were not smooth straight lines. This was attributable to the unavoidable experimental errors in measuring the molecular weight of petroleum oils, which are very complex and undefined mixtures. Similar observations have been reported by other workers(5,131,132).

Therefore, to facilitate the use of the molecular weight values in later calculations, the mixture molecular weights were calculated via equation 9.1.

Table 9.1: Measured Molecular Weights of Crude Oil Binary Mixtures

Mixture	Molecular Weight
Light crude oil	275
Medium crude oil	320
Heavy crude oil	475
Mix 1	280
Mix 2	290
Mix 3	300
Mix 4	305
Mix 5	280
Mix 6	305
Mix 7	340
Mix 8	430
Mix 9	330
Mix 10	355
Mix 11	390
Mix 12	460

The mixtures are identified on p. 160.

Table 9.2: Measured Molecular Weights of Base Oils Binary Mixtures

Mixture	Molecular Weight
Light base oil	290
Medium base oil	335
Heavy base oil	410
Bright stock	590
Mix 1	330
Mix 2	325
Mix 3	320
Mix 4	300
Mix 5	365
Mix 6	350
Mix 7	335
Mix 8	305
Mix 9	510
Mix 10	465
Mix 11	395
Mix 12	320
Mix 13	540
Mix 14	460
Mix 15	420
Mix 16	360
Mix 17	545
Mix 18	535
Mix 19	465
Mix 20	440

The mixtures are identified on p. 162.

Table 9.3: Measured Molecular Weights of Petroleum Products Binary Mixtures

Mixture	Molecular Weight
Kerosene	245
Heavy gas oil	310
Residue > 360^oC	780
Mix 1	270
Mix 2	-
Mix 3	260
Mix 4	250
Mix 5	550
Mix 6	310
Mix 7	285
Mix 8	270
Mix 9	680
Mix 10	430
Mix 11	340
Mix 12	290

The mixtures are identified on p. 161.

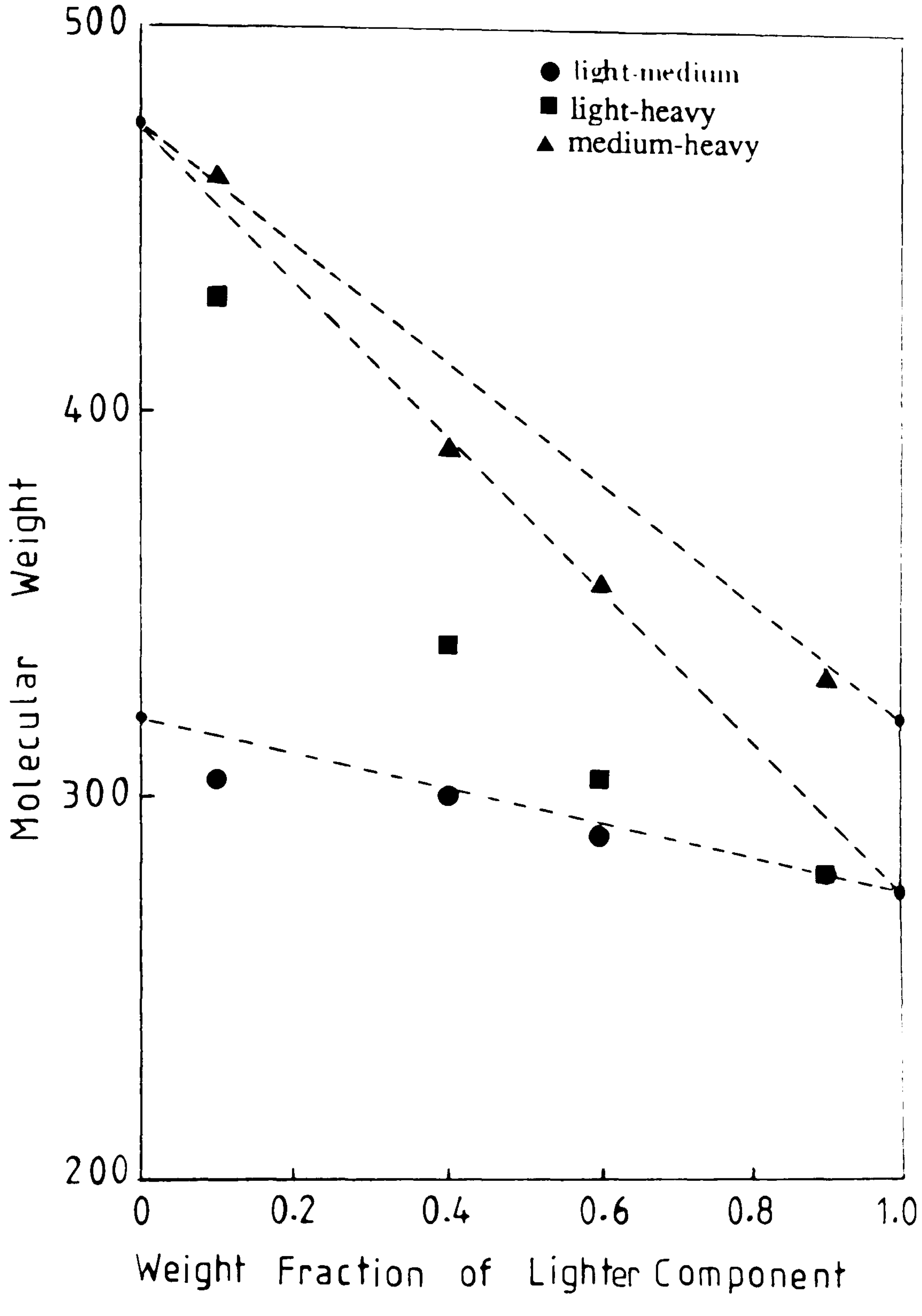


Figure 9.1: Measured Molecular Weights of Crude Oil Binary Mixtures

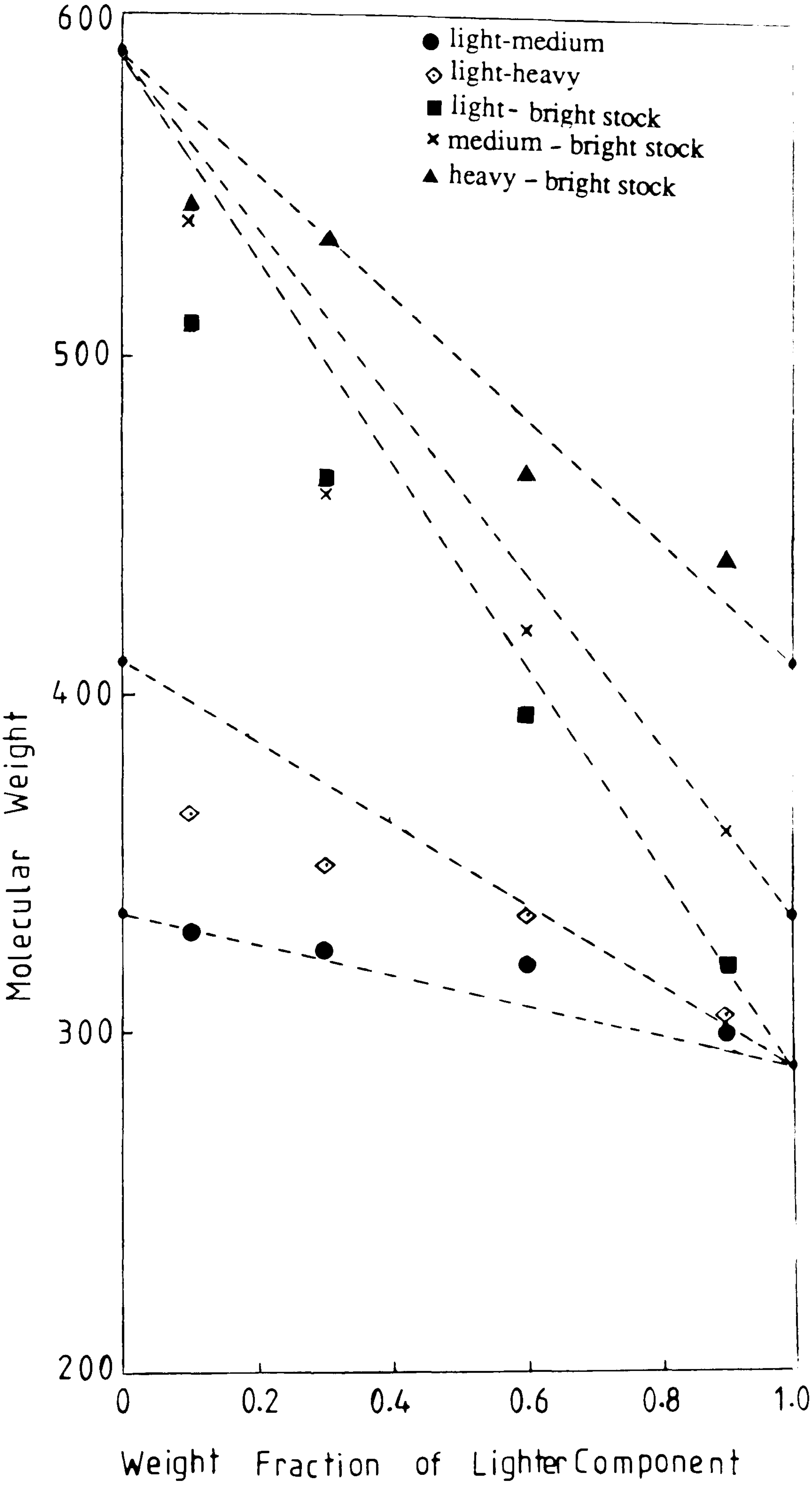


Figure 9.2: Measured Molecular Weights of Base Oil Binary Mixtures

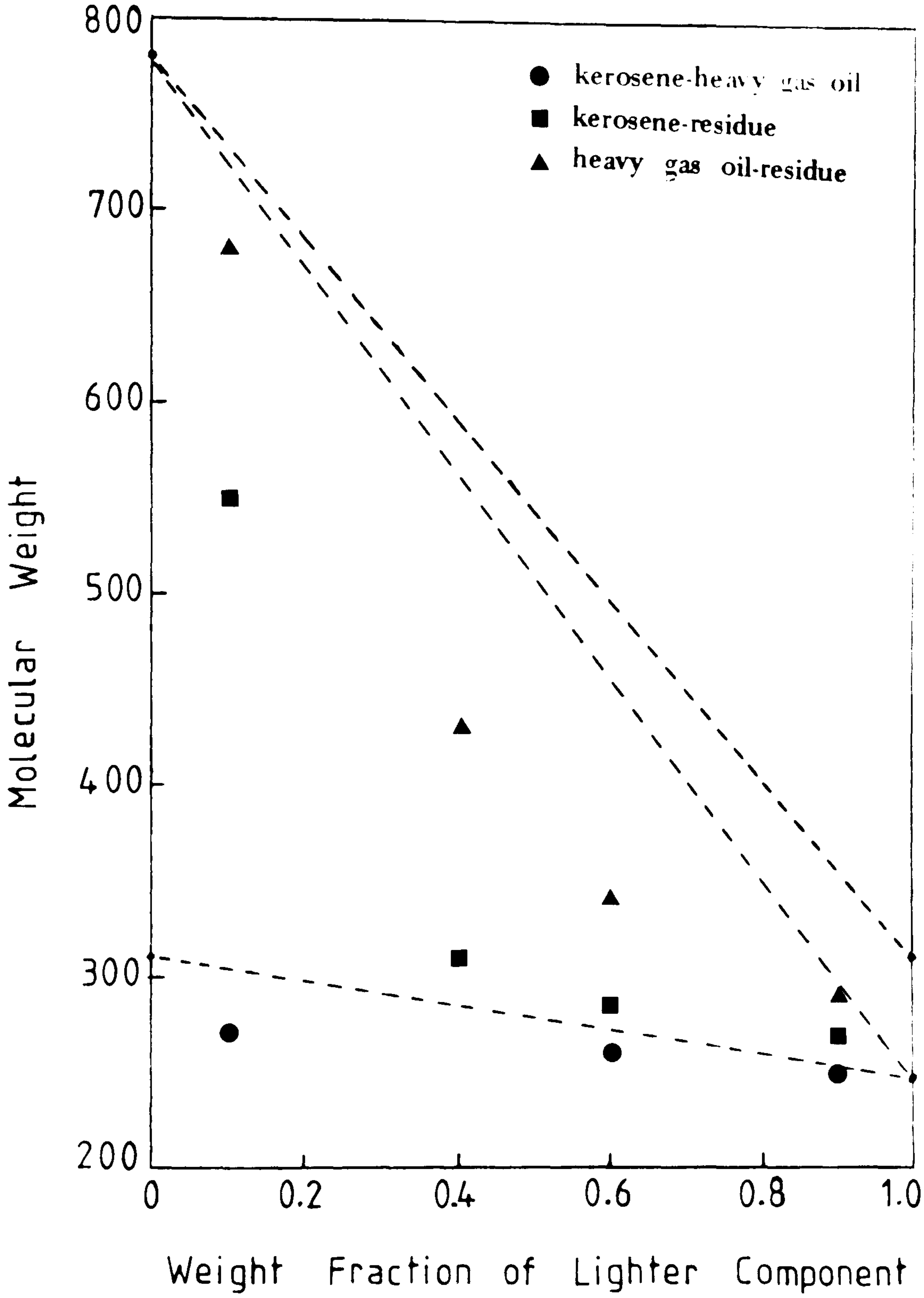


Figure 9.3: Measured Molecular Weights of Petroleum Products Binary Mixtures

9.2 DENSITIES AND MOLAR VOLUMES OF PETROLEUM OILS BINARY MIXTURES

9.2.1 Density

The densities @ 15^{o}C of crude oil, petroleum products and base oil binary mixtures, measured by the method described in Section 8.9, are summarised in Tables 9.4, 9.5 and 9.6; and presented graphically in Figures 9.4, 9.5 and 9.6 respectively.

It is clear that the density did not blend linearly, ie. slightly lower densities were obtained than for the ideal case. Although, in general, the divergence from ideality was very small (especially for mixtures of similar nature, eg. base oils), the density-composition diagrams were not linear, but curved down slightly, indicating the non-ideal behaviour.

Generally, as the difference in the densities of the components ($\Delta\rho$) increased, the divergence from ideality also increased. However, the highest divergence (ie. highest non-ideality) was observed when the two components differed widely in their chemical and physical composition (eg. kerosene and residue).

This "non-ideality" appeared to be real, since if the deviations were due to experimental error, they would have been random. The non-ideal behaviour is, therefore, attributable to minor volume changes on blending, as reported previously, for different pure hydrocarbons binary mixtures by many workers(133-139). The behaviour is presumed to be analogous to that discussed in Section 9.3.

Although the densities of the binary mixtures of crude oils and their products behaved non-linearly, as an approximation, density may be considered as an additive property. Therefore, the density of a mixture can be calculated:

Error
[illegible]

$$\rho_{mix} = \Sigma x_i \rho_i \qquad 9.2$$

$$\frac{\Sigma \rho_i V_i}{\Sigma V_i}$$

where,

ρ_{mix} = density of the mixture

ρ_i = density of each component

x_i = weight fraction

This approximation is permissible, because the non-ideality of the density upon blending is so small, ie. the % deviations of the density, calculated by equation 9.2 from the measured values, are only 0.13%, 0.06% and 0.57% for crude oils, base oils and petroleum products binary mixtures, respectively.

Equation 9.2 is of practical value, because densities of petroleum oils are widely used in petroleum and chemical engineering calculations.

Table 9.4: Measured and Calculated Densities by Equation 9.2 for Crude Oil Binary Mixtures

Mixtures	ρ (measured) (g/ml)	$\Sigma x_i \rho_i$ (g/ml)	% dev.
Light crude oil	0.8445		
Medium crude oil	0.9059		
Heavy crude oil	0.9667		
Mix 1	0.8506	0.8506	0
Mix 2	0.8680	0.8691	0.12
Mix 3	0.8801	0.8813	0.14
Mix 4	0.8998	0.8998	0
Mix 5	0.8550	0.8567	0.20
Mix 6	0.8911	0.8934	0.26
Mix 7	0.9150	0.9178	0.31
Mix 8	0.9530	0.9545	0.16
Mix 9	0.9120	0.9120	0
Mix 10	0.9281	0.9302	0.23
Mix 11	0.9408	0.9424	0.17
Mix 12	0.9606	0.9606	0
Absolute Average % Deviation			0.13

Table 9.5: Measured and Calculated Densities by Equation 9.2 for Base Oils Binary Mixtures

Mixtures	ρ (measured) (g/ml)	$\Sigma x_i \rho_i$ (g/ml)	% dev.
Light base oil	0.8624		
Medium base oil	0.8782		
Heavy base oil	0.8842		
Bright stock	0.8938		
Mix 1	0.8764	0.8766	0.03
Mix 2	0.8730	0.8735	0.05
Mix 3	0.8682	0.8687	0.06
Mix 4	0.8636	0.8640	0.05
Mix 5	0.8812	0.8820	0.09
Mix 6	0.8767	0.8777	0.11
Mix 7	0.8705	0.8711	0.07
Mix 8	0.8640	0.8646	0.07
Mix 9	0.8900	0.8907	0.07
Mix 10	0.8832	0.8844	0.13
Mix 11	0.8739	0.8750	0.12
Mix 12	0.8650	0.8655	0.06
Mix 13	0.8919	0.8922	0.03
Mix 14	0.8899	0.8891	-0.09
Mix 15	0.8840	0.8844	0.05
Mix 16	0.8796	0.8798	0.02
Mix 17	0.8930	0.8928	-0.02
Mix 18	0.8905	0.8909	0.05
Mix 19	0.8875	0.8880	0.06
Mix 20	0.8847	0.8852	0.05
Absolute Average % Deviation			0.06

Table 9.6: Measured and Calculated Densities by Equation 9.2 for Petroleum Products Binary Mixtures

Mixtures	ρ (measured) (g/ml)	$\Sigma x_i \rho_i$ (g/ml)	% dev.
Kerosene	0.8190		
Heavy gas oil	0.9177		
Residue > 360°C	0.9940		
Mix 1	0.9039	0.9078	0.43
Mix 2	0.8725	0.8782	0.65
Mix 3	0.8540	0.8585	0.52
Mix 4	0.8258	0.8289	0.37
Mix 5	0.9712	0.9765	0.55
Mix 6	0.9101	0.9240	1.53
Mix 7	0.8808	0.8890	0.93
Mix 8	0.8332	0.8365	0.40
Mix 9	0.9841	0.9864	0.23
Mix 10	0.9582	0.9635	0.55
Mix 11	0.9440	0.9482	0.45
Mix 12	0.9231	0.9253	0.24
Absolute Average % Deviation			0.57

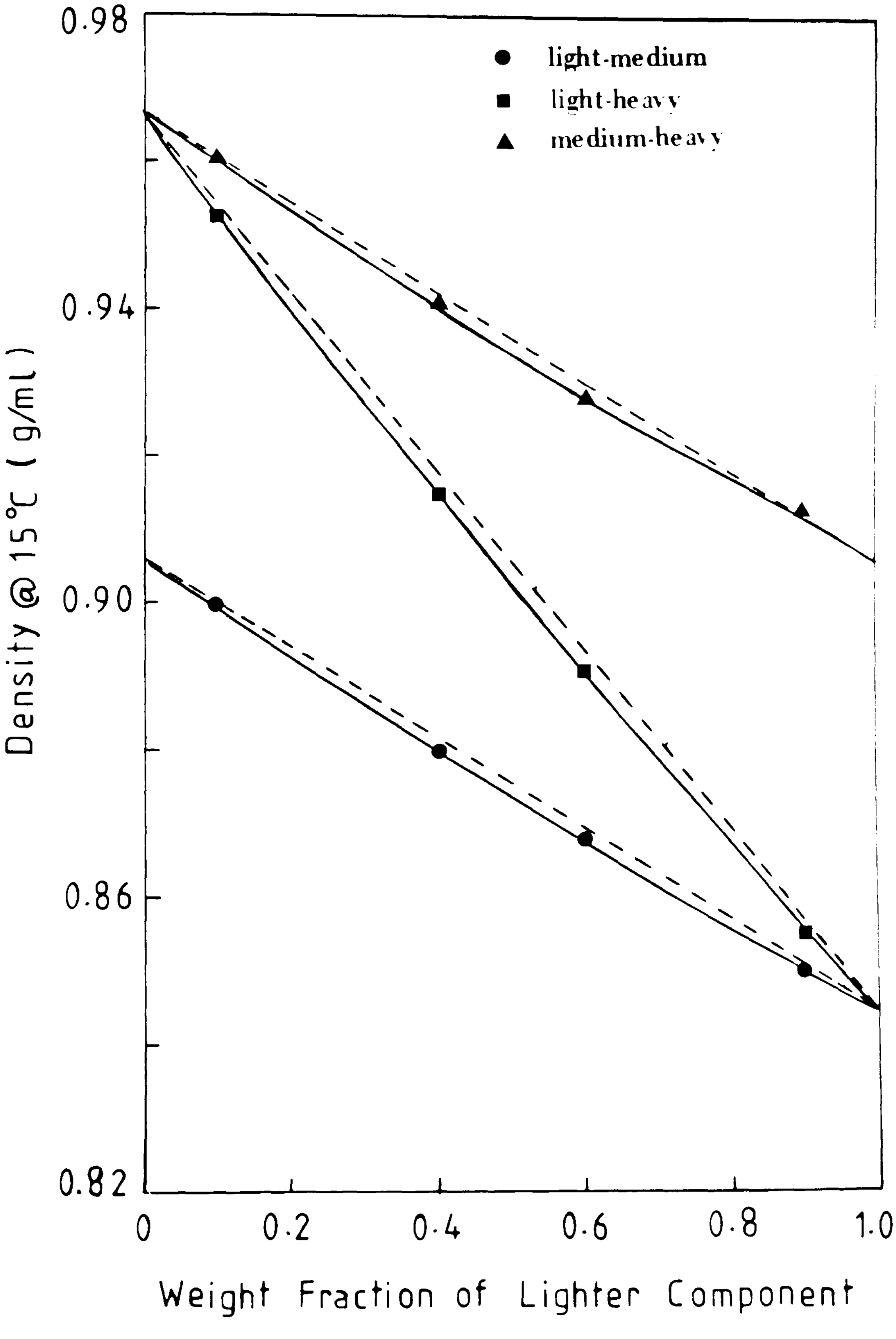


Figure 9.4: Densities of Crude Oil Binary Mixtures

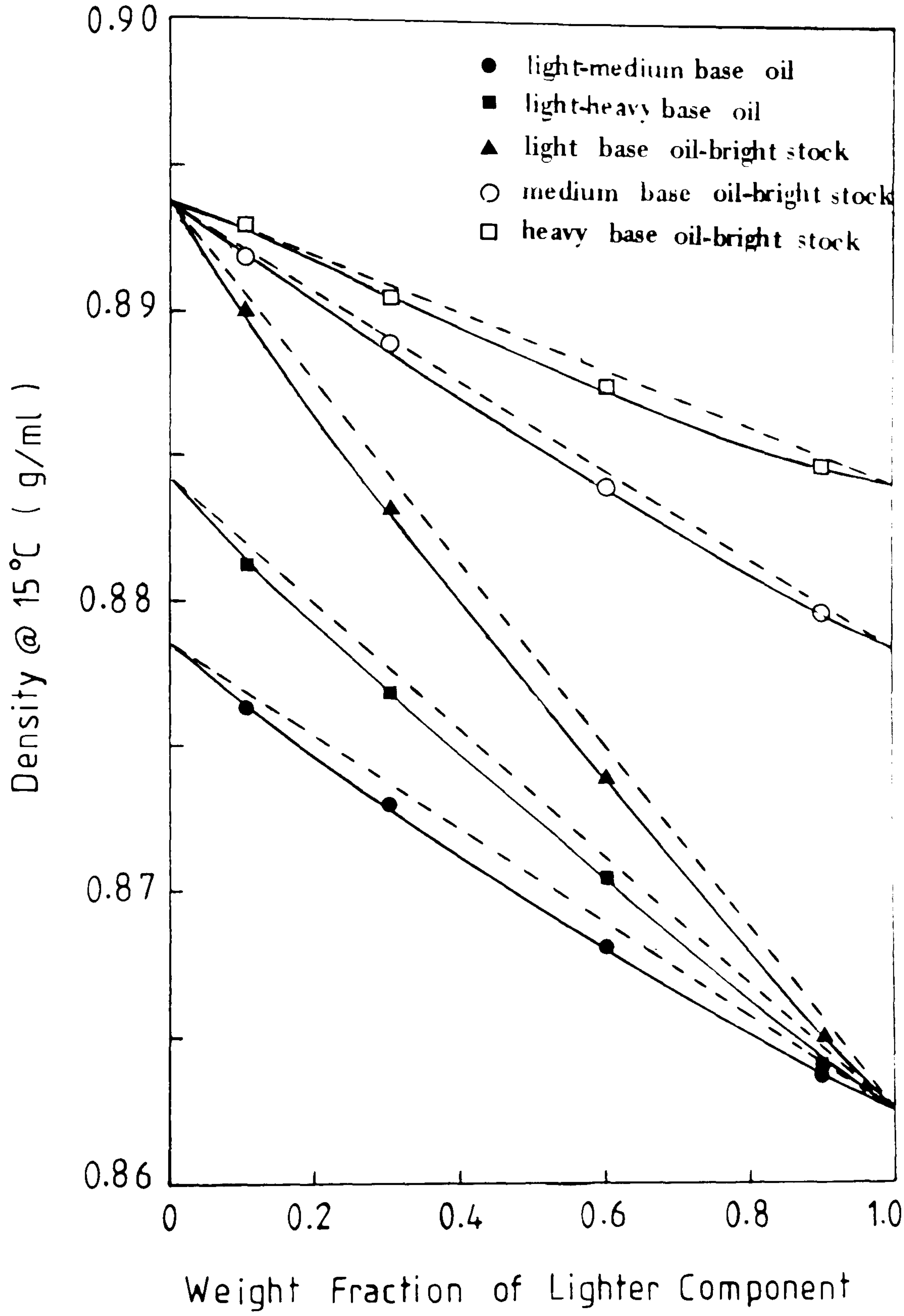


Figure 9.5: Densities of Base Oils Binary Mixtures

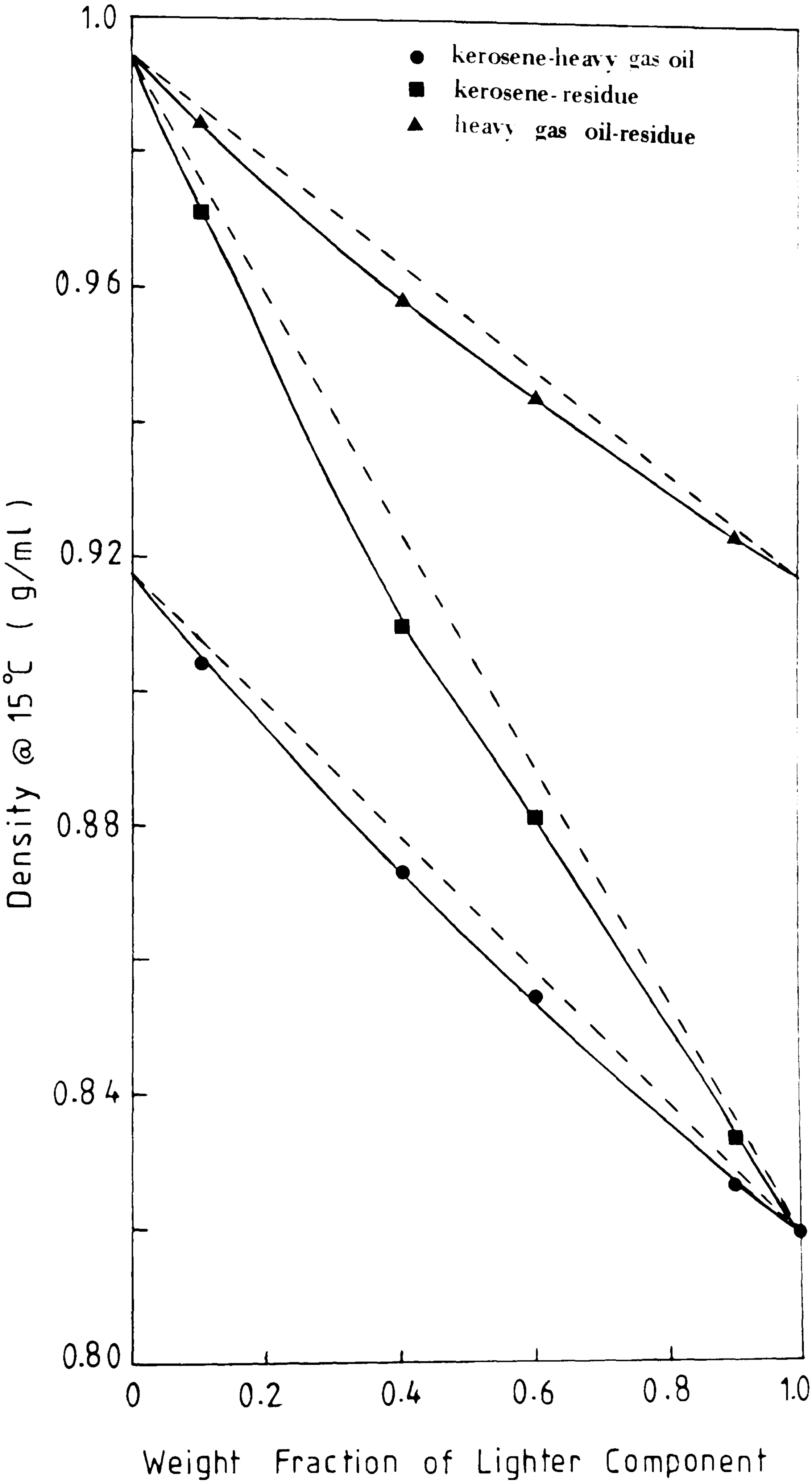


Figure 9.6: Densities of Petroleum Products Binary Mixtures

9.2.2 Molar Volumes

The measured densities of the crude oils, base oils, petroleum products and their binary mixtures summarised in Tables 9.4, 9.5 and 9.6 and the corresponding molecular weights calculated by equation 9.1 were used to calculate the corresponding molar volumes (V_m). The data obtained are summarised in Tables 9.7, 9.8 and 9.9 and presented graphically in Figures 9.7, 9.8 and 9.9.

The molar volumes of all binary mixtures exhibited non-ideal behaviour as indicated in V_m-composition diagrams (Figures 9.7, 9.8 and 9.9), where the actual molar volumes are slightly higher than the ideal molar volumes calculated from the equation,

$$V_{m,\,mix} = \Sigma\, x_i\, V_{m,i} \qquad 9.3$$

where

$V_{m,mix}$ = molar volume of mixture

$V_{m,i}$ = molar volume of each component

x_i = weight fraction

Table 9.7: Calculated Molar Volumes (V_m) of Crude Oils Binary Mixtures

Mixtures	V_m (cm^3)
Light crude oil	326
Medium crude oil	353
Heavy crude oil	491
Mix 1	329
Mix 2	338
Mix 3	343
Mix 4	351
Mix 5	345
Mix 6	398
Mix 7	432
Mix 8	477
Mix 9	368
Mix 10	412
Mix 11	439
Mix 12	479

Table 9.8: Calculated Molar Volumes (V_m) of Base Oils Binary Mixtures

Mixture	V_m (cm^3)
Light base oil	336
Medium base oil	381
Heavy base oil	464
Bright stock	660
Mix 1	377
Mix 2	369
Mix 3	355
Mix 4	342
Mix 5	452
Mix 6	427
Mix 7	388
Mix 8	350
Mix 9	629
Mix 10	566
Mix 11	469
Mix 12	370
Mix 13	634
Mix 14	578
Mix 15	494
Mix 16	409
Mix 17	641
Mix 18	602
Mix 19	543
Mix 20	483

Table 9.9: Calculated Molar Volumes (V_m) of Petroleum Products Binary Mixtures

Mixture	V_m (cm^3)
Kerosene	299
Heavy gas oil	338
Residue > 360°C	785
Mix 1	339
Mix 2	326
Mix 3	317
Mix 4	305
Mix 5	749
Mix 6	622
Mix 7	521
Mix 8	359
Mix 9	745
Mix 10	618
Mix 11	528
Mix 12	387

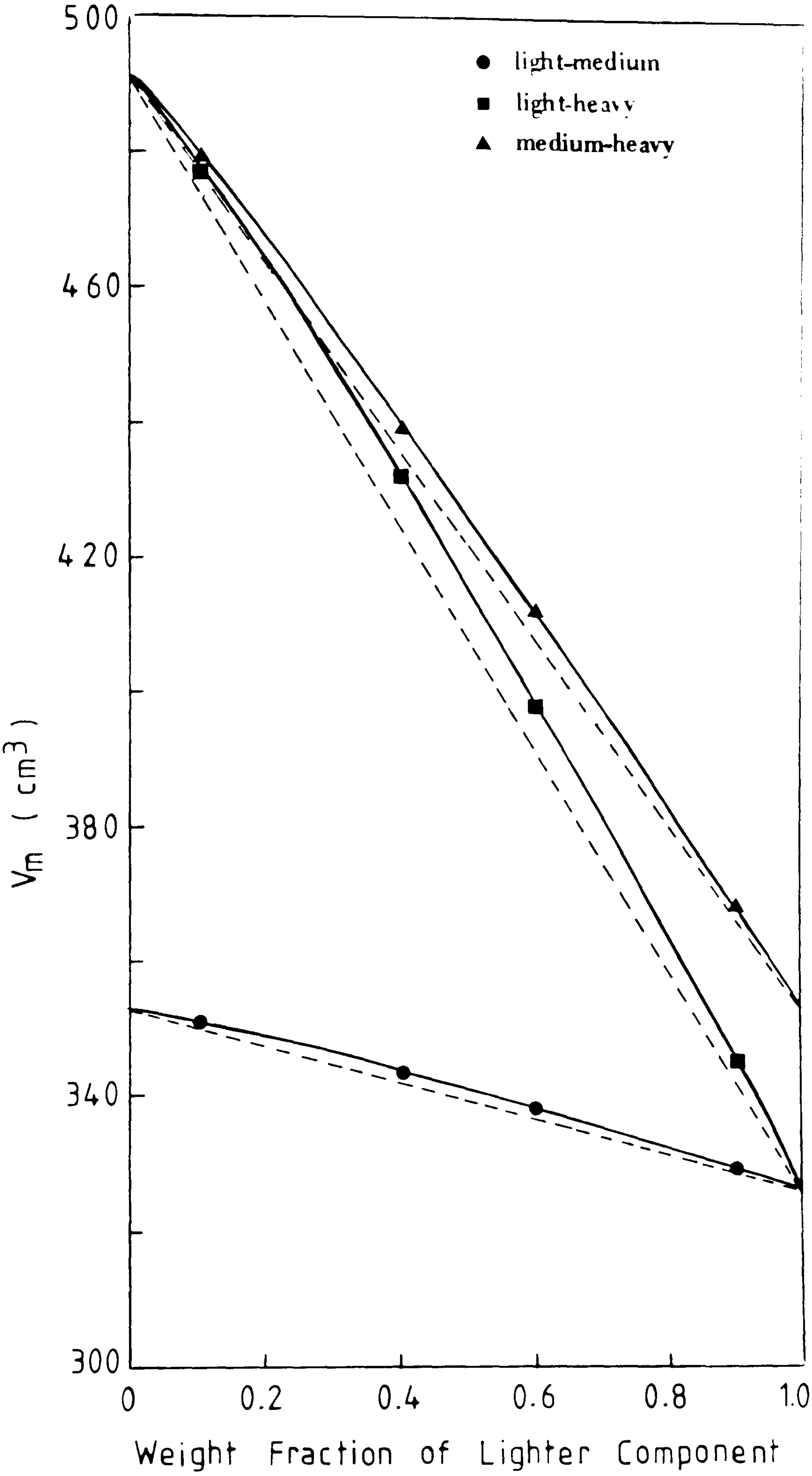


Figure 9.7: Molar Volumes of Crude Oil Binary Mixtures

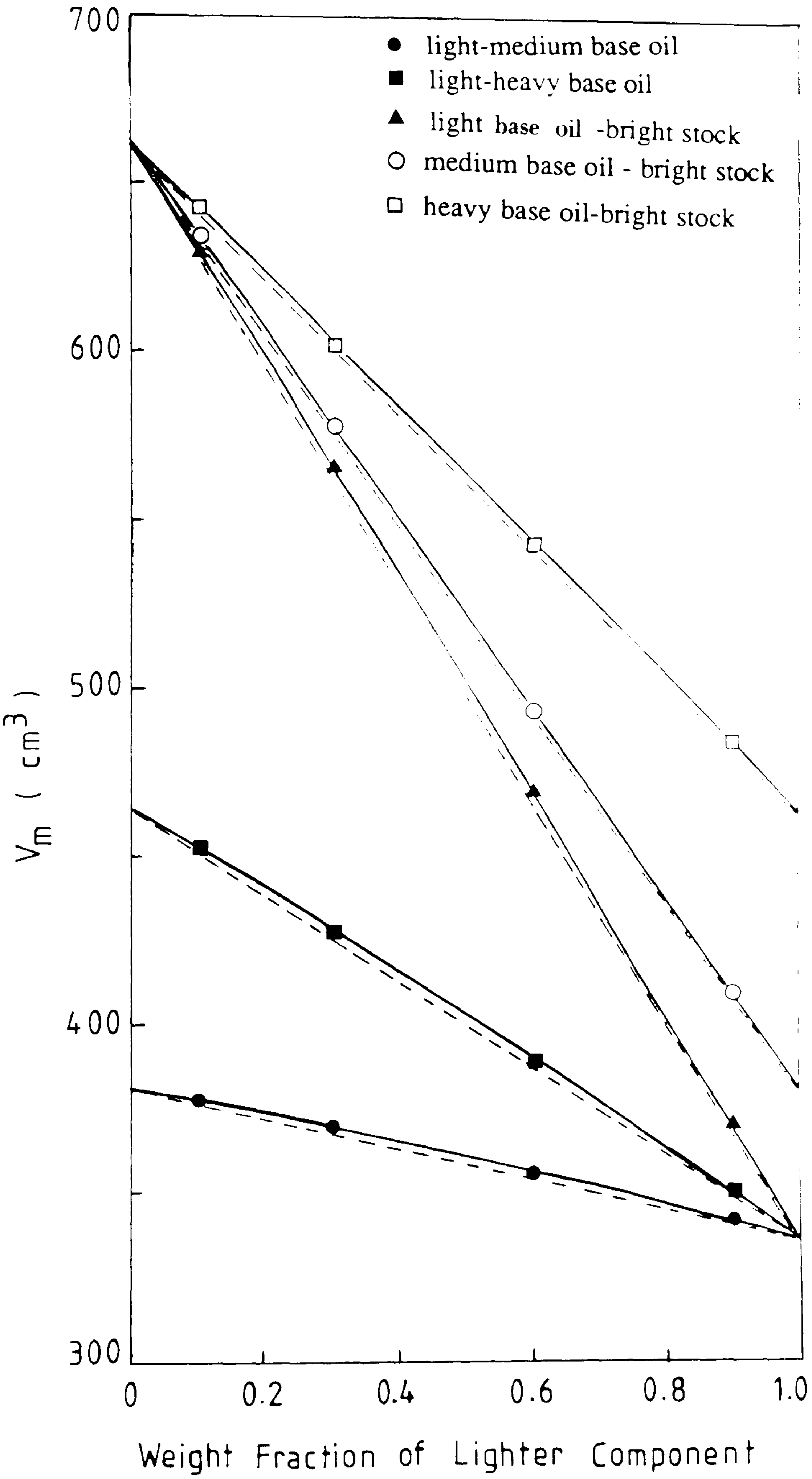


Figure 9.8: Molar Volumes of Base Oils Binary Mixtures

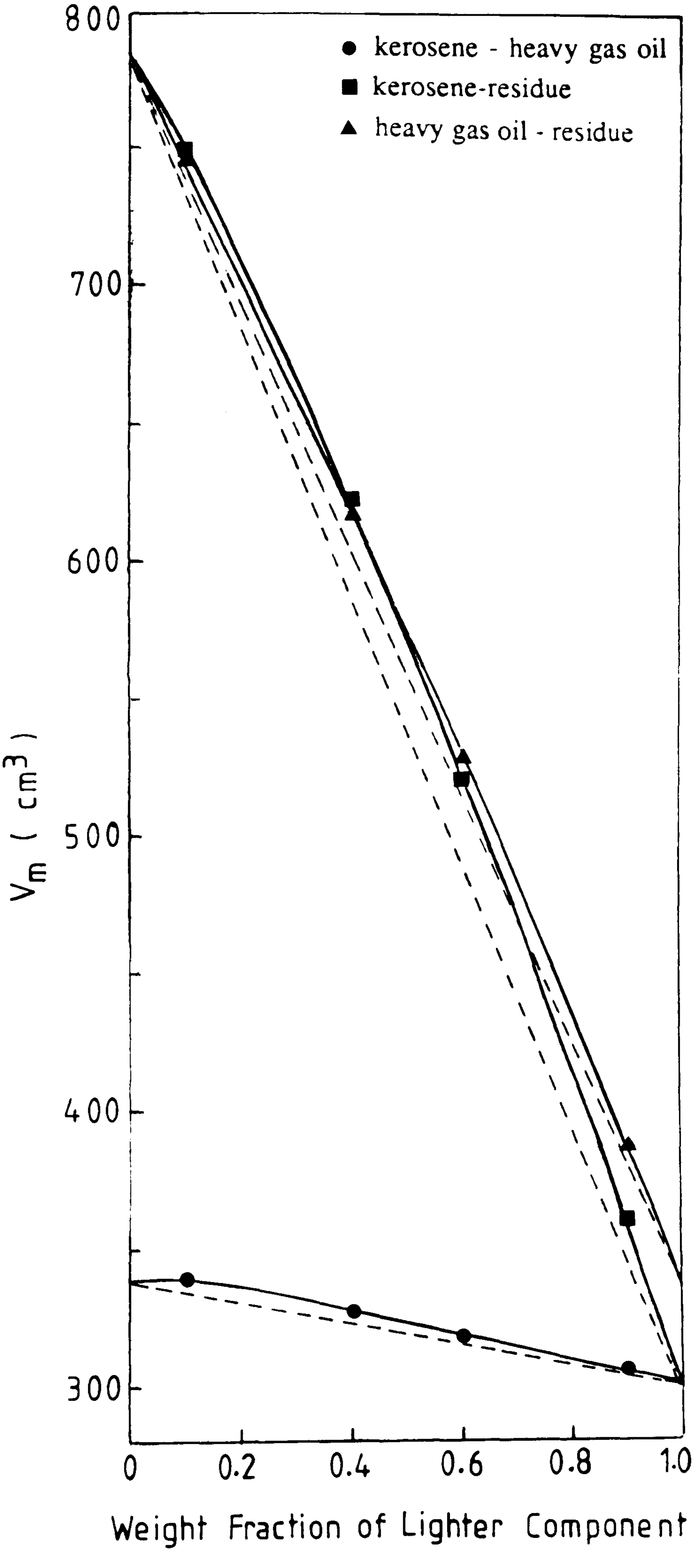


Figure 9.9: Molar Volumes of Petroleum Products Binary Mixtures

9.3 THE KINEMATIC VISCOSITY

Results of kinematic viscosity measurements on crude oils, petroleum products and their mixtures at various temperatures and pressures are presented in this chapter. The effect of temperature and pressure upon viscosity is discussed. The behaviour of the viscosity of binary mixtures prepared from the different petroleum mixtures is also discussed; a mechanism is proposed to explain the behaviour. New correlations are proposed to predict the kinematic viscosity of petroleum liquids and their mixtures at different temperatures and pressures.

9.3.1 The Effect of Temperature:

On Crude Oil Viscosity:

The kinematic viscosities of three crude oils, and binary mixtures of them at atmospheric pressure (14.7 psi) and at temperatures in the range 10°C. to 50°C. are shown in Table 9.10 and presented graphically in Figures 9.10 and 9.11. Clearly an increase in the temperature of the crude oil resulted in a significant decrease in its viscosity. This was expected since the viscosity of a petroleum liquid is known to be extremely sensitive to temperature, i.e. it increases with a decrease in the temperature of the liquid. This behaviour is common for most liquids(63,66,70,77,83,140-143).

The rate of decrease in viscosity of the crude oil with an increase in temperature varied from one crude to another. The highest rate was observed for the heavy crude oil following by the medium crude oil and, then, the light crude oil. The percentage decreases in viscosity associated with an increase in temperature of 10°C (from 10°C to 20°C) where 33.1%, 50.2%, and 59.5% for light, medium and heavy crude oils respectively. Table 9.11 summarises the percentage decreases in crude oil viscosities for incremental 10°C increases in temperature. In general, the rate of decrease in the kinematic viscosity of the heavy crude oil was higher than those of the lighter ones. The slopes of the curves in Figures 9.10 and 9.11 support this observation.

Table 9.10: Measured Kinematic Viscosities (cSt.) of Light, Medium and Heavy Crude Oils and of prepared Binary Mixtures at Atmospheric Pressure

	Kinematic Viscosity (cSt.) @				
Mixture No.	10°C	20°C	30°C	40°C	50°C
Light Crude	14.22	9.512	7.141	5.960	4.850
Medium Crude	163.4	81.46	51.81	34.63	24.98
Heavy Crude	2193	887.9	426.6	223.5	130.0
Mix 1	16.44	10.71	9.171	6.519	5.625
Mix 2	31.71	19.35	14.79	10.79	8.192
Mix 3	49.86	29.96	21.83	14.57	11.95
Mix 4	116.0	64.23	42.18	26.10	17.80
Mix 5	19.02	11.76	10.55	6.952	5.909
Mix 6	54.63	33.17	26.60	15.43	11.98
Mix 7	146.1	78.80	52.10	32.02	20.70
Mix 8	1023	442.5	230.1	129.6	75.02
Mix 9	200.9	101.2	62.65	37.56	25.10
Mix 10	381.6	186.0	109.6	64.41	38.06
Mix 11	643.1	298.6	180.7	97.45	60.81
Mix 12	1676	729.3	372.3	188.6	109.0

Table 9.11:The % Decrease in Crude Oil Viscosities for Incremental 10°C Temperature Increased in the Range 10°C to 50°C

	% Decrease in Kinematic Viscosity @				
Crude Oil	10°C (Initial)	20°C	30°C	40°C	50°C
Light Crude Oil	14.22 cSt.	33.1	49.8	58.1	65.9
Medium Crude Oil	163.4 cSt.	50.2	68.3	78.8	84.7
Heavy Crude Oil	2193 cSt.	59.5	80.6	89.8	94.1

The % decreases in the kinematic viscosities of heavier crude oils as a result of the addition of lighter ones (giving mixtures of compositions summarised in Table 8.4 in Chapter 8), within a temperature range of 10°C - 50°C, are shown in Table 9.12. It is clear that, generally, for a given set of binary mixtures (e.g. addition of 10 % weight of lighter crude to a heavier one), the rate of decrease in kinematic viscosity decreases with increase in temperature.

This implies that the response of the rate of change in viscosity due to temperature is higher for heavy crude oils than light ones, and decreases in magnitude as the temperature increases.

Table 9.12: The Effect of Temperature on the Rate of Decrease in Kinematic Viscosity due to the Addition of Lighter Crude Oil to a Heavier One.

% wt of lighter Crude added to the heavier		Binary System	% Decrease in Kinematic Viscosity @				
			10°C	20°C	30°C	40°C	50°C
10%	L-M	L-M	29.0	21.2	18.6	24.6	28.7
	L-H	L-H	53.4	50.2	46.1	42.0	42.3
	M-H	M-H	23.6	17.9	12.7	15.6	16.1
40%	L-M	L-M	69.5	63.2	57.9	57.9	52.2
	L-H	L-H	93.3	91.1	87.8	85.7	84.1
	M-H	M-H	70.7	66.4	57.7	56.4	53.2
60%	L-M	L-M	80.6	76.3	71.5	68.9	67.2
	L-H	L-H	97.5	96.3	93.8	93.1	90.8
	M-H	M-H	82.6	79.1	74.3	71.2	70.7
90%	L-M	L-M	89.9	86.9	82.3	81.2	77.5
	L-H	L-H	99.1	98.7	97.5	96.9	95.5
	M-H	M-H	90.8	88.6	85.3	83.2	80.7

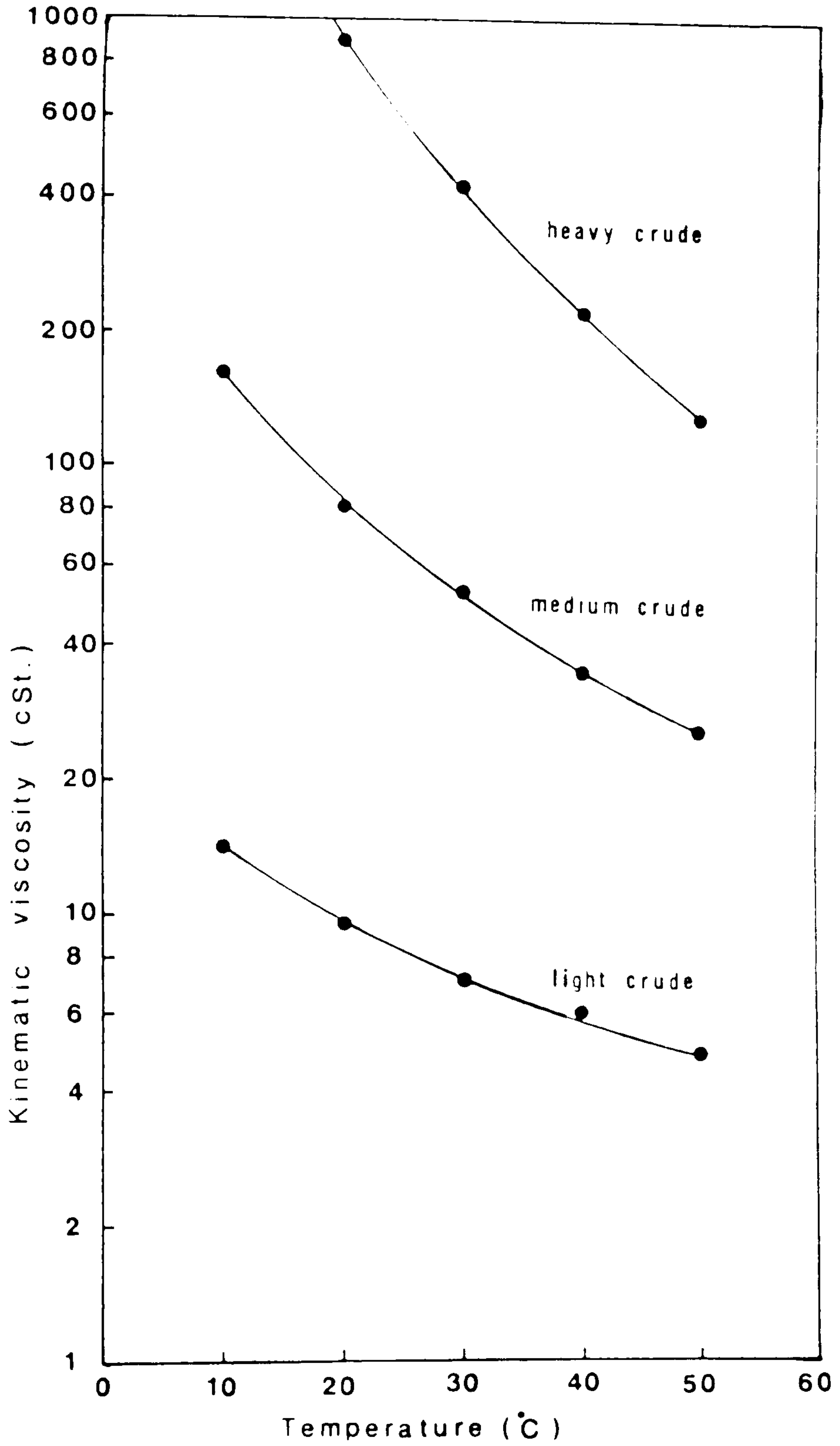


Figure 9.10: Effect of Temperature on the Kinematic Viscosity of Light, Medium and Heavy Crude Oil

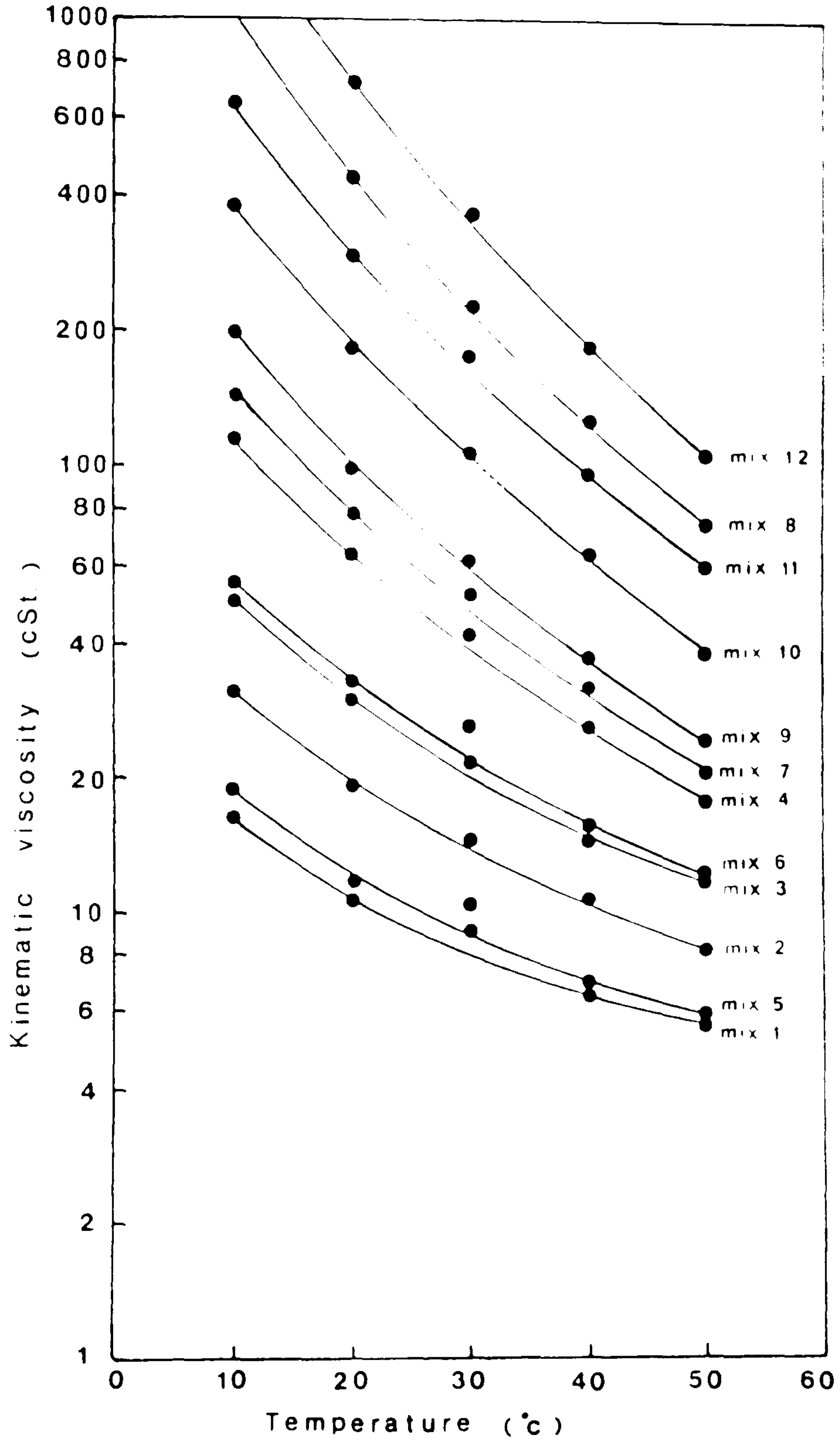


Figure 9.11: Effect of Temperature on the Kinematic Viscosity of Crude Oil Binary Mixtures

On Petroleum Products and Base Oils Viscosities:

The kinematic viscosities of kerosene, heavy gas oil, residue >360°C, light base oil, medium base oil, heavy base oil and bright stock base oil, at atmospheric pressure (14.7 psi) and within a temperature range of 20°C to 100°C are shown in Table 9.13 and presented graphically in Figures 9.12 and 9.13.

As observed previously with crude oils, an increase in the temperature of the petroleum product, or of the base oil, resulted in a significant decrease in its kinematic viscosity. A general trend was observed where the rate of decrease in viscosity increased as the temperature increased i.e. the viscosity increases exponentially as the temperature decreases. It was also observed, as presented in Table 9.14 that the heavier components of petroleum products and base oils exhibited higher rates of decrease in viscosity, with increase in temperature than lighter ones. This behaviour has been reported previously for other hydrocarbons and petroleum products by Mehrotra and Svrcek(73,74,77).

Table 9.13: Measured Kinematic Viscosities (cSt.) of Kerosene, Heavy Gas Oil,Residue >360°C; and Light, Medium, Heavy Base Oil and Bright Stock at Atmospheric Pressure

	Kinematic Viscosity (cSt.) @			
	20°C	40°C	60°C	100°C
Kerosene	1.908	1.381	1.054	0.8450
Heavy Gas Oil	56.95	21.24	10.51	3.941
Residue >360°C	-	2100	433.0	58.60
Light Base Oil	45.34	19.31	-	4.002
Medium Base Oil	177.7	60.21	-	8.025
Heavy Base Oil	424.7	125.9	-	13.17
Bright Stock	1756	425.5	-	29.93

Table 9.14: The % Decrease in Viscosity of Petroleum Products and Base Oils due to increase in Temperature from 20 - 100°C (for residue >360°C. from 40 - 100°C)

	% Decrease in Kinematic Viscosity @		
	40°C	60°C	100°C
Kerosene	27.6	44.8	55.7
Heavy Gas Oil	62.7	81.6	93.1
Residue >360°C	-	79.4	97.2
Light Base Oil	57.4	-	91.2
Medium Base Oil	66.1	-	95.5
Heavy Base Oil	70.4	-	96.9
Bright Stock	75.8	-	98.3

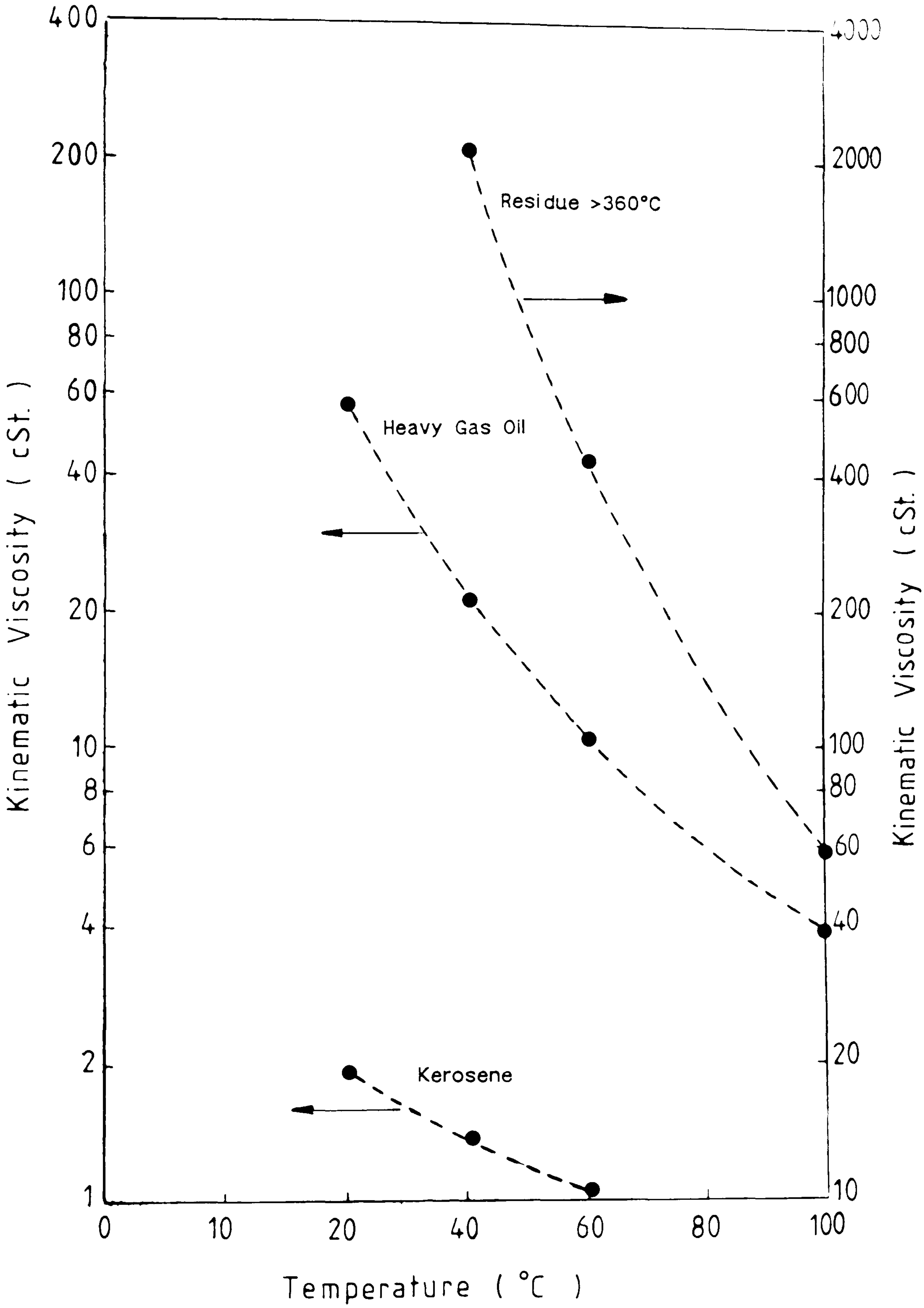


Figure 9.12: Effect of Temperature on the Kinematic Viscosities of Petroleum Products

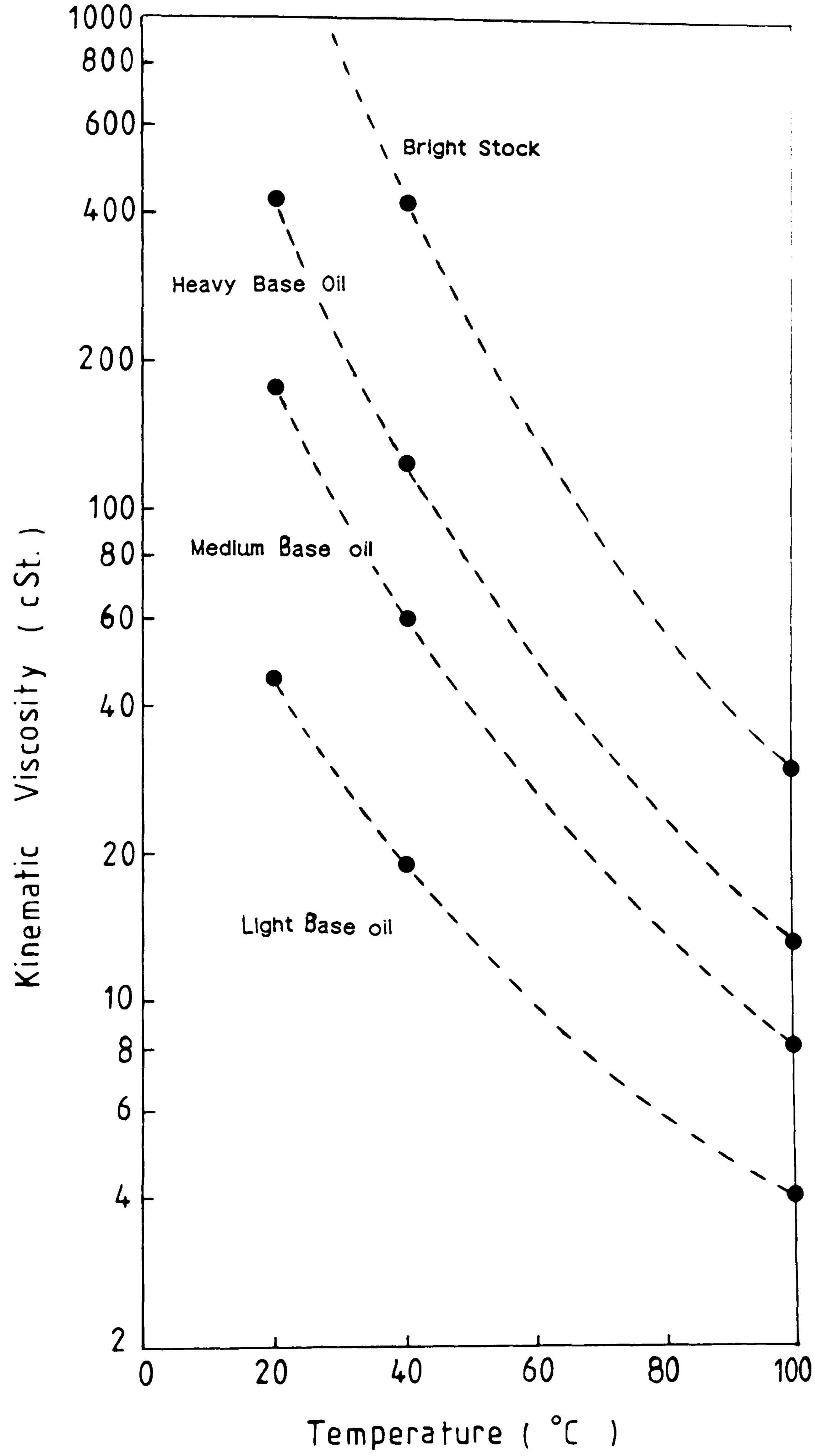


Figure 9.13: Effect of Temperature on the Kinematic Viscosities of Base Oils

9.3.2 The Effect of Pressure on Crude Oil Viscosity;

The measured kinematic viscosities of the three individual crude oils and their binary mixtures in the temperature range 25 - 50°C and at pressures ranging from atmospheric to 8000 psi* are shown in Tables 9.15 and 9.16 and presented graphically, in Figures 9.14, 9.15 and 9.16. The crude oils used in this study was stabilized crudes (dead crudes). i.e., the concentration of the dissolved gases was very low (<1.0% weight). Therefore, the effect of the dissolved gases on the viscosity of the crudes was negligible. Consequently, as expected, the viscosities of the liquid phase crude oils increased as the pressure increased. According to Khan's observation(41,44), the relationship between ln ν and pressure is linear, and straight lines were indeed obtained when ln ν (cSt) of the crudes were indeed plotted against the pressure (psi). This observation is in contrast with the conclusions of Reid, Prausnitz and Sherwood(7). They reported that for pure hydrocarbons, the viscosity - pressure graph is linear up to a pressure of a few thousand atmospheres, but at higher pressure, it would be nearly linear if ln μ were plotted against pressure. It is clear from Figures 9.14, 9.15 and 9.16 that the rate of increase in the viscosity (the slope of a straight line), at a constant temperature, increased as the density of the crude increased e.g. light, medium and heavy crude oils exhibited slopes of 1.00, 1.35 and 1.77 cSt./psi respectively at 25°C. Therefore, the more complex the molecules of the liquid, the higher the increase in viscosity with increasing pressure. As expected, the slopes of the straight lines decreased as the temperature increased, which behaviour is similar to that for dead Athabasca bitumen reported by Mehrotra and Svrcek(74) and Khan et al(41).

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*psi (lbf/in^2) = mbar x0.01450

= N/m^2(Pa) x0.000 145

Table 9.15: Measured Kinematic Viscosity of Light, Medium and Heavy Crude Oils at High Pressure

Crude Oil	Temp. (°C.)	Kinematic Viscosity (cSt.) @				
		14.7 psi	2000 psi	4000 psi	6000 psi	8000 psi
Light Crude	25	8.251	9.801	12.32	15.03	17.81
	30	7.141	8.420	10.49	12.89	15.56
	40	5.960	7.084	8.361	9.905	11.88
	50	4.850	5.671	6.690	7.742	9.011
Medium Crude	25	65.13	84.03	110.8	147.0	189.1
	30	51.81	67.33	88.58	114.10	141.5
	40	34.63	44.25	58.59	74.92	92.55
	50	24.98	31.67	39.69	49.05	60.41
Heavy Crude	25	620.0	842.1	1281	1802	2470
	30	426.6	580.1	870.6	1202	1670
	40	223.5	299.5	428.1	618.3	867.7
	50	130.0	184.9	249.2	351.2	490.4

Table 9.16: Measured Kinematic Viscosities of Crude Oil Binary Mixtures at High Pressure

Mix No.	Temp. (°C)	Kinematic Viscosity (cSt.) @				
		14.7 psi	2000 psi	4000 psi	6000 psi	8000 psi
1	25	9.788	11.58	14.13	17.54	21.14
	30	9.171	11.42	13.50	17.04	19.64
	40	6.519	7.756	9.314	11.78	14.34
	50	5.612	6.625	7.713	9.266	10.90
2	25	16.97	19.90	25.30	32.21	38.92
	30	14.79	17.41	22.69	27.33	33.07
	40	10.79	13.05	15.74	19.61	22.55
	50	8.192	9.721	12.21	14.54	17.43
3	25	25.53	33.01	42.15	53.67	66.68
	30	21.83	27.81	34.81	45.05	53.03
	40	14.57	18.29	23.18	27.55	33.86
	50	11.95	14.89	18.51	22.40	27.52
4	25	51.04	68.79	83.62	105.9	139.2
	30	42.18	51.02	64.04	82.71	105.9
	40	26.10	35.06	46.55	59.89	77.09
	50	17.80	21.82	28.99	35.01	43.31
5	25	11.42	13.38	16.33	20.21	24.44
	30	10.55	12.90	15.28	18.52	22.22
	50	5.909	7.146	8.622	10.48	12.61
6	25	28.15	35.75	45.32	55.62	71.81
	30	26.60	34.37	42.89	52.90	65.91
	40	15.43	20.22	24.06	30.95	37.72
	50	11.98	15.33	18.67	23.01	28.62
7	25	63.67	83.02	110.0	143.2	190.3
	30	52.10	70.47	89.20	111.8	145.3
	40	32.02	40.16	54.29	67.86	86.62
	50	20.70	27.06	34.46	42.65	54.63
8	25	302.5	416.0	561.5	796.1	1111
	40	129.6	182.1	246.1	316.5	435.7
	50	75.02	105.5	141.0	187.4	248.4

Table 9.16 (cont)

9	25	78.58	102.2	130.6	172.9	226.7
	30	62.65	82.22	105.5	141.7	177.9
	40	37.56	48.79	65.05	78.12	100.7
	50	25.10	32.58	41.36	50.51	63.25
10	25	140.2	184.7	250.3	336.9	448.2
	40	64.41	87.90	116.3	149.7	186.6
	50	38.06	50.06	67.21	85.30	110.3
11	25	234.0	312.8	431.0	585.3	795.5
	30	180.7	252.1	347.8	480.6	605.2
	40	97.45	138.3	188.5	255.1	353.5
	50	60.81	83.52	110.1	143.2	190.1
12	25	493.6	701.2	986.9	1346	1881
	30	372.3	513.4	715.7	989.5	1375
	40	188.6	258.4	361.2	495.6	710.3
	50	109.0	150.1	207.2	288.5	396.3

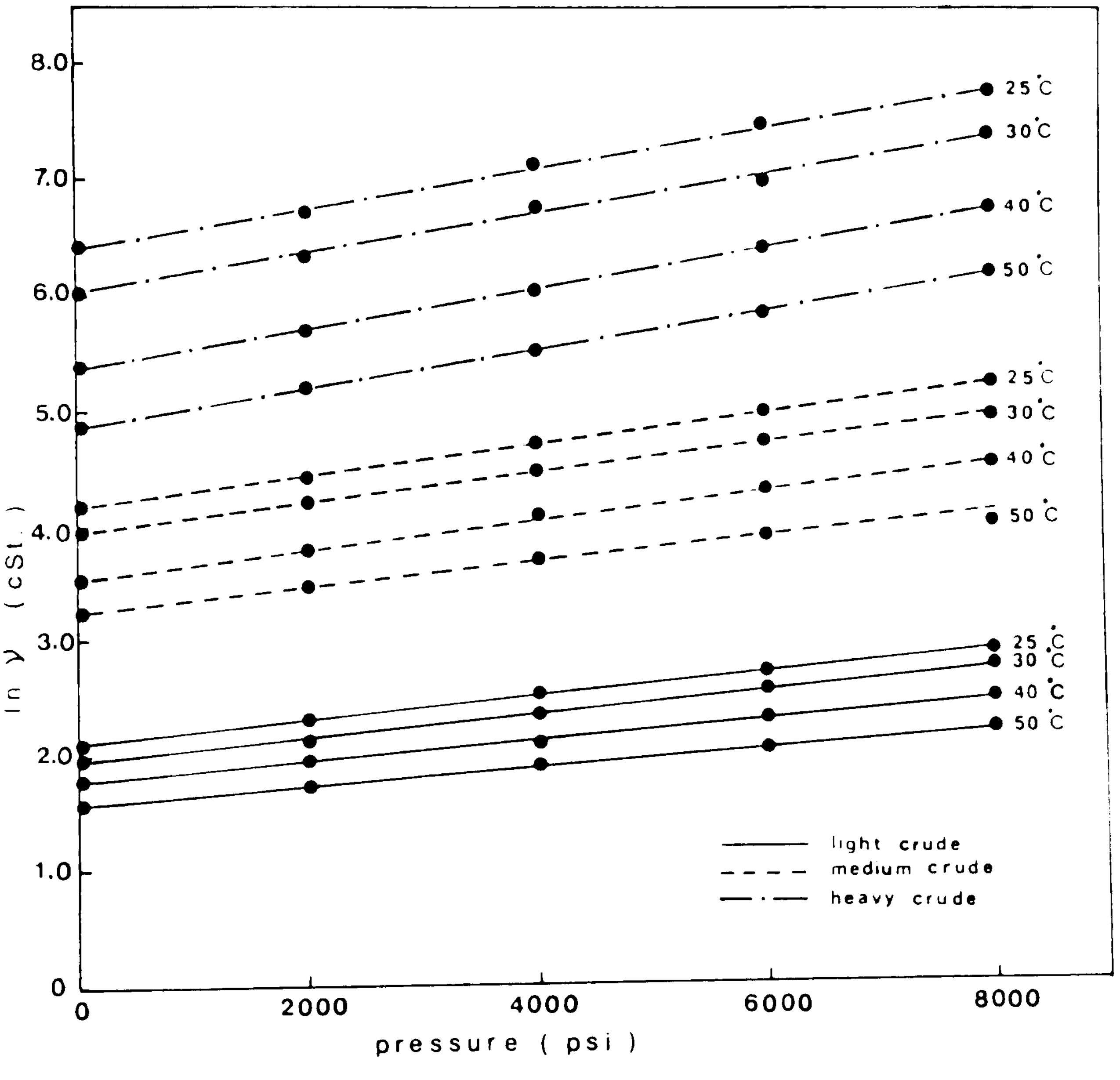


Figure 9.14: Effect of Pressure on the Kinematic Viscosity (v) of Light, Medium and Heavy Crude Oil

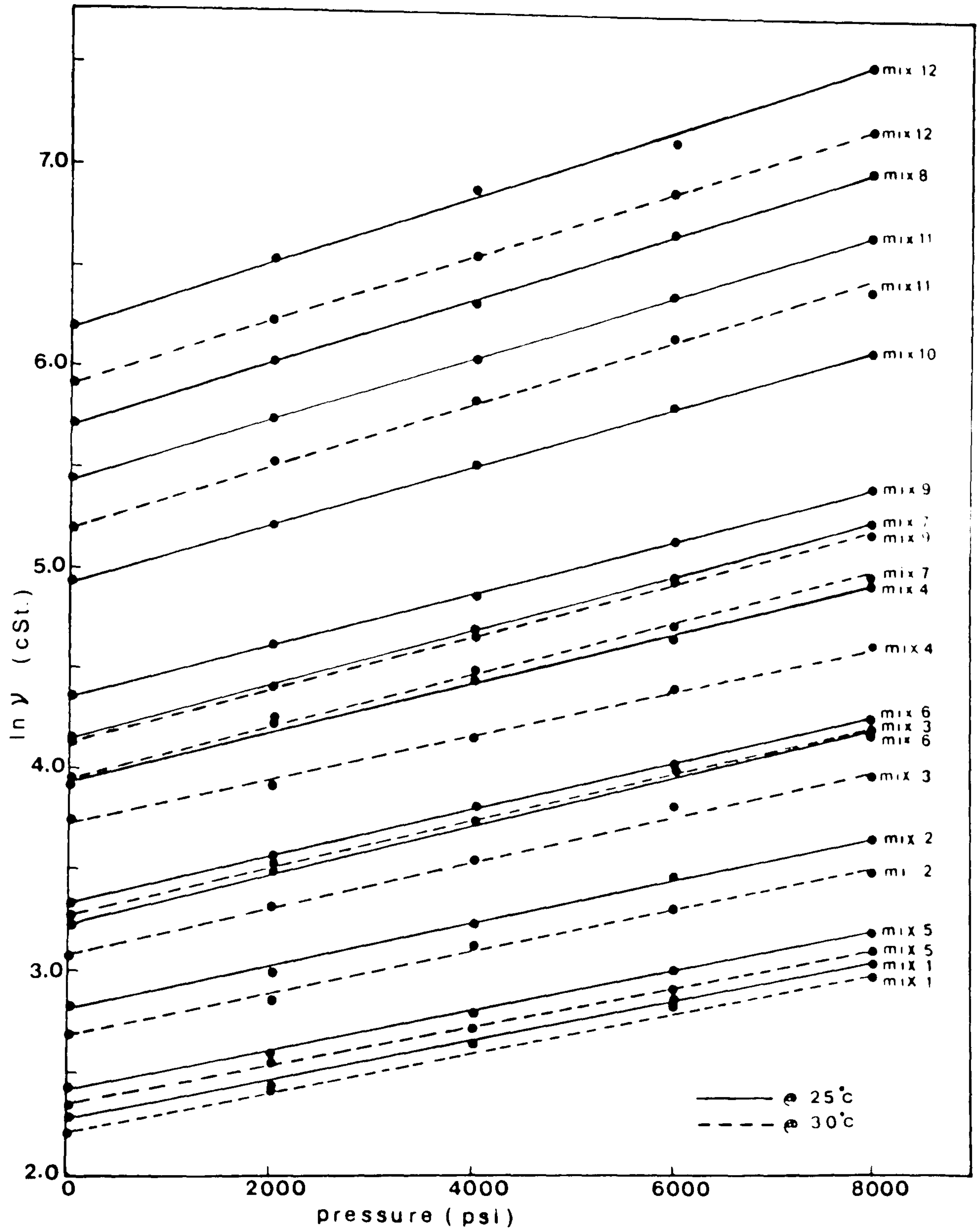


Figure 9.15: Effect of Pressure on the Kinematic Viscosity (v) of Crude oil Binary Mixtures at 25°C and 30°C.

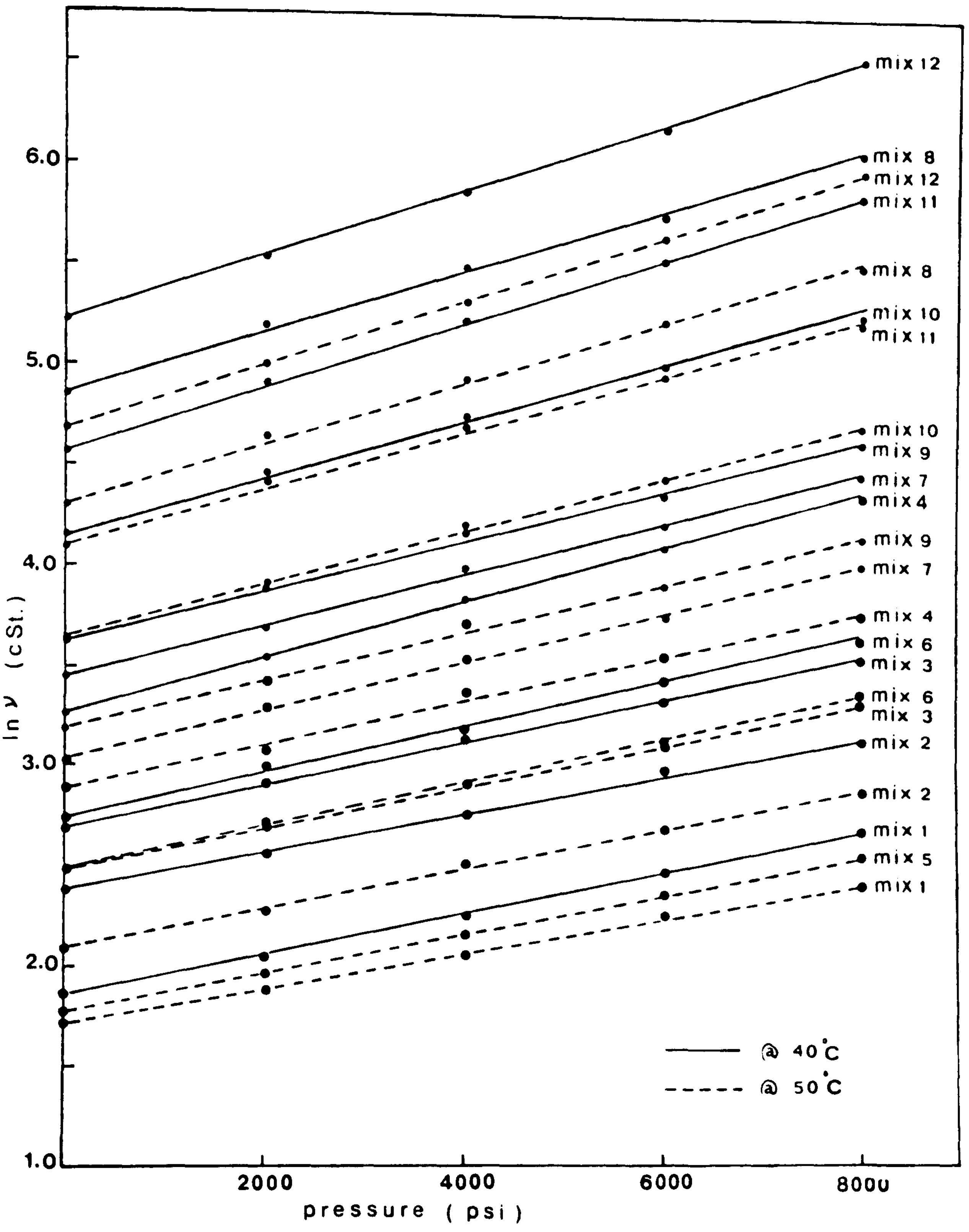


Figure 9.16: Effect of Pressure on the Kinematic Viscosity of Crude Oil Binary Mixtures at 40°C and 50°C

Prediction of Viscosity at High Pressure:

A method was developed to predict the viscosities of crude oils at high pressure and different temperatures. This method considers the change in density (ρ) of the crude oils due to change in temperature. The densities at the required temperature (ρ_T) of the three individual crude oils, (light, medium and heavy) were calculated using the ASTM standard conversion tables for the volumetric measurements of crude oils knowing at least one density measurement at any temperature. The slope($'R$) of the ln ν - Pressure straight lines shown in Figure 9.14 at each temperature for each of the three crudes were calculated, by

$$\text{Slope} = {}'R = \frac{\Delta \ln \nu}{\Delta P} \qquad 9.4$$

where,

ν = Kinematic viscosity, cSt.

ΔP = Change in pressure, psi

Table 9.17 shows ρ_T and $'R_S$ data for each of the three crudes at different temperatures. When the calculated ρ_T's were plotted against the corresponding slopes($'R$'s) a linear relationship was obtained (Figure 9.17). By linear regression, the following equation was obtained.

$$'R = -4.65521 \times 10^{-4} + (6.66906 \times 10^{-4} \times \rho_T) \qquad 9.5$$

where,

$'R$ = the slope of ln ν - pressure straight line

ρ_T = the density of each crude at the required temperature, gm/ml.

Equation 9.4 can be written,

$$'R = \frac{\ln \nu_P - \ln \nu_o}{P - P_{atm.}} \qquad 9.6$$

$$= \frac{\ln \nu_P/\nu_o}{P - 14.7} \qquad 9.7$$

Rearrangement of equation 9.7, yielded,

$$\nu_P = \nu_o \, e^{'R(P - 14.7)} \qquad 9.8$$

where,

ν_P = the kinematic viscosity at the required pressure, in cSt.

ν_o = the kinematic viscosity at atmospheric pressure, in cSt.

P = the pressure, psi

$'R$ = the slope of ln ν - pressure straight line, calculated from equation 9.5

The measured kinematic viscosity data for crude oil binary mixtures, shown in Table 9.16were used to test the proposed method. The percent deviations of the calculated viscosities from the experimental measurements are shown in Table 9.18.

The ρ_T of any mixture $\rho_{T,mix}$ was easily measured, or calculated from the simple mixing rule,

$$\rho_{mix} = \Sigma x_i \, \rho_i \qquad 9.9$$

where,

ρ_{mix} = the density of the mixture

ρ_i = the density of component i

x_i = weight fraction

ρ_{mix} can, also be calculated using the following equation

$$\ln \rho_{mix} = x_1 \ln \rho_1 + x_2 \ln \rho_2 + x_1 x_2 C \qquad 9.10$$

where,

C = constant

x_1 x_2 = the weight fraction of component 1 and 2 respectively

ρ_1, ρ_2 = the densities of component 1 and 2

ρ_{mix} = the density of mixture

The percent deviations of the mixtures' densities calculated by either of these equations from measured values were very low, i.e <0.6% in most cases indicating that they can be used with confidence.

It is clear from Table 9.18 that the deviations of the calculated viscosities at high pressure from the experimental measurements were very low, i.e. less that 8.5% in most cases, with Absolute Average % Deviations of 2.1, 2.4, 3.9 and 5.2 at 2000, 4000, 6000 and 8000 psi respectively. In general, the deviation increased as the pressure was increased, the highest deviation (10.5%) being obtained at 8000 psi and 30°C. for mixture No.4.

Table 9.17: Measured Densities at Different Temperatures (ρ_T) and the slopes of ln ν-Pressure Straight Lines (R), for Light, Medium and Heavy Crude Oils

Temperature	Light Crude Oil		Medium Crude Oil		Heavy Crude Oil	
(oC)	ρ_T	$'R$ (x 10^{-4})	ρ_T	$'R$ (x 10^{-4})	ρ_T	$'R$ (x 10^{-4})
25	0.8376	0.9988	0.8992	1.3475	0.9601	1.7652
30	0.8341	0.9932	0.8958	1.2703	0.9568	1.7315
40	0.8272	0.8583	0.8890	1.2513	0.9502	1.7215
50	0.8201	0.7762	0.8822	1.1034	0.9436	1.6512

Table 9.18: Calculated Kinematic Viscosities of Crude Oil Binary Mixtures at High Pressure Using Equations 9.5. and 9.8

Mix No.	Temp. (°C.)	Kinematic Viscosity (cSt.) @ 2000 psi Calculated	2000 psi %Dev	4000 psi Calculated	4000 psi %Dev	6000 psi Calculated	6000 psi %Dev	8000 psi Calculated	8000 psi %Dev
1	25	11.87	2.5	14.42	2.0	17.51	-0.2	21.27	0.6
	30	11.08	-3.0	13.39	-0.8	16.18	-5.0	19.55	-0.4
	40	7.800	0.5	9.332	0.2	17.17	-5.1	13.38	-6.7
	50	6.651	0.4	7.892	2.3	9.364	1.1	11.11	2.0
2	25	21.09	6.0	26.26	3.8	32.68	1.5	40.68	4.5
	30	18.29	5.0	22.66	-0.1	28.07	-2.6	34.77	5.1
	40	13.22	1.3	16.23	3.1	19.92	1.6	24.45	8.4
	50	9.950	2.4	12.10	-0.9	14.72	1.3	17.91	2.7
3	25	32.25	-2.3	40.81	-3.2	51.64	-3.8	65.34	-2.0
	30	27.45	-1.3	34.57	-0.7	43.54	-3.4	54.83	3.4
	40	18.15	-0.7	22.65	-2.3	28.27	2.6	35.28	4.2
	50	14.76	-0.9	18.26	-1.4	22.58	0.8	27.93	1.5
4	25	66.07	-3.9	85.69	2.5	111.2	4.9	144.2	4.9
	30	54.36	6.6	70.18	9.6	90.61	9.5	117.0	10.5
	40	33.33	4.9	42.64	-8.4	54.55	-8.9	69.82	-9.4
	50	22.54	3.3	28.57	-1.4	36.23	3.5	45.93	6.0
5	25	13.96	4.4	17.10	4.7	20.94	3.6	25.64	4.9
	30	12.83	-0.5	15.64	2.3	19.05	2.9	23.21	4.4
	50	7.060	-1.2	8.445	-2.1	10.10	-3.6	12.09	-4.2
6	25	36.15	1.0	46.47	2.5	59.76	7.4	76.85	7.0
	30	33.99	-1.1	43.51	1.4	55.69	-5.2	71.28	8.1
	40	19.54	-3.4	24.78	3.0	31.43	1.5	39.86	5.7
	50	15.04	-1.9	18.90	1.2	23.76	3.3	29.86	4.3
7	25	84.42	1.7	112.2	1.9	149.1	4.1	198.0	4.1
	30	68.77	-2.4	90.97	2.0	120.33	7.7	159.2	9.5
	40	41.89	4.3	54.92	1.1	71.99	6.1	94.38	8.9
	50	26.84	-0.8	34.86	1.2	45.28	6.2	58.82	7.7

Table 9.18 (cont)

8	25	421.1	1.2	587.9	4.7	820.1	3.0	1145	2.8
	40	178.1	-2.2	245.3	-0.3	337.9	6.8	465.5	6.8
	50	103.1	-2.6	142.0	0.7	195.6	4.3	269.4	8.4
9	25	103.4	1.1	136.3	4.4	179.7	3.9	236.8	4.5
	30	82.07	-0.2	107.8	2.1	141.4	-0.2	185.6	4.3
	40	48.76	-0.1	63.42	-2.5	82.48	5.6	107.3	6.5
	50	32.30	0.9	41.62	0.6	53.65	6.2	69.2	9.3
10	25	188.9	2.3	255.1	1.9	344.7	2.3	465.7	3.9
	40	85.68	-2.5	114.2	-1.8	152.3	1.7	203.0	8.8
	50	50.17	0.2	66.27	-1.4	87.54	2.7	115.6	4.9
11	25	320.6	2.5	440.1	2.1	604.3	3.2	829.7	4.3
	30	246.4	-2.2	337.0	-3.1	460.7	-4.1	630.0	-5.3
	40	131.8	-4.7	178.6	-5.3	242.0	-5.2	327.9	-7.2
	50	81.47	-2.4	109.4	-0.4	146.9	2.6	197.3	3.8
12	25	692.7	-1.2	974.6	-1.2	1371.2	1.9	1929	2.6
	30	520.4	1.4	729.2	1.9	1022	3.2	1432	4.1
	40	261.3	1.1	362.9	0.5	504.1	1.7	700.1	-1.4
	50	149.7	-0.3	206.1	-0.6	283.6	-1.7	390.4	-1.5
Absolute Average % Deviation:			2.1		2.4		3.9		5.2
Mean Average % Deviation:			0.3		0.6		1.7		3.5

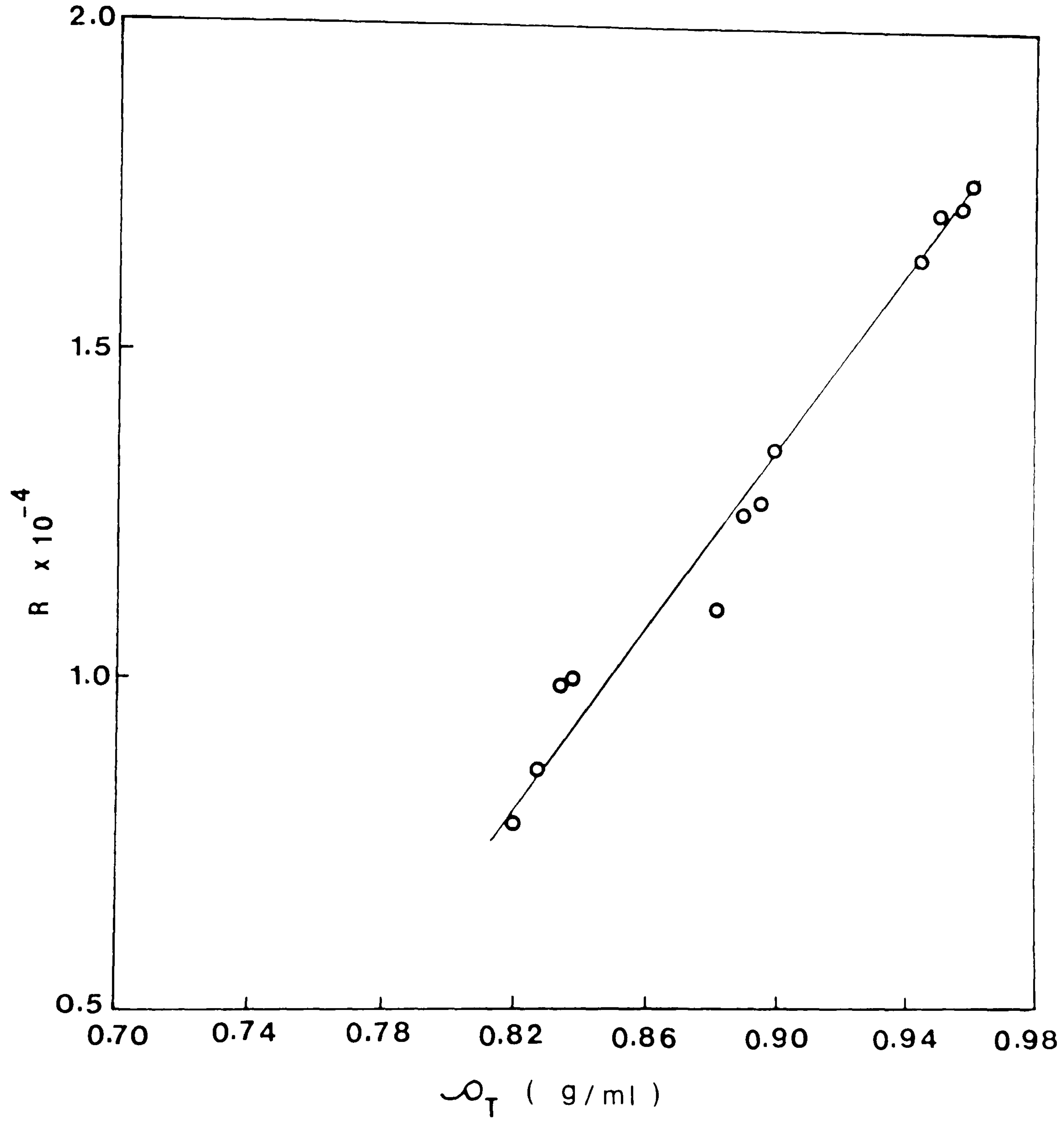


Figure 9.17: Relationship Between the Slopes (R's) of ln v-P Straight Lines, Obtained from Figure 9.14, and Crude Oil Density at the required Temperature (ρ_T).

For comparative purposes, Kouzel method's, equation 5.61.was used to calculate the viscosities of the binary and ternary crude oil mixtures over the same range of temperatures and pressures. The results are summarised in Tables 9.19 and 9.20. The absolute average deviations from the measured values were 6.8%, 14.5%, 23.9% and 34.7% at 2000 psi, 4000 psi, 6000 psi and 8000 psi respectively for the binary mixtures; and 6.7%, 12.1%, 18.8% and 27.7% at 2000 psi, 4000 psi, 6000 psi and 8000 psi respectively for the ternary mixtures.

The measured and calculated viscosities of crude oil ternary mixtures at high pressure using equations 9.5 and 9.8, are shown in Appendix E.2.

Table 9.19: Calculated Kinematic Viscosities of Crude Oil Binary Mixtures at High Pressure Using Equation 5.61

Mix No	Temp (°C)	Kinematic Viscosity (cSt.) @ 2000 psi calc	2000 psi % dev	4000 psi calc	4000 psi %dev	6000 psi calc	6000 psi % dev	8000 psi calc	8000 psi %dev
1	25	12.52	8.1	16.01	13.3	20.48	16.7	26.19	23.9
	30	11.70	2.5	14.93	10.6	19.05	11.8	24.30	23.7
	40	8.217	5.9	10.36	11.2	13.06	10.8	16.46	14.8
	50	7.039	6.2	8.829	14.5	11.07	19.5	13.89	27.4
2	25	22.22	11.6	29.09	15.0	38.08	18.2	49.86	28
	30	19.25	10.6	25.05	10.4	32.60	19.3	42.42	28.3
	40	13.86	6.2	17.81	13.1	22.88	16.7	29.40	30.3
	50	10.42	7.1	13.24	8.4	16.84	15.9	21.41	22.8
3	25	34.09	3.3	45.53	8.0	60.80	13.3	891.19	21.8
	30	28.93	4.0	38.34	10.1	50.81	12.8	67.34	27.0
	40	18.96	3.7	24.67	6.4	32.11	16.5	41.78	23.4
	50	15.43	3.6	19.91	7.6	25.70	14.7	33.17	20.5
4	25	70.90	3.1	98.48	17.8	136.8	29.2	190.0	36.5
	30	57.93	13.6	79.57	24.3	109.3	32.1	150.1	41.8
	40	34.93	0	46.75	0	62.57	4.5	83.75	8.6
	50	23.40	6.0	30.75	6.0	40.40	15.4	53.10	22.6
5	25	14.70	9.8	18.91	15.8	24.34	20.4	31.32	28.1
	30	13.53	4.9	17.36	13.6	22.27	20.3	28.57	28.6
	50	7.425	3.9	9.330	8.2	11.72	11.9	14.73	16.8

Table 9.19 cont ...

Mix	Temp	Kinematic Viscosity (cSt.) @							
		2000 psi		4000 psi		6000 psi		8000 psi	
No	(°C)	calc	% dev	calc	%dev	calc	% dev	calc	%dev
6	25	37.80	5.7	50.77	12.0	68.17	22.6	91.55	27.5
	30	35.62	3.7	47.70	11.2	63.87	20.7	85.52	29.8
	40	20.14	0	26.29	9.2	34.31	10.8	44.78	18.7
	50	15.48	0.01	19.19	7.0	25.81	12.2	33.33	16.5
7	25	89.78	8.1	126.6	15.0	178.5	24.6	251.7	32.2
	30	72.53	2.9	101.0	13.2	140.6	25.8	195.7	34.7
	40	43.35	7.9	58.69	8.1	79.46	17.1	107.6	24.2
	50	27.41	1.3	36.31	5.4	48.08	12.7	63.68	16.6
8	25	486.1	16.8	781.1	39.1	1255	57.7	2017	81.6
	40	192.9	5.9	287.2	16.7	427.5	35.1	636.4	46.1
	50	107.2	1.6	153.3	8.7	219.1	16.9	313.2	26.1
9	25	112.3	9.9	160.6	23.0	229.6	32.8	328.2	44.8
	30	88.23	7.3	124.3	17.8	175.0	23.5	246.4	38.5
	40	51.29	5.1	70.04	7.7	95.64	22.4	130.6	29.7
	50	33.55	3.0	44.85	8.4	59.95	18.7	80.14	26.7
10	25	209.5	13.4	313.2	25.1	468.2	39.0	699.8	56.1
	40	90.97	3.5	128.5	10.5	181.5	21.2	256.3	37.3
	50	52.06	4.0	71.22	6.0	97.42	14.2	133.3	20.8
11	25	366.3	17.1	573.3	33.0	897.3	53.3	1404	76.5
	30	276.2	9.6	422.3	21.4	645.6	34.3	987.1	63.1
	40	141.8	2.5	206.3	9.4	300.1	17.7	436.7	23.5
	50	85.64	2.5	120.6	9.5	169.9	18.7	239.2	25.9
12	25	837.2	19.4	1420	43.9	2409	78.9	4085	117.2
	30	611.9	19.2	1006	40.5	1653	67.0	2716	97.5
	40	290.0	12.2	445.9	23.4	685.5	38.3	1054	48.4
	50	160.2	6.7	235.4	13.6	346.0	19.9	508.4	28.3
Absolute Average % Deviation			6.8		14.5		23.9		34.7

Table 9.20: Calculated Kinematic Viscosities of Crude Oil Ternary Mixtures at High Pressure Using Equation 5.61

Mix psi No	Temp (°C)	Kinematic Viscosity (cSt.) @ 2000 psi calc	2000 psi % dev	4000 psi calc	4000 psi %dev	6000 psi calc	6000 psi % dev	8000 psi calc	8000 psi %dev
1	25	69.48	8.8	96.44	18.3	133.9	28.1	185.9	37.0
	30	50.83	7.0	69.35	12.8	94.63	19.0	129.1	31.6
	40	34.19	6.8	45.73	7.8	61.16	14.0	81.81	22.7
	50	23.95	1.9	31.52	5.3	41.47	10.0	54.58	12.9
2	25	49.59	8.5	67.55	15.4	92.00	22.6	125.3	30.5
	30	38.10	7.1	51.21	11.4	68.82	5.1	92.49	26.8
	40	24.95	4.9	32.87	10.6	43.32	15.4	57.08	22.4
	50	17.26	3.2	22.39	4.9	29.05	10.8	37.69	14.0
4	25	21.20	2.8	27.70	7.8	36.20	15.9	47.31	22.8
	30	17.60	8.6	22.82	14.0	29.60	18.7	38.39	27.8
	40	12.47	6.7	15.98	11.8	20.46	16.9	26.18	19.3
	50	9.706	6.7	12.31	7.0	15.62	10.5	19.82	14.4
5	25	117.6	10.8	168.5	18.5	241.6	35.4	346.4	51.1
	30	88.30	8.3	124.3	14.9	175.1	28.0	246.5	46.8
	40	53.98	2.3	73.90	6.3	101.2	13.8	138.5	24.4
	50	34.84	3.2	46.64	8.3	62.45	16.1	83.61	26.7
6	25	91.86	14.1	129.7	23.1	183.1	31.8	258.5	43.6
	30	70.18	7.9	97.50	15.7	135.5	27.7	188.2	35.4
	40	43.29	8.5	58.59	17.4	79.31	19.2	107.4	25.3
	50	28.81	6.7	38.24	10.7	50.75	16.2	67.36	19.2
Absolute Average % Deviation			6.7		12.1		18.8		27.7

9.3.3 The Non-ideal Viscosity Characteristics of Binary Petroleum Mixtures:

The shape of a viscosity - composition curve at a fixed temperature and pressure is widely used to determine whether a homogeneous liquid mixture is ideal or non-ideal. However, this phenomenon is very complex since it depends upon the type of interactions between the molecules of the components themselves.. Whilst the divergence from ideality is usually attributed to physical interactions between the molecules of the components, the chemical composition of each component strongly affects the behaviour of the mixture, i.e the shape of the viscosity-composition curve. Therefore, it is appropriate to briefly review previous research using mixtures of pure hydrocarbons.

Kendall and Wright(81) examined three mixtures of ester - ester type, i.e. ethyl acetate - ethyl benzoate, ethyl acetate - benzyl benzoate., and ethyl bensoate-benzyl benzoate. These systems were clearly of similar chemical nature with slight changes in the molecular formula of each component. However, the viscosity - composition curves of each system were reported to differ (Fig. 9.18).

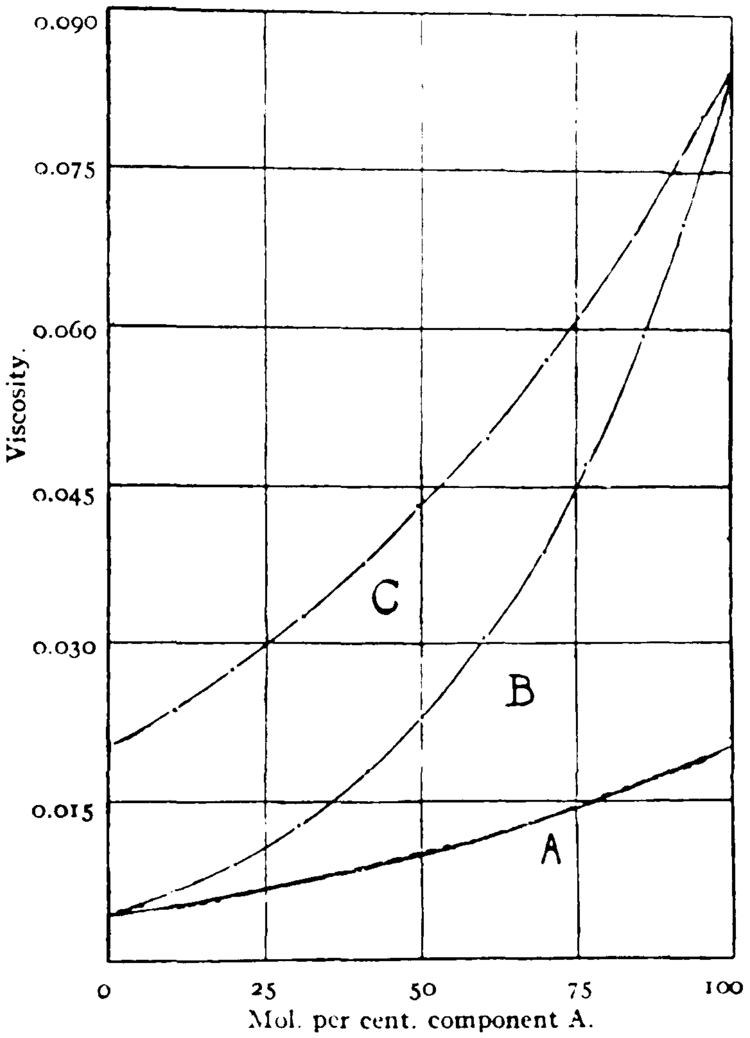


Fig. 9.18: Viscosity vs. Composition Data$^{(81)}$

A = Ethyl acetate - ethyl benzoate
B = Ethyl acetate - benzyl benzoate
C = Ethyl benzoate - benzyl benzoate

Aminabhavi et al.(144) examined the viscosity behaviour of the following binary mixtures of pure chemicals: bromoform - carbon tetrachloride, bromoform-dimethyl sulfoxide, bromoform-cyclohexane, bromoform-bromobenzene, bromoform-dimethylformamide, bromoform-methyl ethyl ketone, bromoform-ethyl acetate, carbon tetrachloride-methanol, carbon tetrachloride-benzene, carbon tetrachloride-ethyl acetate, carbon tetrachloride-dimethyformamide, carbon tetrachloride-cychlohexane, carbon tetrachloride-bromobenzene, carbon tetrachloride-methyl ethyl ketone, carbon tetrachloride-dimethyl sulfoxide and carbon tetrachloride-nitromethane. These mixtures can be classified into two groups: (1) bromoform-binary mixtures and (2) carbon tetrachloride-binary mixtures. Although, the first component in both groups was fixed, the viscosity - composition curves were reported to differ. Some of these mixtures exhibited linear behaviour (ideal), some exhibited negative deviations from linearity, and others exhibited positive deviations with a maxima. Some of the date for these mixtures are shown in Fig. 9.19

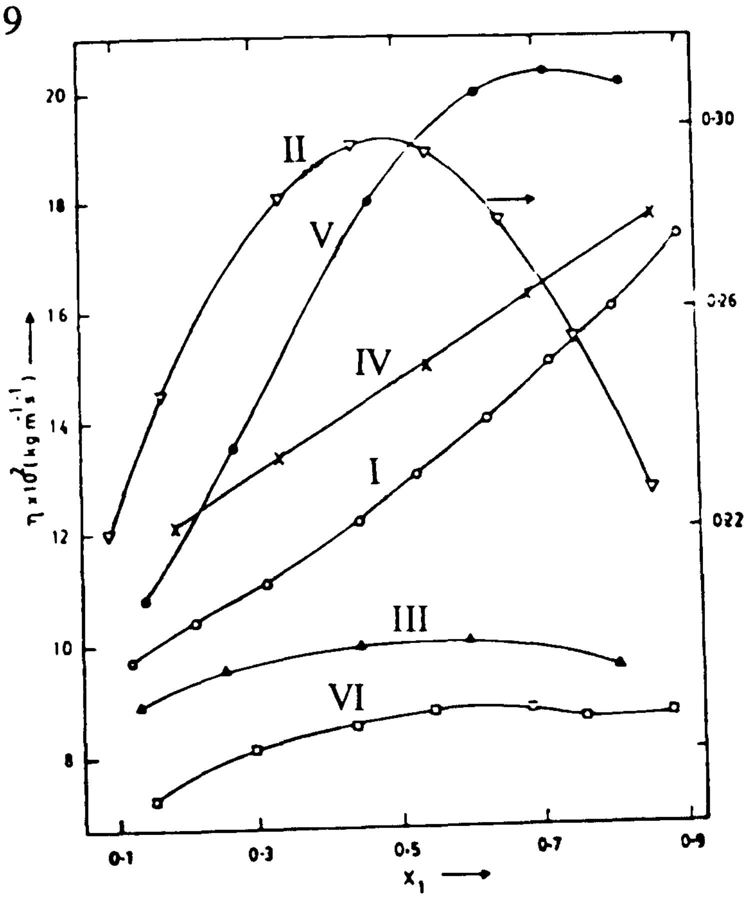


Figure 9.19: Viscosity vs Composition of the Mixture(144).

I- Bromoform-Carbon Tetrachloride; IV- Bromoform-Dimethyformamide

II- Bromoform-Dimethyl sulfoxide; V- Carbon Tetrachloride-Methanol

III- Bromoform-Bromobenzene; VI- carbon Tetrachloride-Dimethylformamide

Manjeshwar and Aminabhavi(145) investigated carbon tetrachloride - binary mixtures with dimethyl sulfoxide, bromobenzene dimethylformamide, cyclohexane, benzene and ethyl acetate. The viscosity - composition curves of these mixtures exhibited different behaviour (Fig. 9.20).

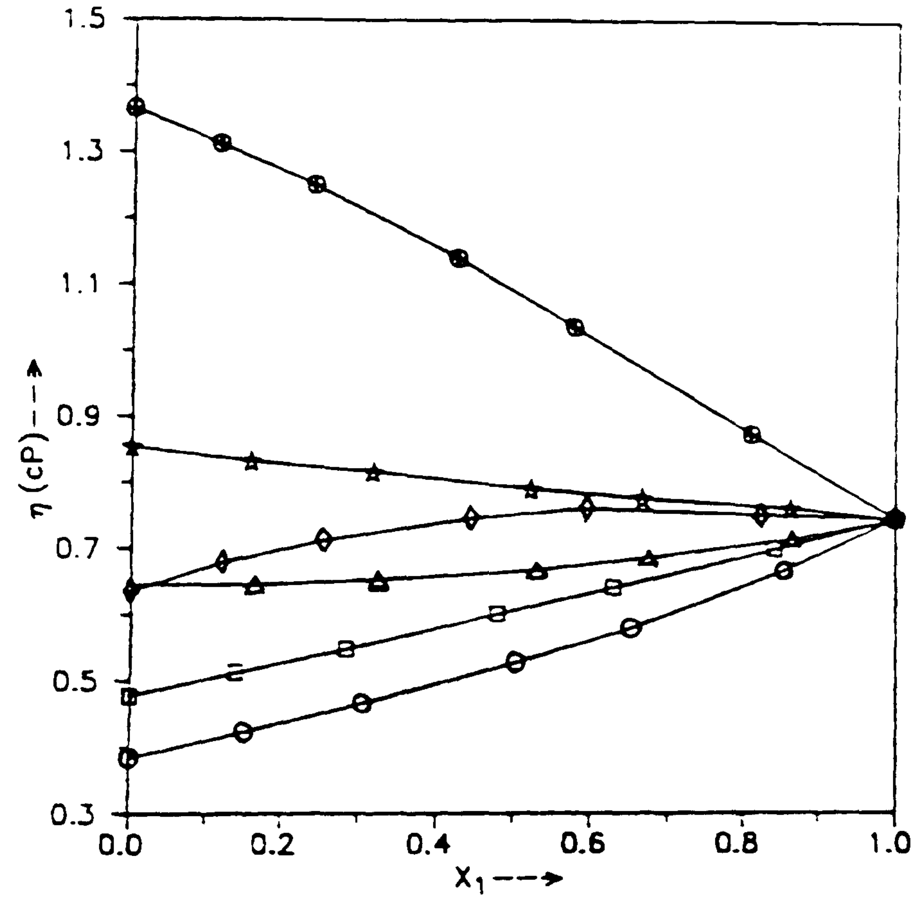


Figure 9.20: Dependence on Viscosity on Mole Fraction of Carbon Tetrachloride at 45°C(145):

(⊕) carbon tetrachloride (1)-dimethyl sulfoxide (2);
(☆) carbon tetrachloride (1)-bromobenzene (2);
(◊) carbon tetrachloride (1)-dimethylformamide (2);
(Δ) carbon tetrachloride (1)-cyclohexane (2);
(□) carbon tetrachloride (1)-benzene (2);
(O) carbon tetrachloride (1)-ethyl acetate (2).

Generally, the chemical composition of each component determined the shape of the viscosity - composition curve, or the type of interaction which occurred between the molecules.

However, whilst it is relatively easy to explain the behaviour of a mixture of two pure hydrocarbons, such as those mentioned, it is extremely difficult to propose a mechanism to explain the non-ideal behaviour when the components are very complex mixtures themselves, such as crude oils. Although crude oil is usually referred to as an "undefined mixture" i.e. its components comprising thousands of all kinds of chemical compound cannot all be determined quantitively, it is logical to consider a specific type of crude oil as one entity, since all the chemical compounds within one particular crude oil, exist in equilibrium. This explains why a particular crude oil has relatively stable and consistent physical properties (e.g. density, viscosity, flash point), although it is composed of so many hydrocarbons. The difficulty arises when one crude oil is mixed with another. The behaviour of a particular physical property (e.g. viscosity) whether ideal or non-ideal, can then be attributed to the interactions between the molecules of each crude oil separately, and/or to disturbance of the equilibrium between the molecules of the first crude component.

It is, also, very important to study the behaviour of petroleum liquid mixtures, in order to be able to suggest and develop models or correlations to predict a particular physical property such as the viscosity. For those mixtures which exhibit non-ideal behaviour, an appropriate correlation must be selected to describe the shape of the viscosity - composition curve and compensate for the deviations from ideality (either positive or negative deviations). Therefore, a particular correlation cannot be claimed to be a general one capable of application to any binary mixture system. Based on the previous discussion, caution is required when using any predictive correlation for a physical property of a particular mixture especially if the correlation is to be used for design purposes.

In general, non-ideal behaviour is attributed to a change in the volume or the force field surrounding the molecules. Association generally increases and dissociation reduces, viscosity from the values it should normally assume. However, this is not necessarily always the case with all liquids, because the non-ideality of viscosity due to mixing is a more complicated phenomenon and there is no general law to explain why, or the manner in which, it happens particularly for those mixtures comprising complex liquids such as crude oils or petroleum products.

The ideal viscosity behaviour of any binary mixture is that which obeys the simple mixing rule, which may be written in terms of kinematic viscosity.

$$v_{mix} = \Sigma x_i \ v_i \qquad 9.11$$

where,

x_i = weight, volume or mole fraction of the component i

v_i = viscosity of component i.

v_{mix} = viscosity of mixture.

The viscosity - composition diagrams of liquids which obey this equation exhibit straight lines indicative of ideal behaviour. Therefore any divergence from ideality (either positive or negative) will be considered as an excess viscosity function (v^E), and its value will be considered as a measure of the non-ideality of any binary mixture. Therefore, equation 9.11 may be modified as follows:

$$v_{mix} = \Sigma x_i v_i + v^E \qquad 9.12$$

where,

x_i = weight, volume or mole fraction of component i.

v_i = kinematic viscosity of component i

v_{mix} = kinematic viscosity of the mixture.

v^E = excess viscosity function.

The Non-Ideal Viscosity Characteristics of Crude Oil Binary Mixtures:

The kinematic viscosities of binary mixtures of the crude oils were determined at 10, 20, 30, 40 and 50°C. The data are shown in Table 9.10, and represented graphically in Figures 9.21, 9.22 and 9.23.

Clearly, the kinematic viscosity of the crude oil binary mixtures exhibited non-ideal behaviour at all test temperatures. The viscosity - composition curves of the mixtures are not straight lines but curve downwards, i.e., the observed kinematic viscosities were less than would be expected. However, the divergence of the viscosity from ideality decreased with an increase in temperature. The excess viscosity function ν^E calculated by the equation 9.12 for the crude oil binary mixtures, at different temperatures, are presented graphically in Figures 9.24, 9.25 and 9.26.

The magnitude of the non-ideality (ν^E) decreased as the temperature was increased from 10°C to 50°C. Each binary mixture exhibited maxima in their ν^E - composition diagrams at all test temperatures. In most cases, the locations of the maximum deviations were in the region 0.2 - 0.4 weight fraction of lighter crude oil. In general there were slight shifts in the location of the maxima towards the heavier component as the temperature decreased, i.e. at lower temperatures a given amount of the lighter component resulted in a larger decrease in viscosity (or increase in fluidity) of the heavier component.

Furthermore, as the difference between the densities (or API gravities) of the components of each binary mixture increased, the non-ideality of the viscosity increased. Therefore, the excess viscosity functions (ν^E) of the light - medium crude mixtures (ΔAPI = 11.34) were less than those of medium - heavy crude mixtures (ΔAPI =9.83) which were in turn less than those of light - heavy crude mixtures (ΔAPI = 21.17).

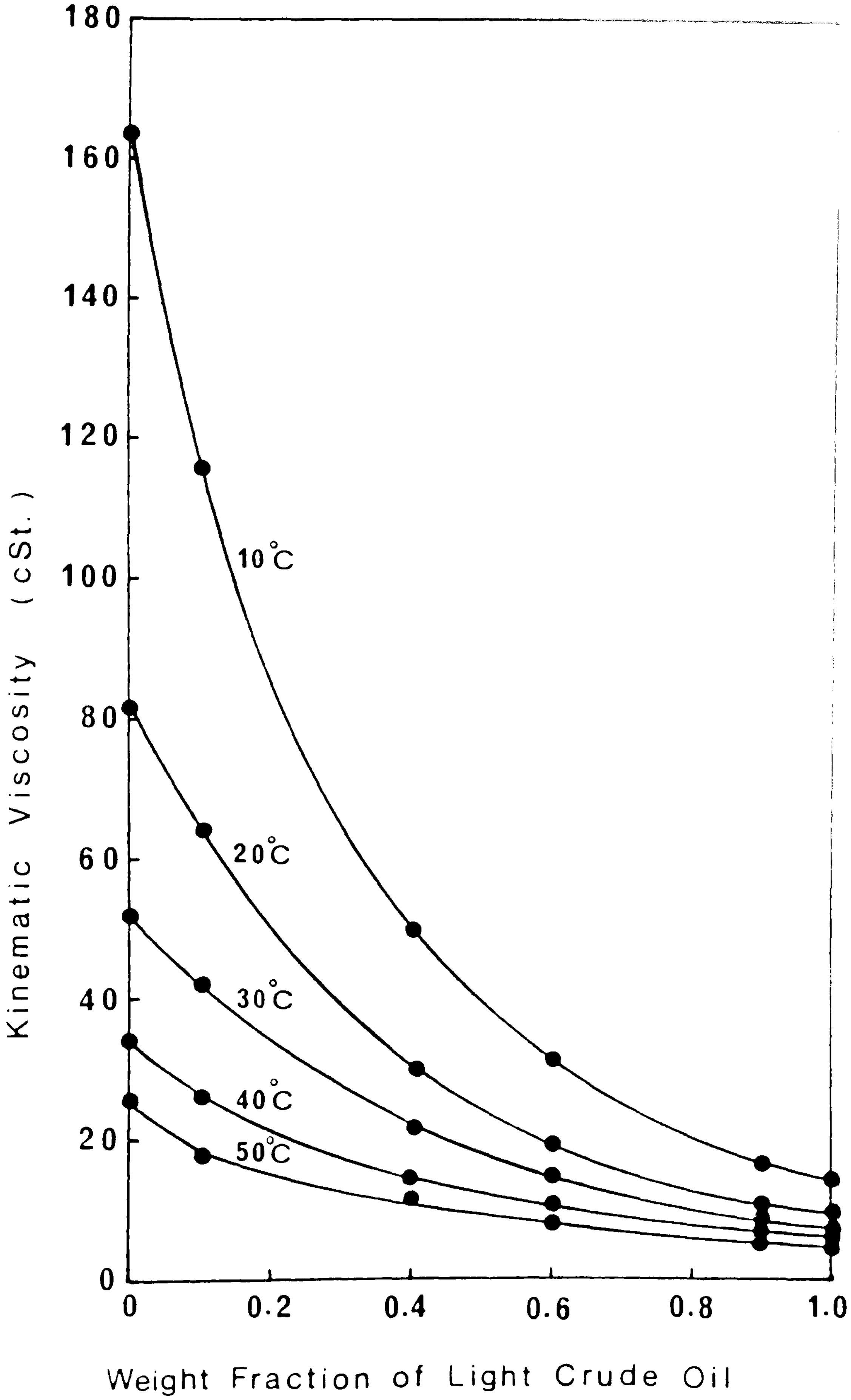


Figure 9.21: Kinematic Viscosities of Light - Medium Crude Oil Binary Mixtures

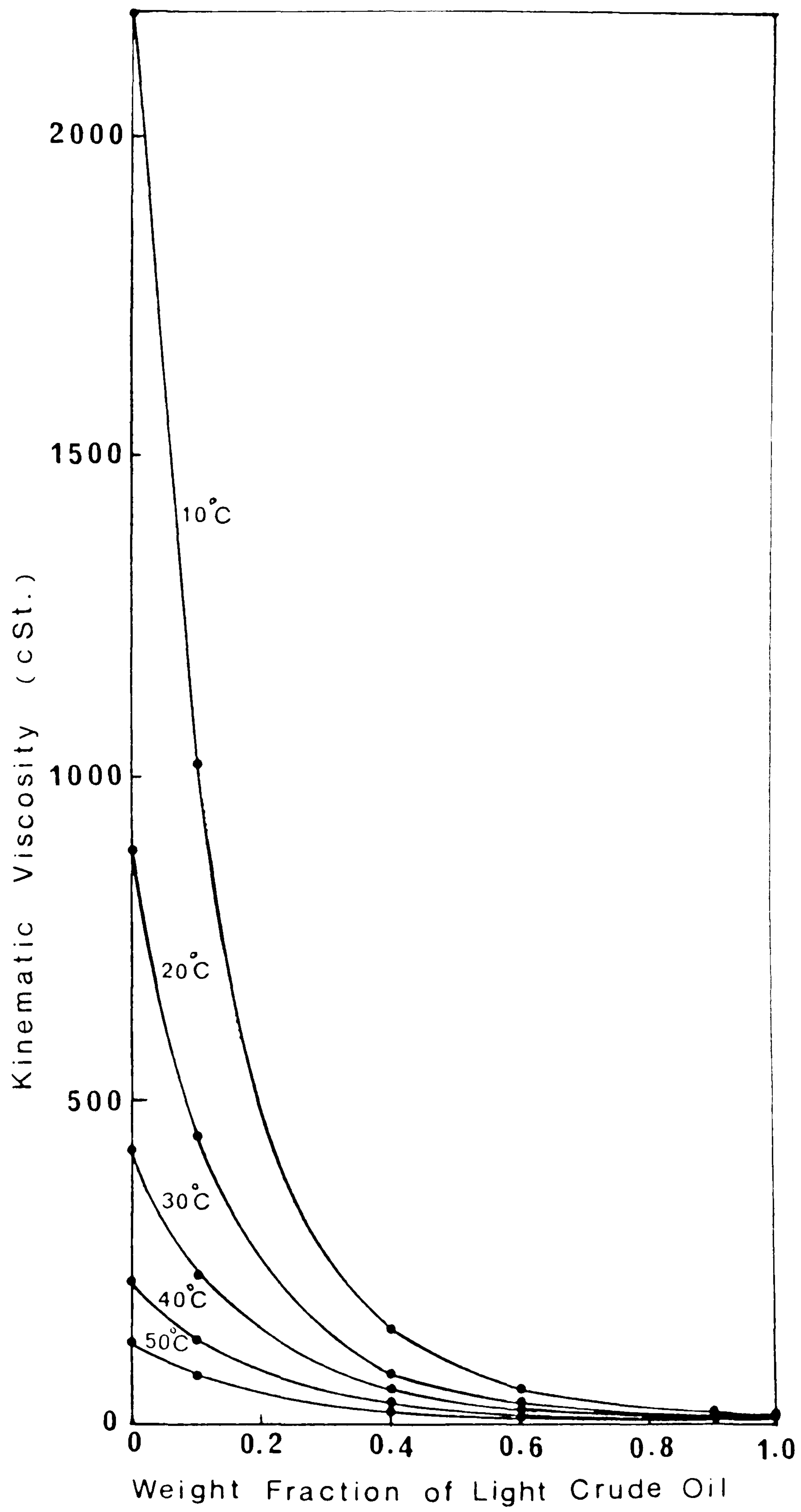


Figure 9.22: Kinematic Viscosities of Light - Heavy Crude Oil Binary Mixtures

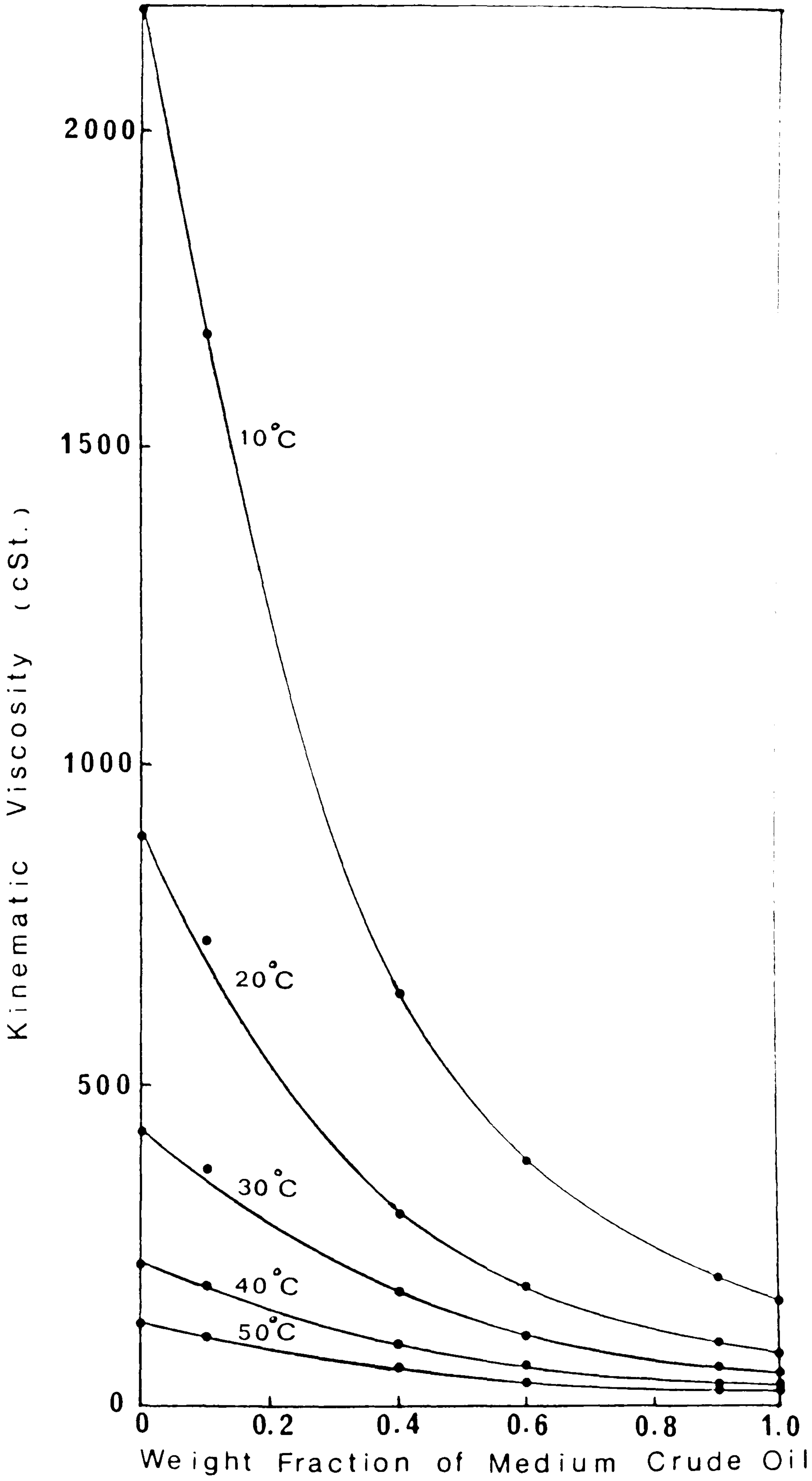


Figure 9.23: Kinematic Viscosities of Medium - Heavy Crude Oil Binary Mixtures

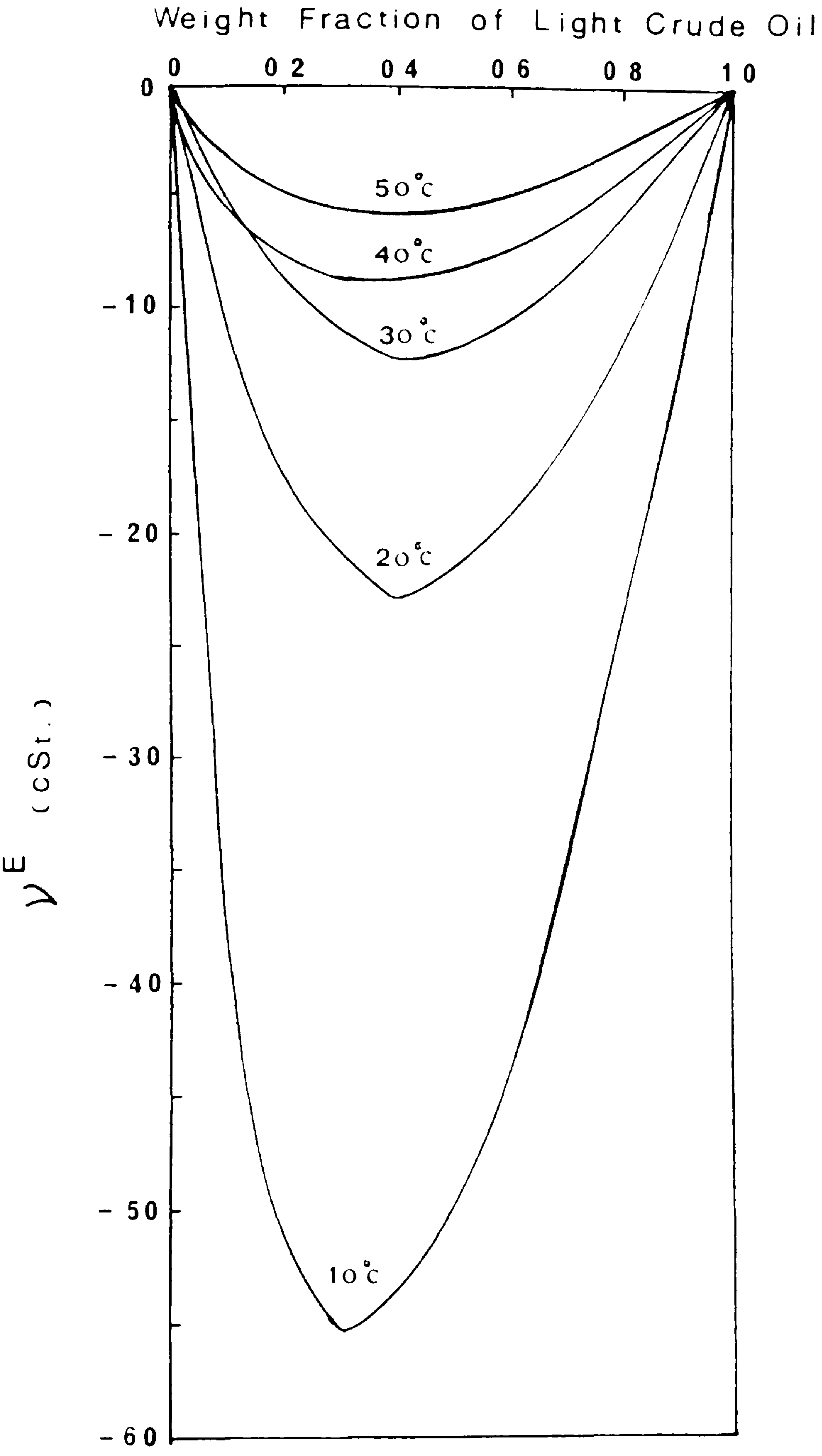


Figure 9.24: Excess Viscosity Function (ν^E) of Light - Medium Crude Oil Binary Mixtures

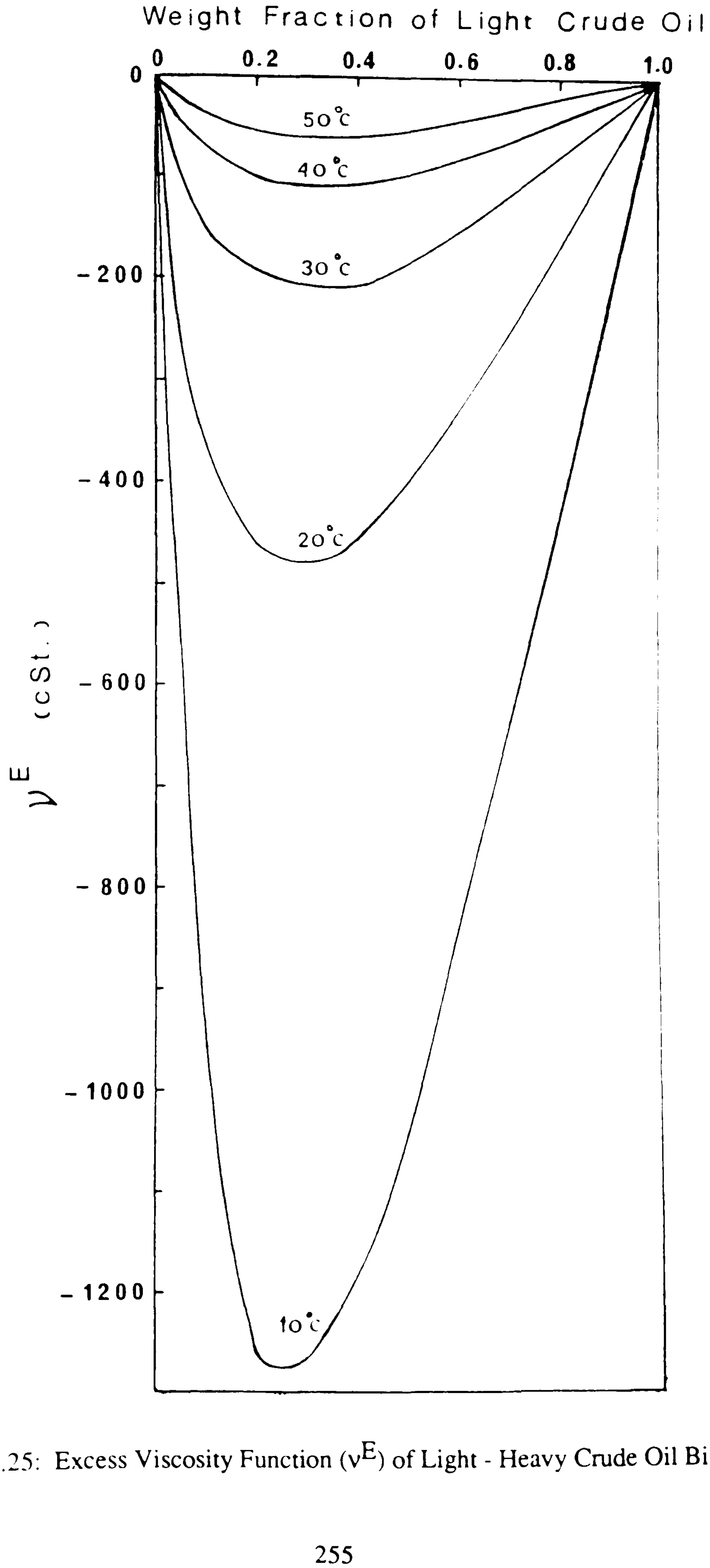


Figure 9.25: Excess Viscosity Function (v^E) of Light - Heavy Crude Oil Binary Mixtures

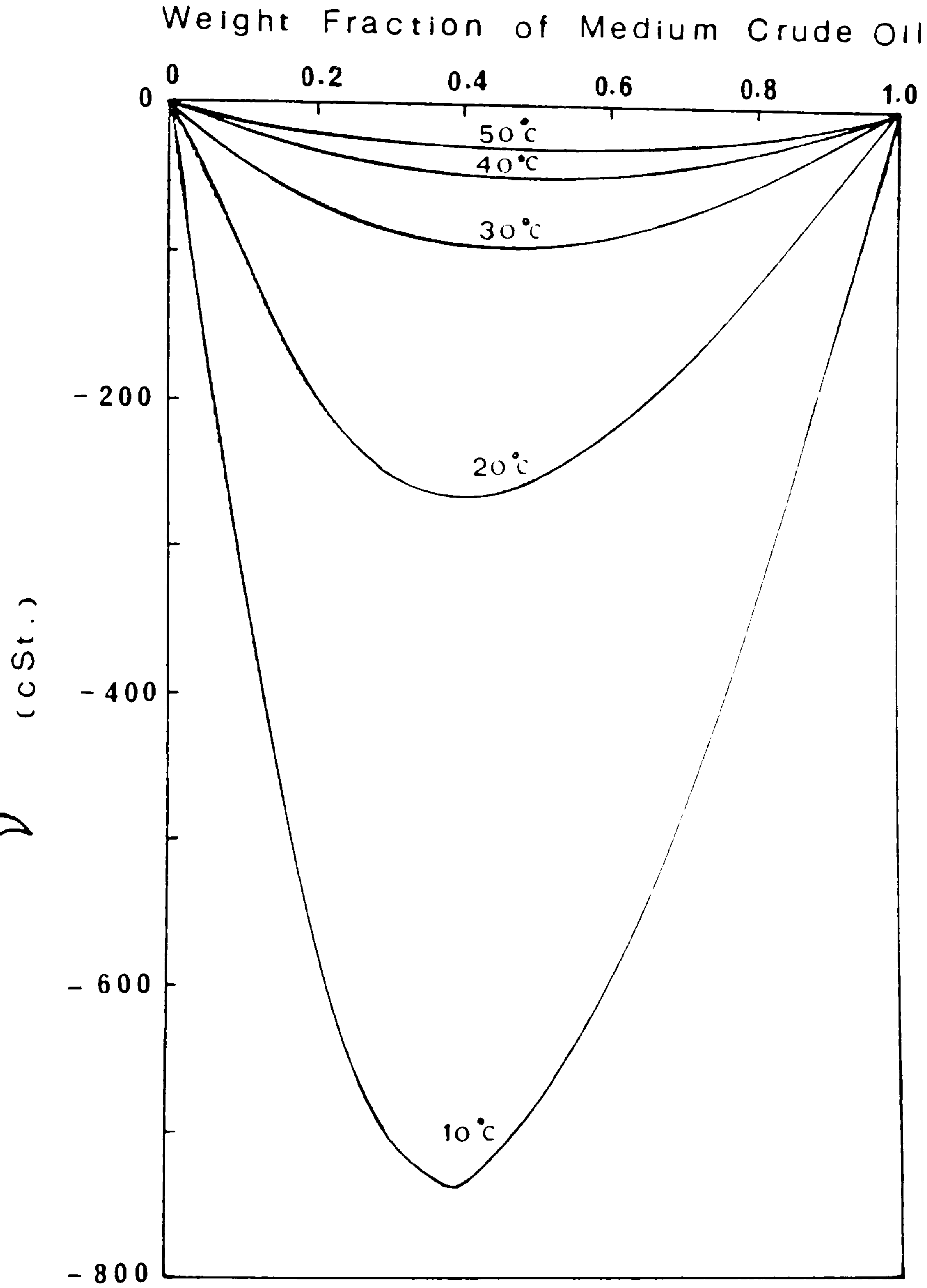


Figure 9.26: Excess Viscosity Function (v^E) of Medium - Heavy Crude Oil Binary Mixtures

The kinematic viscosities of the crude oil binary mixtures were also determined over a pressure range of 14.7 - 8000 psi at 25°C and 50°C. The data obtained are shown in Table 9.16, and presented graphically in Figures 9.27, 9.28 and 9.29. It is clear that the non-ideality of the mixture's viscosities increased as the pressure was increased; the highest divergences from ideality were obtained at 8000 psi for all mixtures at both test temperatures (25°C. and 50°C.)

The excess viscosity functions v^E, calculated by equation 9.12 for mixtures under the same test conditions of pressure and temperature are presented graphically in Figures 9.30, 9.31 and 9.32. The magnitude of v^E at a fixed temperature increased as the pressure was increased. However, the effect of pressure on the magnitude of v^E was much more significant at lower temperatures. All the excess viscosity function - composition curves showed a minima, corresponding to maximum deviations, at the same location observed at atmospheric pressure (0.2 - 0.4 weight fraction of lighter component), with a very slight shift towards the heavier component as the pressure increased.

It was also observed, as before, that the divergence from ideality increased as the ΔAPI gravity of the two components increased.

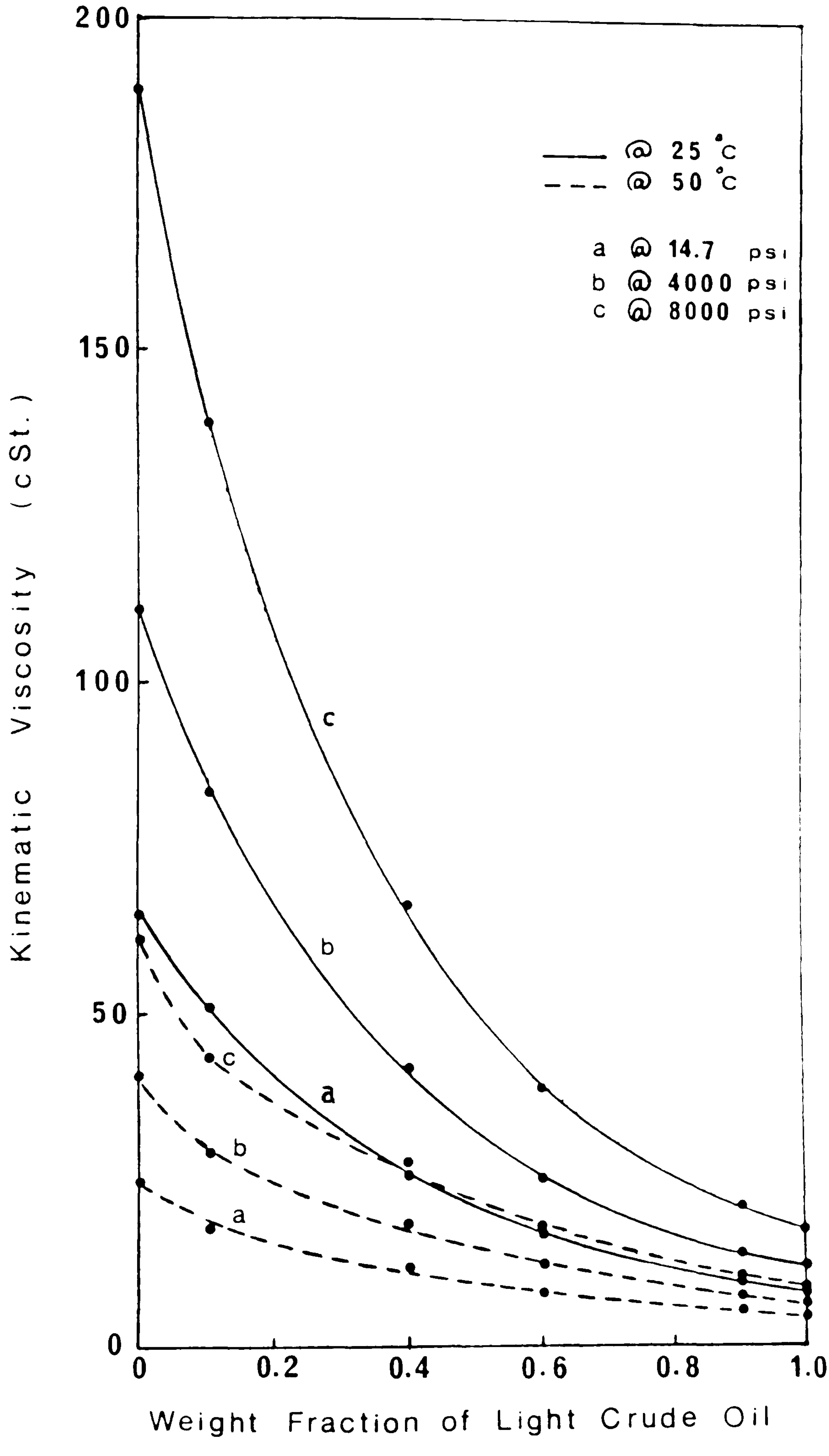


Figure 9.27: Kinematic Viscosities of Light - Medium Crude Oil Binary Mixtures: the Effect of Pressure at 25°C and 50°C

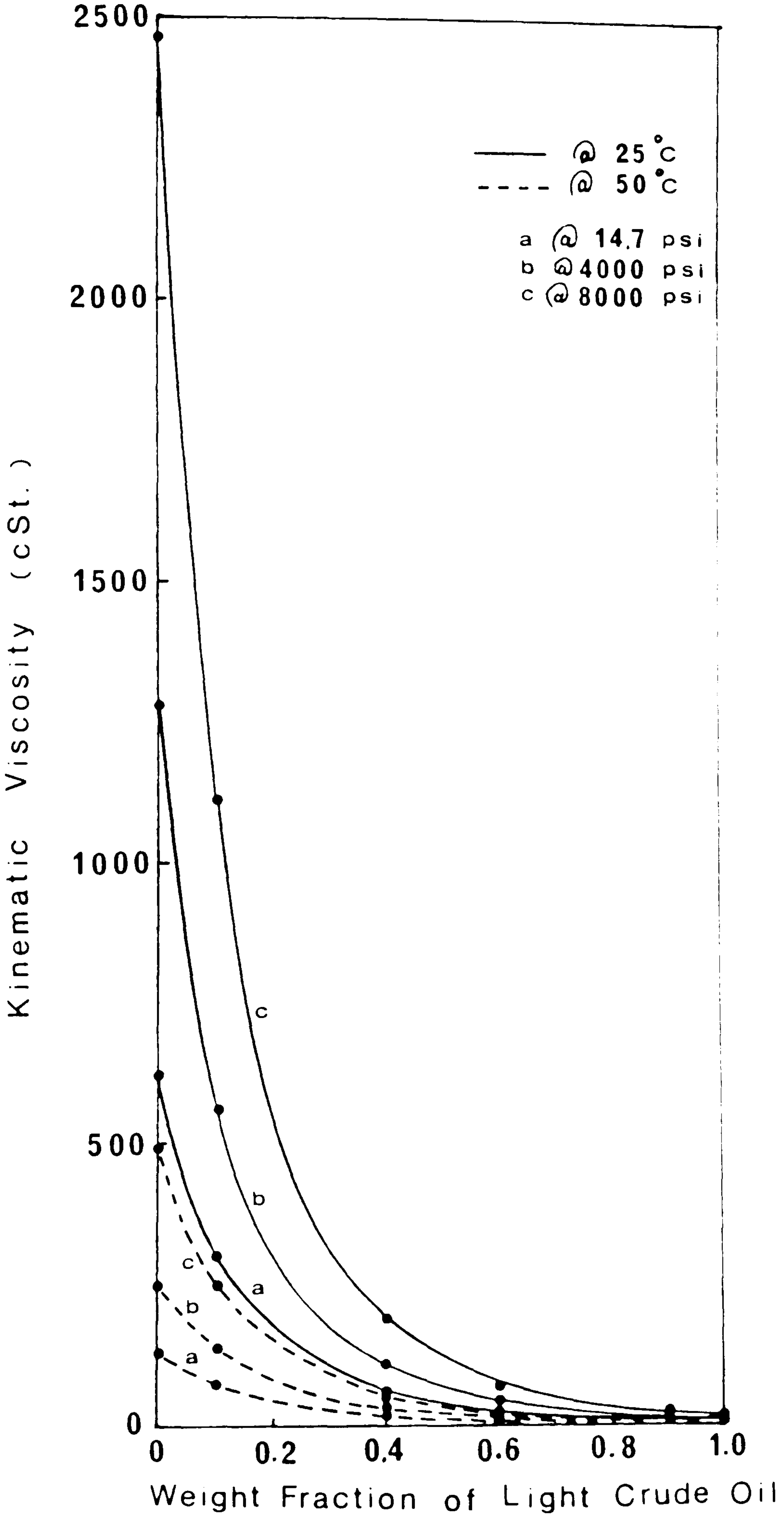


Figure 9.28: Kinematic Viscosities of Light - Heavy Crude Oil Binary Mixtures: the Effect of Pressure at 25°C and 50°C

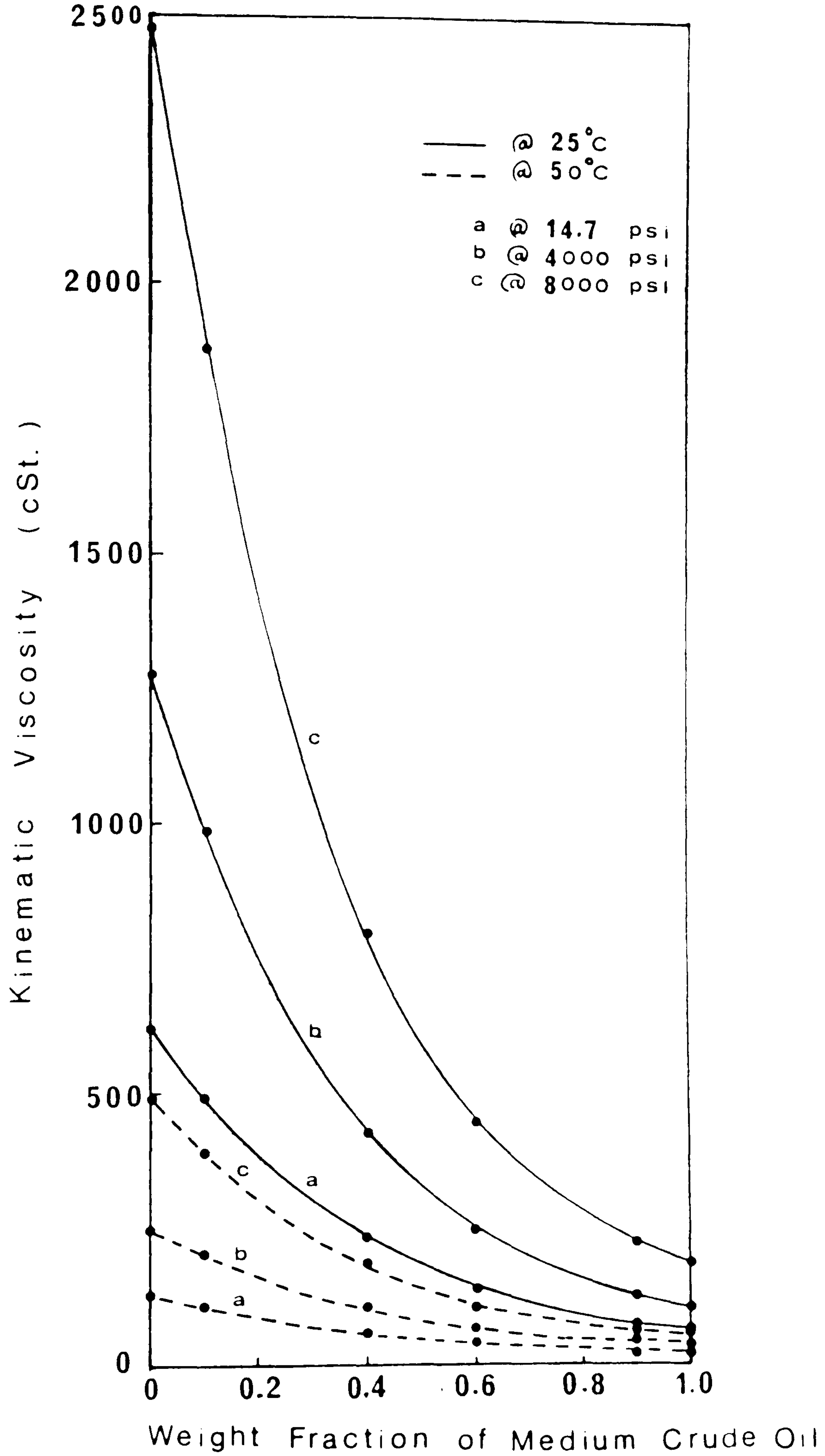


Figure 9.29: Kinematic Viscosities of Medium-Heavy Crude Oil Binary Mixtures: the Effect of Pressure at 25°C and 50°C

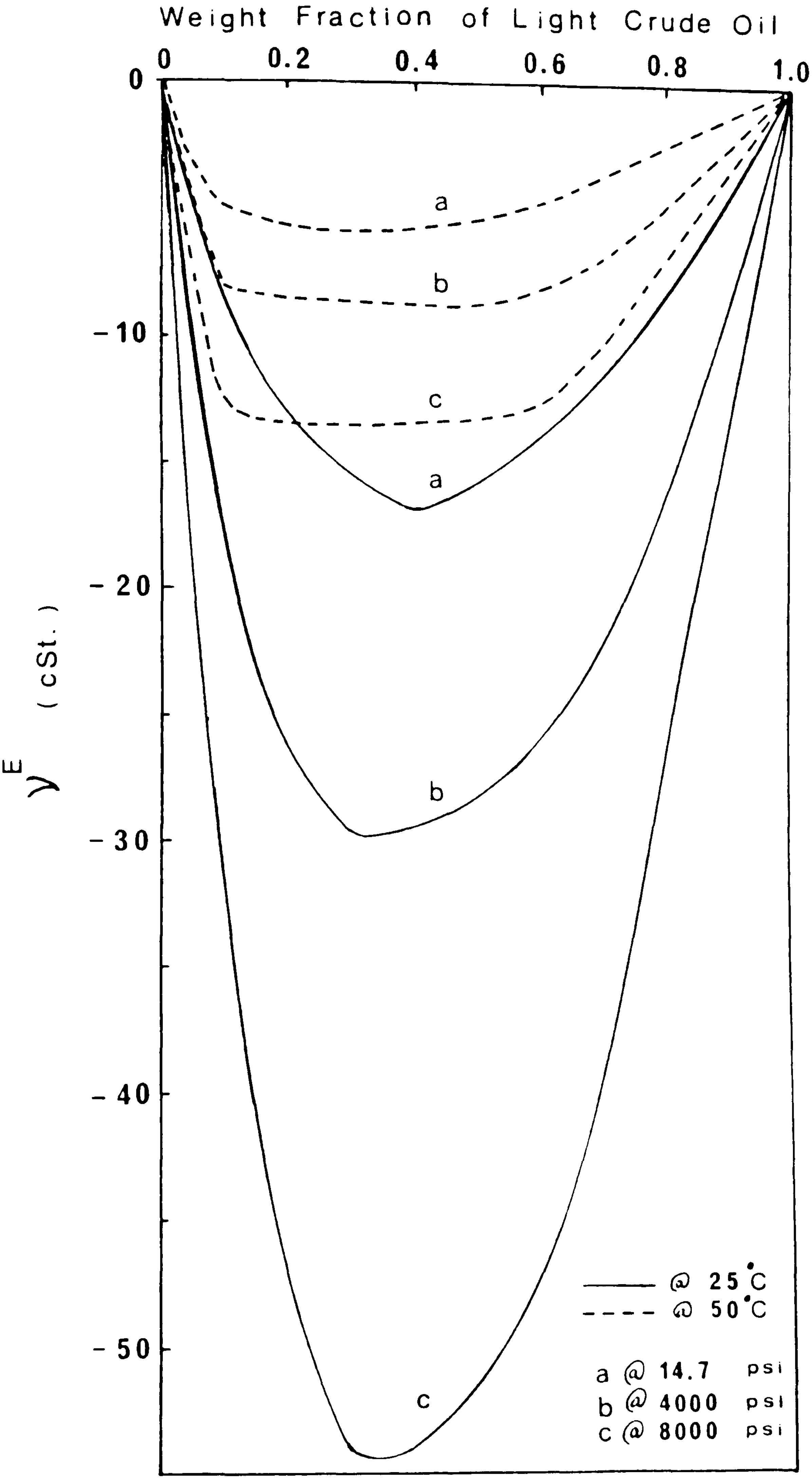


Figure 9.30: Excess Viscosity Function (ν^E) of Light - Medium Crude Oil Binary Mixtures; the Effect of Pressure at 25°C and 50°C

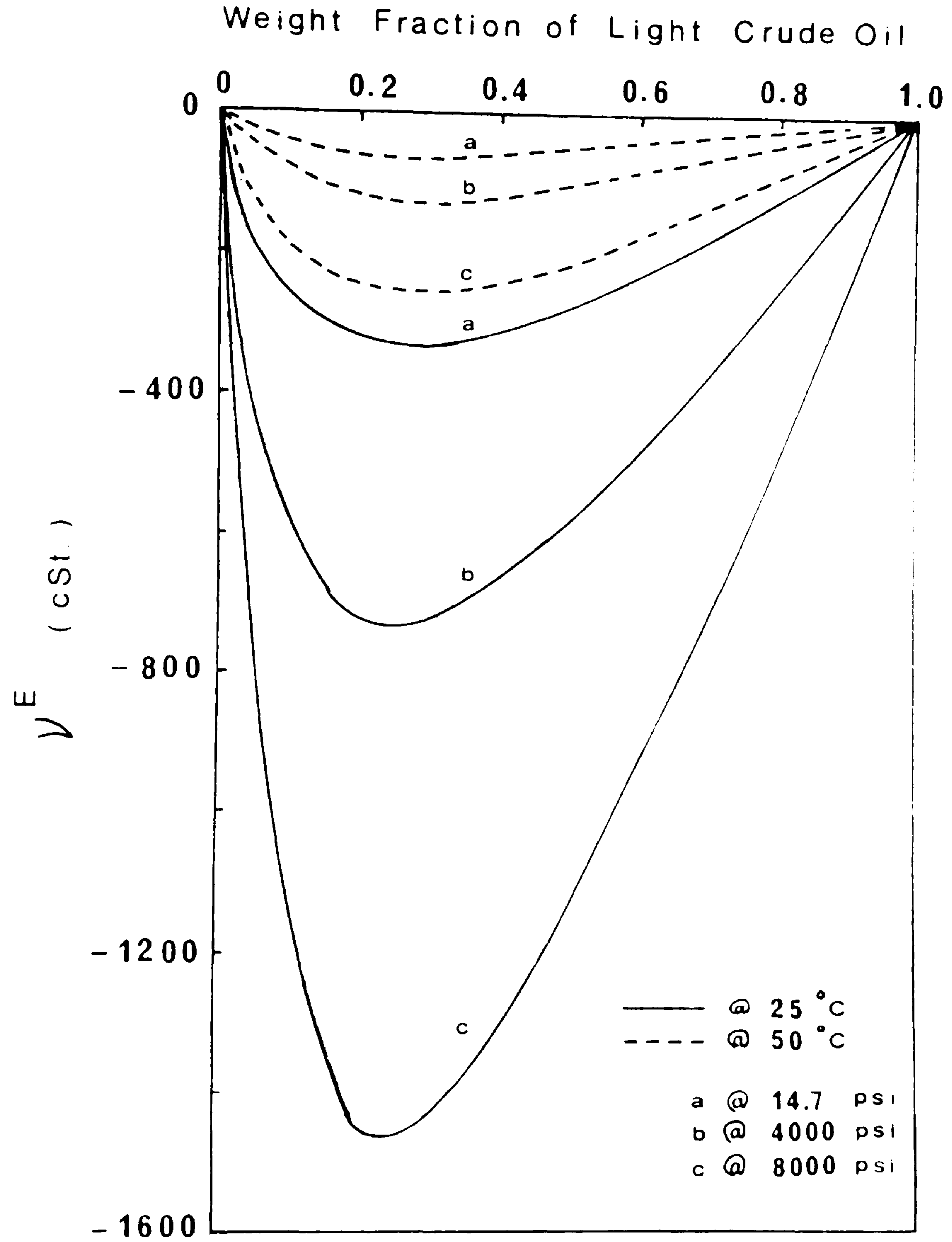


Figure 9.31: Excess Viscosity Function (ν^E) of Light - Heavy Crude Oil Binary Mixtures; the Effect of Pressure at 25°C and 50°C

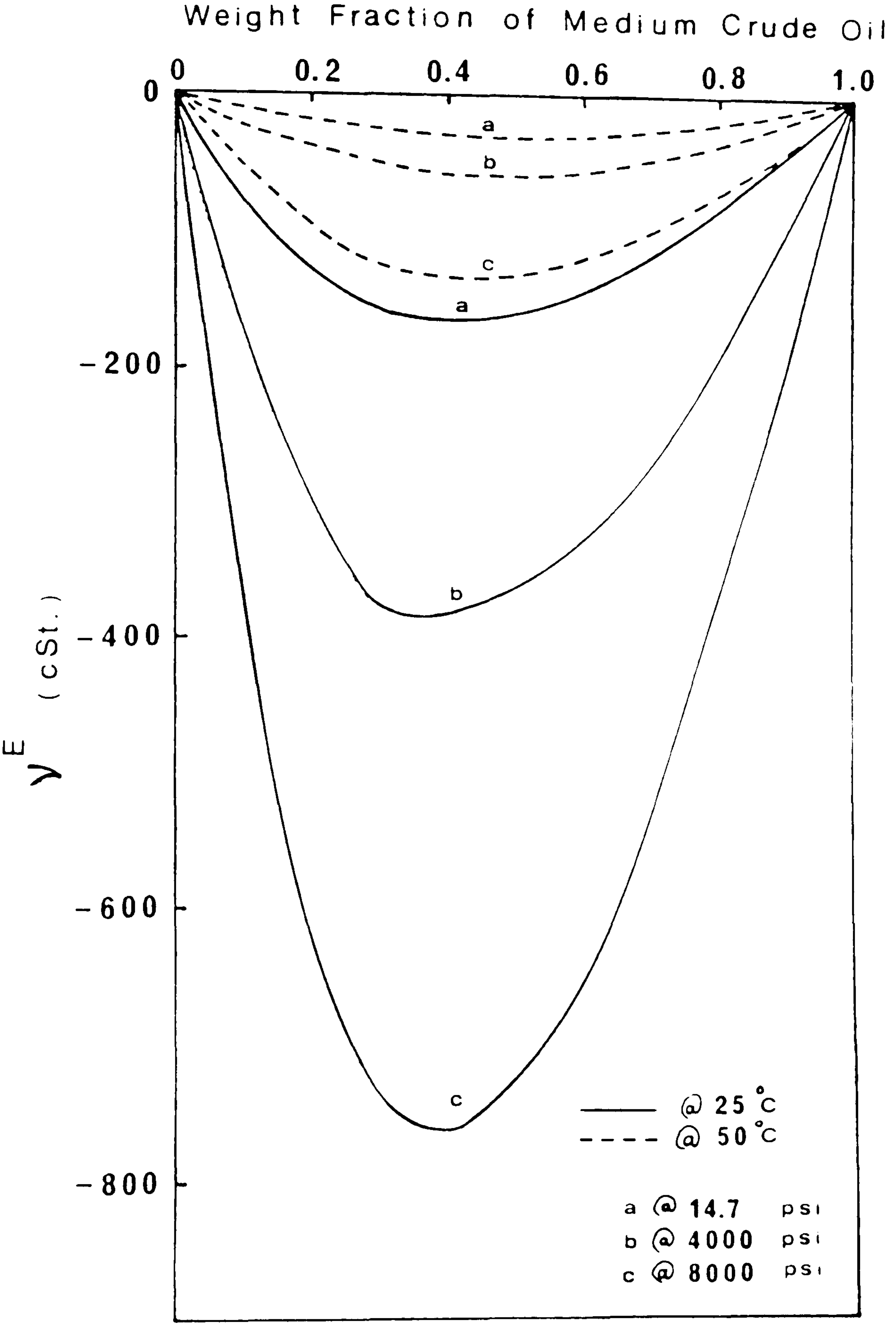


Figure 9.32: Excess Viscosity Function (ν^E) of Medium - Heavy Crude Oil Binary Mixtures:the effect of pressure at 25°C and 50°C

The Non-Ideal Viscosity Characteristics of Petroleum Products and Base Oil Mixtures:

As described in the previous section, crude oil viscosity exhibited non-ideal behaviour upon mixing. The application of a similar approach to the analysis of the viscosity characteristics of the selected binary mixtures of petroleum products and of base oils (kerosene, heavy gas oil, residue >360°C; light, medium, heavy and bright stock base oils) is described below. Viscosity is the most critical property of base oil blends and is always an important property in petroleum product's specification. Therefore, the aim of this part of the study was to investigate the manner in which the viscosity of such mixtures varied with temperature and composition.

Petroleum Products:

The kinematic viscosities of the binary mixtures of products at atmospheric pressure were determined at 20, 40, 60 and 100°C. The measured viscosities are given in Table 9.21 and presented graphically in Figures 9.33, 9.34 and 9.35.

The viscosity - composition curves exhibited similar behaviour to those of crude oil binary mixtures with a negative deviation from ideality. Similarly, the non-ideality increased as the temperature was decreased or as the ΔAPI of the components increased, (ΔAPI of kerosene - heavy gas oil, kerosene - residue and heavy gas oil - residue were 18.6, 30.4 and 11.8 respectively). In the case of kerosene-residue binary mixtures, the viscosity of the residue decreased dramatically from 2100 cSt to 388.4 cSt at 40°C (i.e., an 81.5% decrease in viscosity or increase in fluidity) due to addition of 10% weight of kerosene. At 60°C and 100°C, the percent decreases in viscosity were 73.0% and 54.9% respectively.

Values of the excess viscosity function v^E for the binary mixtures calculated by equation 9.12 are presented graphically in Figures 9.36, 9.37 and 9.38. Similar behaviour was observed to that with crude oil mixtures, with maximum deviations from ideality occurring at about 0.2 - 0.4 weight fraction of lighter component. The tendency of the maxima to shift their locations towards the heavier components as the temperature decreased was greater than observed for the crude oil mixtures, e.g. for the kerosene - residue mixtures the shift was from about 0.3 weight fraction at 100°C to 1.5 weight fraction at 40°C.

The three petroleum product~~s~~ components differed widely in their chemical natures and physical properties. For example, kerosene is a wax-free, asphaltenes-free, relatively low molecular weight, light hydrocarbon comprising predominately saturated hydrocarbons, with a negligible metal content. The residue is a black substance, asphaltenes - bearing, relatively wax-rich, of high molecular weight, high metal content and semi-solid at room temperature. The heavy gas oil is a brown, thick, wax-bearing liquid with chemical and physical properties intermediate between those of kerosene and residue. Hence, the behaviour of viscosity for the extreme case of kerosene-residue mixtures, with a high rate of decrease of viscosity of the residue due to the addition of kerosene and a tendency of the maxima to shift in location with a decrease in temperature, may be attributed to the big difference in the nature of the components, and hence the highest degree of non-ideality.

Table 9.21: Measured Kinematic Viscosities (cSt.) of Kerosene, Heavy Gas Oil and Residue >360°C and of their Binary Mixtures at Atmospheric Pressure

Mixture	Kinematic Viscosity (cSt.) @ 20°C	40°C	60°C	100°C
Kerosene	1.908	1.381	1.054	0.8450
Heavy Gas Oil	65.95	21.24	10.51	3.941
Residue	-	2100	433.0	58.60
Mix 1	31.67	13.58	7.219	-
Mix 2	8.545	4.815	3.095	-
Mix 3	5.152	3.190	2.224	-
Mix 4	2.290	1.629	1.214	-
Mix 5	-	388.4	116.7	26.42
Mix 6	-	21.56	11.38	4.652
Mix 7	-	6.509	4.076	2.218
Mix 8	-	1.886	1.411	0.8880
Mix 9	-	1014	249.3	40.91
Mix 10	-	201.6	67.30	16.06
Mix 11	-	86.39	32.35	9.337
Mix 12	-	28.28	13.57	4.814

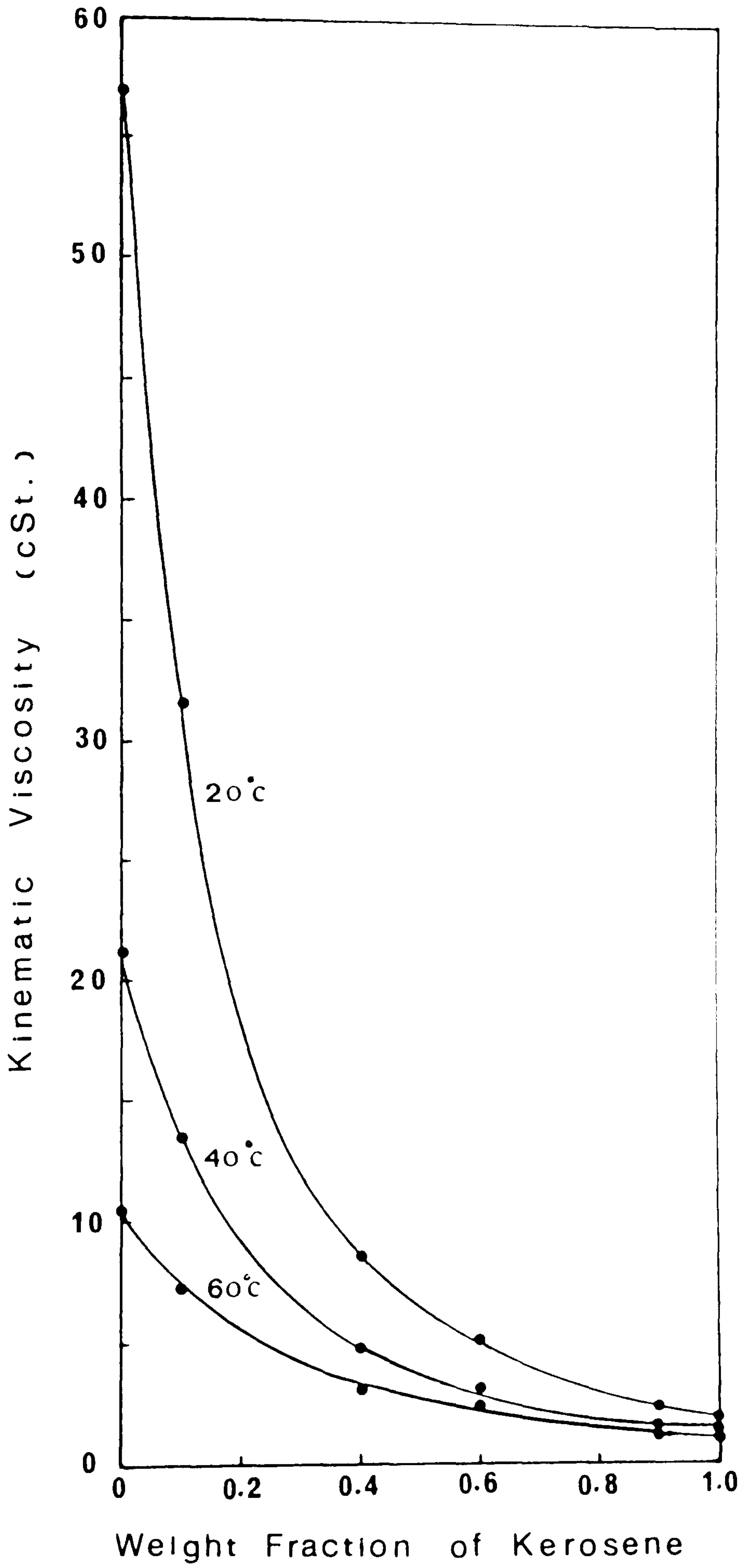


Figure 9.33: Kinematic Viscosities of Kerosene-Heavy Gas Oil Binary Mixtures

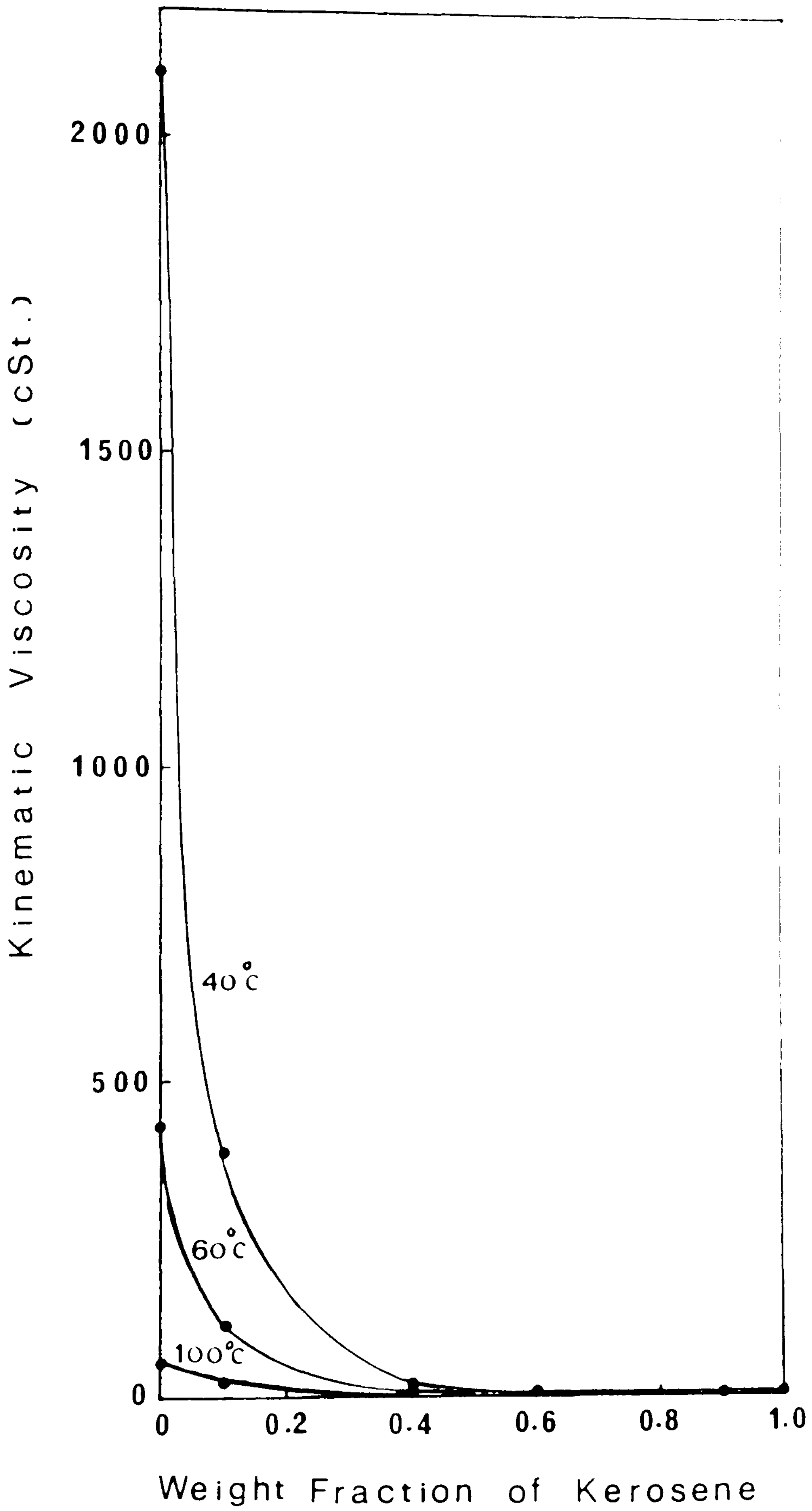


Figure 9.34: Kinematic Viscosities of Kerosene - Residue Binary Mixtures

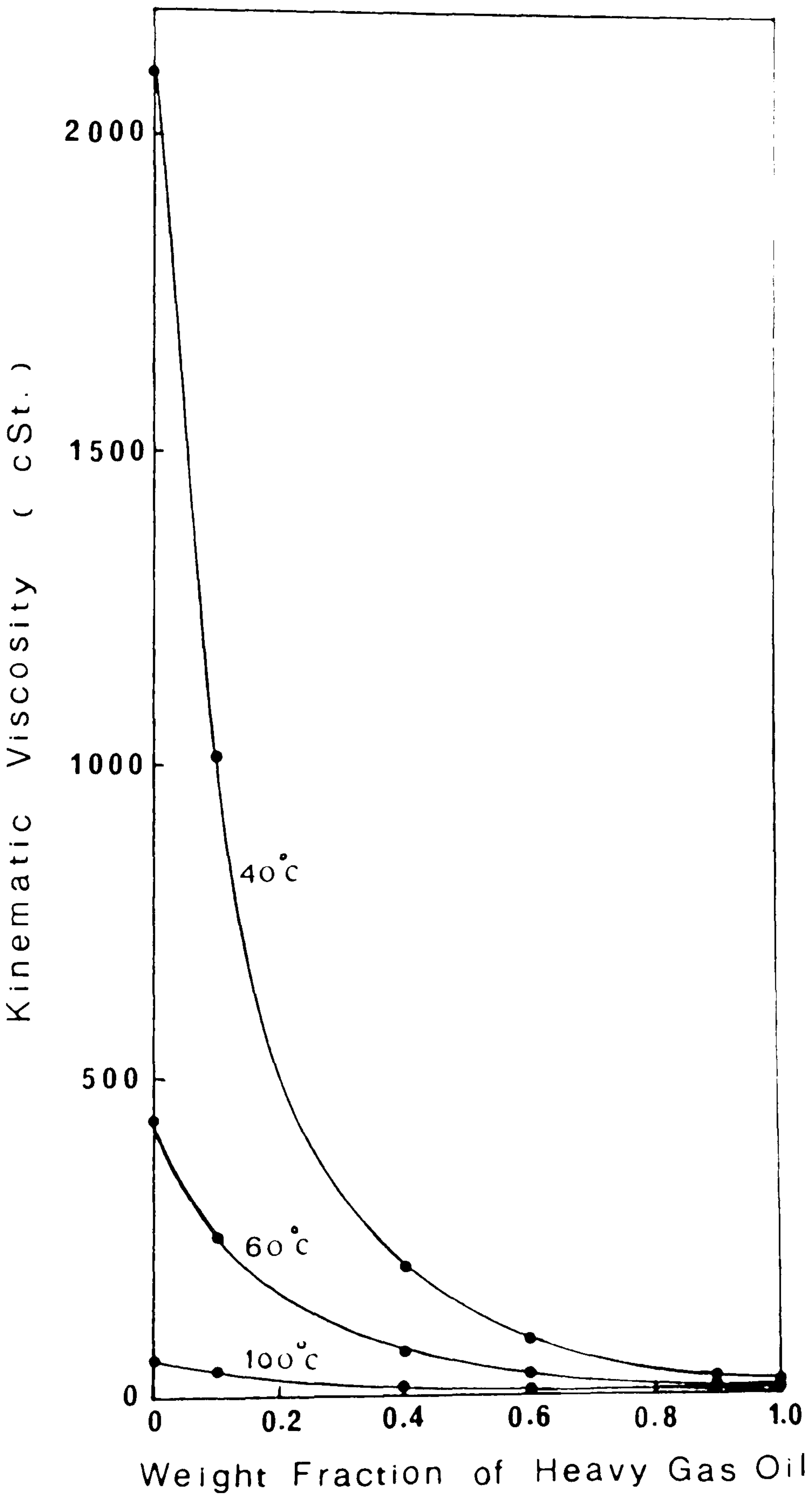


Figure 9.35: Kinematic Viscosities of Heavy Gas Oil-Residue Binary Mixtures

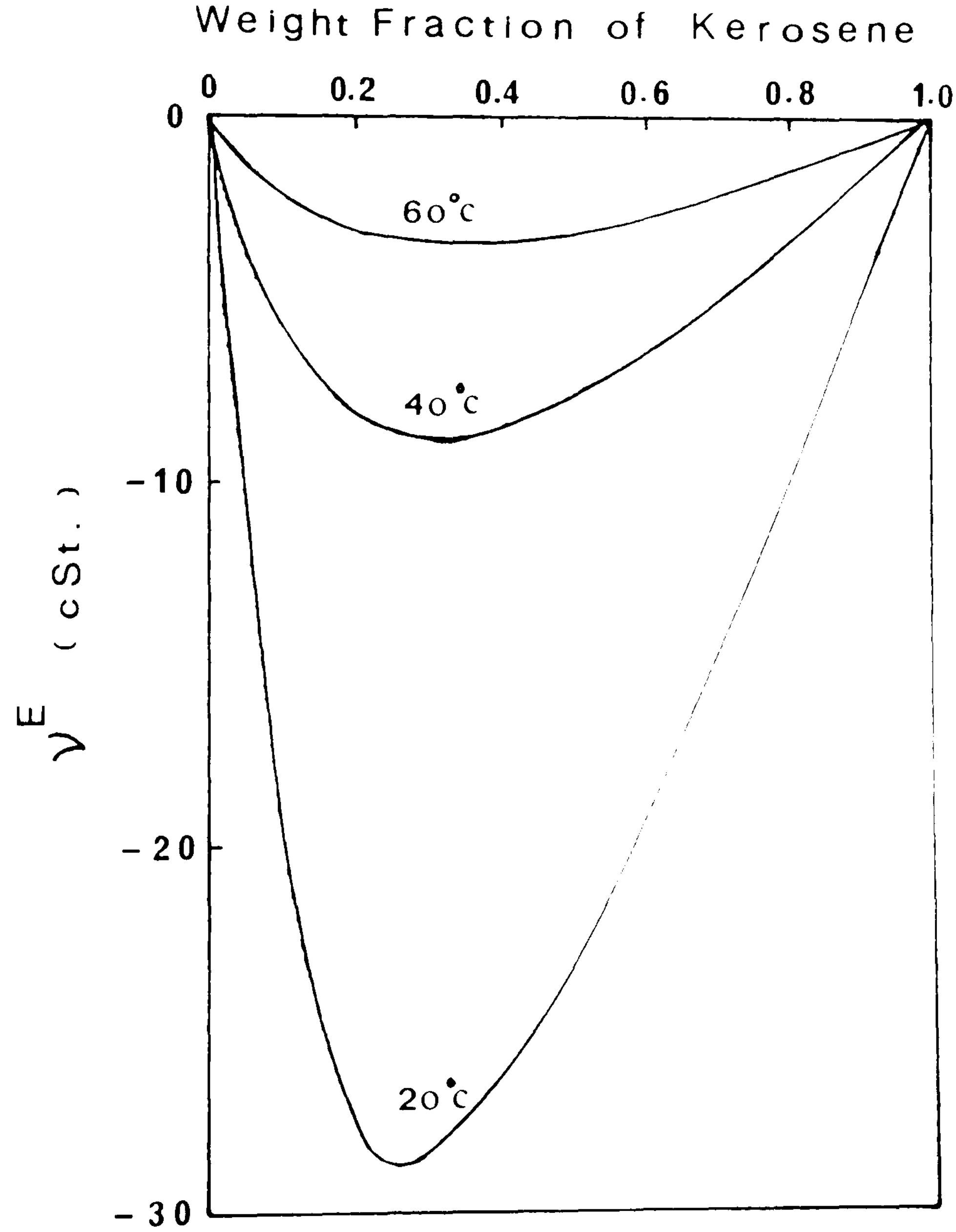


Figure 9.36: Excess Viscosity Function (ν^E) of Kerosene-Heavy Gas Oil Binary Mixtures

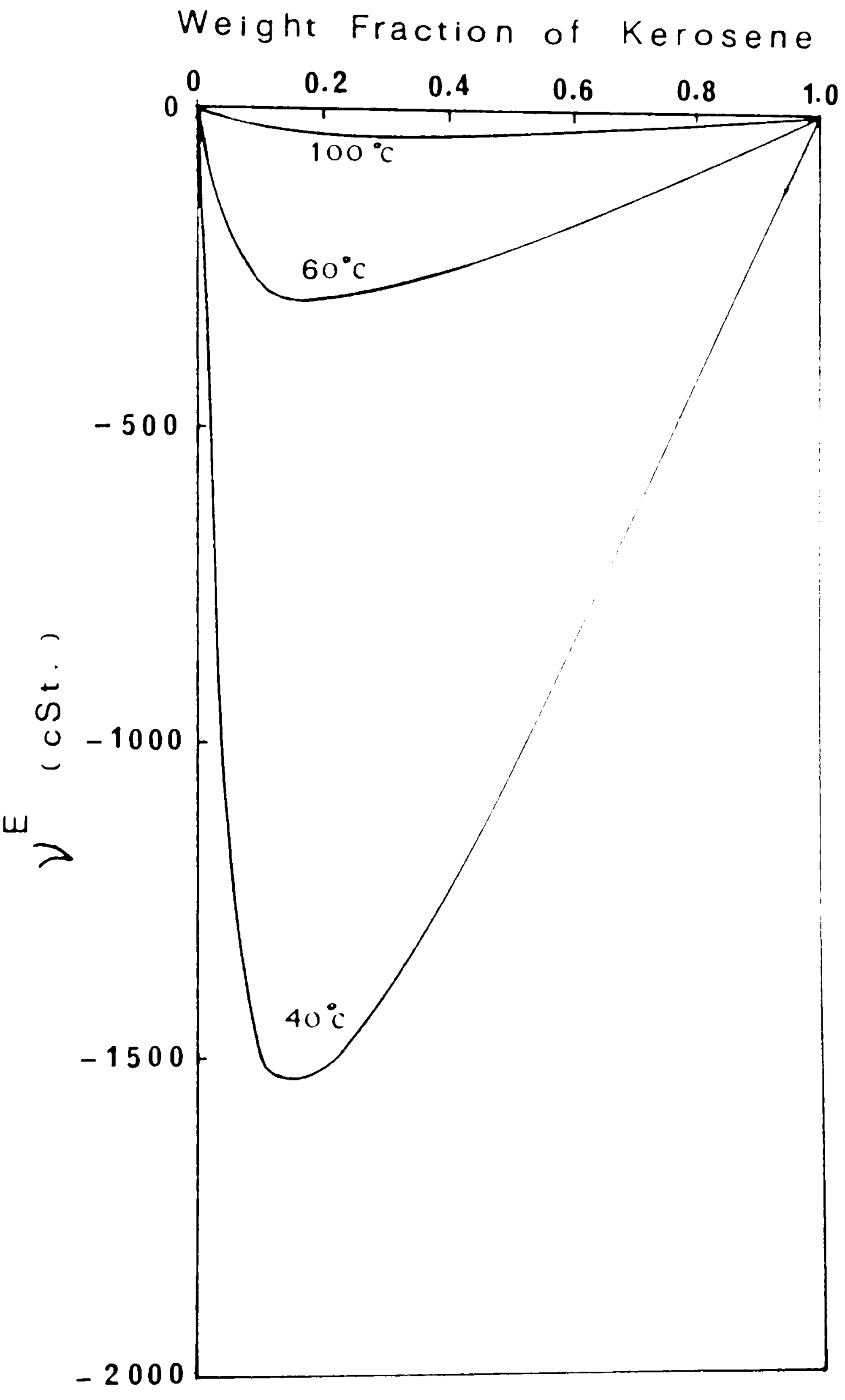


Figure 9.37: Excess Viscosity Function (ν^E) of Kerosene-Residue Binary Mixtures

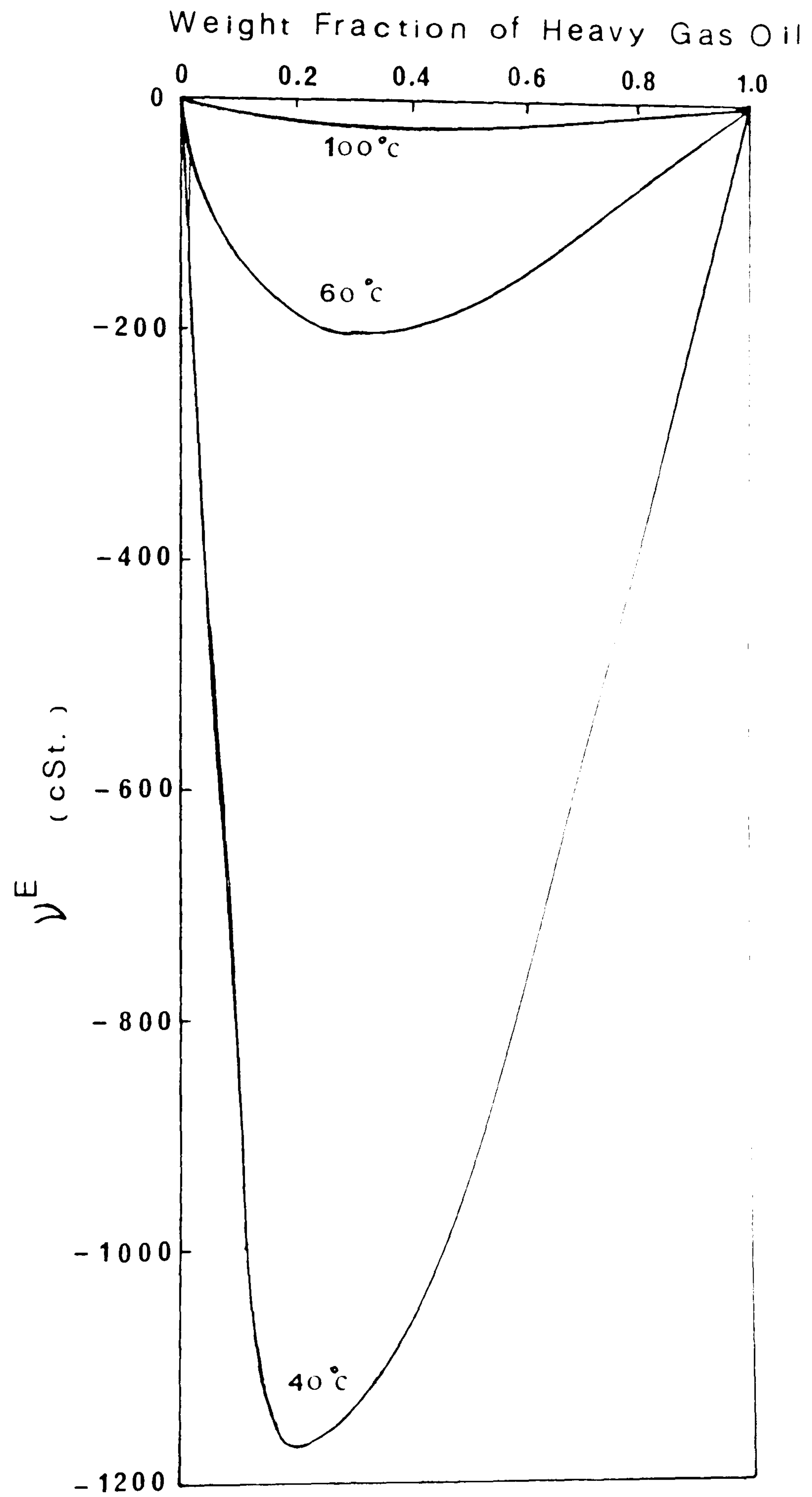


Figure 9.38: Excess Viscosity Function (v^E) of Heavy Gas Oil- Residue Binary Mixtures

Base Oils:

The kinematic viscosities of base oils mixtures were determined at 20, 40 and 100°C, and the data obtained are shown in Table 9.22 and presesnted graphically in Figures 9.39, 9.40, 9.41, 9.42 and 9.43. The viscosity -composition curves exhibited non-ideal behaviour, as observed previously for crude oil mixtures and for petroleum products mixtures. The non-ideal behaviour decreased with an increase in temperature or decrease in ΔAPI of the components (ΔAPI of light-medium base oil, light-heavy base oil, light-bright stock, medium base oil - bright stock, and heavy base oil-bright stock were 2.95, 4.05, 5.80, 2.85 and 1.75 respectively). The curves for 100°C approximate to be straight lines, i.e., the divergence from ideality was very small. These observations are supported by the values of the excess viscosity function ν^E calculated by equation 9.12 and presented graphically in Figures 9.44, 9.45, 9.46, 9.47 and 9.48. It is clear that the viscosities of the base oils mixtures possessed very low values for ν^E at 100°C compared with those at lower temperatures. Therefore, the behaviour of base oil mixture viscosity could be considered, approximately, ideal when subjected to mixing at high temperature.

Although, the differences in the viscosities of the individual base oils were very high, the mixtures exhibited less non-ideality than the petroleum products especially at high temperatures. This might be attributed to the relative similarity in the chemical nature of the base oil components, and in particular to the fact that they are all asphaltenes-free liquids.

Table 9.22: Measured Kinematic Viscosities (cSt) of Light, Medium and Heavy Base Oil and Bright Stock, and Binary Mixtures at Atmospheric Pressure

Mixture (ref. Section 9.3.3)	Kinematic Viscosity (cSt) @		
	20°C	40°C	100°C
Light Base Oil	45.34	19.31	4.002
Medium Base Oil	177.7	60.21	8.025
Heavy Base Oil	424.7	125.9	13.17
Bright Stock	1756	425.5	29.93
Mix 1	152.3	53.13	7.468
Mix 2	113.7	41.49	6 474
Mix 3	75.24	29.47	5.305
Mix 4	51.32	21.56	4.253
Mix 5	326.6	102.4	11.59
Mix 6	200.8	67.90	8.905
Mix 7	102.2	38.37	6.197
Mix 8	55.1	22.86	4.426
Mix 9	1119	295.1	23.56
Mix 10	488.2	146.4	15.05
Mix 11	161.7	57.35	8.276
Mix 12	61.50	24.91	4.709
Mix 13	1343	348.5	25.96
Mix 14	826.0	228.6	19.68
Mix 15	413.7	126.4	13.28
Mix 16	215.8	72.17	9.299
Mix 17	1502	379.5	27.43
Mix 18	1119	295.0	23.21
Mix 19	730.2	203.9	18.09
Mix 20	483.6	143.1	14.27

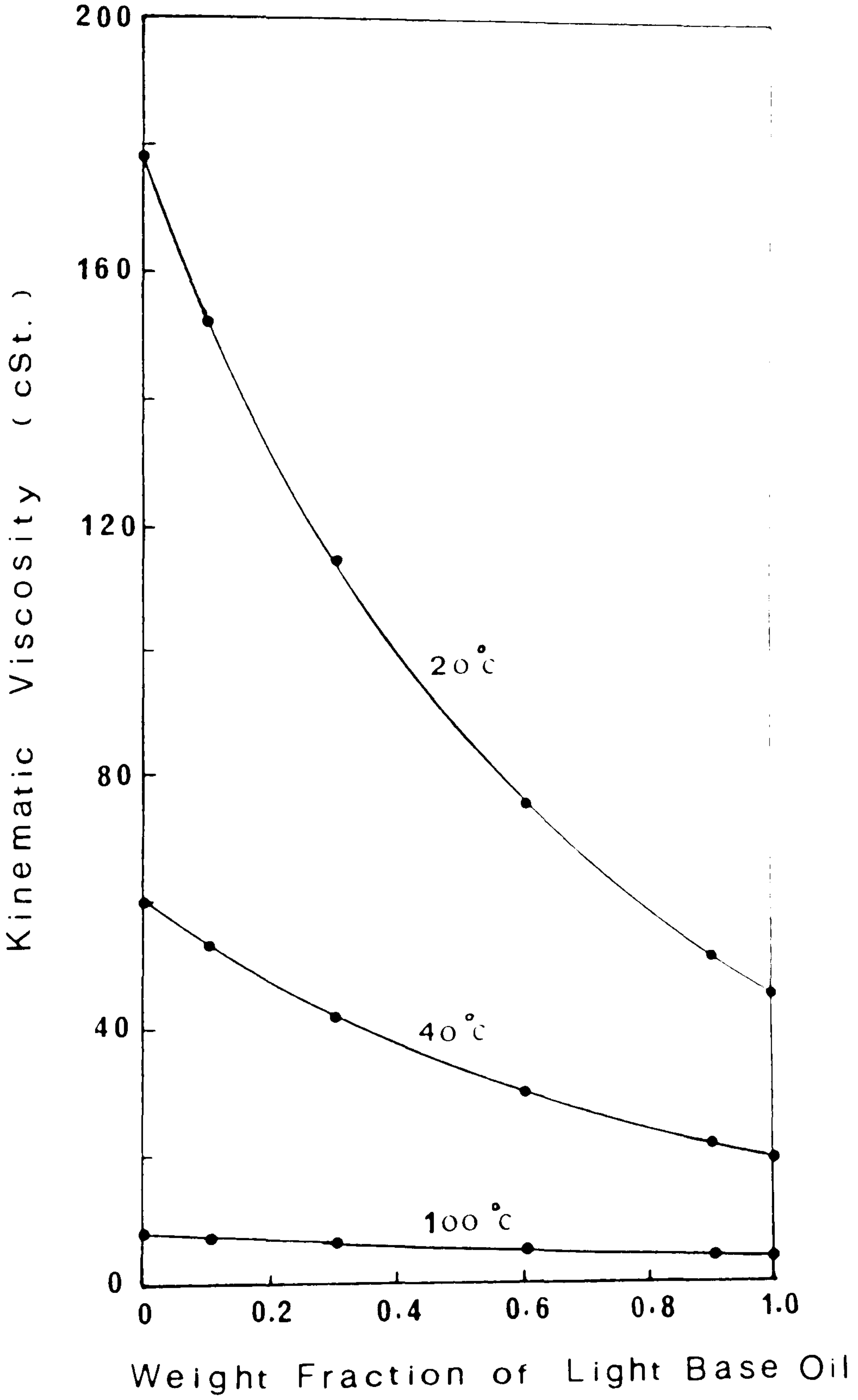


Figure 9.39: Kinematic Viscosities of Light - Medium Base Oil Binary Mixtures

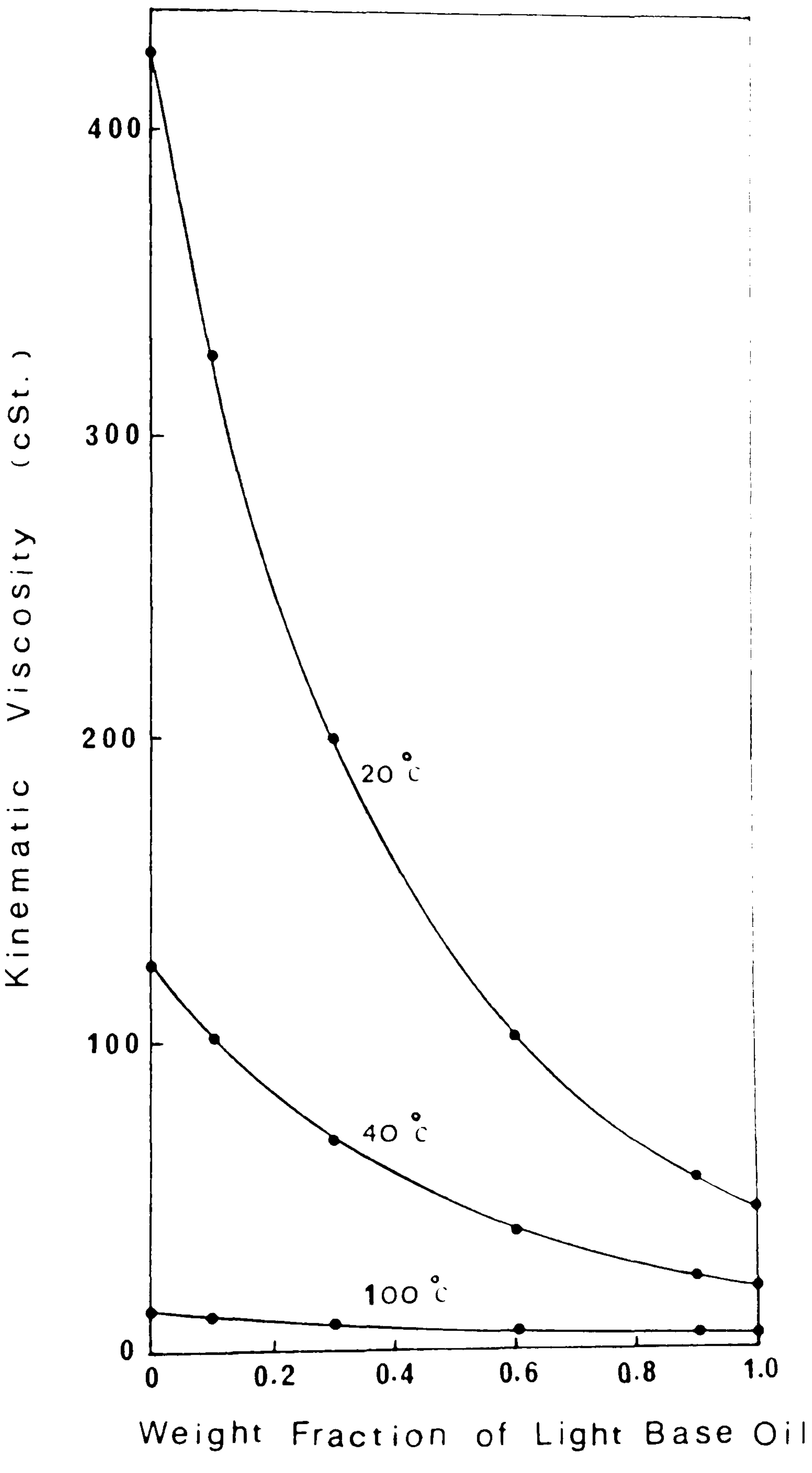


Figure 9.40: Kinematic Viscosities of Light - Heavy Base Oil Binary Mixtures

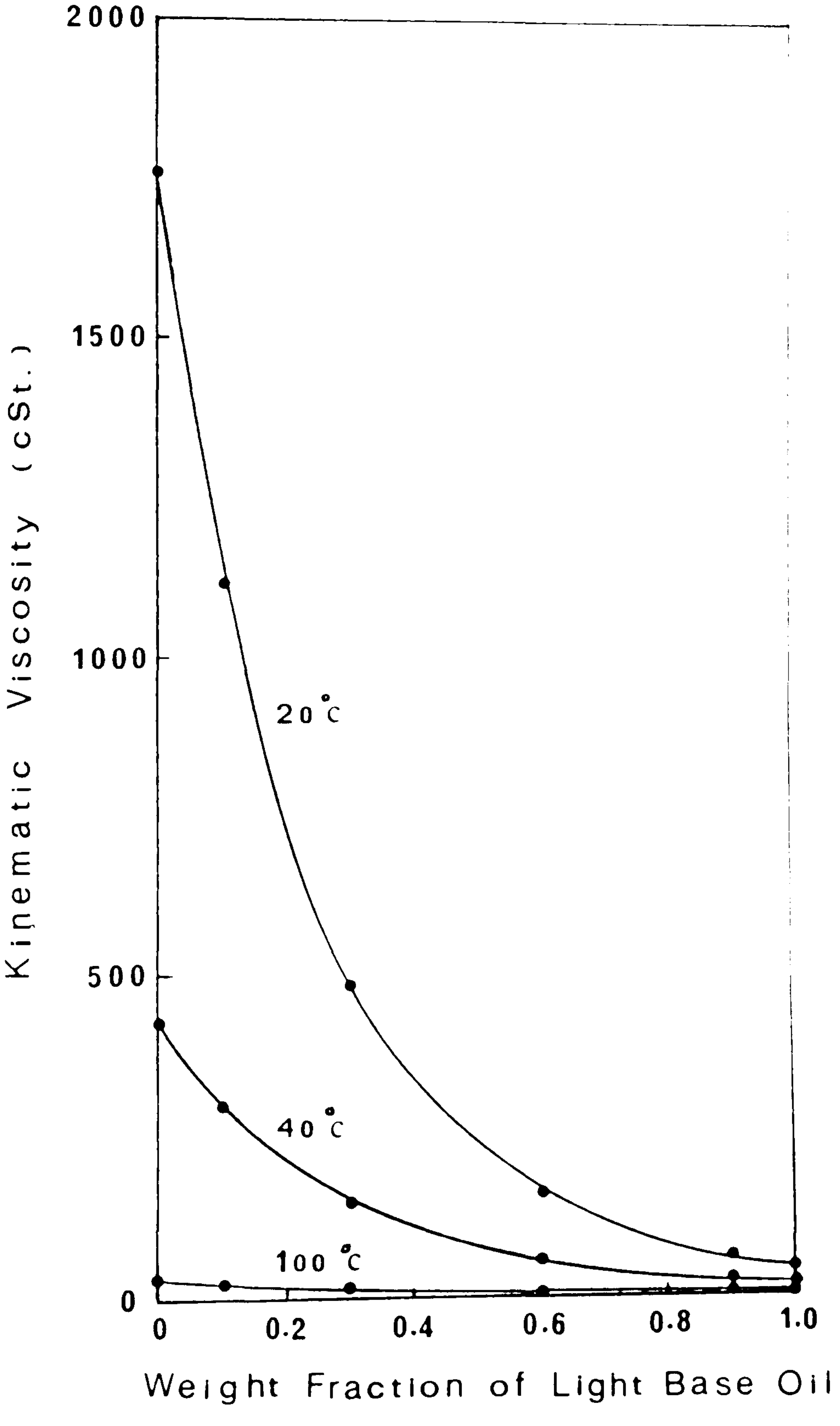


Figure 9.41: Kinematic Viscosities of Light Base Oil - Bright Stock Binary Mixtures

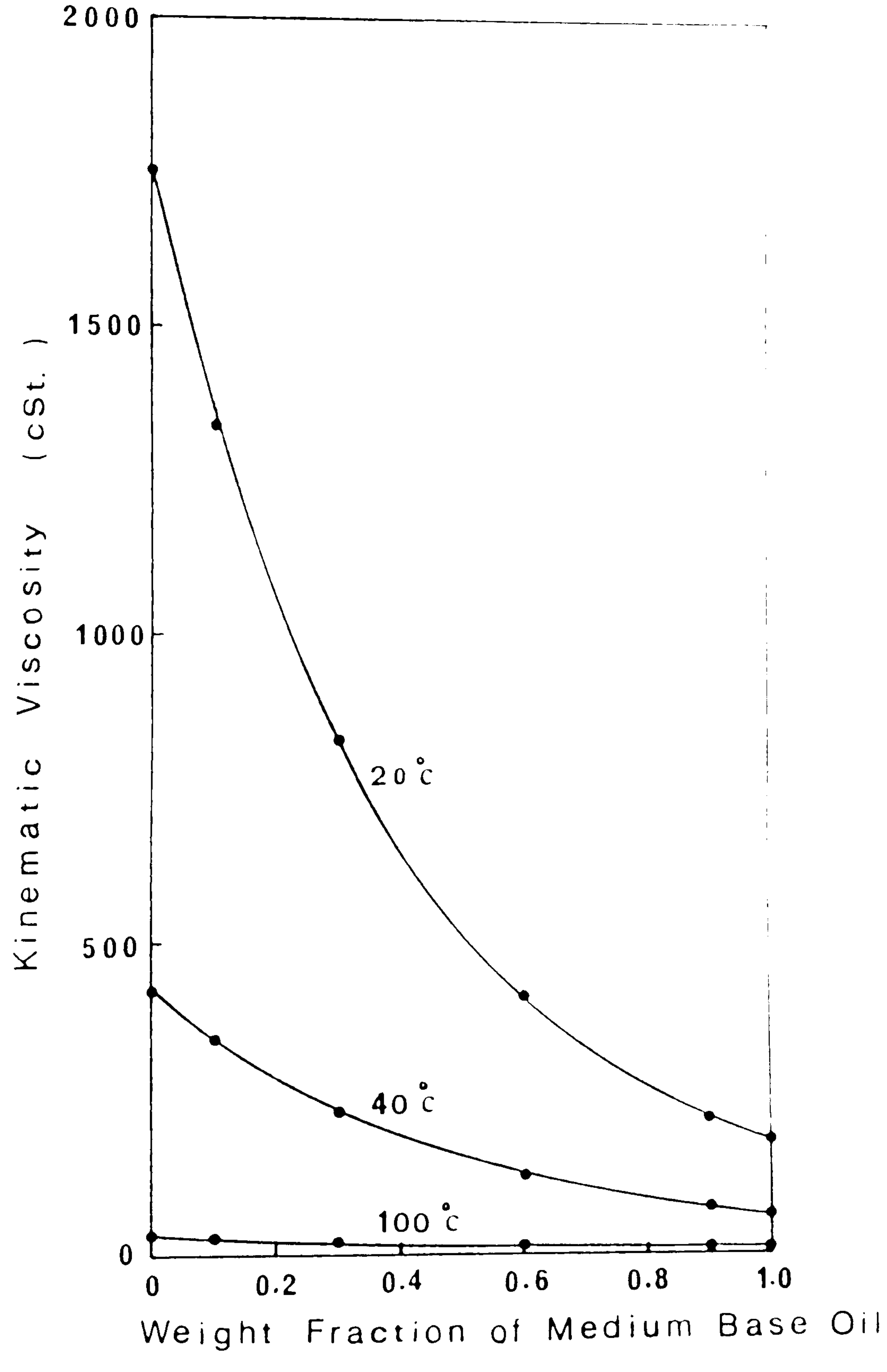


Figure 9.42: Kinematic Viscosities of Medium Base Oil - Bright Stock Binary Mixtures

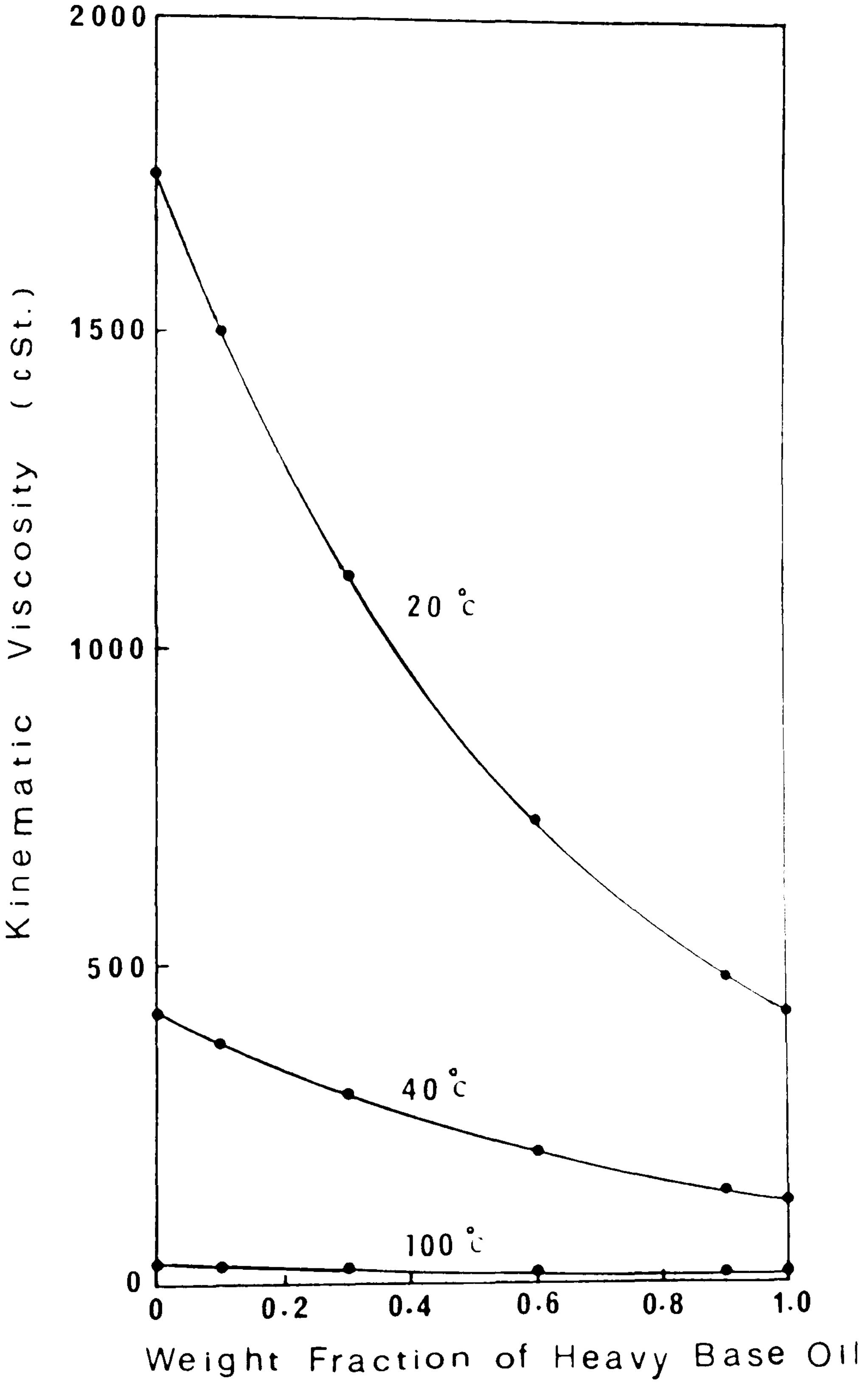


Figure 9.43: Kinematic Viscosities of Heavy Base Oil-Bright Stock Binary Mixtures

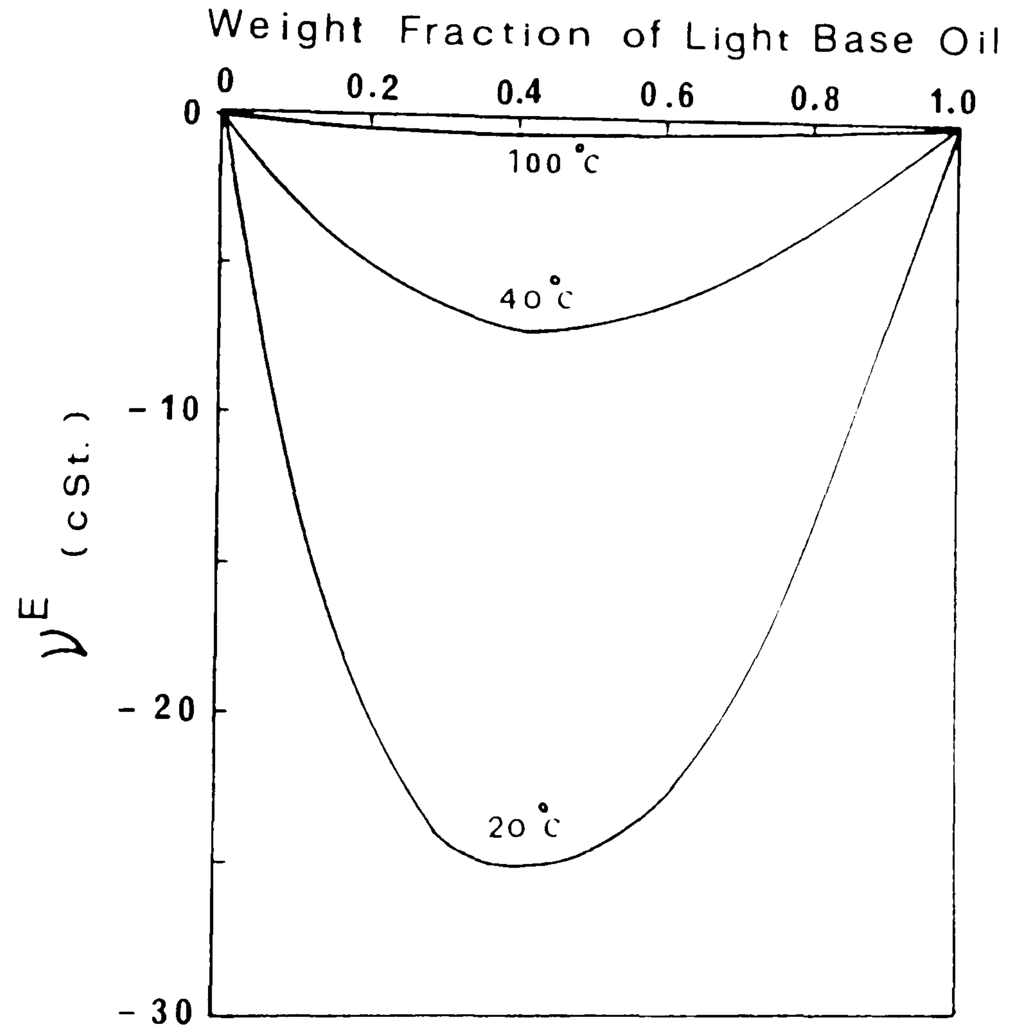


Figure 9.44: Excess Viscosity Function (ν^E) of Light-Medium Base Oils Mixtures

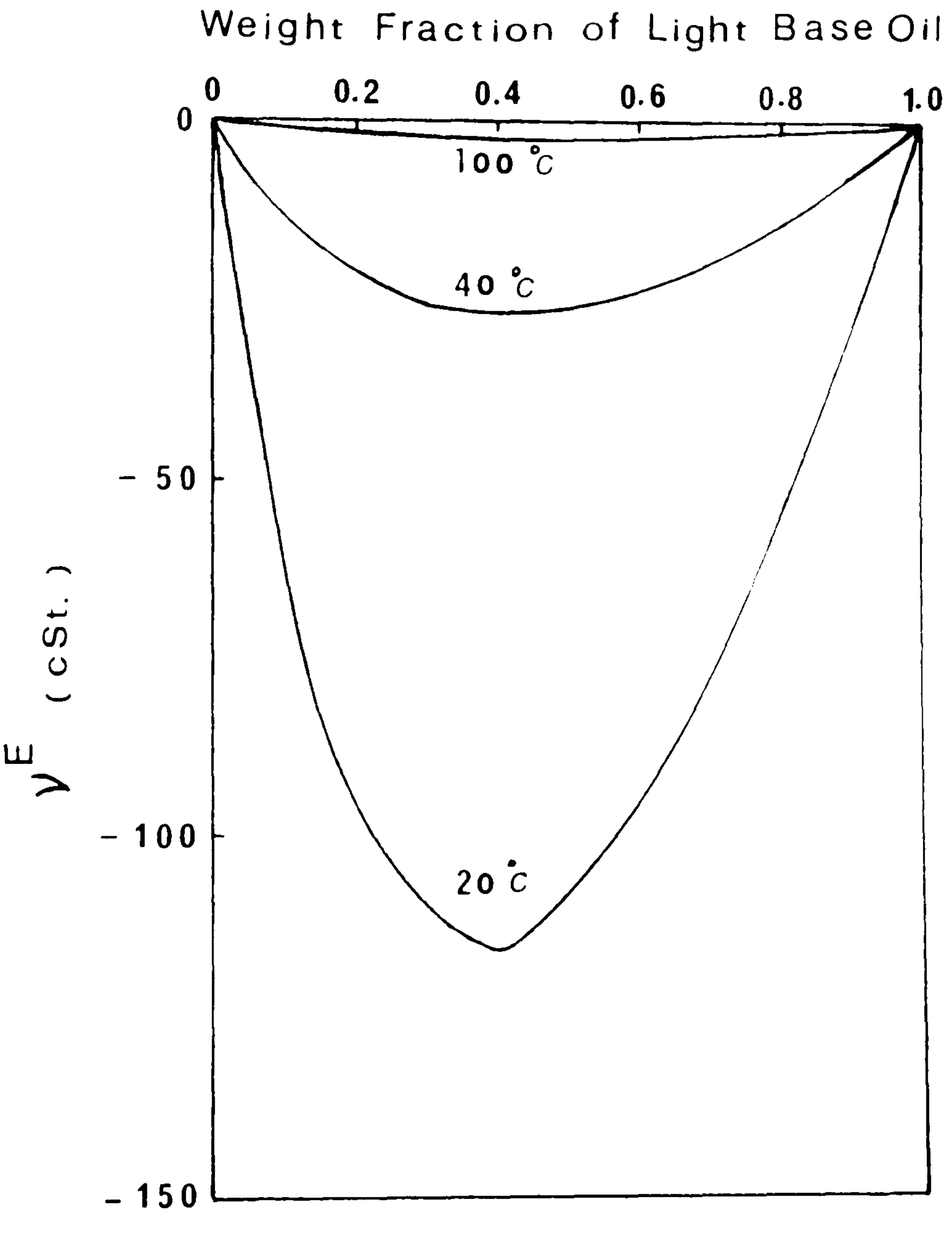


Figure 9.45: Excess Viscosity Function (ν^E) of Light - Heavy Base Oils Mixtures

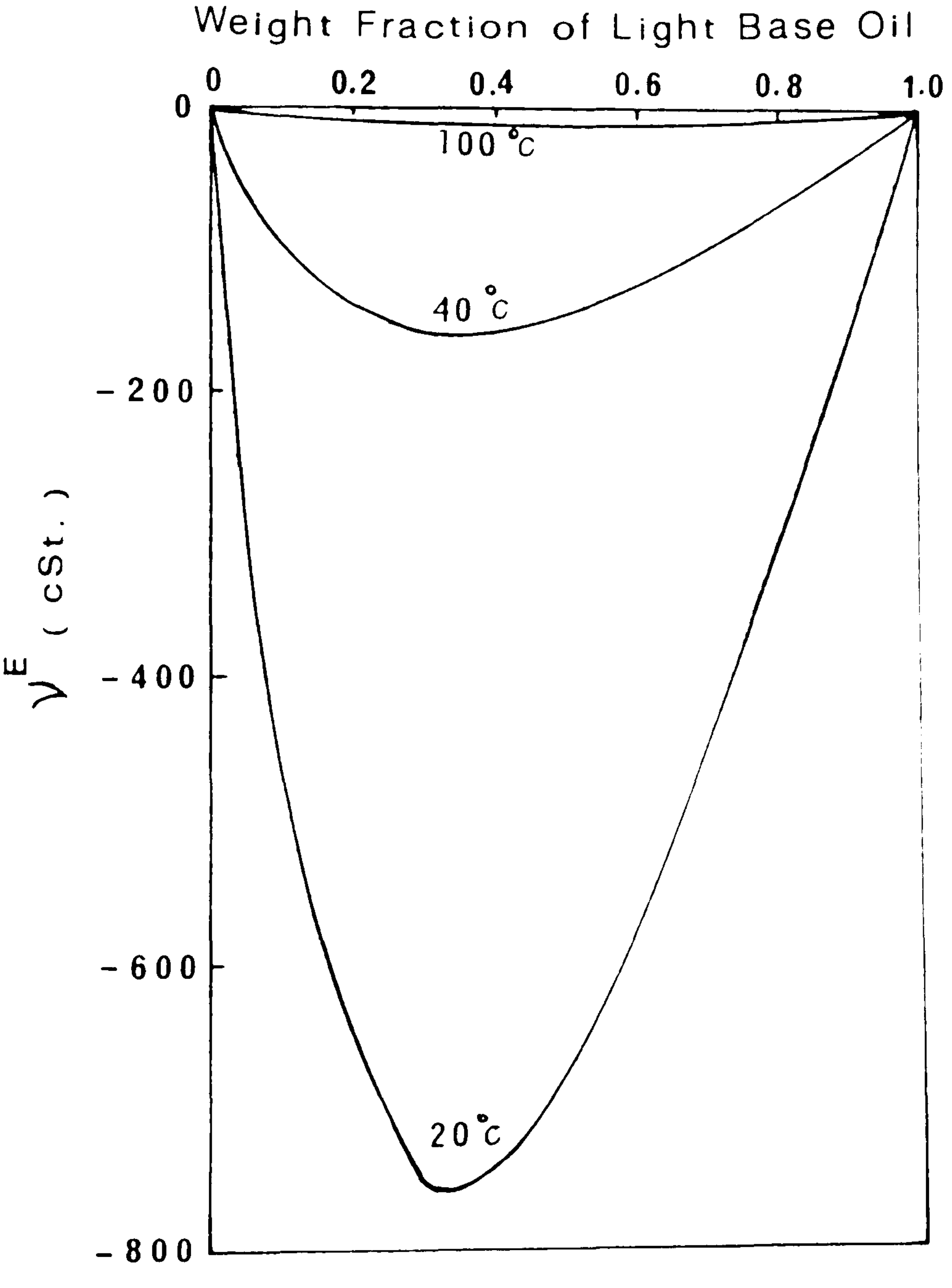


Figure 9.46: Excess Viscosity Function (ν^E) of Light Base Oil - Bright Stock Binary Mixtures

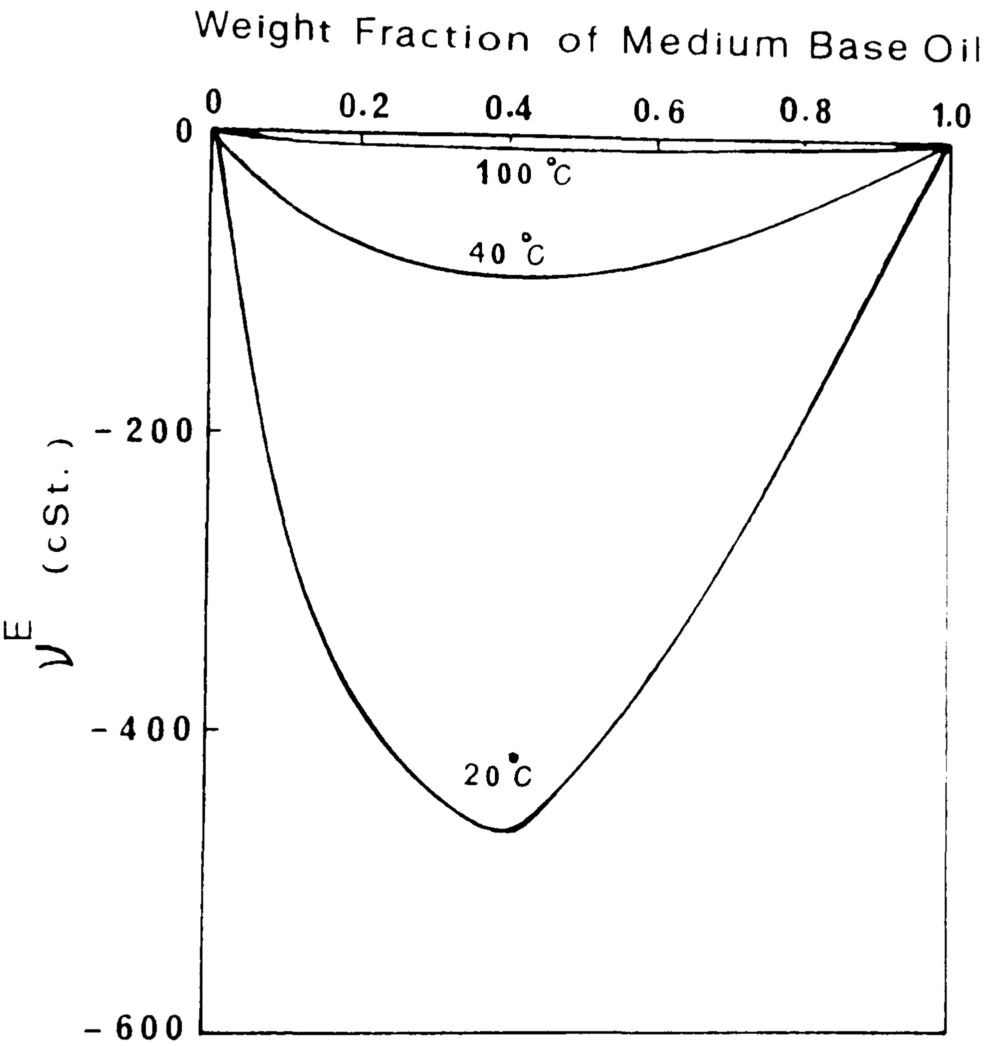


Figure 9.47: Excess Viscosity Function (ν^E) of Medium Base Oil - Bright Stock Binary Mixtures

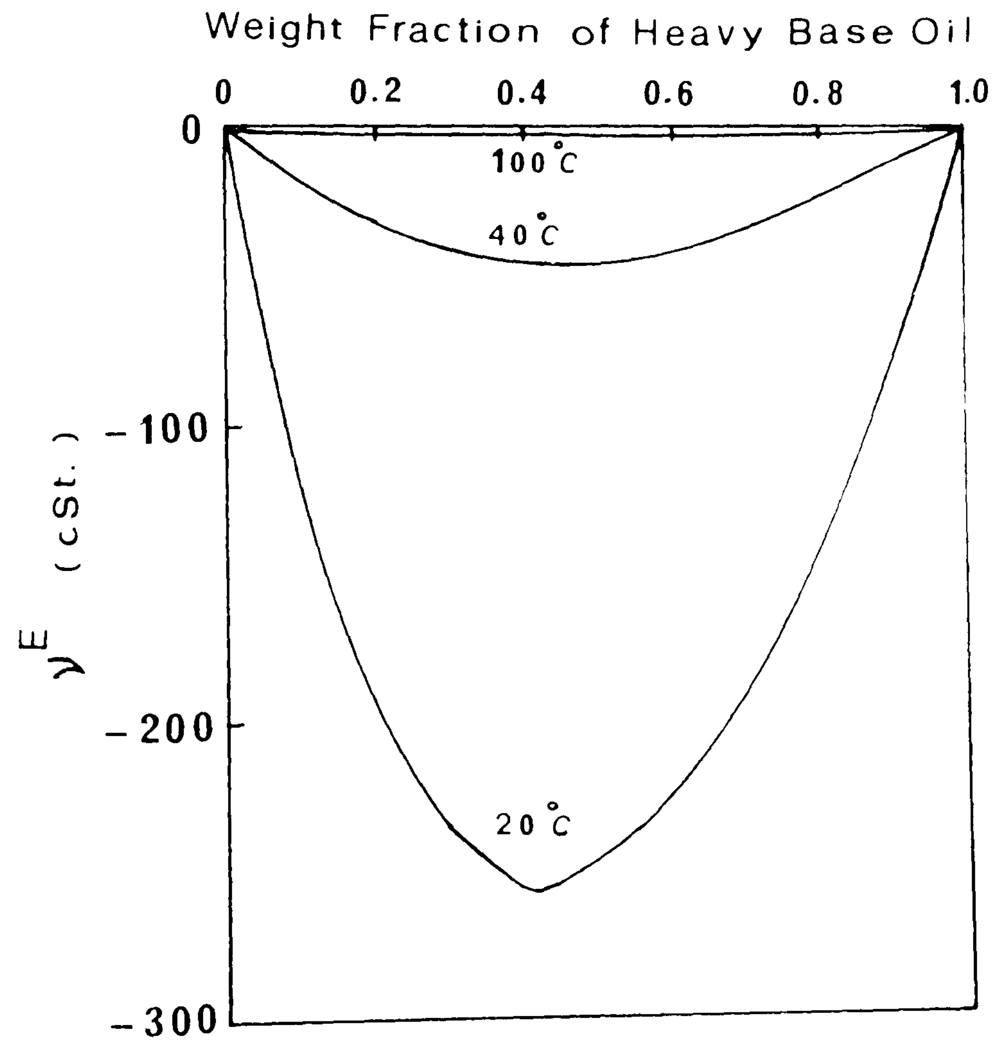


Figure 9.48: Excess Viscosity Function (ν^E) of Heavy Base Oil - Bright Stock Binary Mixtures

Correlation for the Viscosities of Binary Mixtures:

The Grunberg equation, proposed by Grunberg and Nissan(94,95,146) and recommended by Irving(51,52) for prediction of the viscosities of binary mixtures, was considered for modification for the prediction of the viscosities of non-ideal binary mixtures. The equation (eqn 5.67), discussed in Chapter 5, is

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + 2x_1x_2G \qquad 9.13$$

with x defined as mole fraction.

The limitation of this equation was the lack of any method to predict the parameter G. Based upon comparison between equation 9.13 and equations 9.11 and 9.12, it was concluded that $2\,x_1x_2\,G$ is the term that compensates for the non-ideality or v^E. Consequently, equation 9.13 was modified to permit the parameter G to be calculated.

To correlate the kinematic viscosity of crude oil binary mixtures, the experimental data presented in Table 9.10 were used to calculate the empirical parameter G in equation 9.13, for the three crude oil binary mixtures (light - medium, light - heavy and medium - heavy). The average values of G of the crude oil binary mixtures are shown in Table 9.23.

An attempt was made to use the observation that the non-ideal viscosity behaviour increased with an increase in the difference between the densities (i.e. ΔAPI), which reflects the degree of interaction between the molecules of the components. A smooth curve, Fig. 9.49 was obtained, when the average values of G for each crude oil binary mixture system (i.e. light - medium, light - heavy and medium-heavy) were plotted against the corresponding ΔAPI. Applying a curve fitting technique to obtain a relationship between G and ΔAPI resulted in the equation:

$$G = -2.488 \times 10^{-3} (\Delta API)^2 \qquad 9.14$$

Substitution in equation 9.13 resulted in,

$$\ln \nu_{mix} = \Sigma x_i \ln \nu_i - 4.976 \times 10^{-3} x_1 x_2 (\Delta API)^2 \qquad 9.15$$

where,

x_i	is weight fraction of component i
ν_{mix}	is kinematic viscosity of the mixture
ν_i	is kinematic viscosity of component i
ΔAPI	is the difference in API gravities of the components

This equation should enable the viscosity of any crude oil binary mixture to be calculated from a knowledge of the API gravities,which is usually readily available, and viscosities of the components.

Equation 9.15 was subsequently used to calculate the kinematic viscosity of twelve random binary crude oil mixtures. The calculated viscosities and percent deviations from measured values are shown in Table 9.24. Good agreement with the measured values was obtained with percent deviations of 3.3% - 8.3% over a temperature range of 10 - 50°C.

Therefore equation 9.15 was also used to predict the kinematic viscosities of the two systems of binary mixtures (petroleum products and base oils). Very good agreement was obtainedwith the measured values for base oil mixtures (with absolute average deviations of 1.4% - 4.7%), over a temperature range of 10 - 100°C (Table 9.25). However, relatively higher deviations were obtained for binary mixtures of petroleum products (kerosene, heavy gas oil, and residue), particularly with the kerosene - residue system of the highest ΔAPI (Table 9.26). The absolute average deviations were in the range 6.3% - 26.0%. This may be due to the fact that kerosene and residue are extremely different in their chemical and physical properties (Table 8.2). Therefore, equation 9.15 is applicable, with good accuracy, for the prediction of the kinematic viscosities of binary mixtures prepared from components of almost similar chemical properties. Caution should however be applied when using equation 9.15, for mixtures of components which differ widely in their properties.

Table 9.23: Average Values of Grunberg Equation Constant, G, and ΔAPI of Crude Oil Systems

Mixtures	ΔAPI	Av. G
Light-medium	11.34	-0.3539
Light-heavy	21.17	-1.0821
Medium -heavy	9.83	-0.2221

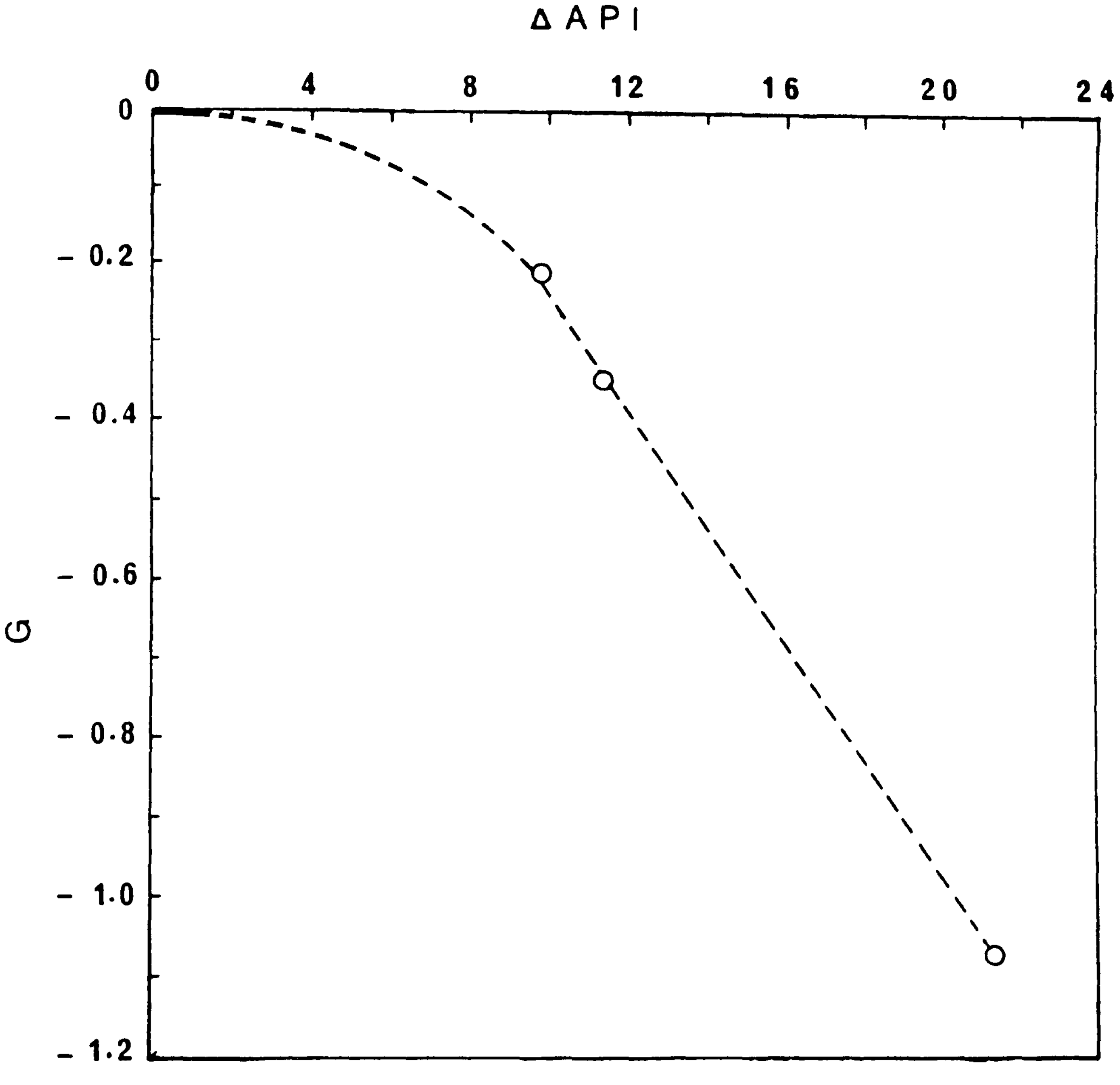


Figure 9.49: Relationship Between G from Equation 9.13 and ΔAPI for Crude Oil Binary Mixtures

G calculated as the average for each binary mixture over the range 10°C to 50°C.

Table 9.24: Calculated Kinematic Viscosities of Crude Oil Binary Mixtures by the Modified Grunberg Equation, 9.15

	Kinematic Viscosity (cSt.) @									
	10°C		20°C		30°C		40°C		50°C	
Mix No.	ν Cal.	%Dev.	ν Cal.	%Dev.	ν Cal.	%Dev.	ν Cal.	%Dev.	ν Cal.	% Dev.
1	17.14	4.2	11.13	3.9	8.219	-10.4	6.709	2.9	5.405	-3.9
2	32.38	6.7	19.26	-0.5	13.53	-8.5	10.33	-4.2	8.079	-1.4
3	52.77	5.8	29.59	-1.2	20.11	-7.9	14.69	0.8	11.26	-5.8
4	120.8	4.2	62.04	-3.4	40.12	-4.9	27.42	5.0	20.39	14.5
5	19.26	1.2	12.25	4.2	8.794	-16.6	7.006	0.8	5.513	-6.7
6	62.47	14.4	34.19	3.1	21.47	-19.3	14.87	-3.6	10.58	-11.7
7	171.1	17.1	84.70	7.5	48.65	-6.6	30.70	-4.1	20.43	-1.3
8	1084	6.0	461.5	4.3	231.9	0.8	127.3	-1.8	76.55	2.0
9	202.9	1.0	99.06	-2.1	61.26	-2.2	39.96	6.4	28.74	14.5
10	411.4	7.0	188.7	1.4	107.3	-2.1	65.05	1.0	43.59	14.5
11	691.5	7.5	304.3	1.9	163.6	-9.5	94.46	-3.1	60.38	-0.7
12	1620	-3.3	669.6	-8.2	330.9	-11.1	117.6	-5.8	105.8	-3.0
Absolute Av. % Dev.		6.5		3.5		8.3		3.3		6.7
Mean Av. % Dev.		6.2		0.9		-8.2		-0.5		0.9

Table 9.25: Calculated Kinematic Viscosities of Base Oil Binary Mixtures by the modified Grunberg equation, 9.15

Mix No.	Kinematic Viscosity (cSt) @ 20°C		40°C		100°C	
	v Cal.	% Dev.	v Cal.	% Dev.	v Cal.	% Dev.
1	154.4	1.4	53.53	0.7	7.457	-0.2
2	116.9	2.8	40.99	-1.2	6.454	-0.3
3	78.03	3.7	30.12	2.2	5.232	-1.4
4	51.77	0.9	21.64	0.4	4.274	0.5
5	337.1	3.2	103.6	1.2	11.61	0.1
6	213.4	6.3	70.52	3.9	9.057	1.7
7	108.8	6.4	40.09	4.5	6.320	2.0
8	56.29	2.2	23.13	1.2	4.475	1.1
9	1200	7.2	307.7	4.3	24.11	2.3
10	565.9	15.9	162.5	11.0	15.8	5.0
11	188.0	16.3	63.92	11.4	8.597	3.9
12	64.38	4.7	25.92	4.1	4.821	2.4
13	1335	-0.6	348.7	0.05	26.14	0.7
14	875.6	6.0	234.7	2.6	20.00	1.6
15	439.9	6.3	103.4	3.1	13.46	1.4
16	222.6	3.2	72.94	1.1	9.121	-1.9
17	1521	1.4	376.2	-0.9	27.53	0.4
18	1143	2.3	294.3	-0.2	23.32	0.5
19	756.5	2.2	204.2	0.2	18.22	0.8
20	488.8	1.1	142.0	-0.7	14.28	0.06
Absolute Av. and Deviation:		4.7		2.7		1.4
Mean Av % Deviation:		4.6		2.4		1.0

Table 9.26: Calculated Kinematic Viscosities of Petroleum Products Binary Mixtures by the Modified Grunberg Equation 9.15

Mix No.	Kinematic Viscosity (cSt) @ 20°C v Cal.	20°C % Dev	40°C v Cal.	40°C % Dev	60°C v Cal.	60°C % Dev.	100°C v Cal.	100°C % Dev.
1	34.73	9.7	13.84	1.9	7.150	-1.0	-	-
2	9.685	13.3	4.708	-2.2	2.770	-10.5	-	-
3	4.910	-4.7	2.726	-14.5	1.749	-21.4	-	-
4	2.295	0.2	1.555	-4.6	1.136	-6.4	-	-
5	-	-	667.2	71.8	156.8	34.4	25.35	-4.0
6	-	-	37.16	72.3	12.93	13.6	3.565	-23.4
7	-	-	8.583	31.9	3.881	-4.8	1.527	-13.1
8	-	-	1.900	7.1	1.272	-9.9	0.853	-3.9
9	-	-	1246	22.9	280.5	12.5	42.03	2.7
10	-	-	283.1	40.4	82.84	23.1	16.86	5.0
11	-	-	113.0	30.7	39.38	21.7	9.824	5.2
12	-	-	31.59	11.7	14.32	5.5	4.850	0.7
Absolute Av.%Dev		7.0		26.0		13.7		6.3
Mean Av. % Dev.		4.6		22.5		4.7		-4.1

9.3.4 Investigation of Eyring's Theory

No single theory has been developed to describe the complexities of molecular interaction described by Newton's Law, equation 5.1. Eyring's theory, the theory of absolute reaction rates or theory of holes, for viscous flow of liquids, discussed in Chapter 5, is well-known and promoted considerable interest.

Eyring (44, 45, 46) proposed the equation:

$$\mu = \frac{Nh}{V} e^{\Delta F/RT} \qquad 9.16$$

or,

$$\nu = \frac{\mu}{\rho} = \frac{Nh}{M} e^{\Delta F/RT} \qquad 9.17$$

From the calculation of ΔF for many compounds, the following relationship was reported:

$$\frac{\Delta E_{vap}}{\Delta F} = 2.45 \qquad 9.18$$

then, by substitution

$$\mu = \frac{hN}{V} e^{\Delta E_{vap}/2.45\,RT} \qquad 9.19$$

Further simplification of the equation was reported,

$$\mu = \frac{hN}{V} e^{3.8T_b/T} \qquad 9.20$$

where,

μ = absolute viscosity, cP

ν = kinematic viscosity, cSt

ΔF = free energy of activation of viscous flow

ΔE_{vap} = internal energy of vaporisation

T_b = normal boiling point (°K)

T = temperature (°C)

ρ = density @ 15°C

V = molar volume

M = molecular weight

h = Plank's constant

N = Avogadro's Number

R = gas constant

These equations were derived after many approximations, which were considered limitations of the theory itself. Because the equation was constructed initially for simple pure hydrocarbons, it should not be expected to apply with high accuracies, particularly with complex liquids, e.g. crude oil or of high molecular weight, e.g. bitumens or residues. For example Bird et. al (36) considered that Eyring's equation should not be used for very long slender molecules, such as $n\text{-}C_{20}\,H_{42}$. Shakhparonov (147) stated that if the liquid is assumed to behave like a compressed monatomic ideal gas, then the equation of Eyring is valid. Therefore, the viscosity of any liquid in which the molecules are non-spherical, or associate, or deform during flow, will deviate widely from Eyring's equation. Nevertheless, this equation is useful, primarily for rough estimation, or as a guide for the interpolation or extrapolation of fragmentary viscosity data.

One objective of this study was to test this theory, noting that Eyring's equation indicates an exponential decrease in viscosity with temperature, which agrees with the observed behaviour for most of the liquids. The modification of Eyring's equation by the introduction of empirical parameters that compensate for the deviations from experimental data was also considered useful. Therefore, in this Section Eyring's equation is tested for possible applications for the prediction of the viscosity of crude oils and their products. Empirical modifications are then proposed.

The viscosity data of crude oils, petroleum products and base oils, and their binary and ternary mixtures were used to investigate the validity of Eyring's equation, using two approaches, a numerical approach and a graphical approach.

The numerical approach involved calculation of the energy of activation of viscous flow (ΔF) according to equation 9.16, which can be transformed to give:

$$\ln \nu = \ln (Nh/M) + \Delta F/RT \qquad 9.21$$

In order to calculate ΔF from this equation, the molecular weight values of crude oils, petroleum products and base oils and their mixtures had to be determined experimentally. The molecular weight values of crude oils, base oils, and petroleum products, given in Tables 9.1, 9.2 and 9.3, were used. The molecular weights of the mixtures were then calculated by equation 9.1, on the basis that the molecular weight is an additive property.

The values of the activation energy of viscous flow (ΔF), calculated numerically by equation 9.17 at different temperatures for crude oils, base oils and petroleum products, are shown in Tables 9.27, 9.28 and 9.29, respectively. It is clear that the values of ΔF vary with temperature.

The graphical approach used to calculate the activation energy of viscous flow (ΔF), was to plot the data and to determine the activation energy of viscous flow from the gradients of these plots.

In equation 9.17, the gas constant (R), Plank's constant (h) and Avogadro's number (N) have fixed values, and if ln (ν) is plotted against $1/T$, a straight line should be obtained of slope = $\Delta F/R$ with an intercept = (hN/M).

Table 9.27 Activation Energies of Viscous Flow (ΔF), Calculated by the Numerical Method, for Crude Oils and Their Binary Mixtures*

Mixtures	ΔF (K cal/g-mol) @					
	10°C	20°C	30°C	40°C	50°C	Average
light crude oil	7.757	7.798	7.891	8.039	8.164	7.930
medium crude oil	9.216	9.136	9.175	9.228	9.313	9.214
heavy crude oil	10.898	10.757	10.682	10.633	10.622	10.718
mix 1	7.849	7.877	8.053	8.106	8.270	8.031
mix 2	8.244	8.248	8.368	8.448	8.541	8.370
mix 3	8.516	8.520	8.620	8.653	8.803	8.622
mix 4	9.016	8.990	9.044	9.044	9.087	9.036
mix 5	7.961	7.962	8.168	8.178	8.335	8.121
mix 6	8.658	8.673	8.837	8.789	8.908	8.773
mix 7	9.271	9.239	9.305	9.310	9.327	9.290
mix 8	10.445	10.326	10.285	10.267	10.245	10.314
mix 9	9.359	9.291	9.391	9.309	9.347	9.325
mix 10	9.792	9.720	9.733	9.724	9.697	9.733
mix 11	10.130	10.041	10.081	10.030	10.048	10.066
mix 12	10.729	10.623	10.581	10.508	10.491	10.586

* In this and subsequent Tables in this Section, the data are, for convenience, reported as computed. This is not intended to imply an order of accuracy greater than the original experimental data, given in Section 9.3.1.

Table 9.28 Activation Energies of Viscous Flow (ΔF), Calculated by the Numerical Method, for Base Oils and Their Binary Mixtures

Base Oil	ΔF (K cal/g-mol) @			
	20°C	40°C	100°C	Average
light base oil	8.738	8.803	9.324	8.955
medium base oil	9.619	9.602	9.949	9.723
heavy base oil	10.242	10.185	10.464	10.297
bright stock	11.280	11.168	11.342	11.263
mix 1	9.518	9.513	9.882	9.638
mix 2	9.334	9.344	9.758	9.479
mix 3	9.068	9.104	9.578	9.25
mix 4	8.820	8.882	9.382	9.028
mix 5	10.071	10.037	10.347	10.152
mix 6	9.752	9.743	10.106	9.867
mix 7	9.300	9.325	9.762	9.462
mix 8	8.875	8.933	9.429	9.079
mix 9	10.987	10.098	11.126	11.007
mix 10	10.438	10.402	10.710	10.517
mix 11	9.680	9.696	10.119	9.832
mix 12	8.972	9.023	9.518	9.171
mix 13	11.099	11.017	11.204	11.107
mix 14	10.761	10.696	10.929	10.795
mix 15	10.264	10.227	10.517	10.336
mix 16	9.772	9.758	10.109	9.880
mix 17	11.170	11.078	11.254	11.167
mix 18	10.961	10.881	11.082	10.975
mix 19	10.651	10.585	10.819	10.685
mix 20	10.342	10.291	10.555	10.396

Table 9.29 Activation Energies of Viscous Flow (ΔF), Calculated by the Numerical Method, for the Petroleum Products and Their Binary Mixtures.

Mixtures	ΔF (K cal/g-mol) @				
	20°C	40°C	60°C	100°C	Average
kerosene	6.795	7.058	7.330	8.045	7.307
heavy gas oil	8.909	8.904	9.007	9.362	9.046
residue >360°C	-	12.335	12.078	12.047	12.153
mix 1	8.560	8.618	8.750	-	8.643
mix 2	7.754	7.926	8.140	-	7.940
mix 3	7.432	7.641	7.891	-	7.655
mix 4	6.918	7.178	7.442	-	7.179
mix 5	-	11.241	11.164	11.404	11.270
mix 6	-	9.288	9.458	9.931	9.559
mix 7	-	8.412	8.640	9.227	8.760
mix 8	-	7.375	7.654	8.231	7.753
mix 9	-	11.843	11.672	11.734	11.750
mix 10	-	10.706	10.664	10.883	10.751
mix 11	-	10.071	10.065	10.353	10.163
mix 12	-	9.170	9.270	9.615	9.352

The calculated values of ΔF by this method of crude oils and their mixtures, base oils and their mixtures, and petroleum products and their mixtures are summarised in Table 9.30. Graphs of the relationships between ln v and 1/T for crude oils, base oils and petroleum products are shown in Figures 9.50, 9.51 and 9.52, respectively.

The values of the intercepts on the ln (v) axes are remarkably different from ln (hN/M), and the calculated values of ΔF obtained do not agree using the two methods. A similar observation was also made by Van Velden (148) and Amin (63). The results suggest that for the oils examined, the energy of activation for viscous flow is a function of temperature.

Table 9.30 compares the values of ΔF calculated by the numerical and graphical approaches; the 'R' values indicate the difference between ΔF values, calculated by the two methods, as:

$$R = \frac{\Delta F_{\text{numerical}} - \Delta F_{\text{graphical}}}{\Delta F_{\text{graphical}}} \times 100 \qquad 9.22$$

R had both positive and negative values for crude oils and petroleum products, unlike those for base oils where it always had positive values. The maximum values of R arose with the light liquids such as kerosene, light crude oil, light base oil and mixtures of low densities. Negative values were obtained for heavy liquids, i.e. heavy crude oil, residue and some of the mixtures of high densities. The values of R shown in Table 9.30 were plotted against the corresponding densities (Figure 9.53). The minimum values of R (i.e. the best agreement between ΔF calculated by the numerical and graphical methods) were found to be for the liquids of density from 0.90 - 0.92 g/ml.

These observations lead to the conclusion that Eyring may have omitted some fundamental relationships in the development of equations 9.16 to 9.20. As a result, Eyring's equation may be considered as semi-empirical. A similar conclusion was reached by other authors (63, 148).

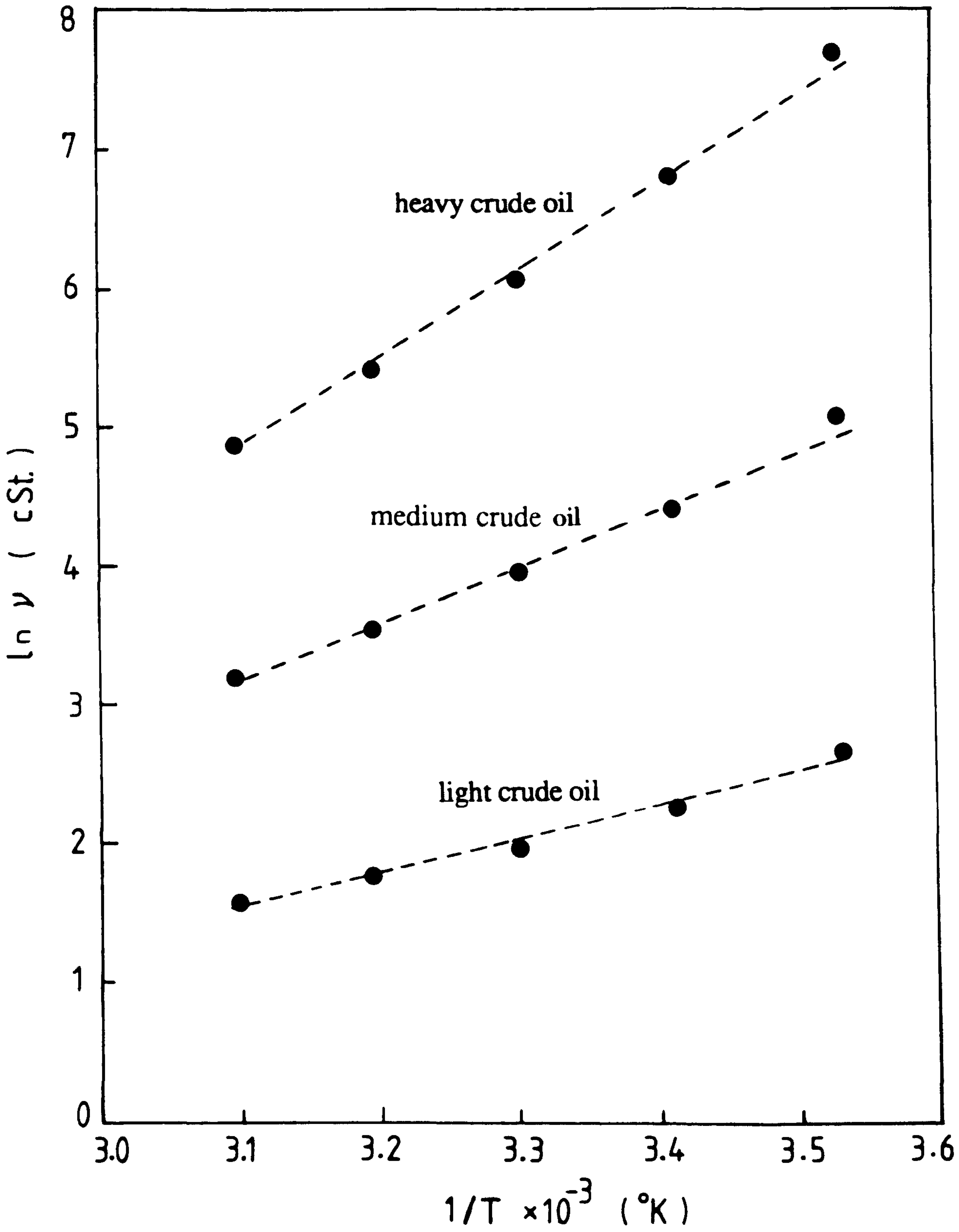


Figure 9.50 Relationship Between ln (v) and 1/T for Crude Oils

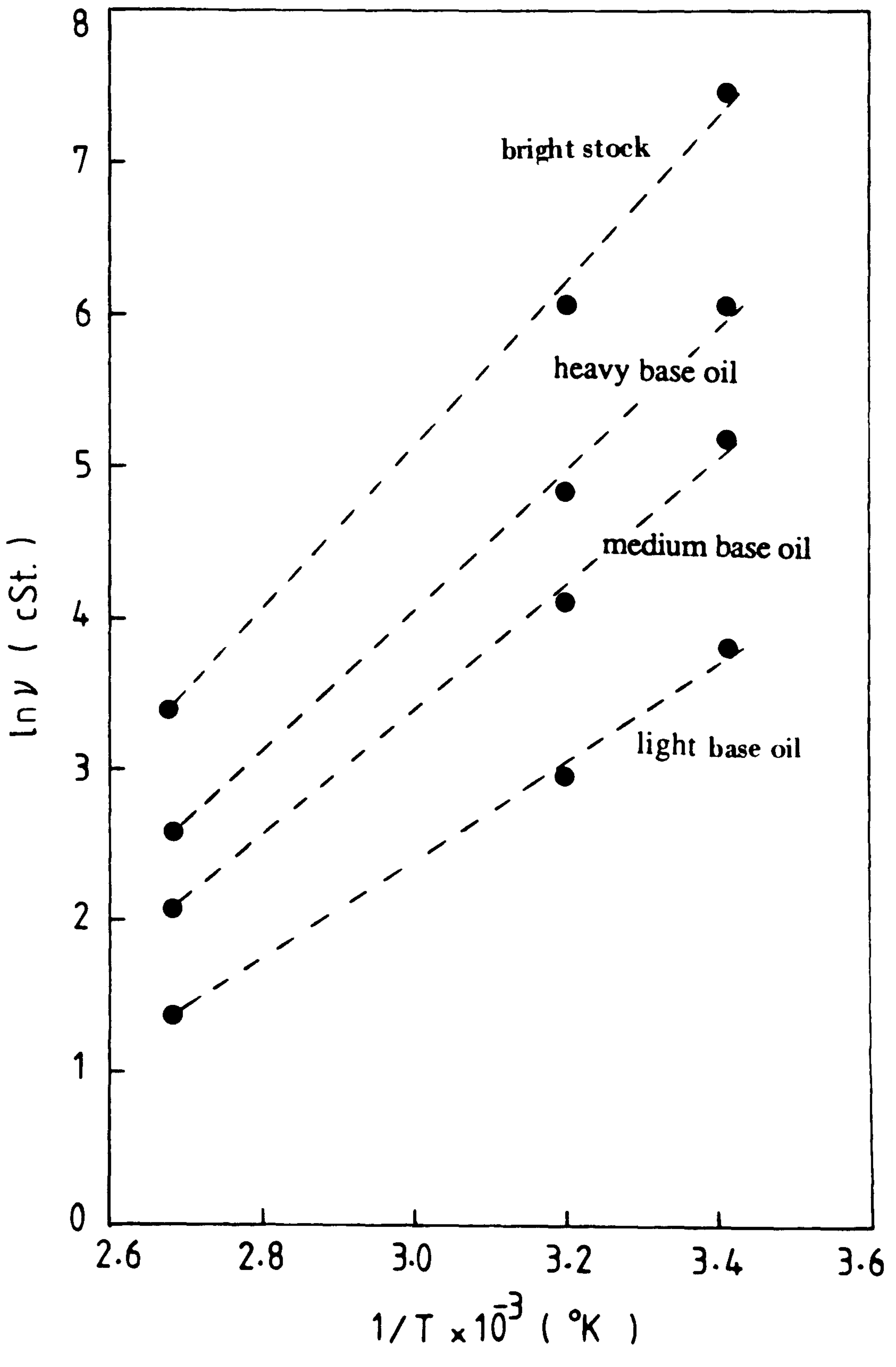


Figure 9.51 Relationship Between ln (v) and 1/T for Base Oils

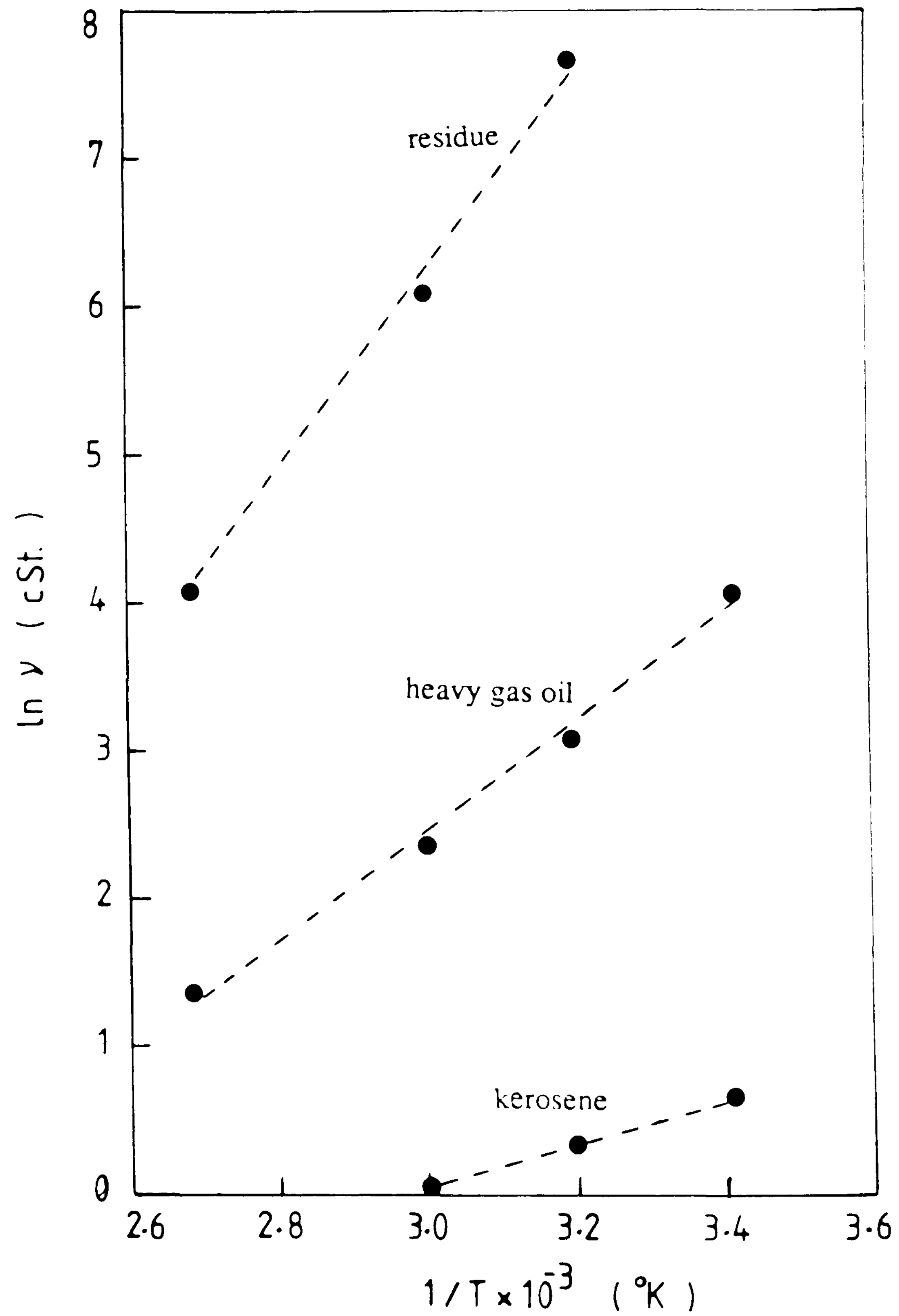


Figure 9.52 Relationship Between ln (v) and 1/T for Petroleum Products.

Table 9.30 ΔF Values of Petroleum Liquids, Calculated by the Numerical and Graphical Methods.

	ΔF (K cal/g-mol) calculated by		*R
	Numerical Method	Graphical Method	
Crude Oils:			
light crude oil	7.871	4.783	66.3
medium crude oil	9.189	8.416	9.6
heavy crude oil	10.742	12.807	-19.5
Binary Mixtures:			
mix 1	8.031	4.816	66.8
mix 2	8.370	5.996	39.6
mix 3	8.622	6.524	32.2
mix 4	9.036	8.457	6.8
mix 5	8.121	5.217	55.7
mix 6	8.773	6.905	27.1
mix 7	9.290	8.745	5.2
mix 8	10.314	11.750	-12.2
mix 9	9.325	9.379	-0.6
mix 10	9.733	10.314	-5.6
mix 11	10.066	10.621	-5.2
mix 12	10.586	12.405	-14.7
Base Oils:			
light base oil	8.955	6.499	31.6
medium base oil	9.723	8.297	17.2
heavy base oil	10.297	9.302	10.7
bright stock	11.263	10.911	3.2

$$*R = \frac{\Delta F_{num.} - \Delta F_{graph.}}{\Delta F_{graph}} \times 100$$

Table 9.30 (continued)

	ΔF (K cal/g-mol) calculated by		
	Numerical Method	Graphical Method	*R
Binary Mixtures:			
mix 1	9.638	8.078	19.3
mix 2	9.479	7.671	23.6
mix 3	9.250	7.097	30.3
mix 4	9.028	6.673	35.3
mix 5	10.152	8.947	13.5
mix 6	9.867	8.349	18.2
mix 7	9.462	7.508	26.0
mix 8	9.079	6.755	34.4
mix 9	11.007	10.353	6.3
mix 10	10.517	9.329	12.7
mix 11	9.832	7.964	23.5
mix 12	9.171	6.879	33.3
mix 13	11.107	10.591	4.9
mix 14	10.795	10.025	7.7
mix 15	10.336	9.224	12.1
mix 16	9.880	8.425	17.3
mix 17	11.167	10.737	4.0
mix 18	10.975	10.394	5.6
mix 19	10.685	9.918	7.7
mix 20	10.396	9.446	10.1
Petroleum Products:			
Kerosene	7.307	2.209	230.8
heavy gas oil	9.046	7.183	25.9
residue	12.153	13.682	-11.2

Table 9.30 (continued)

	ΔF (K cal/g-mol) calculated by		
	Numerical Method	Graphical Method	*R
Binary Mixtures:			
mix 1	8.643	7.179	20.4
mix 2	7.940	4.929	61.1
mix 3	7.655	4.078	87.7
mix 4	7.179	3.077	133.3
mix 5	11.270	10.265	9.8
mix 6	9.559	5.887	62.4
mix 7	8.760	4.120	112.6
mix 8	7.753	2.907	166.7
mix 9	11.750	12.282	-4.3
mix 10	10.751	9.684	11.0
mix 11	10.163	8.505	19.5
mix 12	9.352	6.799	37.5

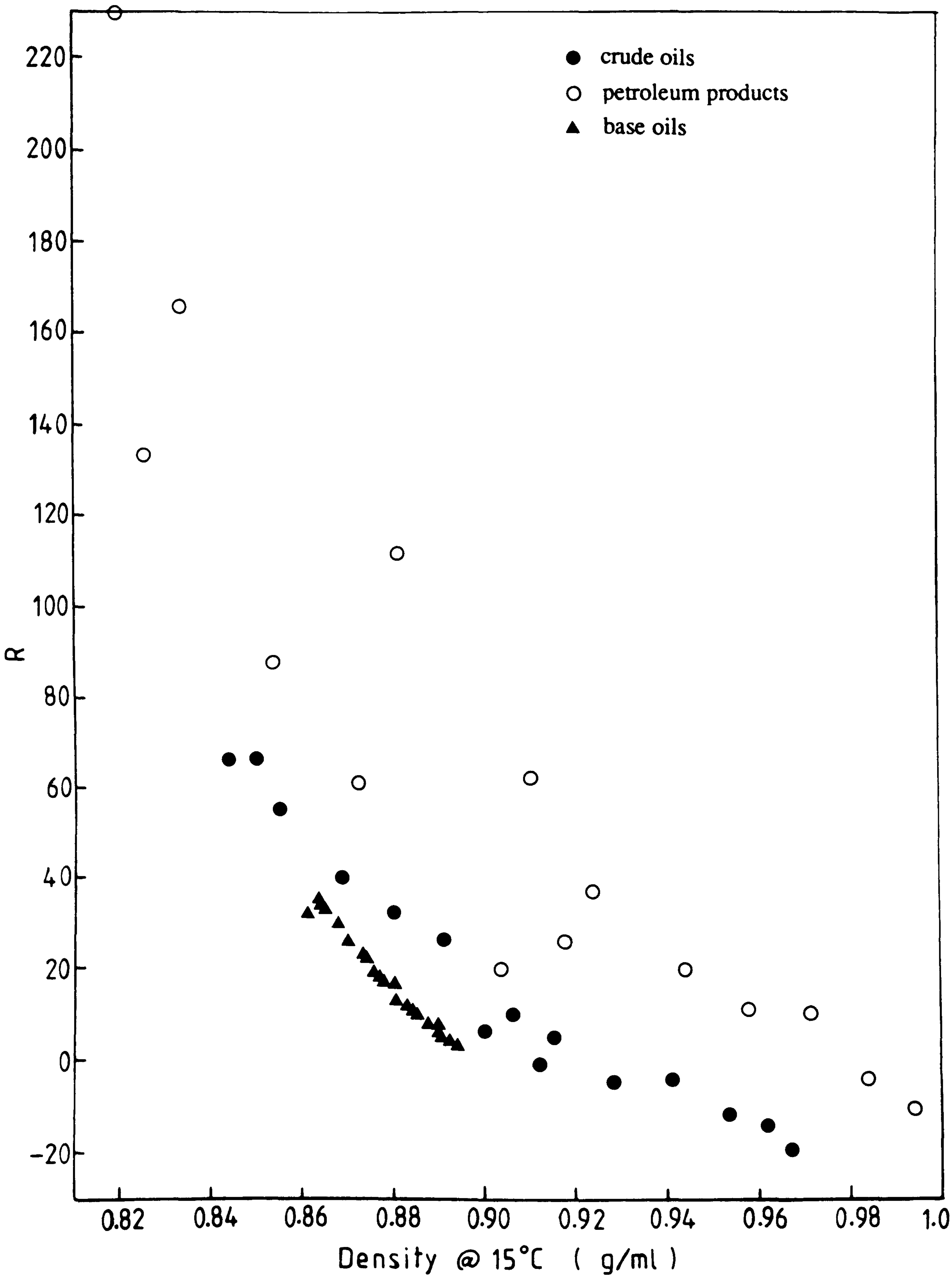


Figure 9.53 Relationship Between R, Calculated via Equation 9.22, and Densities for Crude Oils, Base Oils and Petroleum Products.

Empirical Modification of Eyring's Equation:

The key assumptions upon which Eyring's equation for viscosity was based are:

i The effect of molecular mass is negligibly small, i.e. the molecules behave like material points as in a perfect gas.

ii There are no associative effects in the liquid, i.e. no activation energy is involved in an associated system such as those of hydrogen bonding.

iii The molecules are all similar in size and shape.

For complex hydrocarbon mixtures like crude oils and their products, there are significant deviations from the above assumptions, namely:

i Crude oils and their products contain considerable quantities of high molecular weight materials, i.e. energy is required to overcome the mass inertia before the molecule can move from one position to the next.

ii At relatively low temperatures (below ~40°C), slight associative effects may exist in crude oils and the heavy products, which contain many polar compounds, thus causing the high viscosities exhibited at low temperatures.

iii There is a wide variation of size and shape among the molecules of crude oils and their products.

All the effects of these deviations will be reflected in the value of ΔF, if it is computed theoreticaly.

Consequently, it was believed that the activation energy of viscous flow ΔF is the most important parameter in Eyring's equation for the calculation of the viscosities of liquids, based on logical assumptions of the absolute reaction rate theory. Therefore, accurate application of Eyring's equation requires accurate measurement or estimation of ΔF. Eyring and other workers (44, 45, 46) proposed methods for the calculation of ΔF of pure hydrocarbons from values of their thermodynamic properties such as the internal energy of vaporisation (Δ Evap), the latent heat and entropy. However, it is difficult to use the same approach for liquids which are undefined mixtures, such as crude oils and different types of petroleum products. The basic thermodynamic values are simply not available in the literature; therefore, they must be estimated, and most of the available estimation methods are not of high accuracy, especially with complex liquids such as crude oils.

Consequently, an attempt was made to relate ΔF to other characteristic properties of crude oils and their products, namely density @ 15°C and 50% boiling point ($T_{50\%}$).

Several empirical modifications to Eyring's equation were tested to estimate ΔF. The object was to determine whether these empirical modifications would better-represent the experimental viscosity data.

From the experimental viscosity values of crude oils and their products, the ΔF's of Eyring's equation were calculated by the numerical approach. A correlation was then developed for ΔF in two ways:

1. using the general equation of Riazi $^{(26, 124, 125)}$:

   $\Delta F = f(\text{boiling point } T_{50\%}, \text{density @ } 15°C)$

2. $\Delta F = f(\text{boiling point } T_{50\%})$

The use of a correlated value of ΔF in Eyring's equation does of course represent an empirical modification of the original model.

Applying the minimum sum of squares of normalised error regression techniques, the following models were investigated:

1. $$\ln \ln (\Delta F) = A \quad (d)^{b_1} \quad (T)^{b_2} \qquad 9.23$$

2. $$\ln (\Delta F) = \frac{A}{T^B} \qquad 9.24$$

The regression method employed was to minimise the sum of the squares of the normalised error w defined by,

$$w = \sum \left| \frac{\Delta F_{calc.} - \Delta F_{exp.}}{\Delta F_{exp.}} \right|^2 \qquad 9.25$$

The correlations obtained were:

1. $\ln \ln (\Delta F) = 0.0075 \quad (d)^{-0.0180} \quad (T)^{0.7179}$ 9.26

2. $\ln (\Delta F) = \dfrac{0.0560}{T^{-0.5664}}$ 9.27

where,

ΔF = the activation energy of viscous flow

d = density @ 15°C

$T_{50\%}$ = boiling point of 50% volume recovery, °K

Good agreement was achieved between ΔF values estimated by equations 9.26 and 9.27, and those calculated directly from equation 9.17. The values obtained are shown in Table 9.31. The ΔF values estimated by equations 9.26 and 9.27, were then used to calculate the kinematic viscosities for the crude oils and their products, via equation 9.17. The calculated viscosity values by equation 9.26 for crude oils, base oils and petroleum products are summarised in Tables 9.32, 9.33 and 9.34 respectively; those obtained by equation 9.27 are summarised in Tables 9.35, 9.36 and 9.37.

Since upto 20% deviation of predicted values from measured viscosity, values are considered good agreement in the majority of the literature, reasonable agreement was obtained between the measured and calculated kinematic viscosities, for crude oils and base oils, by both

Table 9.31 Values of ΔF of Crude Oils, Base Oils, Petroleum Products and their Mixtures calculated via Equations 9.17, 9.26 and 9.27

Mixtures	ΔF by eq. 9.17 (K cal./g-mol)	ΔF (K cal./g-mol)			
		by eq. 9.26		by eq. 9.27	
		ΔF	% Dev.*	ΔF	%Dev*
<u>Crude Oils</u>:					
Light crude oil	7.930	7.993	0.8	7.975	0.6
Medium crude oil	9.214	9.254	0.4	9.295	0.9
Heavy crude oil	10.718	10.710	-0.1	10.702	-0.2
Mix. 1	8.031	8.081	0.6	8.071	0.5
Mix. 2	8.370	8.398	0.3	8.411	0.5
Mix. 3	8.622	8.799	2.1	8.829	2.4
Mix. 4	9.036	9.064	0.3	9.103	0.7
Mix. 5	8.121	8.293	2.1	8.297	2.2
Mix. 6	8.773	8.998	2.6	9.034	3.0
Mix. 7	9.290	9.502	2.3	9.543	2.7
Mix. 8	10.314	10.476	1.6	10.482	1.6
Mix. 9	9.325	9.287	-0.4	9.330	0.1
Mix. 10	9.733	9.890	1.6	9.922	1.9
Mix. 11	10.066	10.040	-0.3	10.070	0.04
Mix. 12	10.586	10.618	0.3	10.616	0.3
<u>Base oils</u>					
Light base oil	8.955	9.076	1.4	9.103	1.7
Medium base oil	9.723	9.794	0.7	9.813	0.9
Heavy base oil	10.297	10.280	-0.2	10.275	-0.2
Bright stock	11.263	11.232	-0.3	11.142	-1.1
Mix. 1	9.638	9.701	0.7	9.722	0.9
Mix. 2	9.479	9.426	-0.6	9.454	-0.3
Mix. 3	9.250	9.248	-0.02	9.277	0.3
Mix. 4	9.028	9.162	1.5	9.190	1.8
Mix. 5	10.152	10.083	-0.7	10.088	-0.6
Mix. 6	9.867	9.890	0.2	9.904	0.4
Mix. 7	9.462	9.427	-0.4	9.454	-0.1
Mix. 8	9.079	9.197	1.3	9.225	1.6
Mix. 9	11.007	10.947	-0.6	10.887	-1.1
Mix. 10	10.517	10.382	-1.3	10.369	1.5
Mix. 11	9.832	9.646	-1.9	9.668	-1.7
Mix. 12	9.171	9.197	0.3	9.225	0.6
Mix. 13	11.107	11.077	-0.3	11.004	-0.9
Mix. 14	10.795	10.690	-1.0	10.654	-1.3
Mix. 15	10.336	10.280	-0.5	10.275	-0.6
Mix. 16	9.880	9.927	0.5	9.941	0.6
Mix. 17	11.167	11.077	-0.8	11.004	-1.1
Mix. 18	10.975	10.904	-0.7	10.848	-1.2
Mix. 19	10.685	10.691	0.1	10.654	-0.3
Mix. 20	10.396	10.341	-0.5	10.331	-0.6

Table 9.31 (continued)

Mixtures	ΔF by eq. 9.17 (K cal./g-mol)	ΔF(K cal./g-mol) by eq. 9.26 ΔF	% Dev. *	by eq. 9.27 ΔF	% Dev *
<u>Petroleum products:</u>					
Kerosene	7.307	6.996	-4.3	6.859	-6.1
Heavy gas oil	9.046	9.303	2.8	9.348	3.3
Residue >360°C	12.153	11.808	-2.8	11.686	3.8
Mix. 1	8.643	8.977	3.9	9.017	4.3
Mix. 2	7.940	8.166	2.9	8.167	2.9
Mix. 3	7.655	7.801	1.9	7.770	1.5
Mix. 4	7.179	7.232	0.7	7.130	-0.7
Mix. 5	11.270	10.911	-3.2	10.887	-3.4
Mix. 6	9.559	9.217	-3.6	9.260	-3.1
Mix. 7	8.760	8.179	-6.6	8.183	-6.6
Mix. 8	7.753	7.539	-2.8	7.476	-3.6
Mix. 9	11.750	-	-	-	-
Mix. 10	10.751	10.831	0.7	10.809	0.5
Mix. 11	10.163	10.177	0.1	10.200	0.4
Mix. 12	9.352	9.409	0.6	9.454	1.1
** AAD			1.3		1.5

* Dev. = $\frac{\Delta F\text{cal. by eq. 9.26 or 9.27} - \Delta F\text{cal. by eq. 9.14}}{\Delta F\text{cal. by eq. 9.14}}$ X100

** AAD = Absolute Average Deviations

Table 9.32 Calculated Kinematic Viscosities, by Equations 9.17 and 9.26, for Crude Oils and Their Binary Mixtures

Mixtures	Kinematic Viscosity (cSt.) @									
	10°C		20°C		30°C		40°C		50°C	
	calc.	%Dev.	Calc.	%Dev.	Calc.	%Dev.	Calc.	%Dev.	Calc.	%Dev.
light crude oil	21.62	52.0	13.31	39.9	8.459	18.5	5.535	-7.1	3.718	-23.3
medium crude oil	174.9	7.1	99.76	22.5	59.04	13.9	36.13	4.3	22.79	-8.8
heavy crude oil	1570	28.4	819.5	-7.7	446.5	4.7	252.9	13.2	148.4	14.2
Mix 1	24.83	51.0	15.20	41.9	9.615	4.8	6.262	-3.9	4.188	-25.5
Mix. 2	41.69	31.5	25.04	29.4	15.56	5.2	9.963	-7.7	6.559	-19.9
Mix. 3	82.53	65.5	48.38	61.5	29.38	34.6	18.42	26.4	11.89	-0.6
Mix. 4	126.4	8.9	72.89	13.5	43.60	3.4	26.95	3.2	17.17	-3.6
Mix. 5	34.36	80.6	20.77	76.6	12.98	23.0	8.358	20.2	5.531	-6.4
Mix. 6	100.0	83.1	57.93	74.6	34.78	30.8	21.58	39.8	13.79	15.1
Mix. 7	220.3	50.8	123.7	57.0	72.20	38.6	43.61	36.2	27.17	31.3
Mix. 8	1081	5.7	572.3	29.3	316.0	37.4	181.3	39.9	107.6	43.4
Mix. 9	176.7	-12.1	100.5	-0.6	59.39	-5.2	36.28	-3.4	22.85	-9.0
Mix 10	454.1	19.0	249.2	34.0	142.2	29.8	84.15	30.6	51.43	35.1
Mix. 11	548.4	-14.7	298.2	-0.1	168.8	-6.6	99.06	1.7	60.10	-1.2
Mix. 12	1376	-17.9	722.5	-0.9	395.8	6.3	225.3	19.4	132.8	21.8
*AAD		35.2		32.6		17.5		17.1		17.3

*AAD = Absolute Average Deviation

Table 9.33 Calculated Kinematic Viscosities, by Equations 9.17 and 9.26, for Base Oils and Their Binary Mixtures.

Mixtures	Kinematic Viscosity (cSt.) @					
	20°C		40°C		100°C	
	Cal.	%Dev.	Cal.	%Dev.	Cal.	%Dev.
light base oil	81.08	78.8	29.94	55.1	2.863	28.5
medium base oil	240.9	35.6	82.23	36.6	6.530	-18.6
heavy base oil	453.6	6.8	146.8	16.6	10.28	-22.0
bright stock	1617	-7.9	471.4	10.8	25.81	-13.8
mix 1	208.5	36.9	71.88	35.3	5.847	-21.7
mix 2	133.2	17.2	47.34	14.1	4.135	-36.1
mix 3	102.6	36.3	37.18	26.1	3.400	-35.9
mix 4	92.39	80.0	33.80	56.8	3.161	-25.7
mix 5	333.1	2.0	110.2	7.6	8.117	-30.0
mix 6	254.5	26.7	85.95	26.6	6.658	-25.2
mix 7	127.1	24.4	45.17	17.7	3.944	-36.3
mix 8	95.84	73.9	34.93	52.8	3.237	-26.9
mix 9	1044	-6.7	314.1	6.4	18.51	-21.4
mix 10	443.2	-9.2	141.8	-3.1	9.672	-35.7
mix 11	152.7	-5.6	52.96	-7.7	4.370	-47.2
mix 12	90.45	47.1	32.96	32.3	3.055	-35.1
mix 13	1294	-3.6	383.7	10.1	21.86	-15.8
mix 14	731.7	-11.4	226.4	-1.0	14.26	-27.5
mix 15	425.6	2.9	137.7	8.9	9.644	-27.3
mix 16	281.7	30.5	94.77	31.3	7.271	-21.8
mix 17	1278	-14.8	379.0	-0.1	21.60	-21.3
mix 18	1013	-9.3	306.2	3.8	18.25	-21.4
mix 19	781.6	7.0	241.8	18.6	15.22	-15.8
mix 20	482.5	-0.2	155.1	8.4	10.69	-25.1
A.A.D.		24.0		20.3		26.5

*A.A.D. = Absolute Average Deviation

Table 9.34 Calculated Kinematic Viscosities, by Equations 9.17 and 9.26, for Petroleum Products and Their Binary Mixtures

Mixtures	Kinematic Viscosity (cSt.) @							
	20°C		40°C		60°C		100°C	
	Cal.	%Dev.	Cal.	%Dev.	Cal.	%Dev.	Cal.	%Dev.
kerosene	2.695	41.2	1.250	-9.5	0.6363	-39.6	0.2048	-75.8
heavy gas oil	112.0	96.7	40.35	90.0	16.43	56.3	3.638	-7.7
residue >360°C	-	-	900.2	-57.1	287.8	-33.5	42.46	-27.5
mix 1	64.82	104.7	24.20	78.2	10.17	40.9	-	-
mix 2	17.34	103.0	7.078	47.0	3.217	3.9	-	-
mix 3	9.710	88.5	4.125	29.3	1.942	12.7	-	-
mix 4	3.930	71.6	1.777	9.1	0.8837	-27.2	-	-
mix 5	-	-	228.3	-41.2	79.61	-31.8	13.58	-48.6
mix 6	-	-	19.25	-10.7	7.903	-30.6	1.774	-61.9
mix 7	-	-	4.472	-31.3	2.030	-50.2	0.5392	-75.7
mix 8	-	-	2.453	30.1	1.185	-16.0	0.3490	-60.7
mix 9	-	-	-	-	-	-	-	-
mix 10	-	-	246.5	22.3	86.63	28.7	14.97	-6.8
mix 11	-	-	102.4	18.5	38.32	18.5	7.365	-21.1
mix 12	-	-	41.55	46.9	16.75	23.4	3.645	-24.3
A.A.D.		84.3		37.2		29.5		41.0

*A.A.D. = Absolute Average Deviation

Table 9.35 Calculated Kinematic Viscosities, by Equations 9.17 and 9.27 for Crude Oils and Their Binary Mixtures.

Mixtures	Kinematic Viscosity (cSt.) @									
	10°C		20°C		30°C		40°C		50°C	
	Cal.	%Dev.	Cal.	%Dev.	Cal.	%Dev.	Cal.	%Dev.	Cal	%Dev
light crude oil	20.94	47.2	12.90	35.6	8.210	15.0	5.377	-9.8	3.615	-25.5
medium crude oil	188.2	15.2	107.0	31.4	63.20	22.0	38.59	11.4	24.30	-2.7
heavy crude oil	1548	-29.4	808.3	-9.0	440.6	3.3	249.7	11.7	146.6	12.8
mix 1	24.39	48.4	14.94	39.5	9.457	3.1	6.162	-5.5	4.123	-26.7
mix 2	42.67	34.6	25.61	32.3	15.90	7.5	10.17	-5.7	6.693	-18.3
mix 3	87.05	74.6	50.94	70.0	30.88	41.5	19.33	32.7	12.45	4.2
mix 4	135.4	16.8	77.94	21.3	46.52	10.3	28.70	10.0	18.24	2.5
mix 5	34.60	81.9	20.91	77.8	13.07	23.9	8.412	21.0	5.566	-5.8
mix 6	106.6	95.1	61.62	85.8	36.93	38.8	22.86	48.2	14.58	21.7
mix 7	236.9	62.1	132.8	68.5	77.29	48.3	46.58	45.5	28.97	39.9
mix 8	1093	6.8	578.3	30.7	319.2	38.8	183.0	41.2	108.6	44.8
mix 9	190.7	5.1	108.3	7.0	63.79	1.8	38.88	3.5	24.44	-2.6
mix 10	480.7	26.0	263.2	41.5	150.0	36.9	88.59	37.5	54.06	42.0
mix 11	578.5	-10.0	313.9	5.1	177.4	-1.8	104.0	6.7	62.97	3.6
mix 12	1371	18.2	720.0	1.3	394.4	5.9	224.6	19.1	132.4	21.4
A.A.D.		38.1		37.1		19.9		20.6		18.3

*A.A.D. = Absolute Average Deviation

Table 9.36 Calculated Kinematic Viscosities, by Equations 9.17 and 9.27, for Base Oils and Their Binary Mixtures.

Mixtures	Kinematic Viscosity (cSt.) @					
	20°C		40°C		100°C	
	Cal.	%Dev.	Cal.	%Dev.	Cal.	%Dev.
light base oil	84.93	87.3	31.27	61.9	2.969	-25.8
medium base oil	248.9	40.1	84.78	40.8	6.700	-16.5
heavy base oil	449.7	5.9	145.6	15.6	10.21	-22.5
bright stock	1386	-21.1	407.9	4.1	22.86	-23.6
mix 1	216.1	41.9	74.35	39.9	6.015	-19.5
mix 2	139.8	23.0	49.52	19.4	4.294	-33.7
mix 3	107.8	43.3	38.95	32.2	3.535	-33.3
mix 4	96.95	88.9	35.36	64.0	3.282	-22.8
mix 5	336.0	2.9	111.0	8.4	8.172	-29.5
mix 6	260.7	29.8	87.91	29.5	6.785	-23.8
mix 7	133.2	30.3	47.18	23.0	4.091	-34.0
mix 8	100.6	82.6	36.54	59.8	3.361	-24.1
mix 9	942.0	-15.8	285.2	-3.4	17.07	-27.5
mix 10	433.4	-11.2	138.9	-5.1	9.504	-36.8
mix 11	158.5	-2.0	54.87	-4.3	4.501	-45.6
mix 12	94.91	54.3	34.48	38.4	3.172	-32.6
mix 13	1142	-15.0	341.2	-2.1	19.81	-23.7
mix 14	687.8	-16.7	213.6	-6.6	13.58	-31.0
mix 15	421.9	2.0	136.6	8.1	9.579	-27.9
mix 16	288.6	33.7	96.92	34.3	7.409	-20.3
mix 17	1128	-24.9	337.0	-11.2	19.57	-28.7
mix 18	920.4	-17.7	279.8	-5.2	16.92	-27.1
mix 19	733.5	0.5	227.8	11.7	14.48	-19.9
mix 20	474.3	-1.9	152.6	6.6	10.55	-26.1
A.A.D.		28.9		22.3		27.3

*A.A.D. = Absolute Average Deviation

Table 9.37 Calculated Kinematic Viscosities, by Equations 9.17 and 9.27, for Petroleum Products and Their Binary Mixtures

Mixtures	Kinematic Viscosity (cSt.) @							
	20°C		40°C		60°C		100°C	
	Cal.	%Dev.	Cal.	%Dev.	Cal.	%Dev.	Cal.	%Dev.
Kerosene	2.130	11.6	1.003	-27.4	0.5173	-50.9	0.1702	-79.9
heavy gas oil	121.0	112.5	43.38	104.3	17.59	67.4	3.866	-1.9
residue >360°C	-	-	266 8	27.0	739.9	70.9	36.02	-38.5
mix 1	69.44	119.3	25.81	90.1	10.80	49.6	-	-
mix 2	17.37	103.3	7.090	47.2	3.222	4.1	-	-
mix 3	9.207	78.7	3.924	23.0	1.853	16.7	-	-
mix 4	3.298	44.0	1.508	7.4	0.7575	-37.6	-	-
mix 5	-	-	219.7	-43.4	76.77	-34.2	13.15	-50.2
mix 6	-	-	20.62	-4.4	8.434	-25.9	1.880	-59.6
mix 7	-	-	4.501	-30.8	2.042	-49.9	0.5422	-75.6
mix 8	-	-	2.217	17.6	1.077	-23.7	0.3206	-63.9
mix 9	-	-	-	-	-	-	-	-
mix 10	-	-	238.0	18.1	83.79	24.5	14.53	-9.5
mix 11	-	-	106.3	23.0	39.68	27.7	7.597	-18.6
mix 12	-	-	44.67	58.0	17.93	32.1	3.873	-19.5
A.A.D.		78.2		37.3		36.4		41.7

*A.A.D. = Absolute Average Deviation

equations (9.26 and 9.27). However, both equations gave relatively poor agreement for petroleum products.

Consequently, another attempt was made to estimate ΔF as a function of the densities of the oils. Figure 9.54 shows the relationship between the relative ΔF's and the densities of the petroleum liquids. The ΔF's of crude oils and petroleum products exhibited a linear relationship with the density, but these of base oils exhibited a non-linear relationship. Regression of the ΔF values and densities using the least square techniques gave,

i - for crude oils and petroleum products:

$$\Delta F = -12073 + 23422\, d \qquad 9.28$$

ii - for base oils:

$$\Delta F = 21390 \times (d)^{5.928} \qquad 9.29$$

where,

ΔF = the activation energy of viscous flow

d = density @ 15°C

The ΔF's calculated by equation 9.28 for crude oils and petroleum products are summarised in Tables 9.38 and 9.39, respectively; the ΔF's calculated by equation 9.29 for base oils are summarised in Table 9.40.

The calculated kinematic viscosities for crude oils, base oils and petroleum products, resulted from substituting the ΔF's calculated by equations 9.28 and 9.29, into equation 9.17 are summarised in Tables 9.41, 9.42 and 9.43, respectively. Reasonable agreement was obtained between the measured and calculated viscosities, for crude oils and base oils. However, the agreement was poor for the viscosities of petroleum products, i.e. equation 9.28

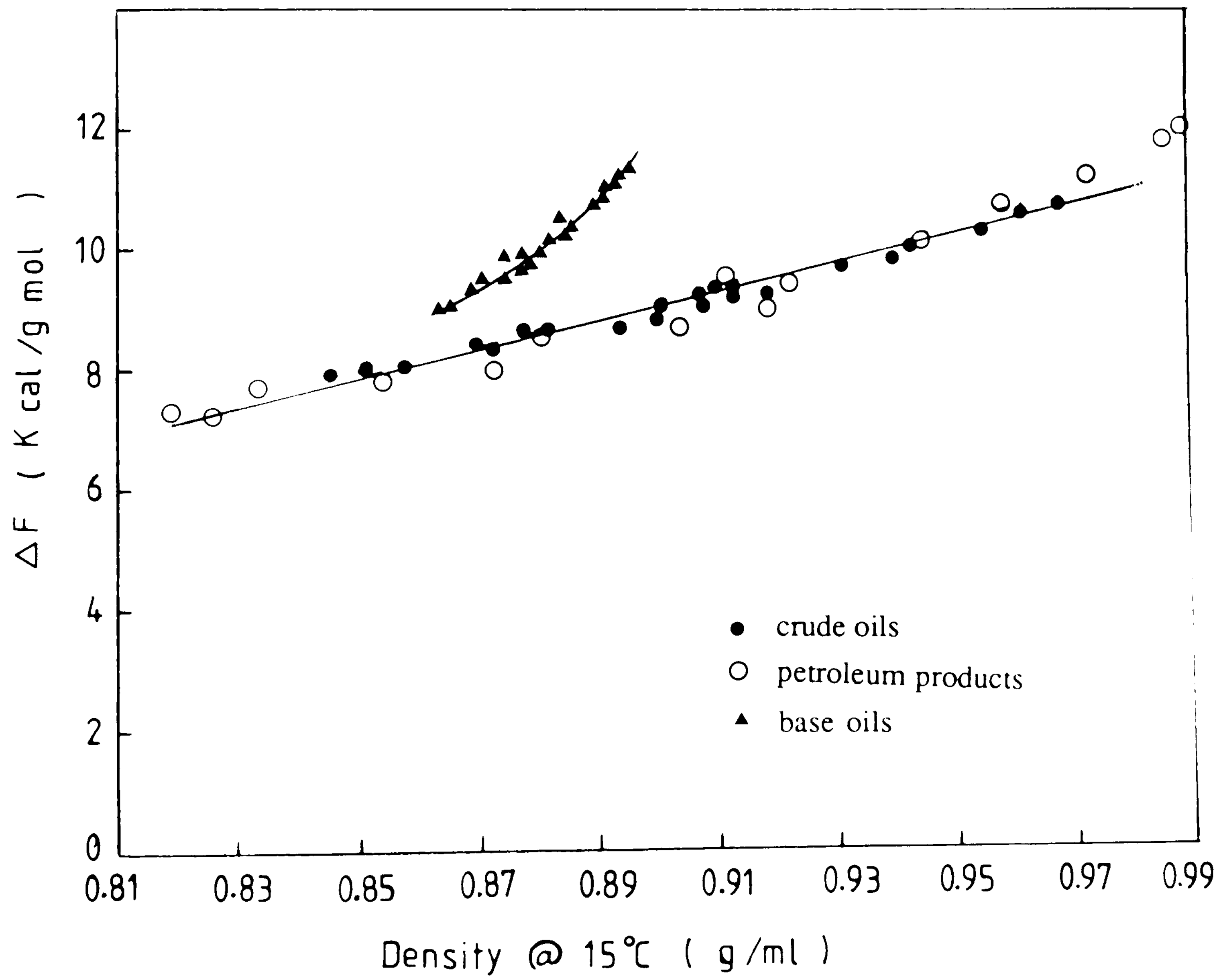


Figure 9.54 Relationship Between ΔF's and the Densities of the Petroleum Liquids

failed to predict the viscosity of the tested liquids.

However, equations 9.26, 9.27, 9.28 and 9.29 together with equation 9.17 permit the prediction of the kinematic viscosity of crude oils and base oils with acceptable accuracy, with ΔF (which, as discussed earlier, is very difficult to determine for petroleum liquids) being estimated from other measureable properties, i.e. density and $T_{50\%}$ boiling point.

Table 9.38 Values of ΔF, of Crude Oils and Their Binary Mixtures, Calculated by Equation 9.28

Crude Oils	ΔF (K. cal/g-mol)	% Dev.
light crude oil	7.707	-2.8
medium crude oil	9.145	-0.8
heavy crude oil	10.569	-0.1
mix 1	7.850	-2.3
mix 2	8.283	-1.0
mix 3	8.569	-0.6
mix 4	9.003	-0.4
mix 5	7.993	-1.6
mix 6	8.853	0.9
mix 7	9.424	1.4
mix 8	10.284	-0.3
mix 9	9.288	-0.4
mix 10	9.715	-0.2
mix 11	10.000	-0.7
mix 12	10.427	-1.5
*AAD		1.0

*AAD = Absolute Average Deviation

Table 9.39 Values of ΔF, of Petroleum Products and Their Binary Mixtures, Calculated by Equation 9.28

Petroleum Products	ΔF (K. cal/g-mol)	% Dev.
kerosene	7.110	-2.7
heavy gas oil	9.422	4.2
residue >360°C	11.209	-7.8
mix 1	9.099	5.3
mix 2	8.363	5.3
mix 3	7.930	3.6
mix 4	7.269	1.3
mix 5	10.675	-5.3
mix 6	9.244	-3.3
mix 7	8.557	-2.3
mix 8	7.443	-4.0
mix 9	10.977	-6.6
mix 10	10.370	-3.5
mix 11	10.038	-1.2
mix 12	9.548	2.1
*AAD		3.9

*AAD = Absolute Average Deviation

Table 9.40 Values of ΔF, of Base Oils and Their Binary Mixtures, Calculated by Equation 9.29

Base Oils	ΔF (K. cal/g-mol)	% Dev.
light base oil	8.894	-0.7
medium base oil	9.905	1.9
heavy base oil	10.313	0.2
bright stock	10.994	-2.4
mix 1	9.785	1.5
mix 2	9.562	0.9
mix 3	9.254	0.04
mix 4	8.974	-0.6
mix 5	10.127	-0.2
mix 6	9.871	0.04
mix 7	9.465	0.03
mix 8	8.980	-1.1
mix 9	10.864	-1.3
mix 10	20.382	-1.3
mix 11	9.745	-0.9
mix 12	9.091	-0.9
mix 13	10.939	-1.5
mix 14	20.713	-0.8
mix 15	10.396	0.6
mix 16	10.005	1.3
mix 17	10.436	-2.1
mix 18	10.756	-0.2
mix 19	10.543	-1.3
mix 20	10.347	-0.5
*AAD		0.9

*AAD = Absolute Average Deviation

Table 9.41 Calculated Kinematic Viscosities, by Equations 9.17 and 9.28 for Crude Oils and Their Binary Mixtures.

Mixtures	Kinematic Viscosity (cSt.) @									
	10°C		20°C		30°C		40°C		50°C	
	Cal.	%Dev.	Cal.	%Dev.	Cal.	%Dev.	Cal.	%Dev.	Cal	%Dev
light crude oil	13.00	-8.6	8.142	-14.4	5.260	-26.3	3.495	-41.4	2.381	-50.9
medium crude oil	144.1	-11.8	82.72	1.5	49.26	-4.9	30.32	-12.4	19.23	-23.0
heavy crude oil	1222	-44.3	643.2	-27.6	353.3	-17.2	201.6	-9.8	119.1	-8.3
mix 1	16.46	0.1	10.22	-4.6	6.551	-28.6	4.319	-33.7	2.922	-48.0
mix 2	33.98	7.2	20.55	6.2	12.43	-16.0	7.752	-28.2	4.974	-39.3
mix 3	54.82	9.9	32.59	8.8	20.05	-8.2	12.73	-12.6	7.766	-35.0
mix 4	113.4	-2.2	65.64	2.2	39.40	-6.6	24.44	-6.4	15.61	-12.3
mix 5	20.15	5.9	12.41	5.5	7.885	-25.2	5.160	-25.8	3.466	-41.3
mix 6	77.28	41.5	45.16	36.1	27.34	2.8	17.09	10.8	11.0	-8.2
mix 7	191.7	31.2	108.2	37.3	63.43	21.7	38.5	20.2	24.06	16.3
mix 8	768.3	-24.9	411.6	-7.0	229.7	-0.2	133.1	2.7	79.78	6.3
mix 9	177.0	-11.9	100.7	-0.5	59.49	-5.0	36.34	-3.2	22.89	-8.8
mix 10	332.7	-12.8	184.5	-0.8	106.4	-2.9	63.51	-1.4	39.16	2.9
mix 11	510.8	-20.6	278.4	-6.8	157.9	-12.6	92.89	-4.7	56.47	-7.1
mix 12	979.9	-41.5	520.4	-28.6	288.2	-22.6	165.7	-12.1	98.61	-9.5
A.A.D.		18.3		12.5		13.4		15.0		21.1

*A.A.D. = Absolute Average Deviation

Table 9.42 Calculated Kinematic Viscosities, by Equations 9.17 and 9.29, for Base Oils and Their Binary Mixtures.

Mixtures	Kinematic Viscosity (cSt.) @					
	20°C		40°C		100°C	
	Calc.	%Dev.	Calc.	%Dev.	Calc.	%Dev.
light base oil	59.31	30.8	22.35	15.7	2.240	-44.0
medium base oil	291.5	64.0	98.30	63.3	7.585	-5.5
heavy base oil	480.1	13.0	154.8	23.0	10.75	-18.4
bright stock	1075	-38.8	321.5	-24.4	18.72	-37.5
mix 1	240.8	58.1	82.28	54.9	6.549	-12.3
mix 2	168.3	48.0	58.91	42.0	4.968	-23.3
mix 3	103.6	37.7	37.54	27.4	3.427	-35.4
mix 4	66.90	30.4	23.55	9.2	1.940	-54.4
mix 5	359.3	10.0	118.2	15.4	8.614	-25.7
mix 6	246.3	22.7	83.36	22.8	6.489	-27.1
mix 7	135.7	32.8	48.02	25.15	4.152	-33.0
mix 8	66.02	19.8	24.64	7.8	2.415	-45.4
mix 9	905.5	-19.1	274.8	-6.9	16.55	-29.8
mix 10	443.2	-9.2	141.8	-3.1	9.672	-35.7
mix 11	181.0	11.9	62.10	8.3	4.994	-39.7
mix 12	75.40	22.6	27.80	11.6	2.648	-43.8
mix 13	1016	-24.4	305.8	-12.3	18.08	-30.4
mix 14	761.2	-7.8	234.9	2.8	15.48	-21.3
mix 15	519.4	25.5	165.9	31.3	11.28	-15.1
mix 16	322.1	49.3	107.4	48.8	8.078	-13.1
mix 17	1003	-33.1	302.1	-20.4	17.85	-34.9
mix 18	785.9	-29.7	241.4	-18.2	14.95	-35.6
mix 19	606.2	-17.0	190.6	-6.5	12.47	-31.1
mix 20	487.5	0.8	156.6	9.4	10.78	-24.5
A.A.D.		27.4		21.3		29.9

*A.A.D. = Absolute Average Deviation

Table 9.43 Calculated Kinematic Viscosities, by Equations 9.17 and 9.28, for Petroleum Products and Their Binary Mixtures

Mixtures	Kinematic Viscosity (cSt.) @							
	20°C		40°C		60°C		100°C	
	Cal.	%Dev.	Cal.	%Dev.	Cal.	%Dev.	Cal.	%Dev.
Kerosene	3.278	71.8	1.502	8.8	0.7559	-28.3	0.2388	-71.7
heavy gas oil	137.4	141.3	48.86	130.0	19.67	87.2	4.272	8.4
residue >360°C	-	-	343.6	-83.6	116.4	-73.1	18.92	-67.7
mix 1	79.93	152.4	29.45	116.9	12.23	69.4	-	-
mix 2	24.33	184.7	9.716	101.8	4.333	40.0	-	-
mix 3	12.12	135.2	5.076	59.1	2.360	6.1	-	-
mix 4	4.187	82.8	1.886	15.8	0.9346	-23.0	-	-
mix 5	-	-	156.2	-59.8	55.72	-52.3	9.878	-62.6
mix 6	-	-	20.10	-6.8	8.232	-27.7	1.840	-60.4
mix 7	-	-	8.212	26.2	3.594	-11.8	0.8980	-59.5
mix 8	-	-	2.102	11.5	1.025	-27.4	0.3067	-65.5
mix 9	-	-	251.8	-75.2	87.24	-65.0	14.72	-64.0
mix 10	-	-	117.5	-41.7	43.16	-35.9	8.038	-50.0
mix 11	-	-	81.89	-5.2	31.06	-4.0	6.105	-34.6
mix 12	-	-	51.96	83.7	20.66	52.2	4.397	-8.7
A.A.D.		128.0		55.1		40.2		50.3

*A.A.D. = Absolute Average Deviation

ΔF of Mixtures:

The average values of the activation energy of viscous flow ΔF calculated by the numerical method and shown in Table 9.30 for the binary mixtures of crude oils, base oils and petroleum products are presented graphically in Figures 9.55, 9.56 and 9.57, respectively. It is clear that ΔF values exhibited non-ideal behaviour on mixing similar to that for kinematic viscosity. The divergence from ideality increases as the difference in the density (Δ API) of the components increases for each binary mixtures system. The highest non-ideality was exhibited by light-heavy crude oils mixtures, light base oil-bright stock base oil mixtures, and kerosene - residue mixtures.

The excess activation energies of viscous flow ΔF^E of each binary mixture system, as a compensation for the non-ideality, were calculated from

$$\Delta F^E = \Delta F_{mix} - \sum x_i \Delta F_i \qquad 9.30$$

where,

ΔF^E = excess activation energy of viscous flow

ΔF_{mix} = activation energy of viscous flow of the mixture

ΔF_i = activation energy of viscous flow of component i

x_i = weight fraction of component i.

The calculated values of ΔF^E are presented graphically in Figures 9.58, 9.59 and 9.60. As with v^E, discussed in Section 9.3.3, the absolute values of ΔF^E increase with increasing difference in densities between the mixture components.

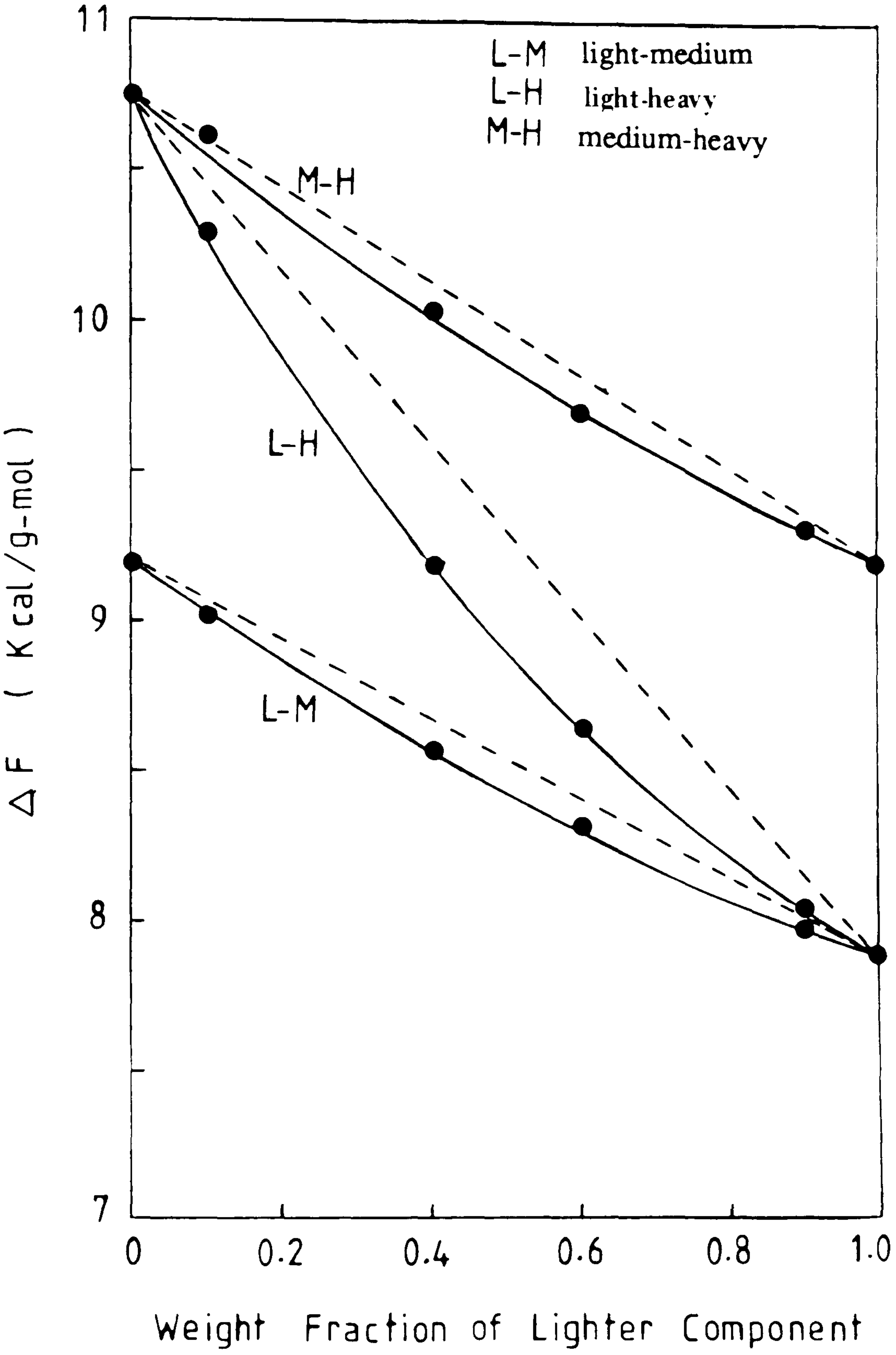


Figure 9.55 ΔF's of Crude Oils Binary Mixtures as a Function of Composition

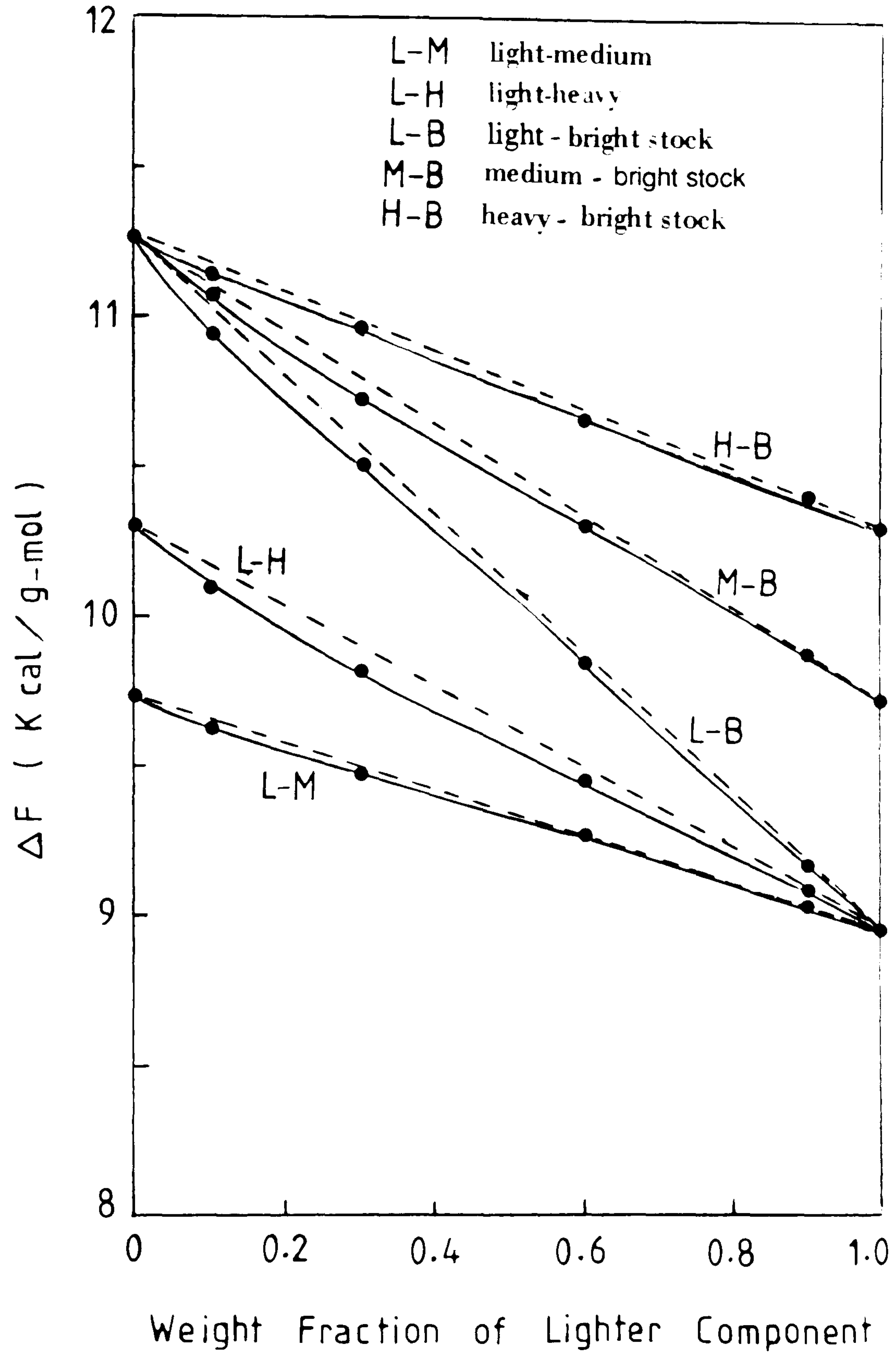


Figure 9.56 ΔF's of Base Oils Binary Mixtures as a Function of Composition

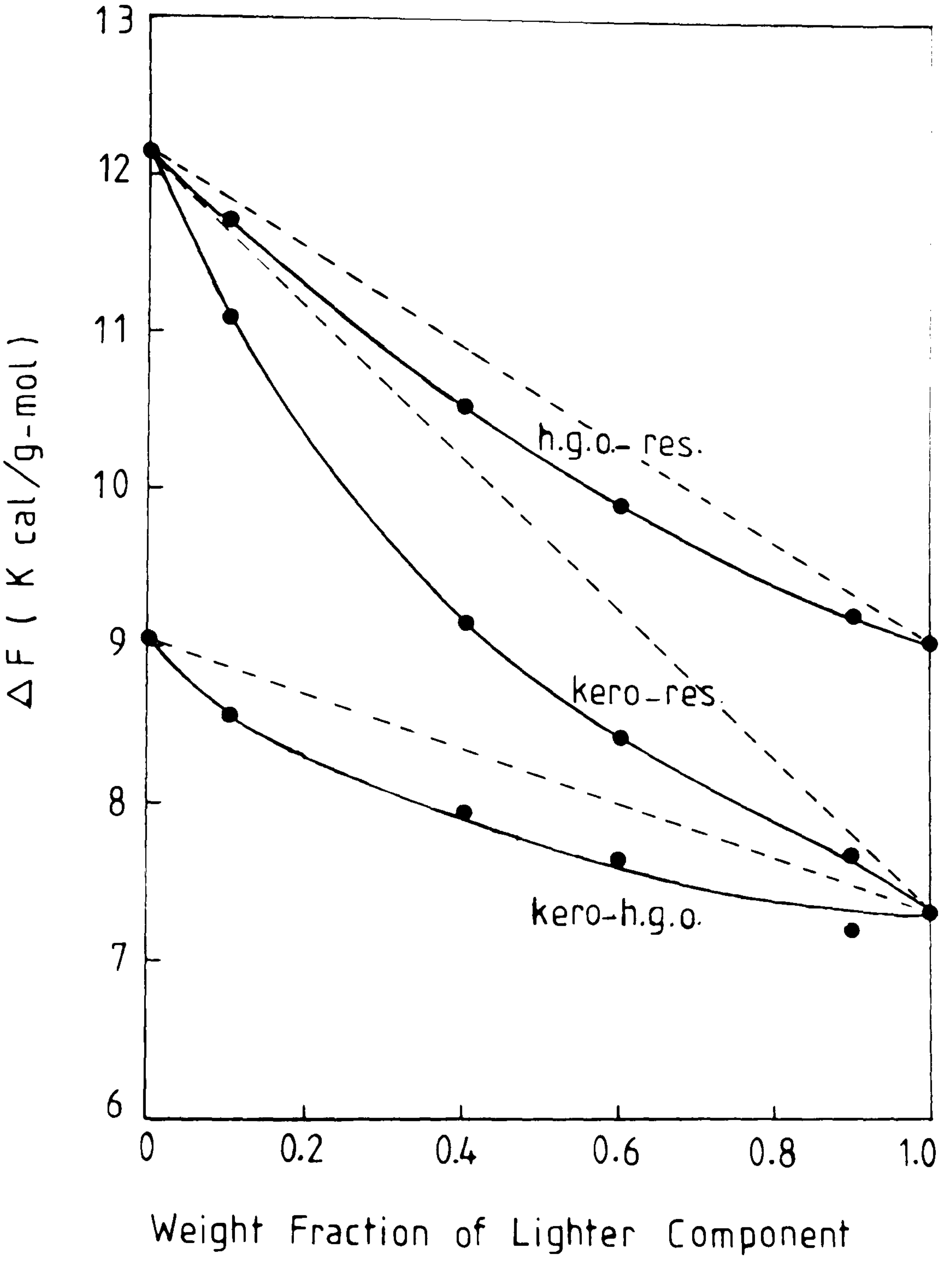


Figure 9.57 ΔF's of Petroleum Products Binary Mixtures as a Function of Composition

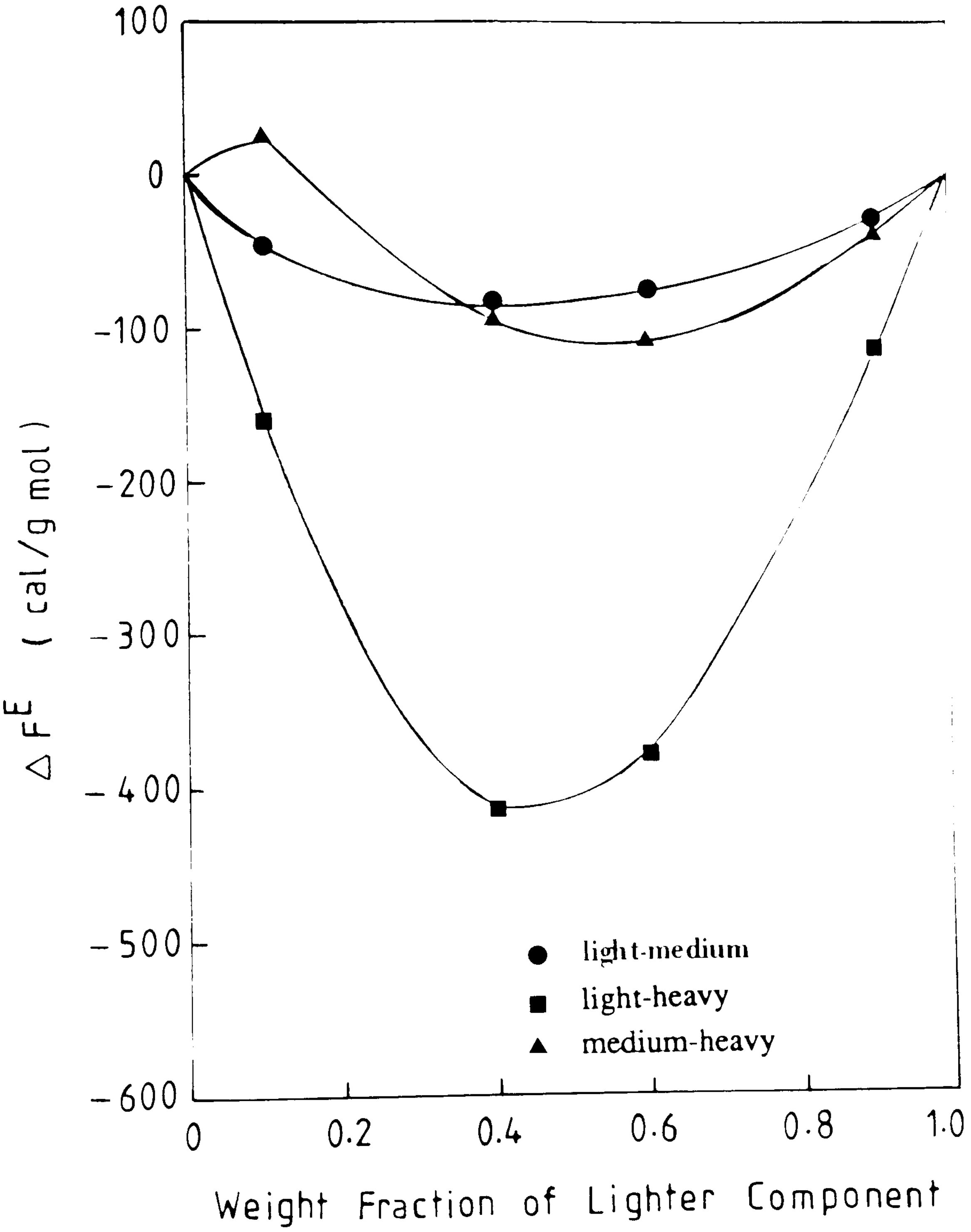


Figure 9.58 Excess Activation Energy of Viscous Flow (ΔF^E) of Crude Oil Binary Mixtures

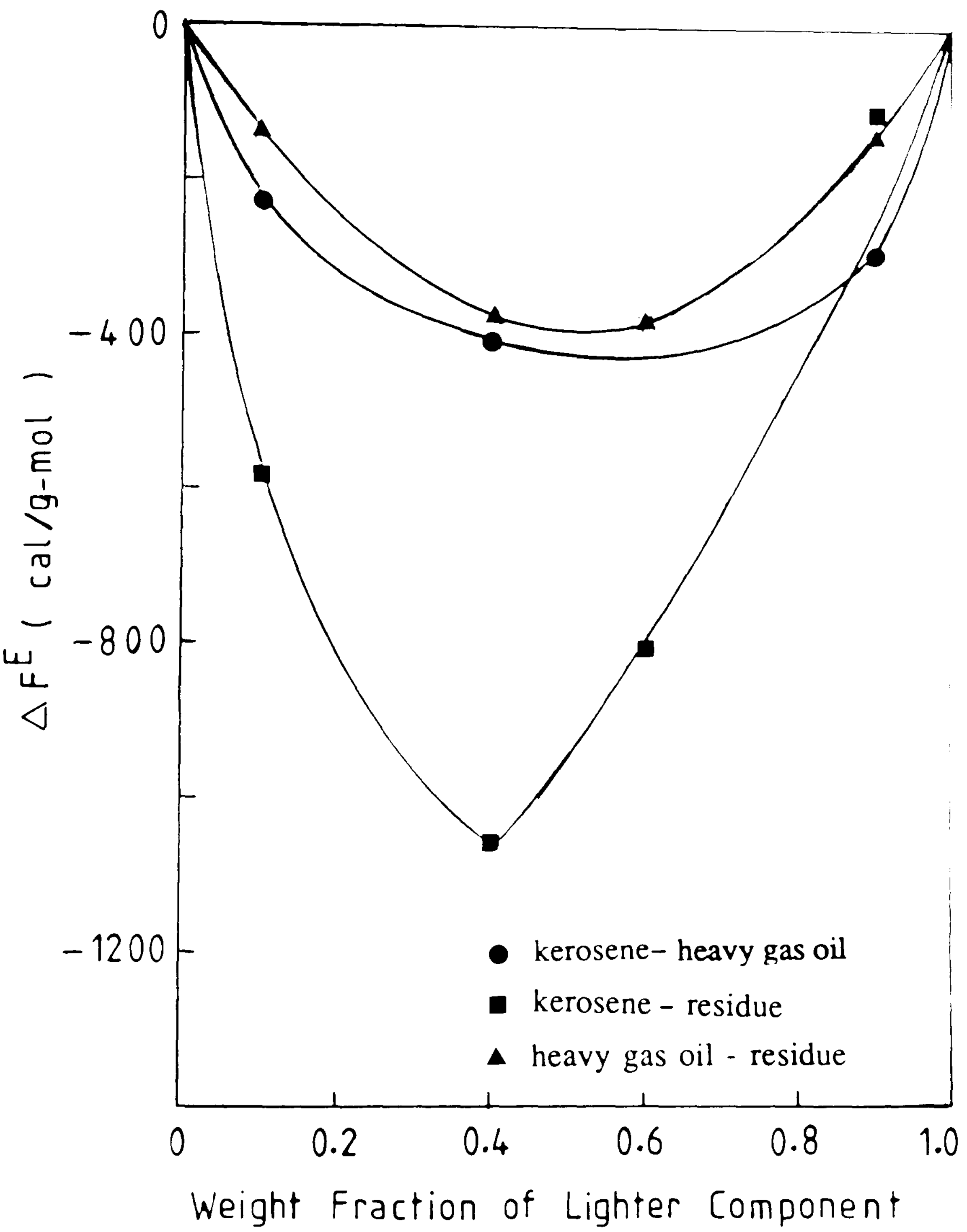


Figure 9.59 Excess Activation Energy of Viscous Flow ΔF^E of Petroleum Products Binary Mixtures

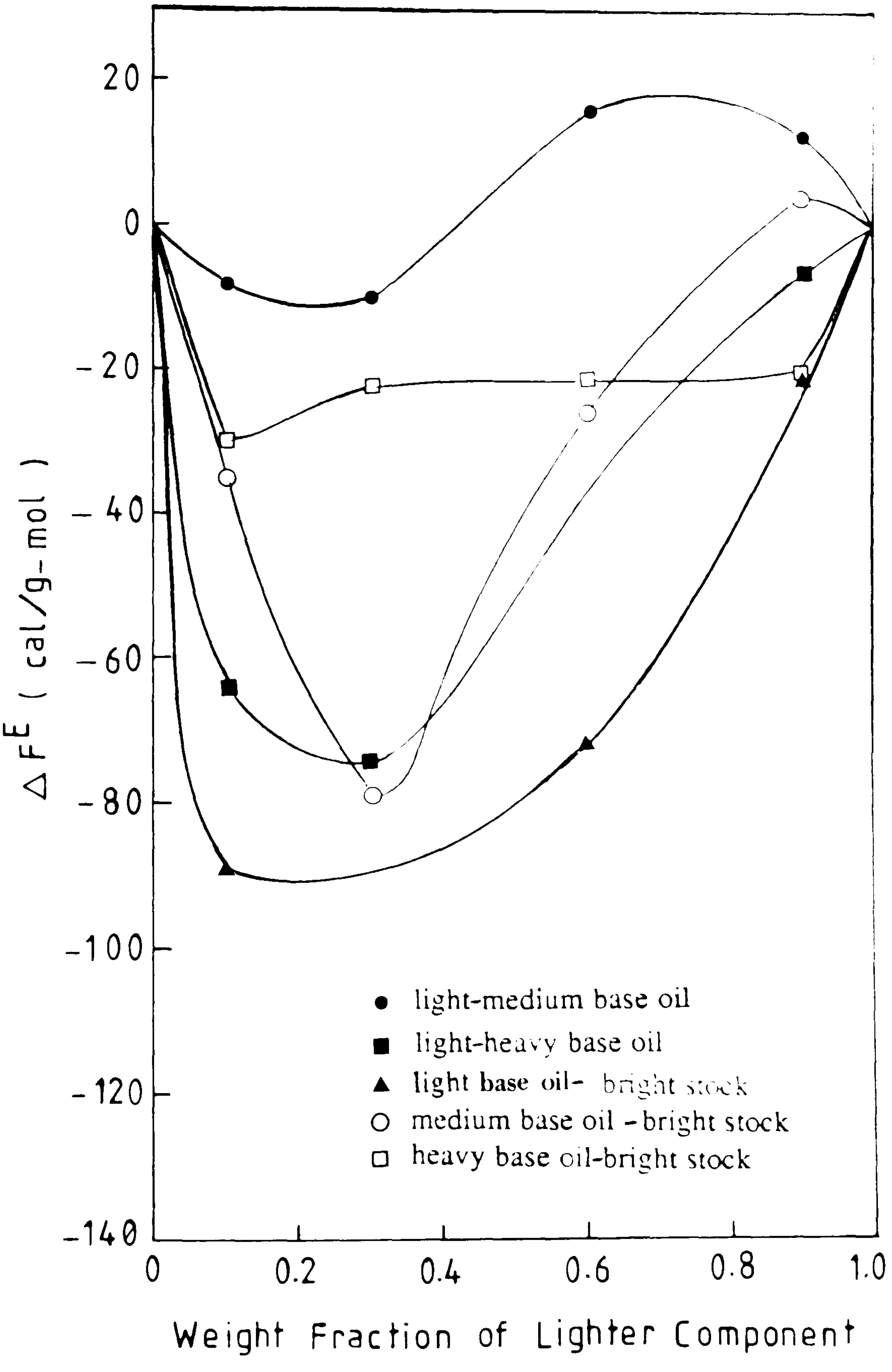
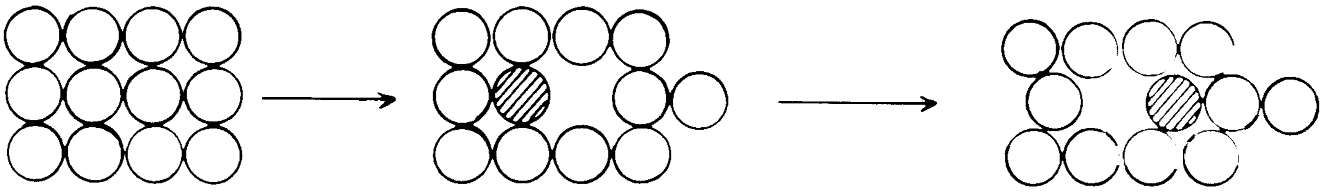


Figure 9.60 Excess Activation Energy of Viscous Flow (ΔF^E) of Base Oil Binary Mixtures

9.3.5 A Proposed Mechanism for the Non-Ideal Behaviour of the Viscosity of Mixtures

The majority of work to describe the mechanism of the viscous flow of a liquid has been based upon Eyring's theory or the theory of free volume, both described in Chapter 5. According to Eyring's theory, molecules in a liquid are quite closely-packed, and the empty space between them (free volume) is insufficient to allow free movement of one molecule past another. For any one molecule to move, its neighbours must first give way, or a "hole" must form. The activated molecule then moves into the hole. This process of motion is shown in Figure 9.61.



State of Rest

A hole is formed

Activated molecule moves into hole

Figure 9.61: Viscous Flow According to Eyring's Model of Viscosity

Only a few molecules have sufficient energy to overcome the attractive forces of their neighbours, and undergo the process shown in Figure 9.61. Eyring$^{(44,45,46)}$ reported that the concentration of the activated molecules is inversely proportional to the kinematic viscosity of a liquid.

The free volume theory of viscous flow utilizes a similar approach in describing the mechanism of liquid viscosity. The main assumption is that the viscosity of a liquid is inversely proportional to the free volume between the molecules. Hence, in addition to the dependence of the viscosity on molecular weight, it is also dependent on the molar volume, the type of interaction between molecules, and how close they are packed. Thus, a liquid of very closely-packed molecules would be expected to be viscous and a liquid of loosely-packed molecules to be of low viscosity.

Therefore, the molar volume of a liquid is believed to be the controlling parameter which affects the viscosity, and determines the type of behaviour that the liquid may exhibit when exposed to changes, eg. due to mixing, or variations in temperature or pressure.

Many workers have investigated the effect of mixing upon the molar volume of gases(85) and pure hydrocarbons(65,133,134,135,149,150). However, no reports were found in the literature relating to petroleum liquids or similar complex mixtures.

As described in Section 9.3.3, the measured viscosities of binary mixtures examined in this study exhibited values less than anticipated. This non-ideal behaviour is believed to be due to an initial increase in the molar volume of the binary mixtures. In effect, when a small quantity of a lighter oil is mixed with a heavy one, the molar volume of the mixture initially increases above the expected values, ie. the total molar volume becomes greater than the ideal molar volume V^i_m defined by,

$$V^i_m = \Sigma V_i \quad X_i \qquad 9.31$$

where,

V^i_m = the ideal molar volume of the mixture

V_i = molar volume of component i

X_i = mole, volume, weight fraction.

Two types of mechanism may be proposed for the increase in the molar volume due to mixing, which is actually an average molar volume since petroleum liquids consist of many different hydrocarbon molecules.

Swallowing of smaller molecules by larger ones:

According to this proposed mechanism, a long molecule of high molecular weight, such as asphaltenes or > C_{20} aliphatic compounds, tends to coil loosely. Consequently, a lattice space is formed inside the molecule itself forming a cage. When small molecules (light liquid) are added to it, they are occluded inside the lattice space of the coiled molecule, increasing its volume (Figure 9.62).

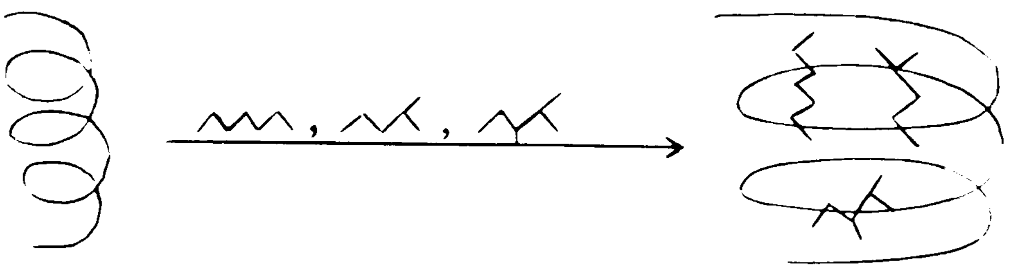


Figure 9.62: Diagrammatic Illustration of Small Molecules Swallowed by Larger Ones

The free volume thus increases and so, the viscosity decreases significantly causing the steep decline on the viscosity-composition diagrams and giving high v^E values. This phenomena predominates during initial addition of the small molecules (light liquid or solvent). The growth of volume of the long molecules continues until it reaches a stage, at which associative interactions commence between the grown molecules (clusters). This tends to produce higher molecular weights, by forming an associative network, which in turn will increase the viscosity. Meanwhile, the amount of the light liquid (low molecular weight molecules) in the mixture increases to a stage at which its solvation effect will predominate, so that the viscosity of the mixture decreases at a reduced rate, ie. less v^E. Consequently the effect of the molar volume increase will decrease, as more of the light liquid is added until it diminishes to zero.

This mechanism is, probably, enhanced by the existence of asphaltenes which are highly polar hydrocarbons of high molecular weight. The structure and the effect of asphaltenes on the viscosity of liquids is discussed later.

The Formation of Solvated Shell:

According to the solvated shell mechanism, the light liquid (low molecular weight molecules) and the heavy liquid (high molecular weight molecules) are considered as solvent and solute, respectively. It is then assumed that a solvated shell is formed by the molecules of solvent, added initially, which surround the large molecules of the heavy liquid solute, causing an initial increase in the volume of the newly-formed cluster (Figure 9.63). The immediate effect of solvated shell formation is to minimize the associative bonds between the large molecules of the heavy liquid and to break down the associative network. This, together with the creation of more free volume, facilitates the fluidity of the large molecules causing a steep drop in the viscosity of the heavy liquid. This phenomenon was observed in the viscosity-composition diagrams after the addition of up to 30% of the light component.

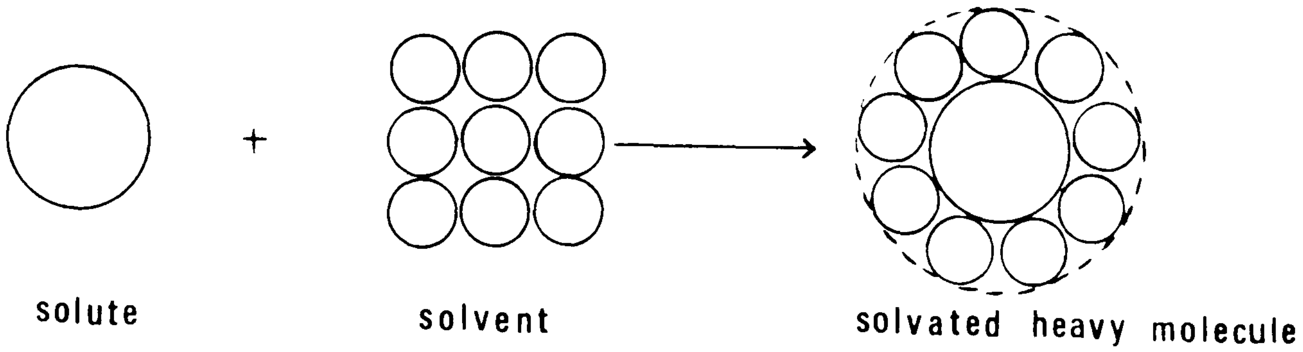


Figure 9.63: Diagrammatic Illustration of the Solvated Shell Formation Mechanism

As the addition of solvent (light liquid) is continued, more solvated clusters are formed, resulting in a steep rate of decrease in the viscosity and increase in the absolute values of the excess viscosity function v^E. However once a certain stage, ~0.3-0.4 weight fraction of the light component, is reached the rate of decrease in the viscosity is reduced. At this stage most of the large molecules are solvated (consumed) and the solvent (light liquid) predominates as the addition continues.

This mechanism also, is considerably enhanced by the presence of the asphaltenes.

A somewhat similar mechanism was reported by other researchers(6, 151, 152, 153, 154) who investigated the stability of petroleum oils against aggregation when used as feedstocks to the refining industry, mainly the heavy feedstocks such as residues. An attempt was made to improve the quality of the feedstock in order to decrease the tendency for undesirable coke formation inside the reactors or the heating coils. They studied the effect of additives (light petroleum products) on the stability against aggregation of petroleum oils containing high molecular weight hydrocarbons. Viscosity was dealt with as the characteristic indicative of the stability or instability of the petroleum system.

Syunyaev(6,151) proposed that the intermolecular interactions of high-molecular weight compounds in petroleum crudes will lead to the formation of complex structural units (CSU), termed "clusters" in the present study, due to Van der Waals forces. These units consist of "supermolecular structures" termed "micelles" in the present study, and solvated shells around these structures. This will give the petroleum system specific properties and will change the system from a thermodynamically stable to an unstable state and tend to produce phase separation.

Seliverstov et al$^{(154)}$ proposed that association of molecules should change both the energy of viscous flow of the system and its molar volume, and hence the distance between moving layers of the structural units. Molecules in a petroleum system are in the free state if the energy of thermal motion is greater than the energy of intermolecular interaction; they are in a bound state if the relationship is the reverse. He presented the following expression to calculate the energy of viscous flow ΔE:

$$\Delta E = RT\left(1 - \frac{T}{\eta}\frac{d\eta}{dT}\right) \qquad 9.32$$

where,

R = gas constant

T = temperature

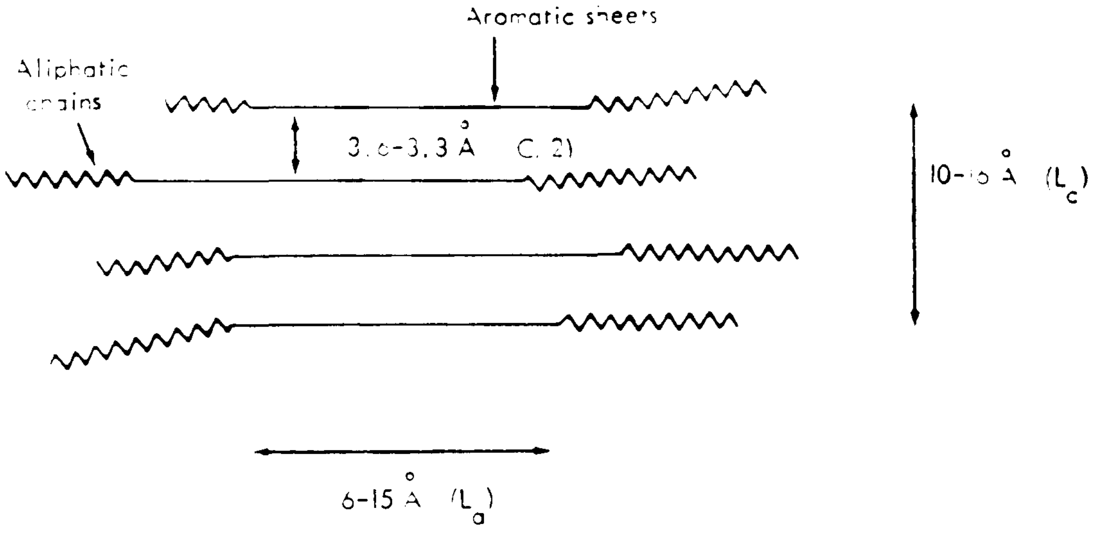
η = dynamic viscosity

However, Syunaev and co-workers and the other investigators did not specify which component of petroleum crudes will cause the formation of the (CSU). Moreover, they only studied the effect of small amounts of the additives (light petroleum products ≤4%) on the viscosity of heavy hydrocarbon materials, ie. they did not examine a full range of viscosity-composition diagrams.

The Effect of Asphaltenes

Structure of Asphaltenes in Crude Oils

Asphaltenes are complex, highly polar, molecules which, when present in any crude oil or petroleum product, have a broad distribution of molecular weights. It is now generally accepted that they are the final products from oxidation reactions(43). X-ray analysis characterises the structure of asphaltenes, and using this technique Altegelt and others(155) have proved that asphaltenes consist of several sheets of condensed aromatic and naphthenic ring systems, to which are attached some side chains of different lengths. These sheets are interconnected by short side chains or bridges. The nature of these bridges is uncertain. Figure 9.64 shows the dimensions of a unit cell, or micelle, of an asphaltene determined by x-ray analysis(43). Asphaltenes may also contain metal atoms and inorganic elements, such as nitrogen and sulphur.



where,

C/2 = interlamellar distance

La = layer diameter

Lc = height of unit cell

Nc = Lc/C/2 = number of lamellae contributing to the micelle.

Figure 9.64: Diagrammatic Representation of an Asphaltene from X-Ray Analysis

Dickie and Yen(5) proposed a macrostructure for asphaltenes, extracted from different crude oils, based on x-ray studies. This structure is shown in Figure 9.65. Figures 9.66, 9.67 and 9.68 show other structures presented by Khan(43), Winniford(156)and Tissot(157), respectively.

It is clear that the asphaltenes possess very complex structures and play an important role in determining the viscous flow behaviour of a petroleum liquid.

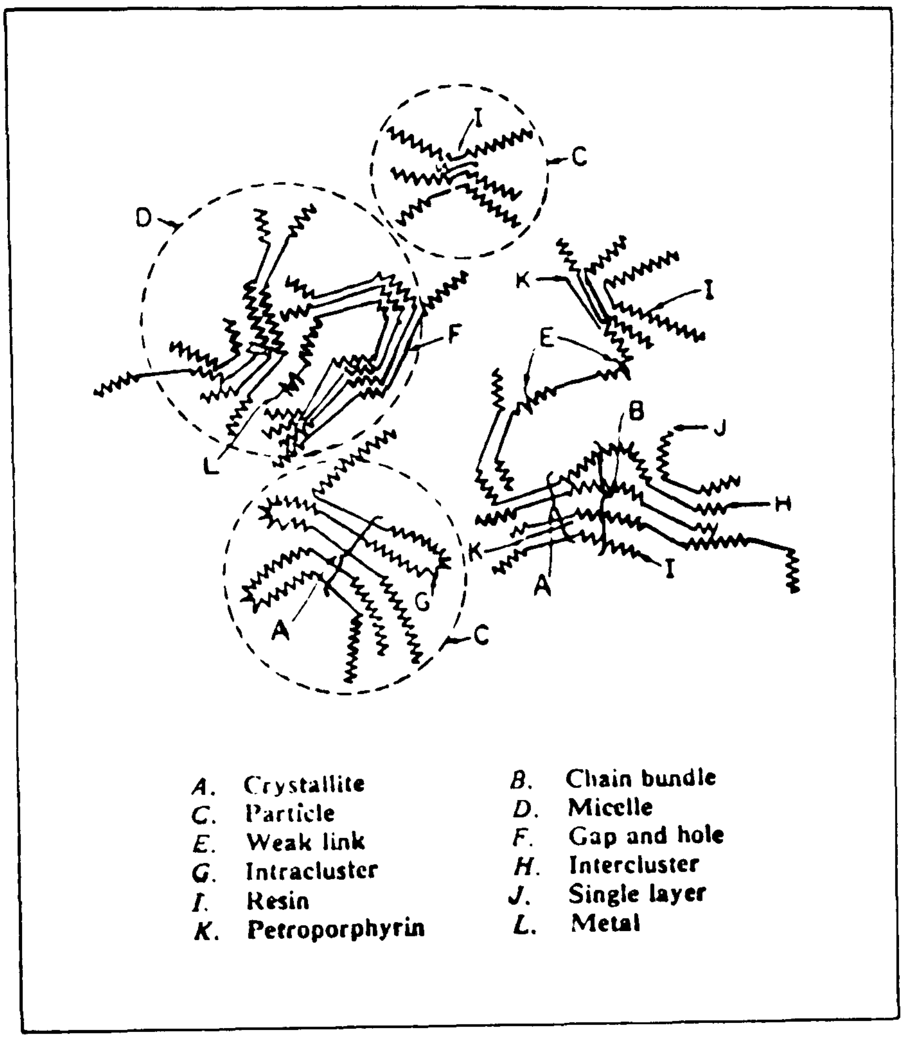


Figure 9.65: Macrostructure of Asphaltenes According to Dickie and Yen(5)

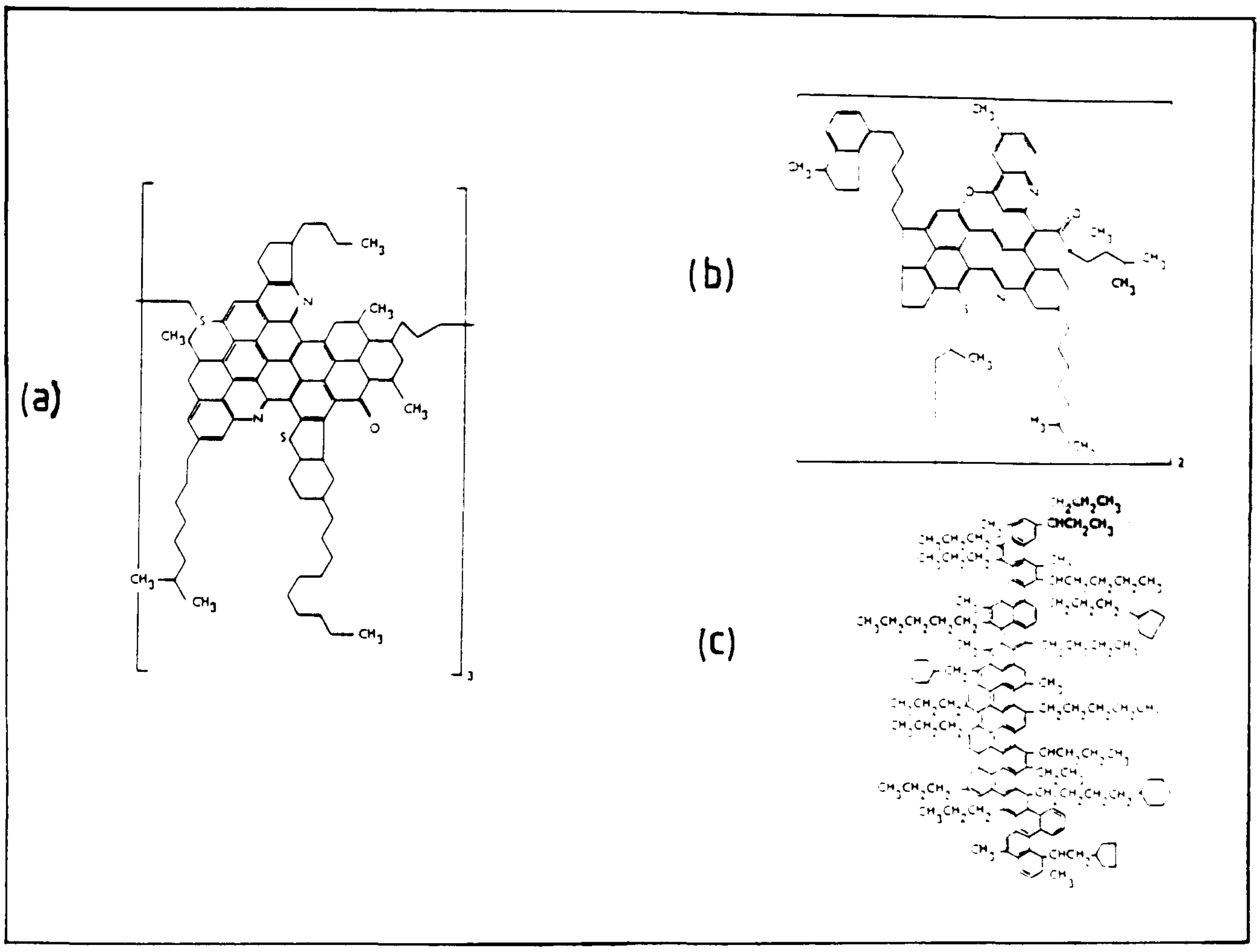


Figure 9.66: Hypothetical Structures for Asphaltenes from

(a) Venezuelan Crude Oil

(b) Californian Crude Oil, and (c) Iraqi Crude Oil, according to Khan(43)

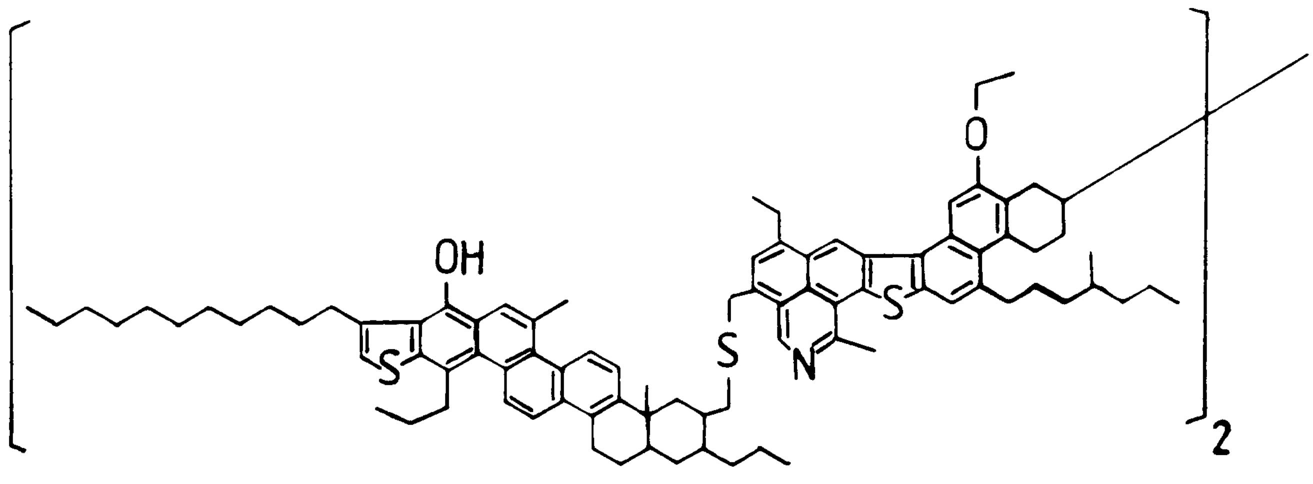


Figure 9.67: Average Structural Models of Asphaltenes from Athabasca Bitumen According to Winniford(156)

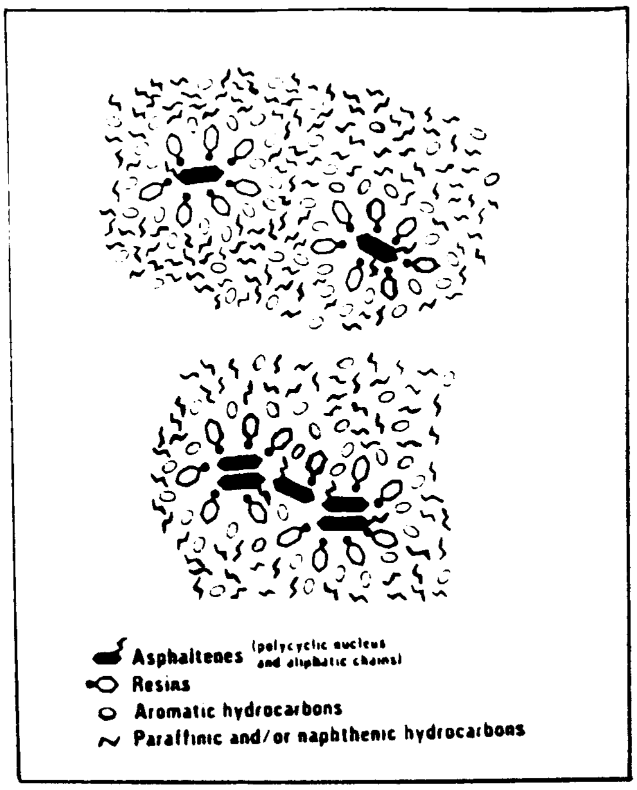


Figure 9.68: Macrostructure of Resins and Asphaltenes According to Tissot(157)

Effect of Asphaltenes on the Viscosity of the Binary Mixtures

The presence of asphaltenes strongly affects the viscosity behaviour of a liquid upon mixing. Those liquids which contain asphaltenes are usually termed "asphaltenes-bearing liquids" and those which do not "asphaltenes-free liquids".

The two mechanisms, previously proposed for the non-ideal viscosity behaviour of mixtures, are considerably enhanced by the presence of asphaltenes due to their polarity. If the heavy molecule (high molecular weight) is a polar asphaltene molecule, then coiling of the molecule and the occlusion of small molecules inside the lattice space (cage) will occur more easily. Therefore, the formation of clusters (micelles) is more probable so that increased non-ideality of viscosity behaviour would be expected for such mixtures.

Considering the solvated shell mechanism, the presence of asphaltenes will enhance the formation of the solvated shell, surrounding the asphaltenes micelle, due to their high polarity. Therefore the weak attraction forces between the solvent and the solute increase, resulting in a higher degree of non-ideality in the mixture viscosity.

To test this assumption, three powerful halogenated solvents of similar chemical structure, namely, carbon tetrachloride CCl_4, chloroform $CH\,Cl_3$, dichloromethane $CH_2\,Cl_2$; and tetrahydrofuran C_4H_8O (THF) were chosen to prepare binary mixtures with the heavy crude oil, which was asphaltenes-bearing, and of high viscosity, as described in Chapter 8. These solvents are of low viscosities compared to the heavy crude oil. However, their polarities differ widely, the dipole moments of CCl_4, $CHCl_3$, CH_2Cl_2 and THF being 0, 1.1, 1.8 and 1.7, respectively(7). The compositions of the binary mixtures are shown in Table 9.44. The measured values of the kinematic viscosity @ 10°C are shown in Table 9.45 and presented graphically in Figure 9.69.

Table 9.44: Composition of Heavy Crude Oil-Solvents Binary Mixtures

Mixtures	% weight of				
	Heavy Crude	CCl_4	$CHCl_3$	CH_2Cl_2	THF
Mix 1	90%	10%	-	-	-
Mix 2	70%	30%	-	-	-
Mix 3	30%	70%	-	-	-
Mix 4	90%	-	10%	-	-
Mix 5	70%	-	30%	-	-
Mix 6	30%	-	70%	-	-
Mix 7	90%	-	-	10%	-
Mix 8	70%	-	-	30%	-
Mix 9	30%	-	-	70%	-
Mix 10	90%	-	-	-	10%
Mix 11	70%	-	-	-	30%
Mix 12	30%	-	-	-	70%

Table 9.45: Kinematic Viscosities (cSt) at 10°C of Heavy Crude Oil-Solvents Binary Mixtures

Mixture	Kinematic Viscosity (cSt) @ 10°C
Heavy Crude Oil	2193
CCl_4	0.7084
$CHCl_3$	0.4248
CH_2Cl_2	0.4176
THF	0.6161
Mix 1	866.7
Mix 2	123.8
Mix 3	4.980
Mix 4	546.8
Mix 5	50.08
Mix 6	2.376
Mix 7	243.4
Mix 8	20.99
Mix 9	1.520
Mix 10	292.6
Mix 11	24.22
Mix 12	1.979

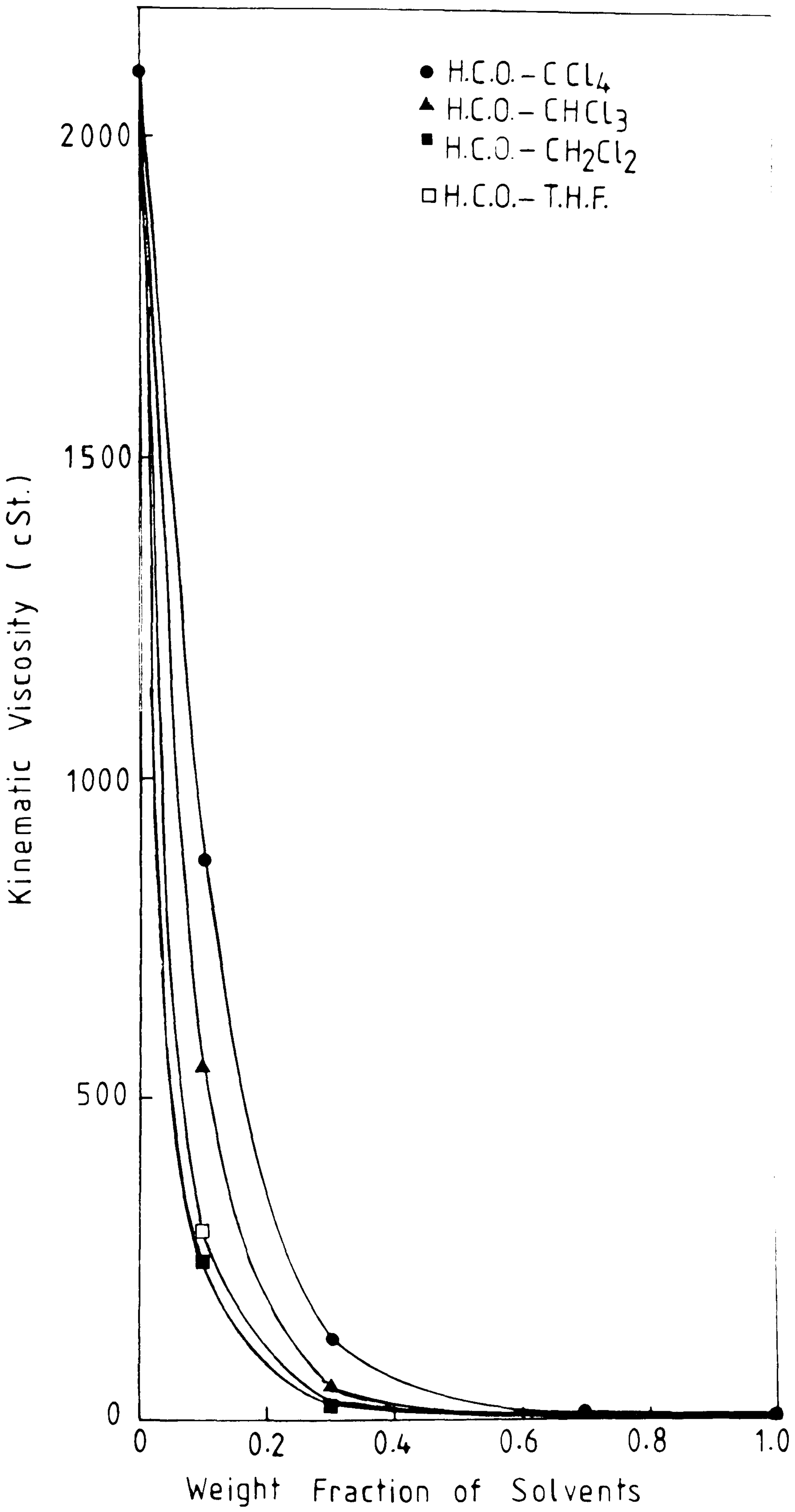


Figure 9.69: Kinematic Viscosities of Heavy Crude Oil-Solvents Binary Mixtures

It is clear from the data shown in Table 9.45 and presented in Figure 9.69, that the non-ideality of the mixtures viscosity increased with an increase in the polarity of the solvent, ie. the rate of decrease in the viscosity increased as the polarity of the solvent increased.

This observation provides evidence that the asphaltenes content plays a key role in the two proposed mechanisms discussed previously, mainly in enhancing the formation of clusters due to the initial addition of the lighter liquids. This is strongly supported by the measured viscosity values of all the binary mixtures tested in this study in that the highest non-ideality, ie. the highest rate of decrease in the viscosity, was exhibited by the mixtures comprising a component of high asphaltenes content, namely heavy crude oils and residue > 360°C.

9.3.6 Prediction of the Viscosity of Ternary Mixtures:

Crude Oils

Ternary mixtures were prepared by blending light, medium and heavy crude oil at different weight fractions (Table 8.5). The kinematic viscosities of mixtures were measured at 10, 20, 30, 40 and 60°C, by the ASTM D445(66)/IP7(16) standard method. The results are summarised in Table 9.46.

For real multi-component mixtures, the kinematic viscosity can be calculated using the equation,

$$\ln v_{mix} = \Sigma x_i \ln v_i \qquad 9.33$$

where,

v_{mix} = kinematic viscosity of mixture

v_i = kinematic viscosity of component i

x_i = mole, volume or weight fraction of component i.

As discussed previously, an excess function must be included to account for deviation from ideality. Thus equation 9.33 can be modified to give:

$$\ln v_{mix} = \Sigma x_i \ln v_i \pm (\ln v)^E \qquad 9.34$$

where

$(\ln v)^E$ is the excess function.

Table 9.46: Measured Viscosities of Crude Oils and Their Ternary Mixtures

	Kinematic Viscosity, cSt @				
Mixtures	10°C	20°C	30°C	40°C	60°C
Light crude oil	14.22	9.512	7.141	5.960	4.013
Medium crude oil	163.4	81.46	51.81	34.63	17.76
Heavy crude oil	2193	887.9	426.4	223.5	78.71
Mix 1	122.10	70.75	37.25	25.56	13.88
Mix 2	88.12	48.47	28.35	18.93	10.34
Mix 3	68.25	34.32	22.03	14.08	8.391
Mix 4	36.25	19.81	13.57	9.755	6.525
Mix 5	207.2	110.3	62.71	39.43	19.70
Mix 6	171.8	83.38	50.51	31.98	16.27
Mix 7	27.09	16.01	11.59	8.427	5.611
Mix 8	499.4	234.4	127.6	73.77	32.40

The excess function for a ternary mixture can be expressed by a three parameter equation as:

$$(\ln v)^E = a_{12} x_1 x_2 + a_{23} x_2 x_3 + a_{13} x_1 x_3 \qquad 9.35$$

where a_{ij} is the so-called interaction parameter between components i and j. To determine the value of these parameters, the viscosities of the pure components and three blends must be measured experimentally. Equations 9.34 and 9.35 can then be used to calculate corresponding interaction parameters.

Table 9.47 presents calculated values of a_{12}, a_{23} and a_{13} at five temperatures: 10, 20, 30, 40 and 60°C. The values are based on measured viscosities of mixtures 6, 7 and 8. To check the validity of this model, viscosities of mixtures 1, 2, 3, 4 and 5 were calculated by equations 9.34 and 9.35. Calculated and measured viscosities are in good agreement for mixture 1, in which the deviation is less than 8.1% at all temperatures (Table 9.48). For other mixtures however, the deviation, particularly at low temperatures, is rather high. For example, the percentage error in predicted viscosity for mixture 3 at 20°C is 26.1%. The lowest deviations were obtained at the higher temperatures (40° and 60°C).

The fourth interaction parameter (a_{123}) was added to equation 9.35 to account for interactions between components 1, 2 and 3:

$$(\ln v)^E = a_{12}\, x_1\, x_2 + a_{23}\, x_2\, x_3 + a_{13}\, x_1\, x_3 + a_{123}\, x_1\, x_2\, x_3 \qquad 9.36$$

The four parameters can be calculated by solving a set of four simultaneous equations and using experimental data on mixtures 1, 6, 7 and 8 (Table 9.49). Based on these results, the viscosities of mixtures 2, 3, 4 and 5 were calculated by equations 9.34 and 9.36. Table 9.48 shows that predicted and measured viscosities are in excellent agreement. The deviation in most cases is less than 6%.

The ASTM D341(66) method and Refutas index method(96) are very widely used in the oil industry to predict the viscosity of petroleum products mixtures. However, although introduced in the early 1940's, these two methods are only for petroleum products. No approaches have been published or adopted by the oil industry to predict the viscosity of multi-mixtures of crude oil. This may be due to the complex nature of crude oils resulting in large deviations from actual values. Consequently, an attempt was made to test these two methods using data for ternary crude oil mixtures, and to compare the results with those obtained from the 4-parameter correlation which had been developed, equations 9.34 and 9.36.

The ASTM D341(66) method is based on conventional viscosity-temperature charts. The kinematic viscosity of a binary mixture can be determined at any temperature provided the kinematic viscosities at two temperatures are known for each component. Seven standard charts are available covering wide viscosity and temperature ranges.

The procedure to obtain blend viscosities requires that viscosity-temperature lines of components be plotted and then blended by linear proportioning at a constant viscosity (measuring the distance along a horizontal line). Since measuring the distance on the chart is time-consuming and inaccurate, Twu and Bulls(90) used a modified Wright's equation(67,68) to predict blend viscosity:

$$\ln \ln (v + 0.7) = m \ln T + b \qquad 9.37$$

where v is the kinematic viscosity in centistokes, T is the absolute temperature, and m and b are constants for a particular oil. The two parameters m and b can be calculated from two viscosity measurements. To calculate the viscosity of a multi-component mixture, the mixture is split into a series of binary blends.

This method was used to predict the viscosities of crude oil mixtures 1, 2, 3, 4 and 5 (Table 9.50). However, the deviation is clearly rather high in most cases. For example, at 60°C, the error is 23% for all blends except mixture 5. It can therefore be concluded that the ASTM D341 method cannot predict the viscosities of crude oil ternary mixtures with reasonable accuracy.

Similar results were obtained when the Refutas index method was applied to crude oil mixtures. This method was developed to predict blend viscosities of all petroleum components from gasoline to vacuum residue. The Refutas function or blending index is given by:

$$I = f(v) = 23.097 + 33.468 \log_{10} \log_{10} (v + 0.8) \qquad 9.38$$

where I is the Refutas index and v is the kinematic viscosity.

To determine the viscosity of a mixture by this method, Refutas indices of components are determined based on known viscosities. The Refutas index of the mixture is then calculated, based on the weight fraction of each component:

$$I_{\beta} = \sum_{i}^{n} I_i \, x_i \qquad 9.39$$

where I_{β} is the Refutas index of the mixture, and x_i is the weight fraction of component i. Once I_{β} is determined, the mixture viscosity can be read directly from a corresponding table or deduced from equation 9.38.

This method was used to predict the viscosities of mixtures 1, 2, 3, 4, and 7 at 10, 20, 30, 40 and 60°C. However, as shown in Table 9.50, calculated and measured viscosities are not in good agreement. The deviation for most cases is 15%.

Finally, a comparison between the three methods, ASTM D341, Refutas Index, and the 4-parameter model is shown in Figures 9.70, 9.71, 9.72 and 9.73. The figures present experimental and calculated viscosities for mixtures 2, 3, 4 and 5 over a temperature range of 10-60°C. It is clearly demonstrated that, the 4-parameter model gives the best representation of experimental data over the whole temperature range, and that the greatest deviations with the ASTM D341 and Refutas index methods are over low temperatures. Figure 9.74 presents the deviations of the calculated kinematic viscosities by the 4-parameter equation of mixtures, 2, 3, 4 and 5 as a function of temperature.

Table 9.47: Calculated Values of a_{12}, a_{23} and a_{13} as a Function of Temperature

Temp °C	a_{12}	a_{23}	a_{13}
10	-0.569	-3.869	-0.769
20	1.188	-3.566	-1.791
30	-1.493	-3.303	-0.553
40	-0.567	-3.269	-1.227
60	-0.730	-2.315	-0.990

Table 9.48: Measured and Calculated Viscosities (cSt) of Mixtures 1, 2, 3, 4, and 5 Using the 3-Parameter and 4-Parameter Models

Mixture	Temp oC	Measured	3-Parameter Expression		4-Parameter Expression	
			Calculated	Deviation %	Calculated	Deviation %
1	10	122.1	120.9	-1.03		
	20	70.75	65.06	-8.05		
	30	37.25	36.56	-1.85		
	40	25.56	23.85	-6.68		
	60	13.88	12.99	-6.44		
2	10	88.12	78.61	-10.79	97.17	10.27
	20	48.47	51.81	6.89	51.46	6.17
	30	28.35	24.22	-14.57	29.08	2.57
	40	18.93	18.25	-3.59	19.60	3.54
	60	10.34	10.26	-0.77	10.97	6.09
3	10	68.25	56.89	-16.65	67.60	-0.95
	20	34.32	43.28	26.09	32.51	-5.27
	30	22.03	17.81	-19.16	20.90	-5.13
	40	14.08	14.89	5.80	13.62	-3.27
	60	8.390	8.410	0.23	8.060	-3.93
4	10	36.25	38.83	7.13	44.56	22.92
	20	19.81	32.43	63.71	20.49	3.44
	30	13.57	12.85	-5.32	14.79	9.02
	40	9.760	11.54	18.32	9.540	-2.22
	60	6.530	6.680	2.38	5.690	-8.70
5	10	207.2	184.0	-11.20	209.2	0.97
	20	110.3	92.02	-16.57	113.7	3.06
	30	62.71	52.71	-15.95	59.63	-4.91
	40	39.43	32.39	-17.85	38.63	-2.03
	60	19.70	17.01	-13.66	19.33	-1.88

Table 9.49: Calculated Values of a_{12}, a_{23}, a_{13} and a_{123} as a Function of Temperature

Temp °C	a_{12}	a_{23}	a_{13}	a_{123}
10	0.178	-1.259	4.442	1.978
20	-1.279	-1.483	-4.499	10.586
30	-0.714	-0.916	-3.274	-0.298
40	-1.595	-1.198	-3.515	5.204
60	-1.391	-1.078	-2.511	4.475

Table 9.50: Measured and Predicted Viscosities (cSt) for Mixtures 1, 2, 3, 4 and 5 Using ASTM D341 and Refutas Index Method

			ASTM D341		REFUTAS Index	
Mixture	Temp oC	Measured	Calculated	Deviation %	Calculated	Deviation %
1	10	122.1	114.2	-6.45	142.0	16.29
	20	70.75	59.41	-16.03	61.60	-12.93
	30	37.25	34.69	-6.88	46.90	25.90
	40	25.56	21.61	-15.45	32.10	25.58
	60	13.88	10.25	-26.13	16.50	18.87
2	10	88.12	79.59	-9.67	95.30	8.72
	20	48.47	42.41	-12.51	47.70	-1.59
	30	28.35	25.30	-10.74	34.10	20.28
	40	18.93	16.09	-15.01	24.10	27.31
	60	10.34	7.890	-28.64	13.00	25.72
3	10	68.25	52.55	-23.00	61.00	-10.62
	20	34.32	28.94	-15.67	33.24	-3.26
	30	22.03	17.17	-19.33	23.50	6.67
	40	14.08	11.59	-17.65	17.30	22.86
	60	8.390	5.930	-29.31	9.920	18.22
4	10	36.25	22.94	-22.91	38.60	6.48
	20	19.81	17.66	-10.88	22.76	14.58
	30	13.57	12.04	-11.29	16.20	19.38
	40	9.760	8.550	-12.32	12.50	28.13
	60	6.530	4.940	-24.35	7.520	15.24
5	10	207.2	253.3	22.25	245.0	18.26
	20	110.3	123.6	12.09	93.80	-14.80
	30	62.71	68.31	8.93	73.20	16.72
	40	39.43	40.46	2.61	47.40	20.21
	60	19.70	17.67	-10.29	22.70	15.22

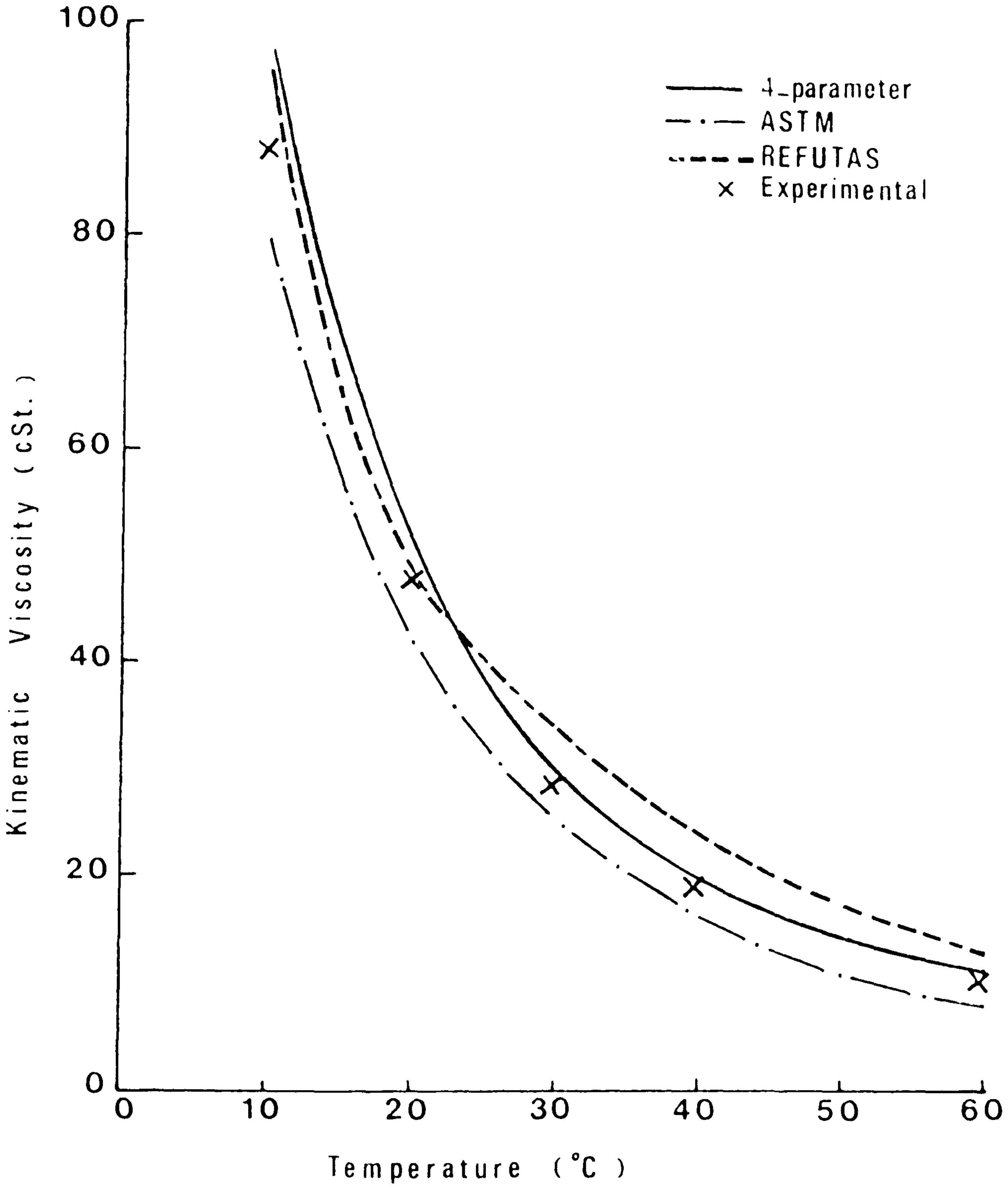


Figure 9.70: Experimental and Predicted Viscosities, as a Function of Temperature, for Mixture 2

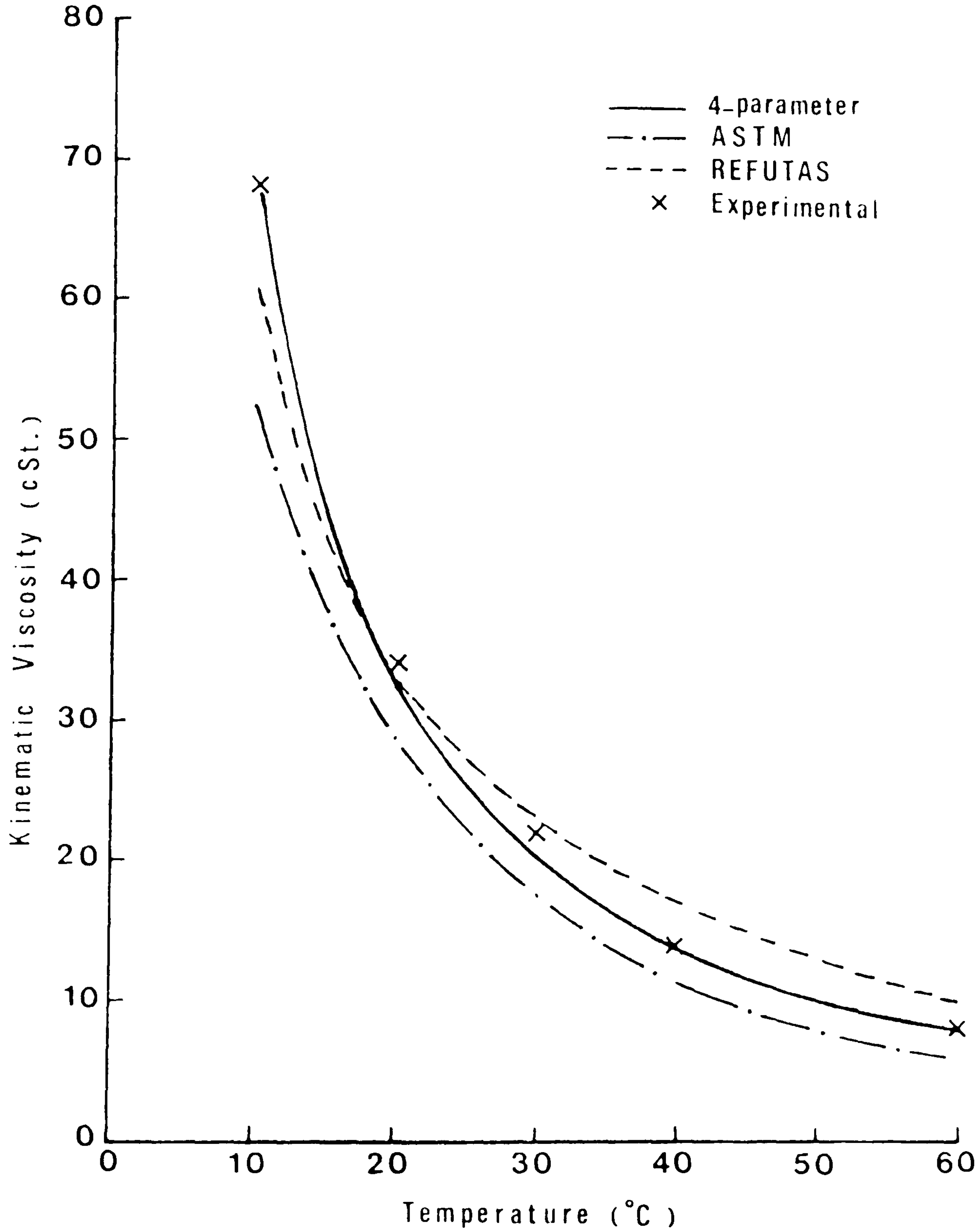


Figure 9.71: Experimental and Predicted Viscosities, as a Function of Temperature, for Mixture 3

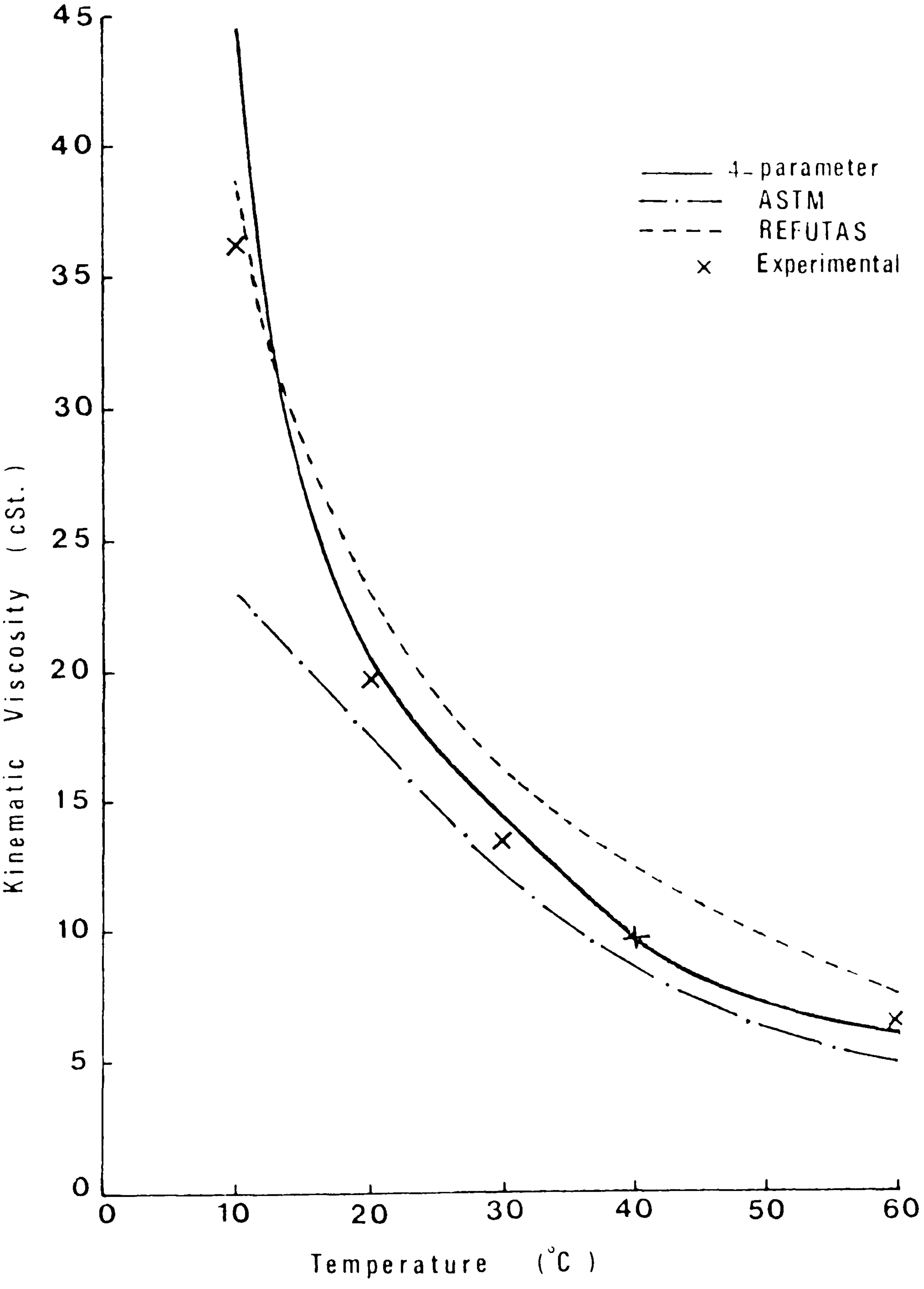


Figure 9.72: Experimental and Predicted Viscosities as a Function of Temperature for Mixture 4

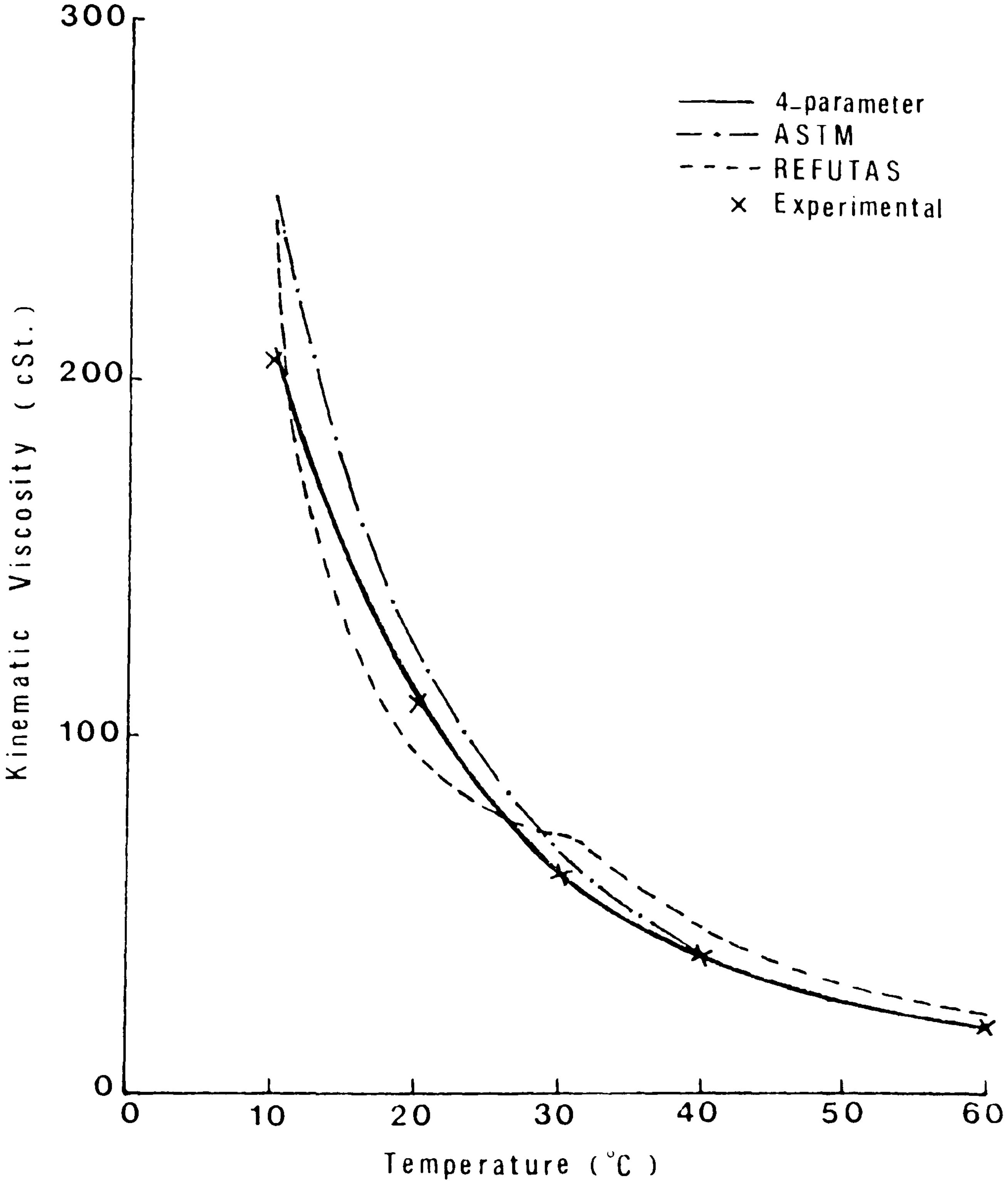


Figure 9.73: Experimental and Predicted Viscosities, as a Function of Temperature, for Mixture 5

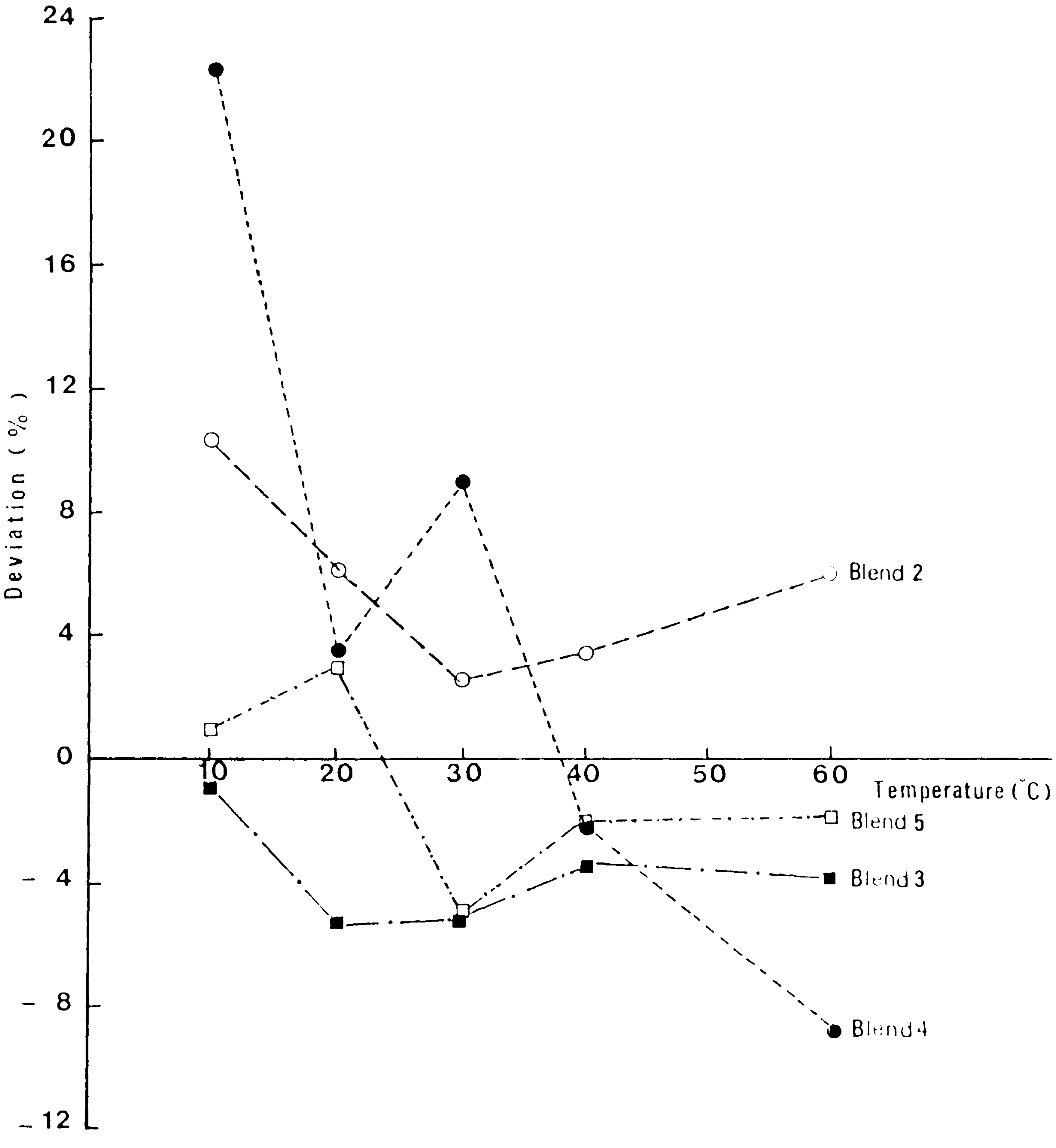


Figure 9.74: Deviations of the Calculated Kinematic Viscosities by the 4-Parameter Equation for Mixtures 2, 3, 4 and 5 as a Function of Temperature

Base Oils:

Viscosity is considered as the most important criteria in lube oil manufacture. Different types of base oils are usually blended together to produce the end-use lube oil to the required specifications. Hence, accurate prediction of the viscosity of the final blends is essential in planning for the production of newly formulated lube oils. Moreover, many calculations and estimations of other characteristics of the end-use lube oil formulation depend strongly upon the accuracy of estimation of the final mixture viscosity.

Therefore, an attempt was made to test the validity of the modified 4-parameter correction (equations 9.34 and 9.36), for the prediction of the kinematic viscosity of base oils ternary mixtures.

Three new types of additive-free base oils (spindle oil (light), base oil (medium), and bright stock (heavy)) were chosen to test the correlation. These base oils were provided by Kuwait Lube Oil Company (KLOC). Eigh mixtures of different compositions by weight were prepared from the three individual base oils. The compositions of the mixtures are shown in Table 9.51.

The kinematic viscosity of the components and mixtures at different temperatures are shown in Table 9.52. Mixtures 1, 6, 7 and 8 were used to compute the interaction parameters a_{ij} and a_{ijk}.

A comparison was made between the ASTM-D341$^{(66)}$ method, Refutas index method$^{(96)}$, and the 4-parameters correlation (equations 9.34 and 9.36). The percent deviation of the calculated viscosity from the measured values for each method are presented in Table 9.53. Mixtures 1, 6, 7 and 8 were not included in Table 9.53 because they were used to compute the interaction parameters.

It is clear that the predictions from all three methods are in excellent agreement with the experimental data. However, the new correlation gave the best results, with average absolute deviations of 1.95% to 2.0% over a temperature range from 20-100°C. The data obtained by this method is presented in Figure 9.75.

Table 9.51: Weight Fractions of Base Oil Mixtures

Blend No	Light Base Oil	Medium Base Oil	Heavy Base Oil
1	0.30	0.30	0.40
2	0.30	0.50	0.20
3	0.40	0.50	0.10
4	0.55	0.40	0.05
5	0.20	0.30	0.50
6	0.10	0.70	0.20
7	0.70	0.10	0.20
8	0.10	0.20	0.70

Table 9.52: Kinematic Viscosities of the Individual Base Oils and their Mixtures at Different Temperatures

Blend No	Kinematic Viscosity (cSt) @		
	20°C	40°C	100°C
Light base oil	68.43	26.05	4.655
Medium base oil	369.4	109.1	12.01
Heavy base oil	2011	454.0	29.46
1	396.0	115.8	12.48
2	288.5	89.32	10.44
3	210.8	67.40	8.787
4	152.0	51.46	7.312
5	561.0	155.5	15.41
6	419.6	121.5	13.10
7	146.6	49.76	7.271
8	951.3	242.3	20.36

Table 9.53: Calculated Kinematic Viscosities of Base Oil Mixtures (2, 3, 4 and 5) using the 4-Parameter Correlation, ASTM-D341 Method and Refutas Index Method

Mix No	Temp (°C)	Exp vis. (cSt)	4-Parameters model		ASTM-D341		REFUTAS Index	
			Calc vis (cSt)	% dev*	Calc vis (cSt)	% dev	Calc vis (cSt)	% dev
2	20	288.5	294.1	1.96	292.1	1.24	278.0	-3.65
	40	89.32	87.63	-1.88	92.67	3.75	85.77	-3.97
	100	10.44	10.60	1.60	11.45	9.70	10.93	4.73
3	20	210.8	215.7	2.32	208.3	-1.20	201.1	-4.62
	40	67.40	65.84	-2.31	68.09	1.03	64.83	-3.82
	100	8.787	8.950	1.90	9.058	3.05	9.308	5.89
4	20	152.0	156.7	3.11	157.0	3.30	154.5	1.65
	40	51.46	49.68	-3.47	55.17	7.20	49.29	-4.21
	100	7.312	7.520	2.90	8.202	12.20	7.907	8.16
5	20	561.0	558.8	-0.39	563.5	0.45	530.1	-5.51
	40	155.5	156.7	-1.74	154.6	-0.61	146.7	-5.68
	100	15.41	15.17	-1.60	15.05	-2.30	14.35	-6.85
%AAD**								
	20			1.95		1.55		3.86
	40			2.1		3.15		4.42
	100			2.0		6.81		6.42
%MAD***								
	20			1.75		0.95		-3.03
	40			-1.73		2.84		-4.42
	100			1.2		5.66		2.98

$$* \ \% \text{ Deviation} = \frac{\text{Calculated value - Experimental value}}{\text{Experimental value}} \times 100$$

** % AAD = Absolute Average Deviation

*** % MAD = Mean Average Deviation

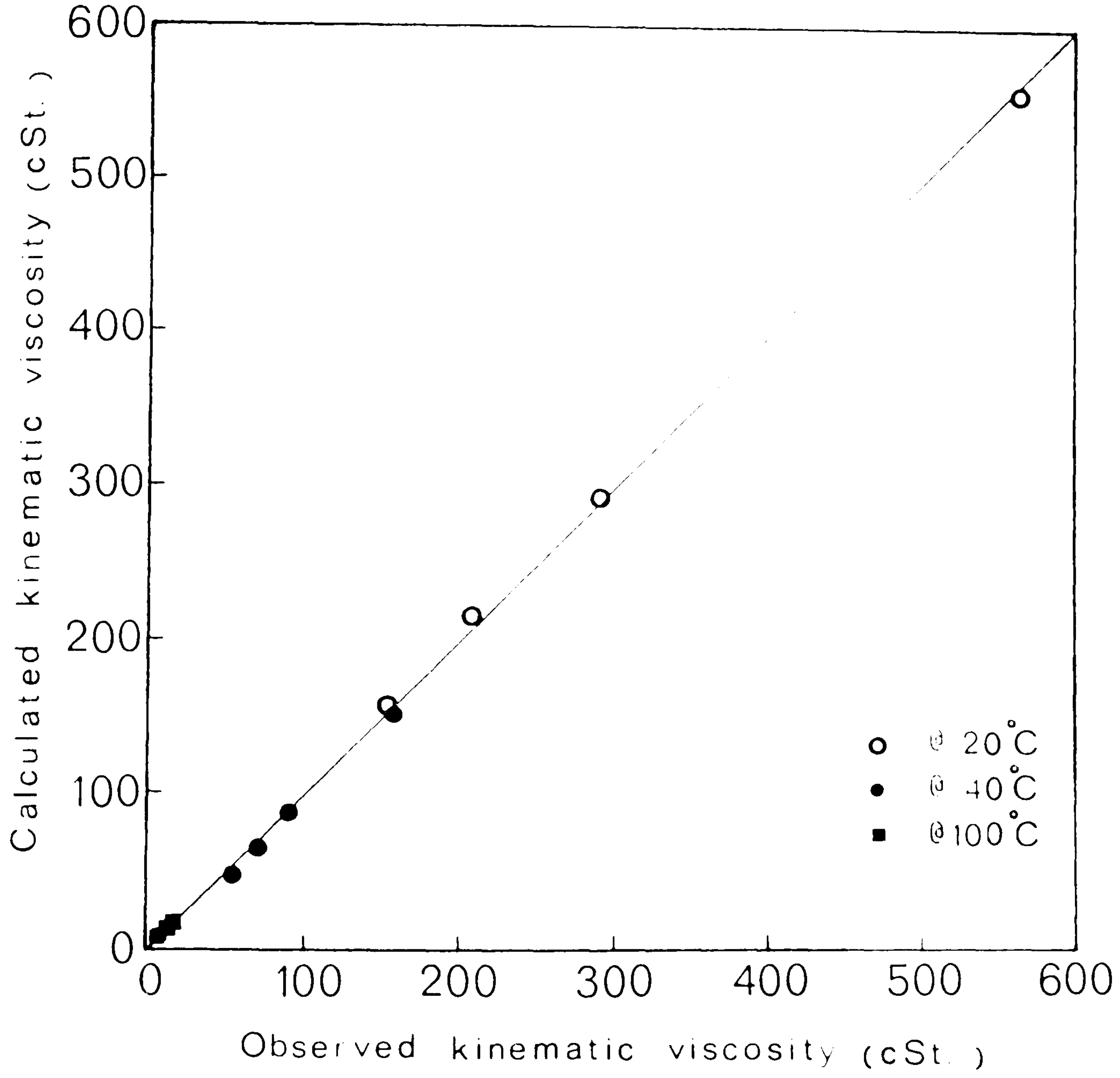


Figure 9.75: Kinematic Viscosities of Base Oil Mixtures 2, 3, 4 and 5 Using the 4-Parameter Equation

9.4 POUR POINTS OF CRUDE OILS AND PETROLEUM PRODUCTS

As discussed in Chapter 6, pour point is considered, together with the viscosity, as one of the most important low - temperature flow properties of petroleum oils. Since the determination of freezing point for dark liquids or multi-component mixtures (such as petroleum oils) is difficult, pour point measurements are usually considered as an alternative to provide a very good indication of freezing point.

Pour point reflects the behaviour of the molecules of a liquid upon cooling, which depends on the type of interactions between them. Generally, the interactions between molecules depend strongly on the chemical compositions of the liquid (e.g. the type of chemical bonding, existing functional groups, wax content, asphaltenes content and the existence of polar and non-polar compounds). Therefore, changes in the type and/or the intensity of the interactions between the molecules due to external forces, e.g. mixing, may lead to changes in the pour point of the liquid.

Consequently, the measured effects of mixing on the pour points of crude oils, base oils and petroleum products are presented in this section. The effect of wax content and of asphaltenes content upon the pour points of binary mixtures is also discussed.

9.4.1 Pour Point of Crude Oil Mixtures

The pour points of crude oils and their binary mixtures were determined by the standard method ASTM (66) /IP (16). The results are summarised in Table 9.54. The wax content and asphaltenes content were also determined and these data are also summarised in Table 9.54.

The heavy crude oil would be expected to have the highest pour point, since it has a high density and a high molecular weight. However, it actually exhibited a lower pour point than the other crudes examined, due to its lower wax content. Figure 9.76 shows the relationship between the pour points of the crude oils and their corresponding wax contents.

Clearly, the pour point increased linearly with wax content, which would be expected since it is controlled by the formation of a net-work of wax, which solidifies on cooling. The, mainly paraffinic, wax net-work causes "wax-interlocking" which traps other oil molecules causing total prevention of liquid flow (corresponding to the pour point). Thus high wax contents (i.e. high paraffins contents) in a liquid result in the formation of a wax net-work at higher temperatures, resulting in higher pour points.

Table 9.54 Pour Points, Wax Contents and Asphaltenes Contents for Crude Oils and Their Binary Mixtures

Crude Oil Asphaltenes	% Composition			Pour Point	Wax Content	Asphaltenes Content
	L	M	H	(°C)	% wt	% wt
Light crude oil	100			-18	4.8	0.9
Medium crude oil		100		-14	5.4	4.4
Heavy crude oil			100	-23	0.7	7.8
mix. 1	90	10		-13	5.0	1.2
mix. 2	60	40		-13	4.9	2.1
mix. 3	40	60		-12	5.3	3.2
mix. 4	10	90		-12	5.1	3.9
mix. 5	30	70		-13		
mix. 6	50	50		-13		
mix. 7	90		10	-16	4.1	1.6
mix. 8	60		40	-26	3.1	3.8
mix. 9	40		60	-36	2.4	5.1
mix. 10	10		90	-28	1.4	7.0
mix. 11	30		70	-36		
mix. 12	50		50	-34		
mix. 13		90	10	-17	5.0	4.5
mix. 14		60	40	-28	3.6	5.8
mix. 15		40	60	-32	2.7	6.5
mix. 16		10	90	-25	0.9	7.5
mix. 17		30	70	-31		
mix. 18		50	50	-29		

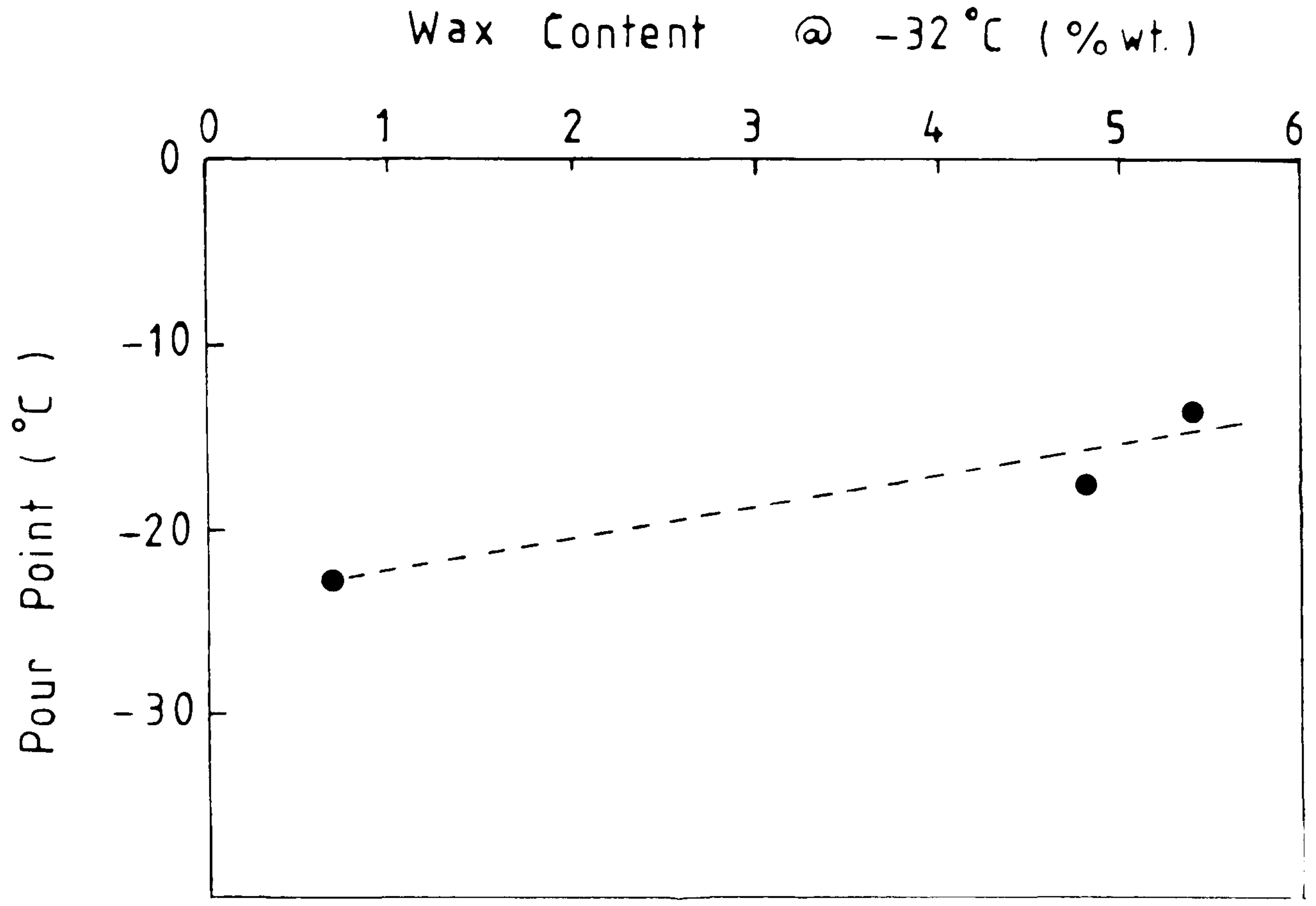


Figure 9.76 The Relationship between the Wax Contents @ -32°C of the Crude Oils and Their Corresponding Pour Points

Effect of mixing upon pour point

The pour point data given in Table 9.54 are presented graphically in Figures 9.77, 9.78 and 9.79. It is clear that the pour point does not blend ideally and that its behaviour varies with the nature of the complex.

For the light-heavy and medium-heavy crude oil mixtures, the mixture pour points were less than those of the components. Thus each component acted as a pour point depressant to the other, i.e. mixing light or medium crude oil with the heavy crude oil improved the pour point of the mixture and hence the storage and transportation properties at low temperatures. This is also achieved in practice by adding polymeric pour point depressants to the oils.

The minimum pour point of light-heavy and medium-heavy crude oil mixtures systems were observed at 0.3 - 0.4 weight fraction of the lighter component. This proportion is similar to that observed for the greatest non-ideality of the binary mixtures viscosity (v^E) for the crude oils.

The pour points of the light-medium crude oil binary mixtures were slightly higher than those of the two components (Figure 9.77).

9.4.2. Pour Point of Base Oils and Petroleum Products Mixtures

The pour points of the light, medium, heavy and bright stock base oils and their binary mixtures are summarised in Table 9.55 and presented graphically in Figure 9.80. It is clear that the pour points of the mixtures are higher than those of the components, i.e. in all cases mixing elevated the pour points.

Light and heavy base oils were mixed, separately, with asphaltenes - bearing (4.8% wt.) straight run residue > 360°C having the characteristics shown in Table 9.11. The compositions and pour points of the prepared binary mixtures are summarised in Table 9.56.

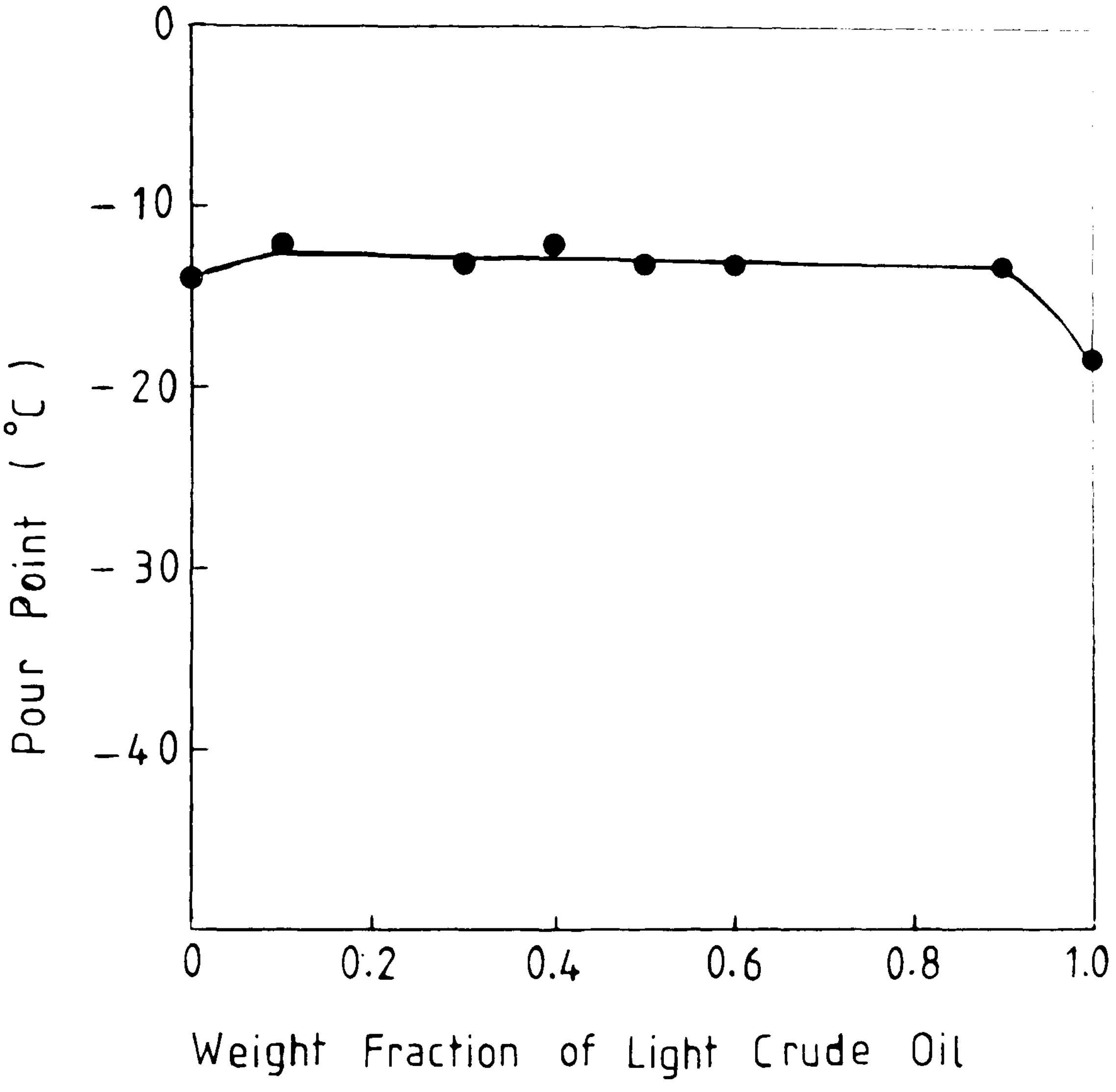


Figure 9.77 Pour Points of Light-Medium Crude Oils Binary Mixtures

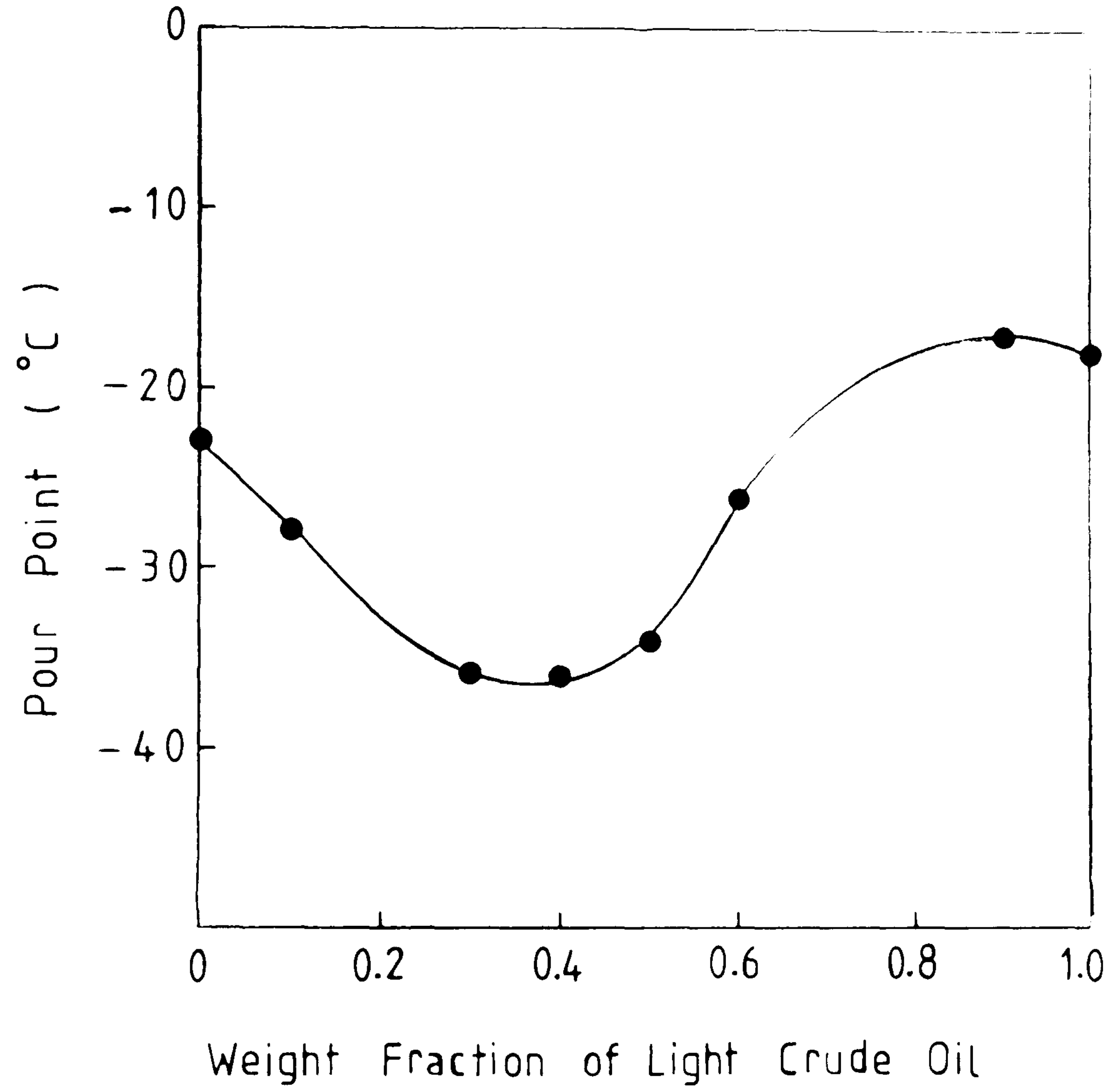


Figure 9.78 Pour Points of Light-Heavy Crude Oils Binary Mixtures

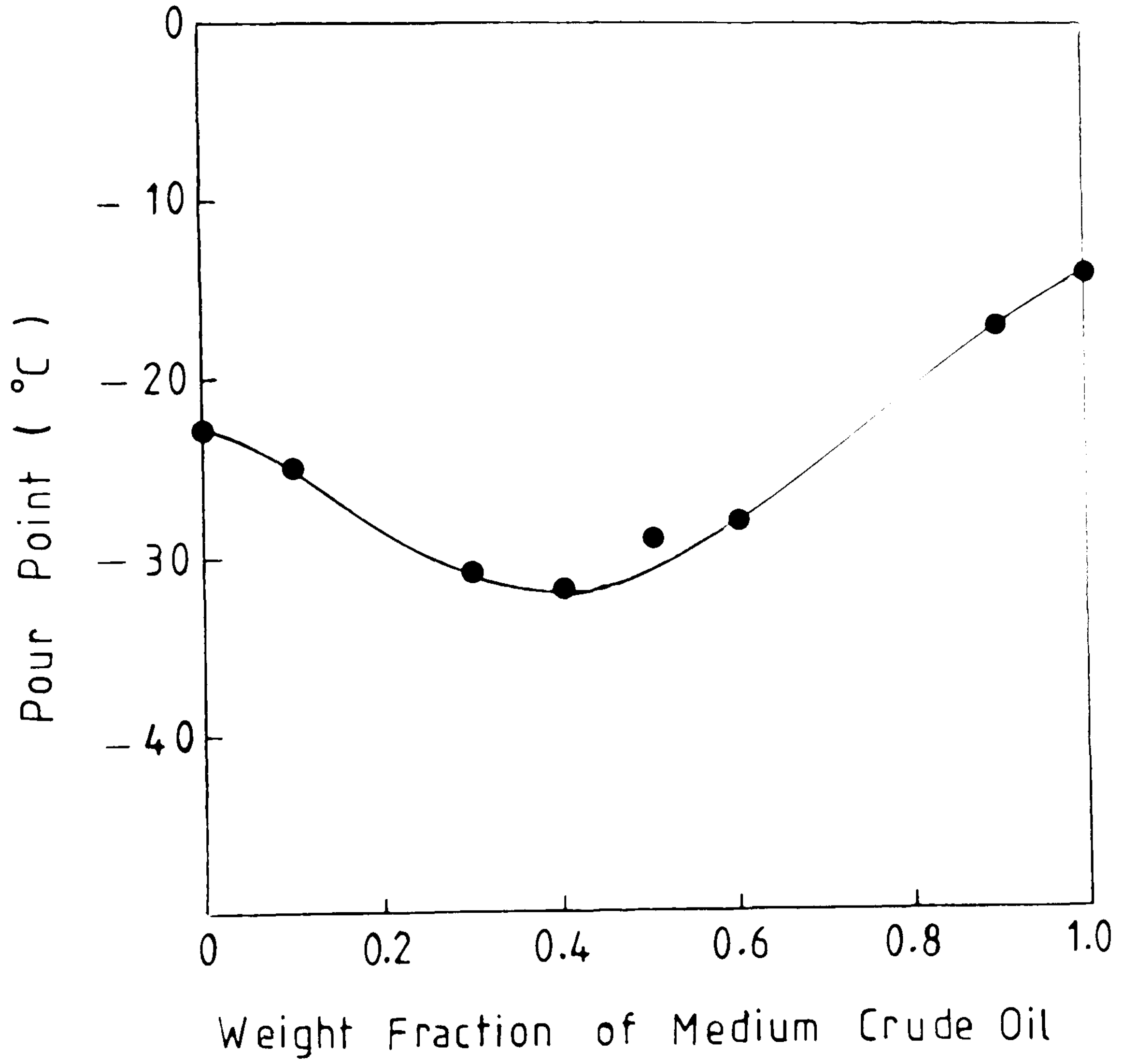


Figure 7.79 Pour Points of Medium-Heavy Crude Oils Binary Mixtures

and presented graphically in Figure 9.81. A depression of pour point occurred with both binary mixtures.

Table 9.55 Pour Points of Base Oils and Their Binary Mixtures

Base Oils	Pour Point (°C)
light base oil	-21
medium base oil	-17
heavy base oil	-15
bright stock	-14
mix. 1	-14
mix. 2	-14
mix. 3	-14
mix. 4	-14
mix. 5	-13
mix. 6	-14
mix. 7	-14
mix. 8	-16
mix. 9	-15
mix. 10	-14
mix. 11	-14
mix. 12	-16
mix. 13	-13
mix. 14	-14
mix. 15	-14
mix. 16	-14

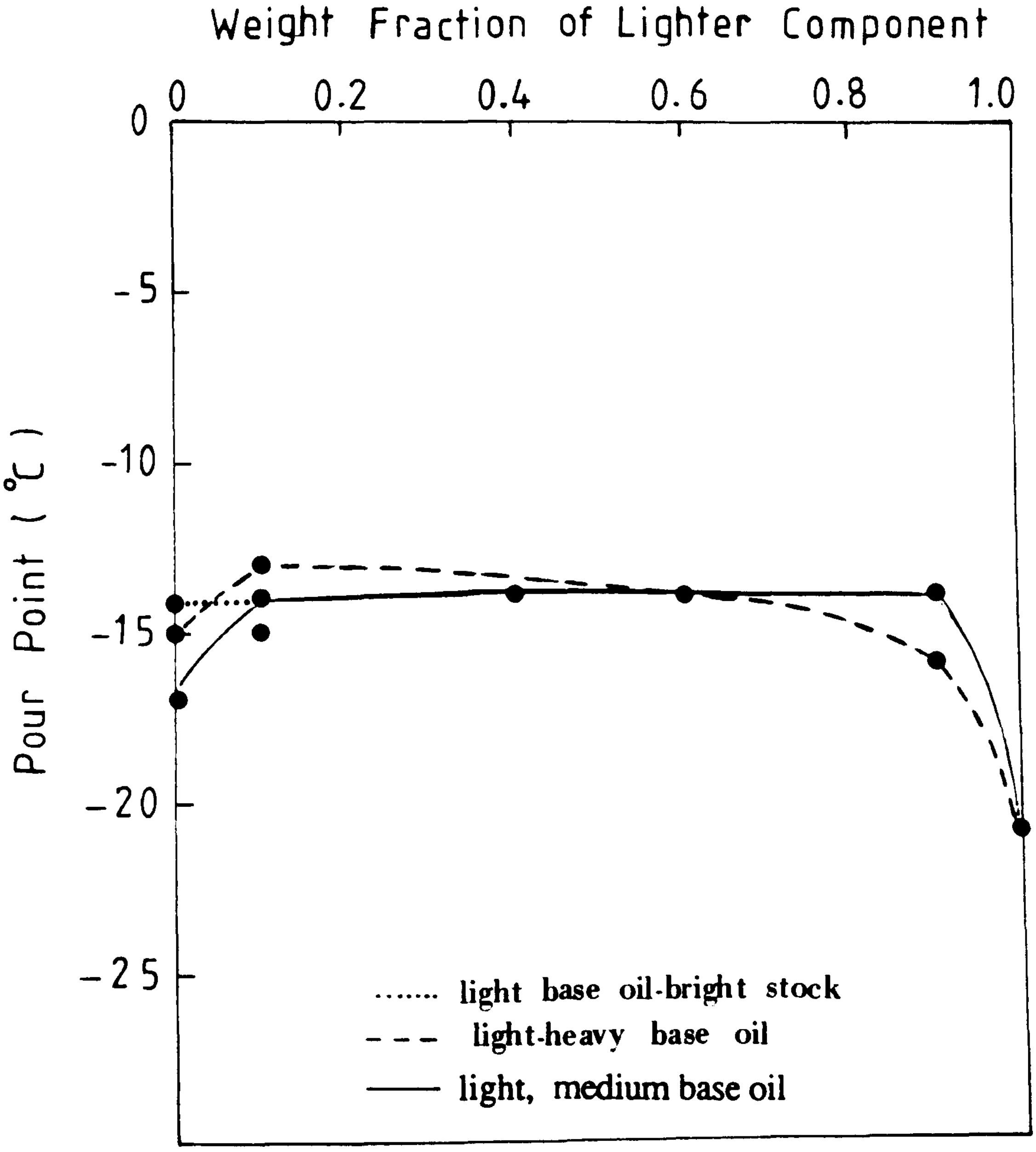


Figure 9.80 Pour Points of Base Oils Binary Mixtures

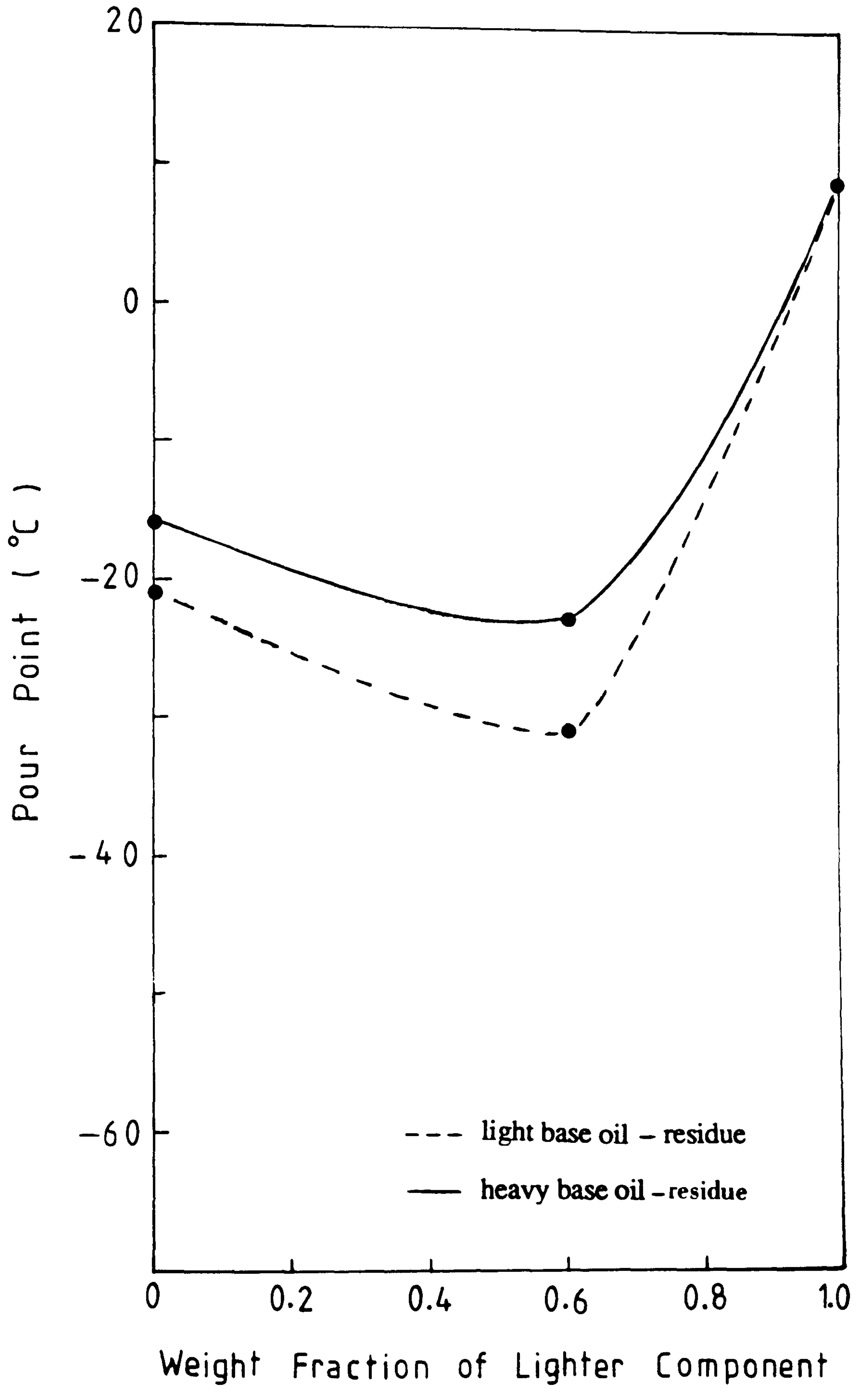


Figure 9.81 Pour Points of Binary Mixtures of Light Base Oil, Heavy Base Oil and Residue

Table 9.56 Pour Point of Selected Base Oils - Petroleum Products (Asphaltenes Rich) Binary Mixtures

	Composition (%wt)			Pour Point
	LBO	HBO	Res.	(°C)
light base oil	100	-	-	-21
heavy base oil	-	100	-	-15
residue >360°C	-	-	100	+10
mix. 1	60		40	-31
mix. 2		60	40	-23

9.4.3 The Effect of Wax Content and Asphaltenes Content

Wax content and asphaltenes content, both blend linearly, i.e. they obey the simple mixing rule,

$$P_{mix} = \sum x_i P_i \qquad 9.40$$

where,

P_{mix} = wax, or asphaltenes, content of mixture.

P_i = wax, or asphaltenes, content of component i.

x_i = mole, volume or weight fraction.

Table 9.54 summarises the wax contents and asphaltenes contents of the curde oils and their mixtures in this study. The data are presented graphically in Figures 9.82 and 9.83.

Because petroleum oils comprise mixtures of many hydrocarbons, the waxes precipitate by cooling over a temperature range which varies according to the paraffin content of the oil. Table 9.57 shows the proportions of wax separated - out from the light, medium and heavy crude oils at different temperatures. The data are presented graphically in Figure 9.84.

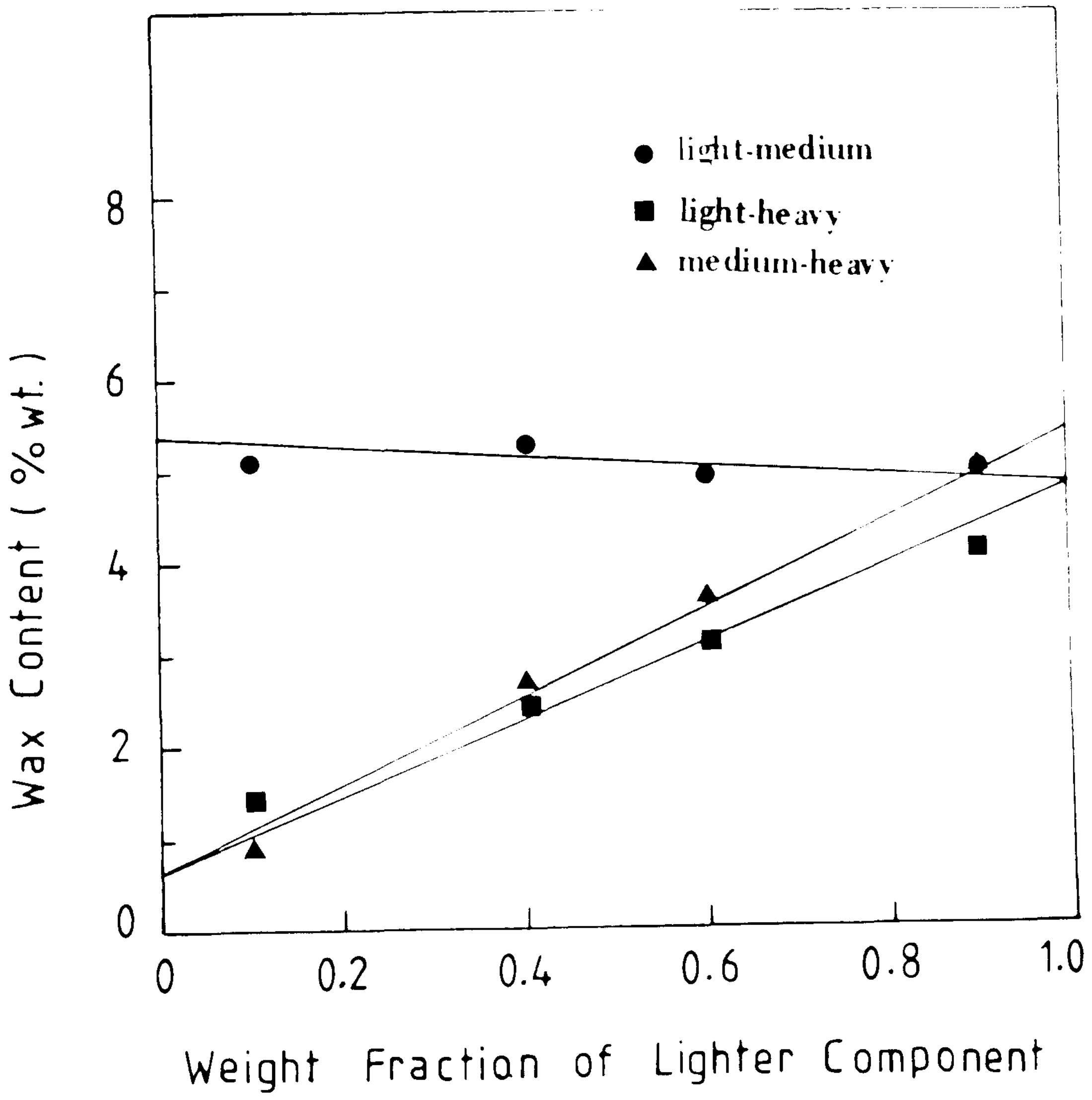


Figure 9.82 Wax Content @ -32°C of Crude Oil Binary Mixtures

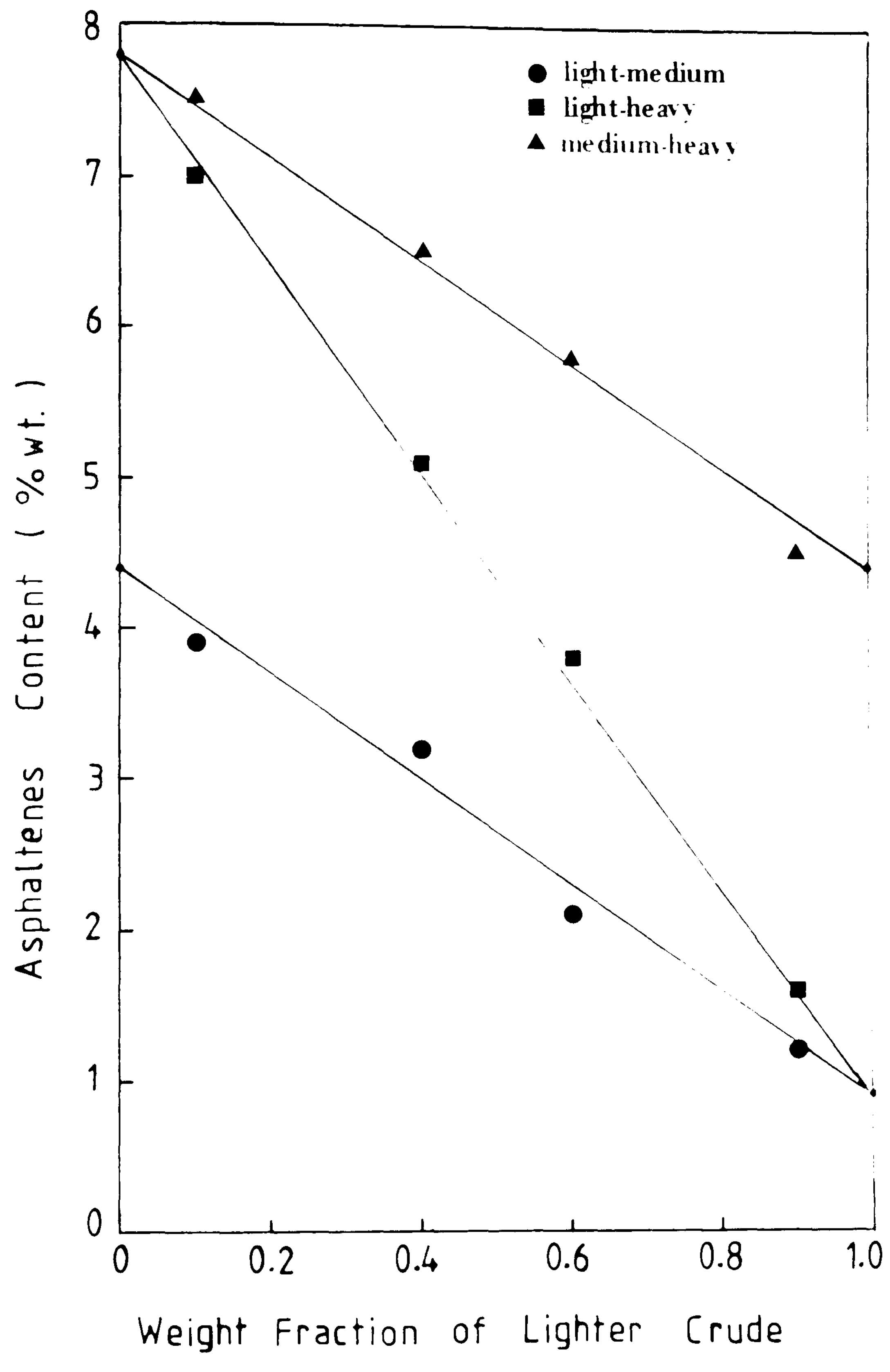


Figure 9.83 Asphaltenes Contents of Crude Oil Binary Mixtures

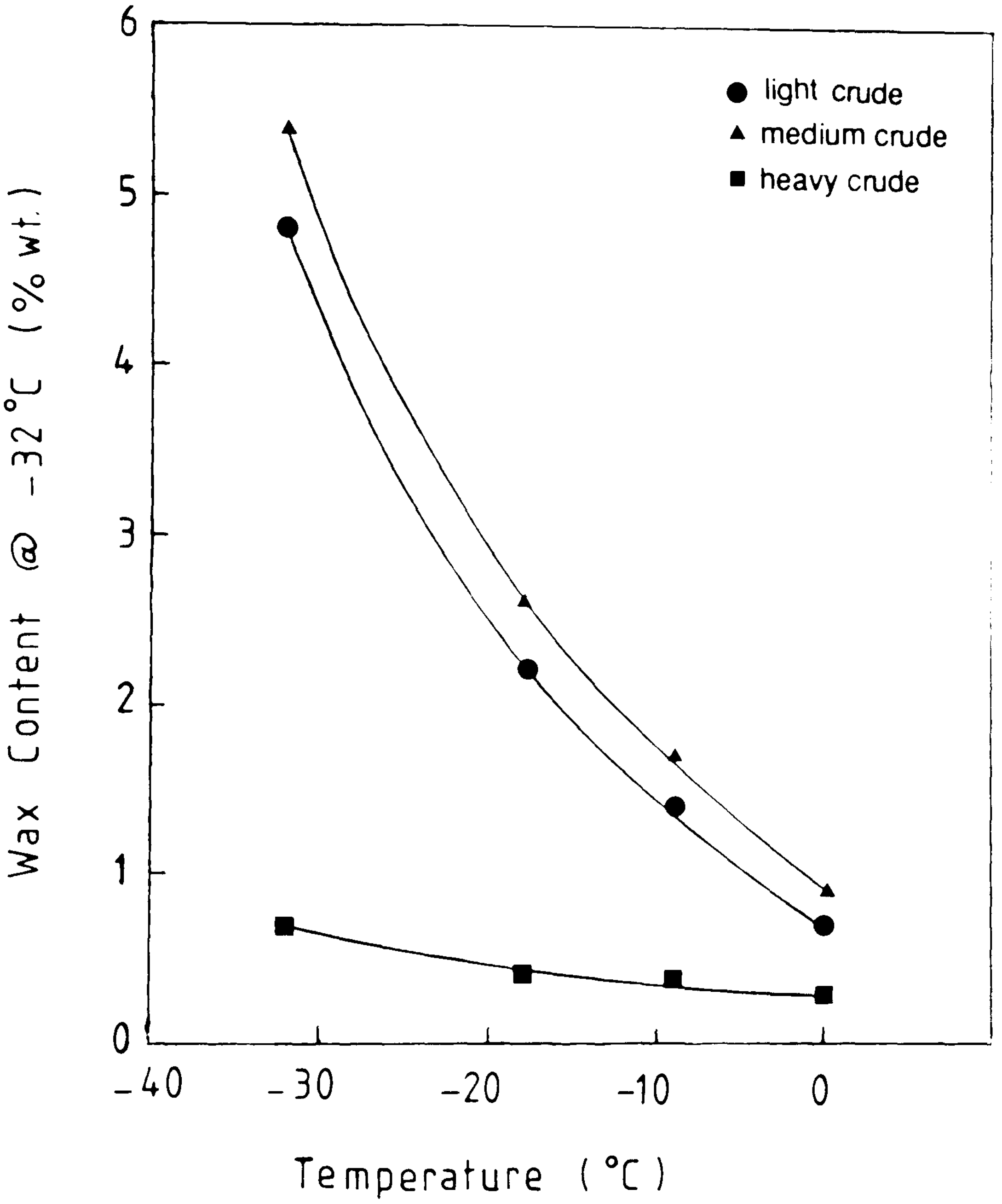


Figure 9.84 Wax Content of Light, Medium and Heavy Crude Oils Separated at Different Temperatures

Table 9.57 The Proportions of Wax Separated - out from the Light, Medium and Heavy Crude Oils at Different Temperatures

Crude Oil	Wax proportions (wt %) separated-out at			
	0°C	-9°C	-18°C	-32°C
light crude oil	0.7	1.4	2.2	4.8
medium crude oil	0.9	1.7	2.6	5.4
heavy crude oil	0.3	0.4	0.4	0.65

Clearly, the amount of wax separated from the heavy crude (low wax content) did not vary significantly with temperature. The proportion separated from the light and medium crudes, of initially high wax content, increased significantly with decreasing temperature. It can be deduced from this that petroleum oils of low wax content solidify, as a bulk, sharply when the pour point is reached although it occurs at lower temperatures. Conversely, although petroleum oils of high wax contents have higher pour points, they solidify gradually over a wide temperature range until a complete solidification (pour point) is reached. Hence,low wax-content (or wax-free) oils transfer from a liquid to a solid-like phase upon cooling, while those of high wax content pass through an intermediate stage, in which the wax crystals remain in suspension. However the rheological characteristics of petroleum liquids at low temperatures are complex and depend strongly upon the chemical composition of the oil and the rate of cooling.

It is believed that, due to its high polarity and the complex nature, asphaltenes may have an effect on the formation of wax net-work leading to changes in the pour points of petroleum liquids. Therefore, to test the effect of asphaltene content on the pour point of oils, small amounts of asphaltenes-rich short residue > 530°C were added to the asphaltenes - free base oils. The asphaltene content of the short residue > 530°C obtained by high vacuum distillation of Wafra Ratawi Crude Oil (the medium crude oil) was 19.0% by weight; the characteristics of the residue are summarised in Appendix C. The residue was added to the base oils in small amounts as listed in Table 9.58. The experimental data are presented graphically in Figure 9.85. A 38.0% depression in pour point of light base oil was obtained by the addition of 0.29% weight of the short residue. Although the residue did not dissolve completely in the medium base oil, a depression was also achieved in its pour point. No changes were observed in the pour point of heavy base oil and bright stock, simply because the residue did not dissolve in them even when the temperature was raised to ~90°C. The relationship between residue concentration and pour point was not linear. The highest depressions were achieved at an optimum concentration above which the pour points decreased very slightly or increased. This observation is of great practical importance, i.e. care should be taken not to exceed the optimum amount of asphaltenes, otherwise undesirable results may occur.

It was not practicable to test the effect of added short residue on the pour point of crude oils, since evaporation of light products would have occurred on heating to obtain dissolution.

Table 9.58 Pour Points of Base Oils as a Function of Addition of Residue > 530°C (Asphaltenes-Rich)

	% wt of added residue > 530°C		
	0.029	0.14	0.29
	Pour point, °C		
light base oil	-25	-28	-29
medium base oil	-19	-17	-15
heavy base oil	-	-	-
bright stock	-	-	-

It may be concluded that the asphaltenes content plays the key role in depression of the pour points of crude oils and petroleum products upon mixing. If both mixture components are of high wax content (highly paraffinic) then the effect of wax precipitation predominates leading to slight elevation of pour point, even if one or both of the components are asphaltenes - bearing. If one of the components is wax-free, i.e. naphthenic or low paraffinic in character, and asphaltenes - bearing then the effect of asphaltenes predominates leading to a depression in the pour point.

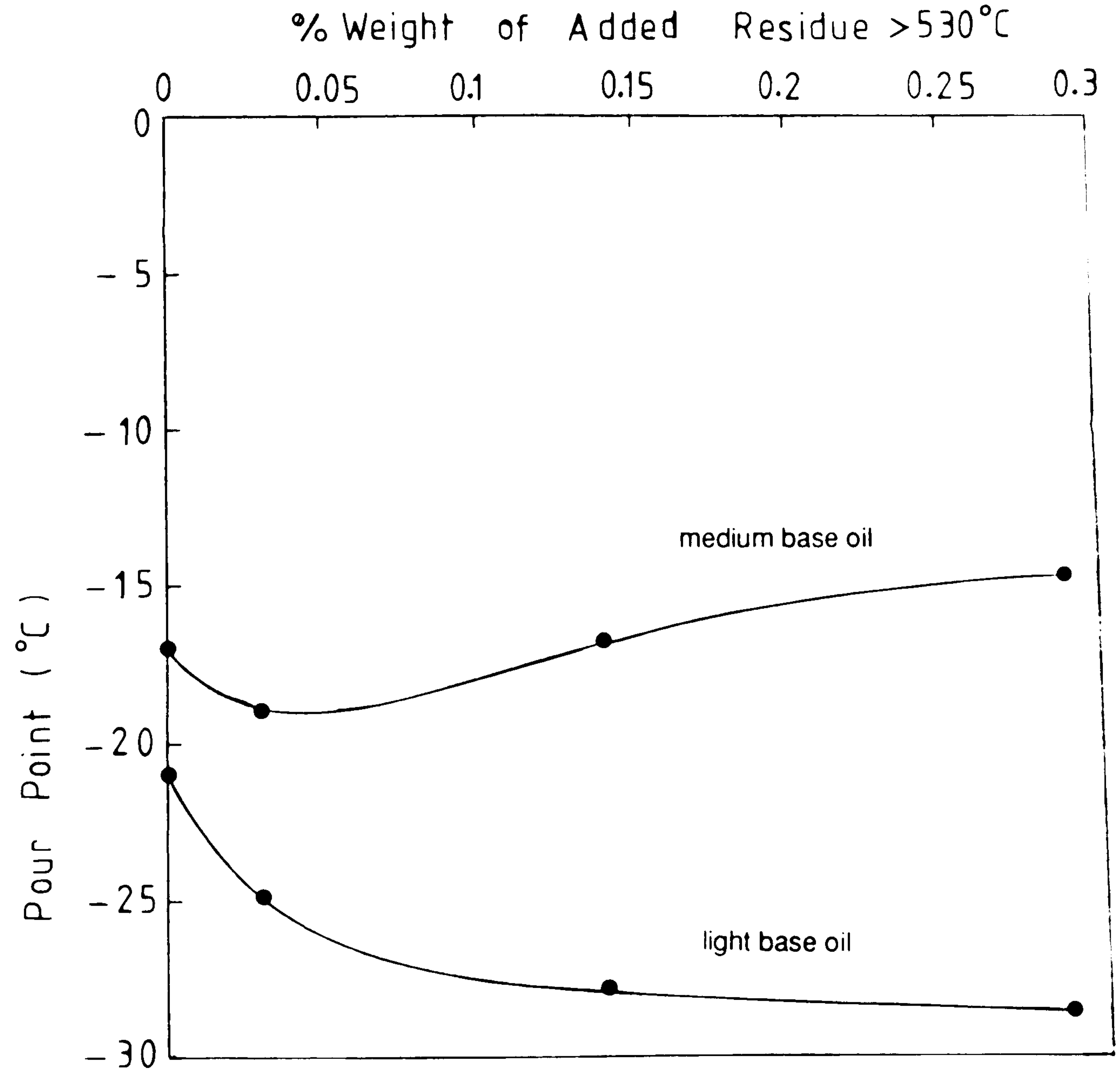


Figure 9.85 The Effect of Addition of Residue > 530°C Upon the Pour Point of Base Oils

9.4.4 Behaviour of Oils at Low Temperature

An oil subjected to very low temperature may undergo changes in its physical properties exemplified by:

1. Solidification without precipitation of a solid phase. This is simply due to a progressive increase in viscosity on cooling; when the viscosity reaches some critical value the oil no longer flows under its own weight. Oils which exhibit this phenomenon include those of predominatingly naphthenic characteristics, i.e. the heavy crude oil studied in this project.

2. Solidification with preciptiation of a solid phase, due to the appearance of (102):

   (a) Macrocrystals of paraffins which cause total solidification of oil,

or

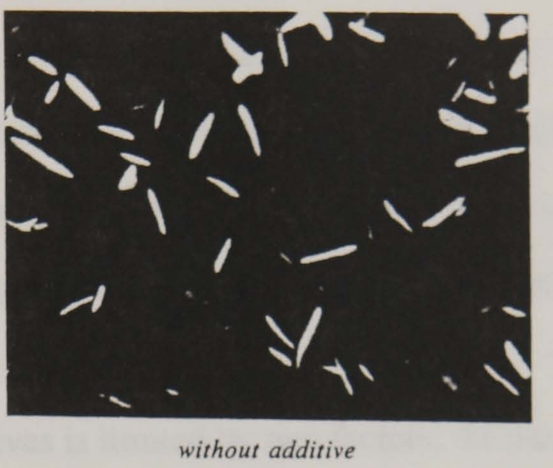
   (b) Microcrystals of wax which swell, forming a crystalline structure trapping a significant volume of oil.

Oils which exhibit such phenomena usually have high pour points and hence the addition of pour point depressants is necessary to improve the fluidity properties at low temperatures.

Pour Point Depressants:

The mechanisms of pour point depressants are relevant to the understanding of the pour point behaviour of petroleum oils observed on mixing.

A pour point depressant is a chemical which in low concentration (~1% wt), restricts the growth and interlocking of the first crystals formed and hence ensures the free flow of oil at temperatures lower than the normal pour point. Thus the depressant does not modify the appearance of crystals but lowers the pour point.



without additive

with additive

Figure 9.86 Photomicrographs of an Oil with, and without 0.5% of a Pour Point Depressant at 15°C; Magnification X120 (102).

A pour point depressant should have no deleterious effect on any other essential property of the oil. Some products usually used as pour point depressants are listed in Appendix D.

Mechanism of the Pour Point Depressant Action

The generally-accepted theory of the action of pour point depressants is that of surface adsorption. Adsorption of the depressant on the surface of the wax particles simultaneously inhibits their growth and their capacity to absorb oil and form gels-depending on crystal type (i.e. small or large, and originally of n-paraffins or iso-paraffins). In the absence of long interlocking crystals and/or swollen particles, oil can move freely even when solid wax particles are suspended in it. This theory has received support from x-ray studies (158) and measurements of the heat of solidification (159).

The phenomenon is clearly illustrated in the micrographs reproduced as Figure 9.86. The oil with additive contains wax particles of fine crystalline structure (no interlocking crystals), termed "microcrystalline wax" or "petroleum ceresin" (102).

The effect of additives is limited by two factors; the nature of the oil and the nature and concentration of the additive itself.

9.4.5 Mechanism of Pour Point Behaviour of Mixtures

From the previous discussion, the most probable mechanism of the depression of the pour point of crude oils and petroleum products upon mixing is that based upon the formation of clusters or aggregates of molecules proposed to explain the kinematic viscosity behaviour of petroleum mixtures (Section 9.3).

Depression of the pour point is believed to be due to the presence of asphaltenes and resins. The asphaltenes, of very complex chemical composition, facilitate the formation of clusters either by swelling and absorbing smaller hydrocarbons or the formation of a solvated shell surrounding the asphaltenes aggregates. Iso-paraffins are less probable to be absorbed than n-paraffins of the same carbon atoms number, while aromatics are the least probable to be absorbed. This is due to the fact that the n-paraffins occupy less volume; hence, they are easier to absorb and accommodate inside the cavities of the clusters. In solvated-shell formation, the branched paraffins and polar hydrocarbons are more likely to surround the asphaltenes aggregates than the n-paraffins. This is due to the polar nature of the asphaltenes, as discussed in Section 9.3.

Both mechanisms lead to absorption of the paraffins either inside or on the outer shell of the asphaltenes aggregates; this effectively prevents the paraffins from forming an interlocking "wax-net work" upon cooling and, hence, lowers the pour point of the mixture. This phenomenon continues until the stage at which further addition of the asphaltenes - bearing component increases the pour point until, eventually, it reaches its normal level. This point coincides with the optimum concentration of the asphaltenes - bearing component in the mixture, i.e. the best low temperature characteristics. Increase in the pour point beyond this point is attributed to the increase in concentration of the paraffins in the mixture, resulting from continuous addition of the heavy crude oil, which will promote wax interlocking at higher temperature than at the optimum concentration.

Depression in the pour point of mixtures represents thermodynamic instability. Although the asphaltenes aggregates originally existed in equilibrium with the other chemical compounds in the crude oil, this was disrupted due to the addition of a second crude oil of similar chemical nature but at a different equilibrium state. The variations in the equilibrium states between one crude and another are attributable to differences in the concentrations of the chemical species in the crude oils. Therefore mixing of two significantly different types of crude oil (e.g light and heavy crude oils) changes the concentrations of these chemical species and hence, promotes instability of the equilibrium state. This instability is envisaged to be the driving force which leads to the absorption of the paraffins by the asphaltenes aggregations or the formation of solvated shell around the asphaltenes aggregates. This leads in turn to depression of the pour point as a compensation for the thermodynamic instability.

The elevation of the pour point of the base oils mixtures (Figure 9.80) is attributed to the enhancement of wax crystal - interlocking. This behaviour was unexpected since, in the absence of asphaltenes, the pour points of base oils should behave ideally. The maximum elevation in the pour point of mixtures occurred at high concentrations of light base oil (~0.9 weight fraction). Normally regardless of their concentration the heavier base oils contain paraffins of higher molecular weights, i.e. they solidify forming wax crystals at higher temperatures compared with the light base oil. Whilst no definitive mechanism can yet be proposed, it may be that the paraffin molecules in the first portion of added heavier base oil act as nuclei on which the other paraffins molecules within the mixture start to crystalize and construct a wax -net work, leading to elevation of the pour point.

9.5 BOILING POINT

For completion, an investigation was made of the effect of blending upon the boiling point ranges of binary mixtures of crude oils, base oils and of petroleum products. The true boiling point, T.B.P., data obtained by distillation, for the binary mixtures of crude oils and petroleum products are summarised in Tables 9.59 and 9.60 respectively. The boiling point ranges of base oil binary mixtures obtained by the ASTM D1160 method are summarised in Table 9.61. The boiling point curves of crude oils, petroleum products and base oils are shown in Figures 9.87, 9.88 and 9.89, respectively.

It is clear that the boiling point ranges of the crude oils and the residue > 360°C (Figures 9.87 and 9.88) are not full ranges and do not form full range distillation curves, i.e. not all the charged oil was distilled and recovered. This was due to thermal cracking at Atmospheric Equivalent Temperature > 520°C. Therefore, the crude oils were distilled up to ~ 520°C (AET) leaving the rest of the undistilled material as heavy residue. However the base oils, kerosene and heavy gas oil exhibited full-range distillation curves, i.e. all the charged oil was distilled and 99% recovery was achieved.

It has also been observed that the slopes of the distillation curves of all the tested oils increased as the oils became heavier, i.e. as the density increased.

However, the distillation data shown in Tables 9.59, 9.60 and 9.61, demonstrate that the distillation curves were additive, and blended almost linearly.

With reference to the distillation data of oils, the temperature of 50% recovery, $T_{50\%}$, which is analogous to the normal boiling point, T_b for pure hydrocarbons, can be related to other properties. Figures 9.90, 9.91 and 9.92 demonstrate the relationship between $T_{50\%}$ and density, molecular weights and viscosity. These results suggest that such types of relationship may be used for estimating some properties of petroleum oils, which could be related to the boiling point of the oils in question, and their mixtures provided that the boiling point data are additive.

In addition, knowing the densities of the crude oils, it seemed possible that the shape of their distillation curves could be deduced from Figure 9.93. The distillaltion curve was therefore divided into segments according to the % volume recovery, e.g. 5%, 10%, 20%, 50%, 60% and 70%. Knowing the density of a crude, the distillation temperature of each % volume recovery segment was then read from the corresponding curve. Subsequently, connecting the determined points resulted in a continuous distillation curve, as shown in Figure 9.94 for crude oil mixtures No. 3, 7 and 11. Therefore this may be a useful means for predicting or checking the continuous distillation curves of mixtures of crude oils.

Table 9.59 Distillation Data of Crude Oils and Their Binary Mixtures

Mixture No.	temperature (°C) at % volume recovery of						
	IBP*	5%	10%	30%	50%	60%	70%
light crude oil	20	84	111	212	317	377	450
medium crude oil	28	97	136	260	396	469	558**
heavy crude oil	69	159	212	352	473	545	566
Mix 1	20	84	112	219	323	381	
Mix 2	21	89	123	228	344	420	
Mix 3	27	94	129	240	369	430	
Mix 4	27	96	132	257	385	464	
Mix 5	29	91	124	228	337	390	
Mix 6	42	107	148	264	381	450	
Mix 7	46	116	170	292	410	481	
Mix 8	67	149	200	333	461	531	
Mix 9	30	100	141	274	398	471	
Mix 10	44	124	169	303	431	501	
Mix 11	52	132	182	319	439	515	
Mix 12	67	156	205	340	468	543	

* IBP = Initial Boiling Point

** Values obtained by extrapolation of the distillation curve.

Table 9.60 Distillation Data of Petroleum Products and Their Binary Mixtures

Mixture	temperature (°C) at % volume recovery of							
No.	IBP*	5%	10%	30%	50%	70%	90%	95%
Kerosene	218	230	235	240	244	248	264	273
heavy gas oil	315	345	352	374	399	433	481	494
residue > 360°C	351	418	449	532 **	610 **	-	-	-
Mix 1	308	332	348	364	380	412	457	476
Mix 2	269	303	309	322	329	364	395	412
Mix 3	250	278	286	290	304	319	352	366
Mix 4	221	242	248	251	262	270	291	298
Mix 5	331	380	412	461	482	-	-	-
Mix 6	284	321	339	370	394	-	-	-
Mix 7	247	281	298	311	330	-	-	-
Mix 8	230	243	255	271	285	-	-	-
Mix 9	-	-	-	-	-	-	-	-
Mix 10	329	371	394	448	478			
Mix 11	305	348	373	419	446			
Mix 12	294	339	351	380	405			

* IBP = Initial Boiling Point

** Values obtained by extrapolation of the distillation curve.

Table 9.61 Distillation Data of Base Oils and Their Binary Mixtures

Mixture	temperature (°C) at % volume recovery of							
No.	IBP*	5%	10%	30%	50%	70%	90%	95%
light base oil	341	362	371	380	385	390	399	404
medium base oil	360	387	396	412	425	438	456	463
heavy base oil	384	409	421	440	450	462	479	485
bright stock	412	445	452	478	495	519	-	-
Mix 1	357	384	393	409	420	435	452	460
Mix 2	356	383	387	399	405	420	438	447
Mix 3	345	369	378	389	395	408	418	425
Mix 4	340	467	372	382	390	396	406	416
Mix 5	381	403	418	435	440	453	469	475
Mix 6	374	392	404	421	430	442	456	464
Mix 7	356	378	389	401	405	415	429	434
Mix 8	342	362	374	385	392	400	409	415
Mix 9	402	430	444	467	482	508	-	-
Mix 10	388	419	427	447	455	478	-	-
Mix 11	364	390	400	410	417	432	-	-
Mix 12	340	367	376	388	392	405	-	-
Mix 13	405	435	445	470	488	510	-	-
Mix 14	393	422	437	459	470	497	-	-
Mix 15	384	410	417	436	450	472	-	-
Mix 16	368	390	400	420	432	449	-	-
Mix 17	407	443	451	472	488	511	-	-
Mix 18	400	435	441	465	480	504	-	-
Mix 19	398	421	430	452	470	488	-	-
Mix 20	384	410	422	443	453	467	-	-

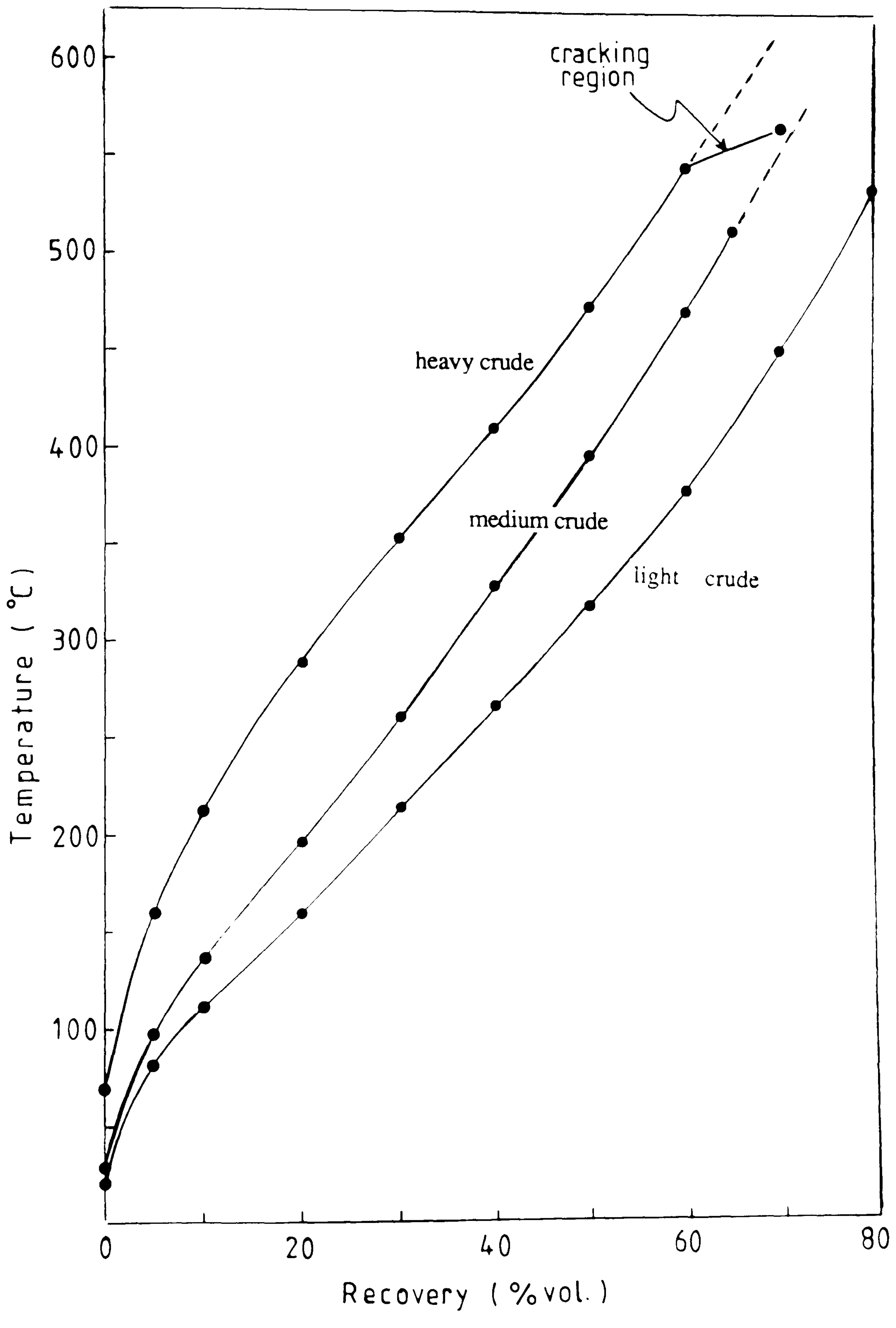


Figure 9.87 Crude Oils TBP Distillation Curves

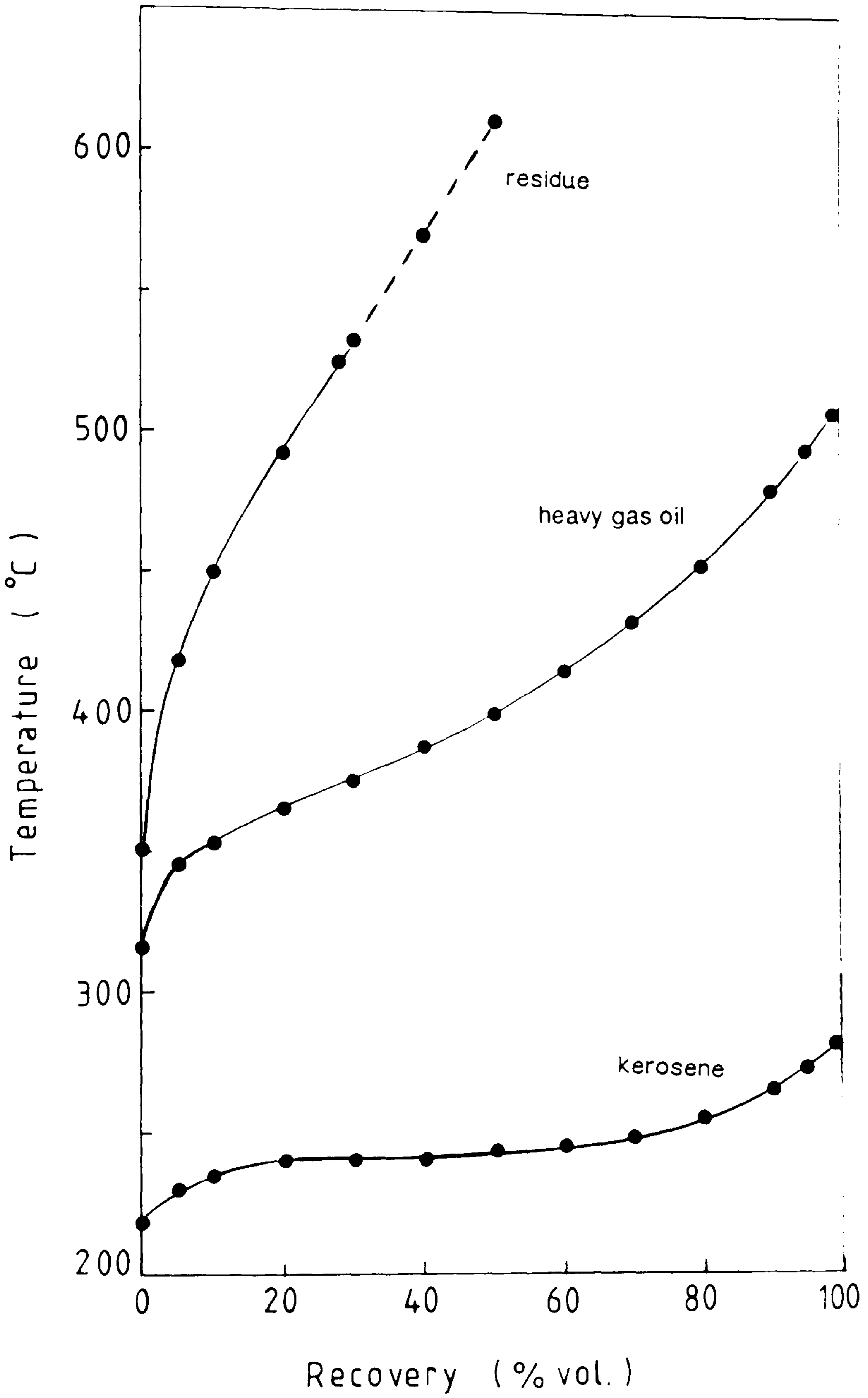


Figure 9.88 Distillation Curves of Petroleum Products

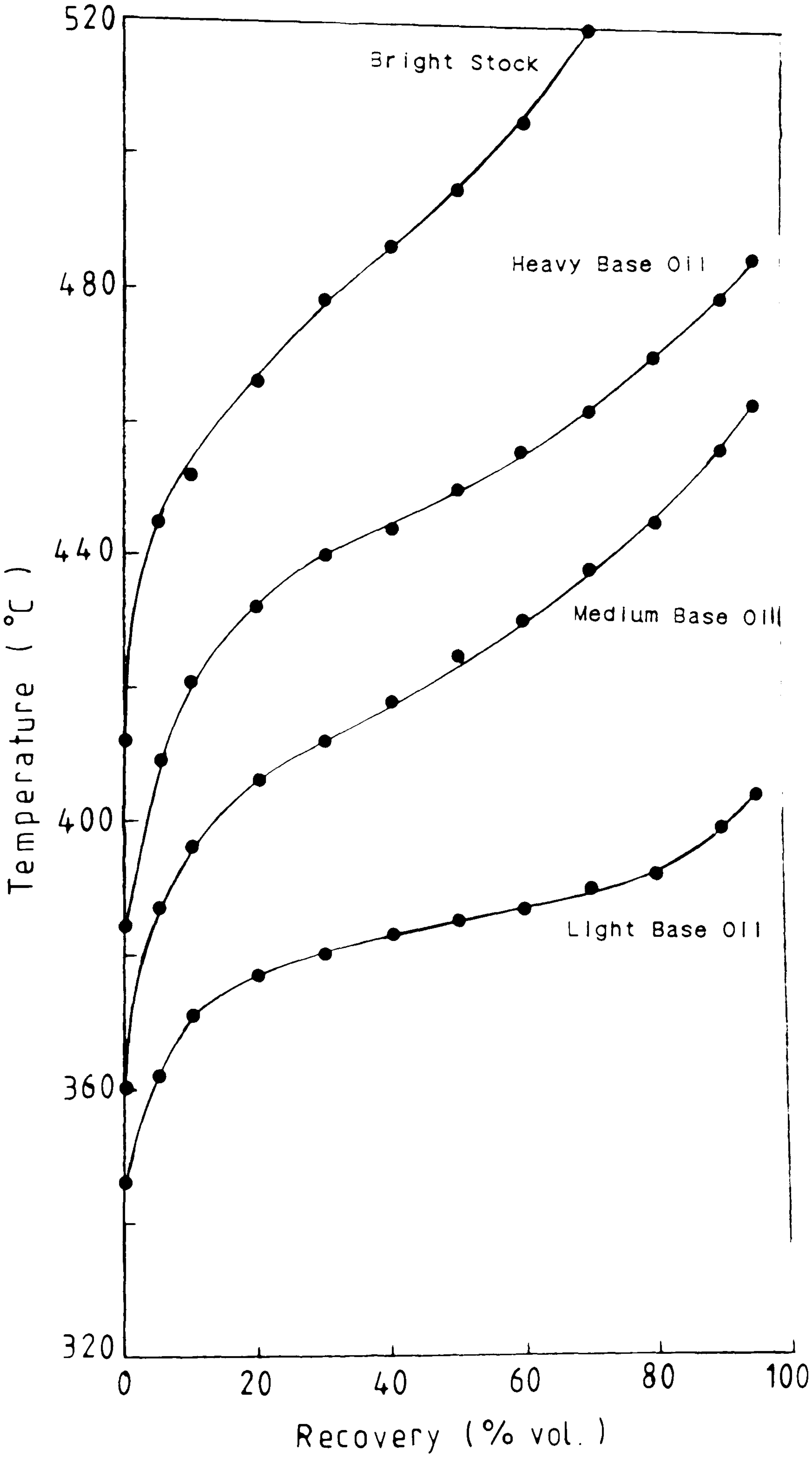


Figure 9.89 Distillation Curves of the Base Oils

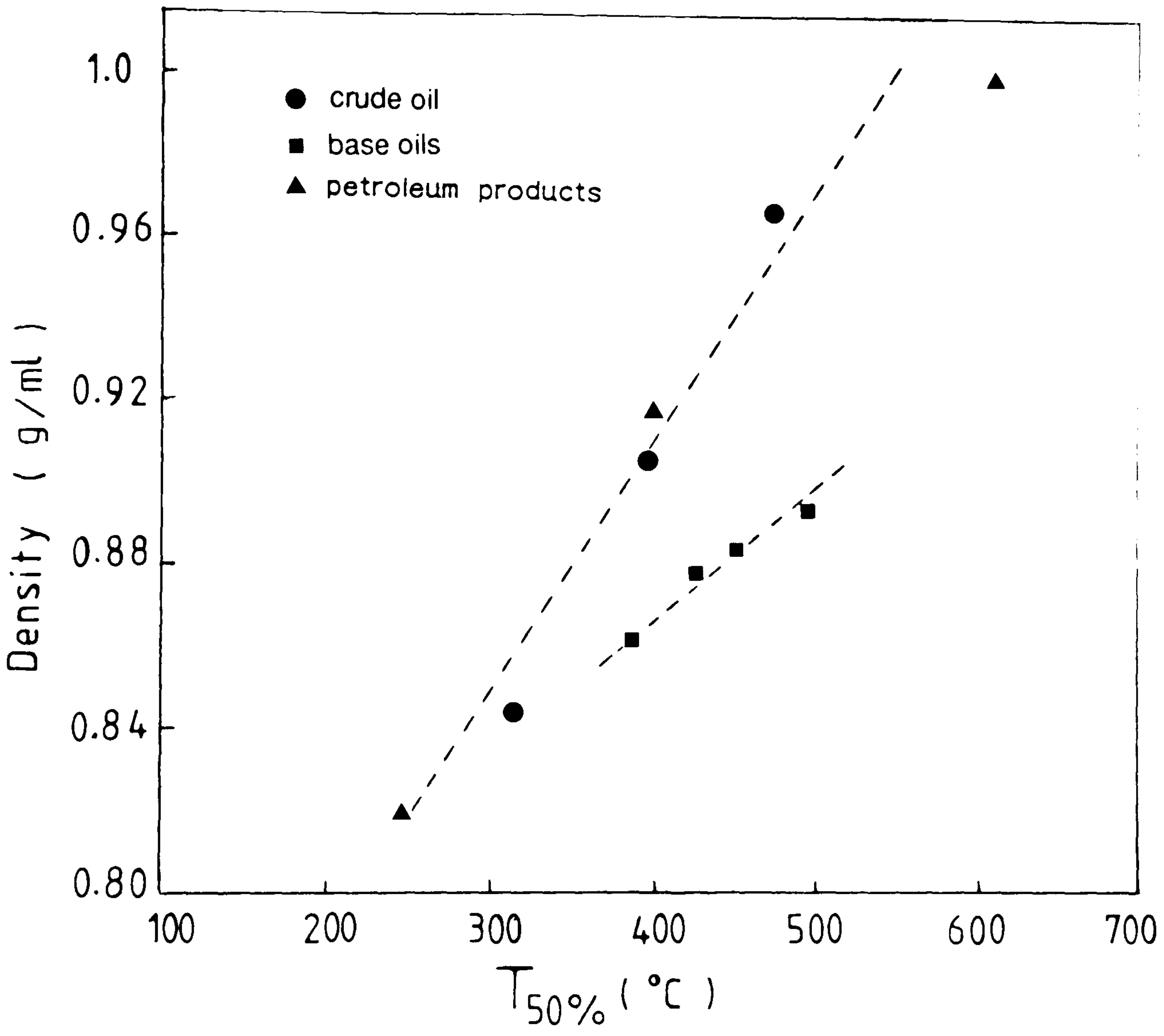


Figure 9.90 Relationship Between $T_{50\%}$ and Density @ 15°C of Petroleum Oils.

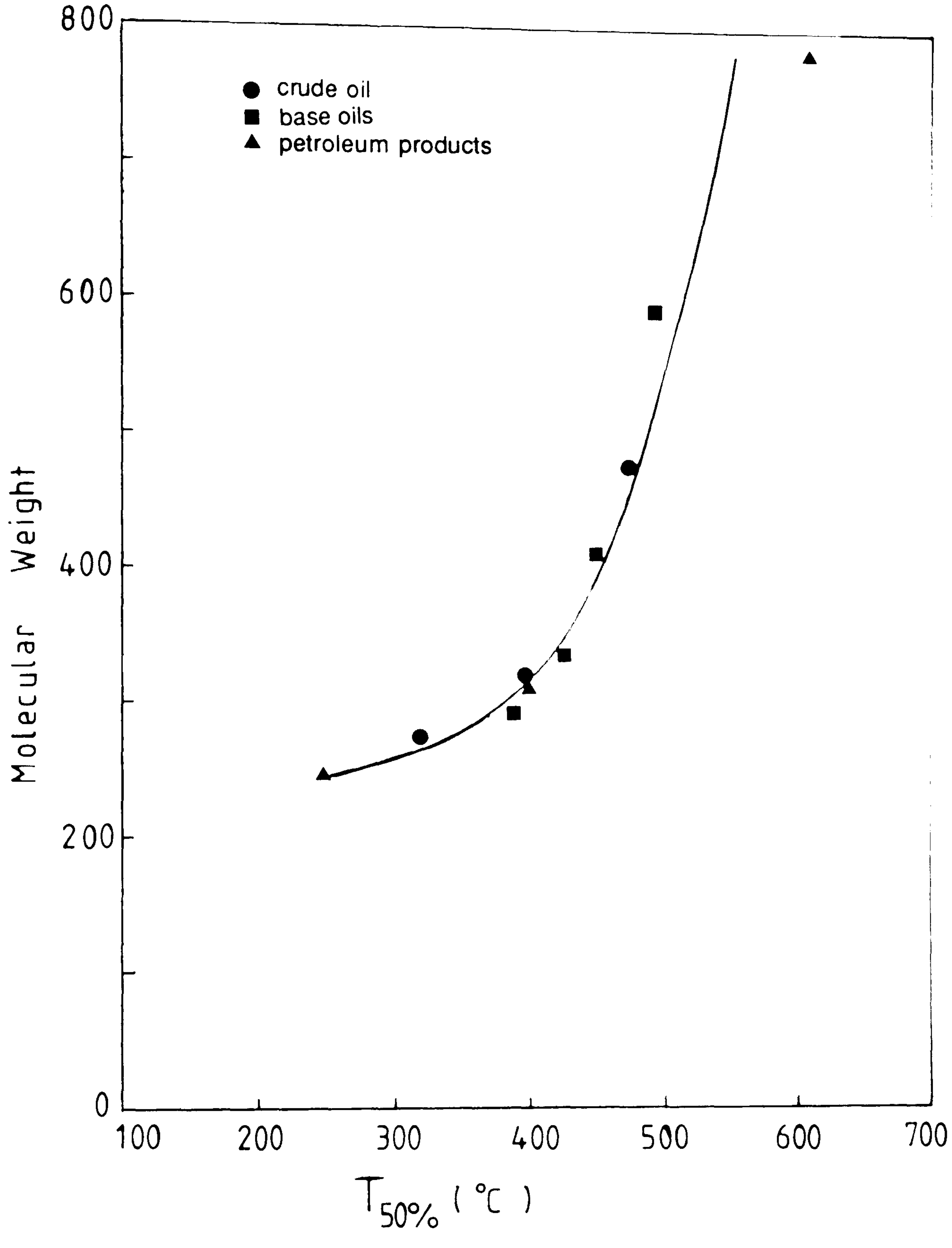


Figure 9.91 Relationship Between $T_{50\%}$ and Molecular Weights of Petroleum Oils

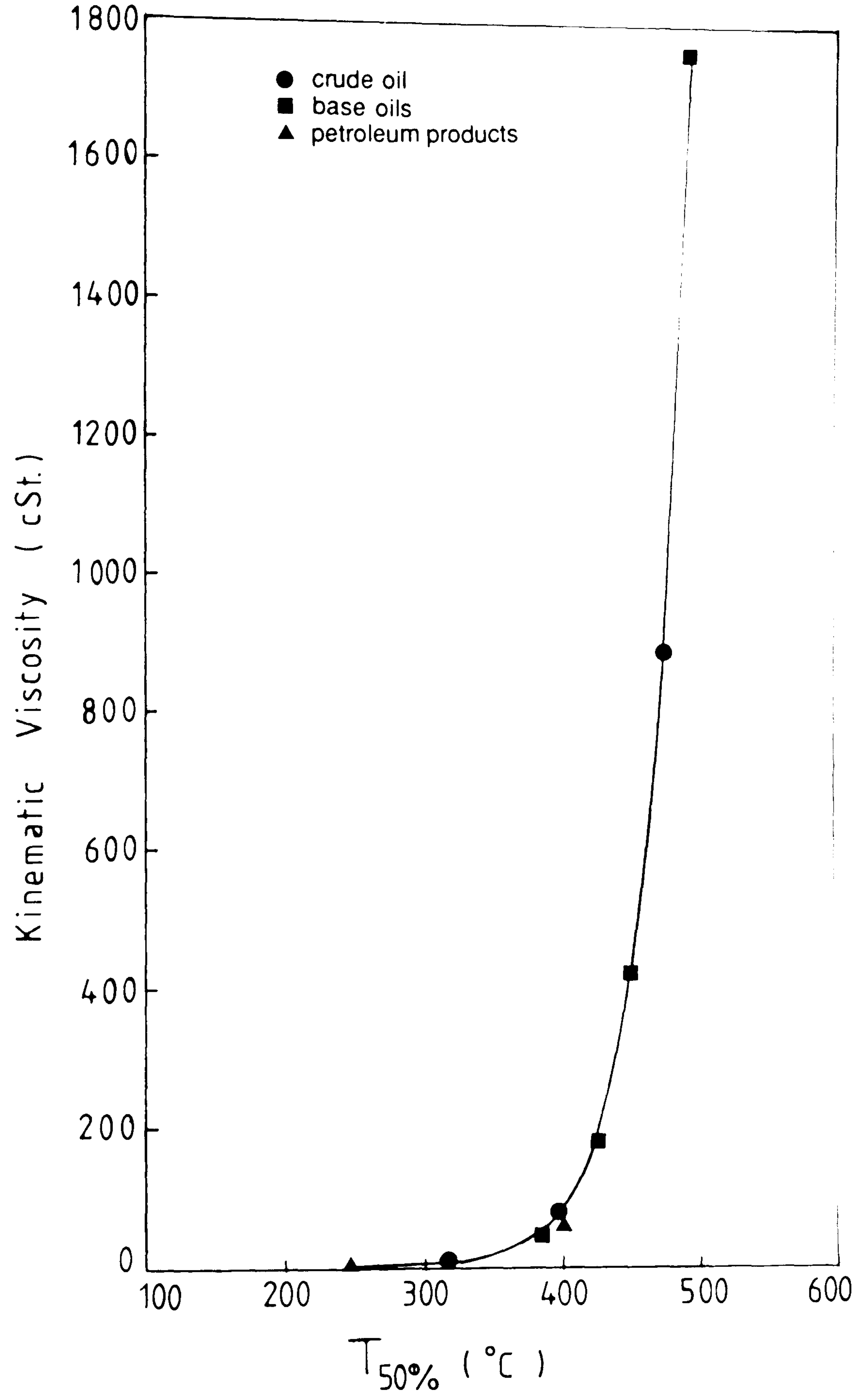


Figure 9.92 Relationship Between $T_{50\%}$ and Kinematic Viscosity @ 20°C of Petroleum Oils

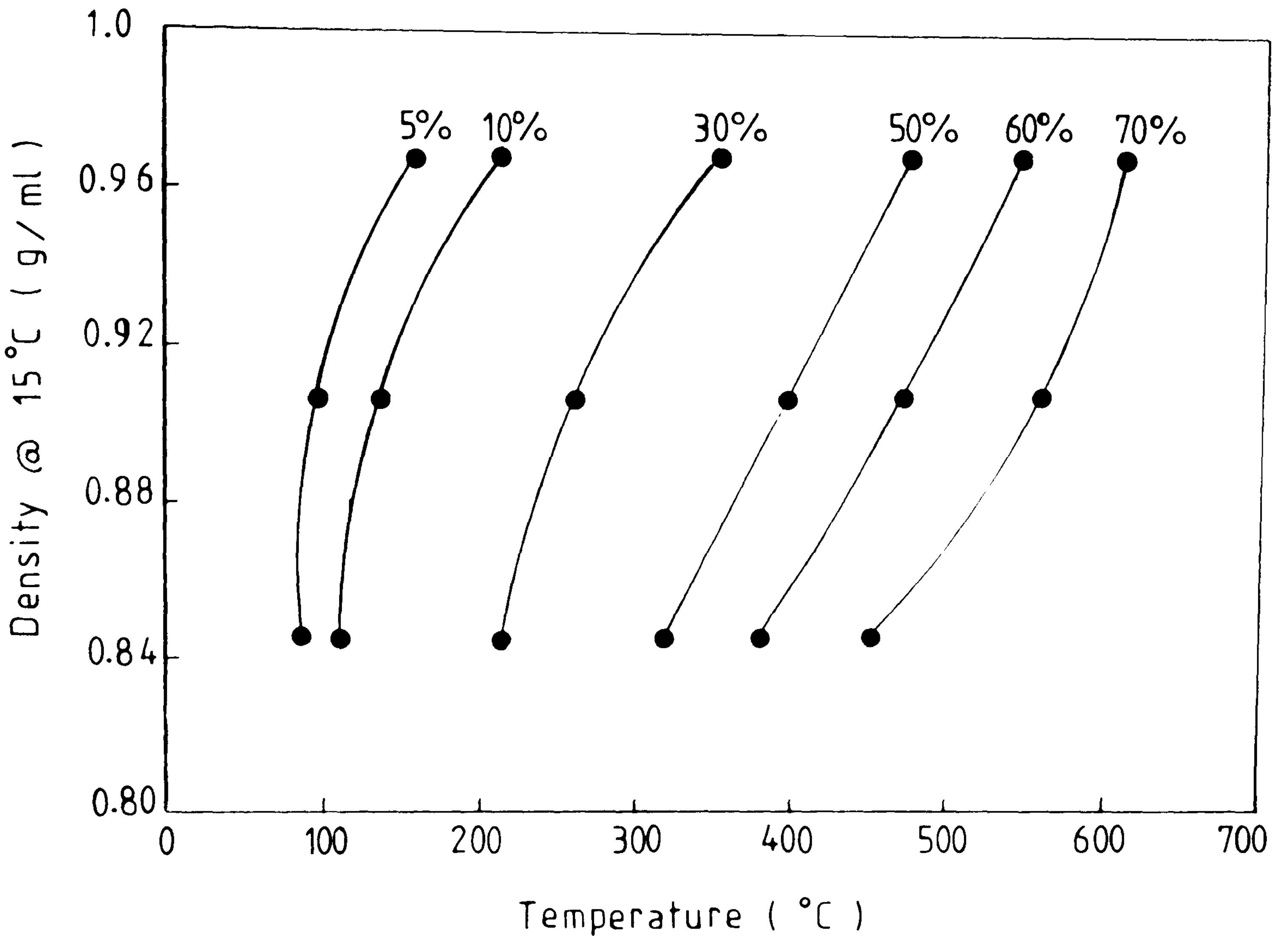


Figure 9.93 Relationship Between the Distillation Temperatures and Densities @ 15°C of Crude Oils

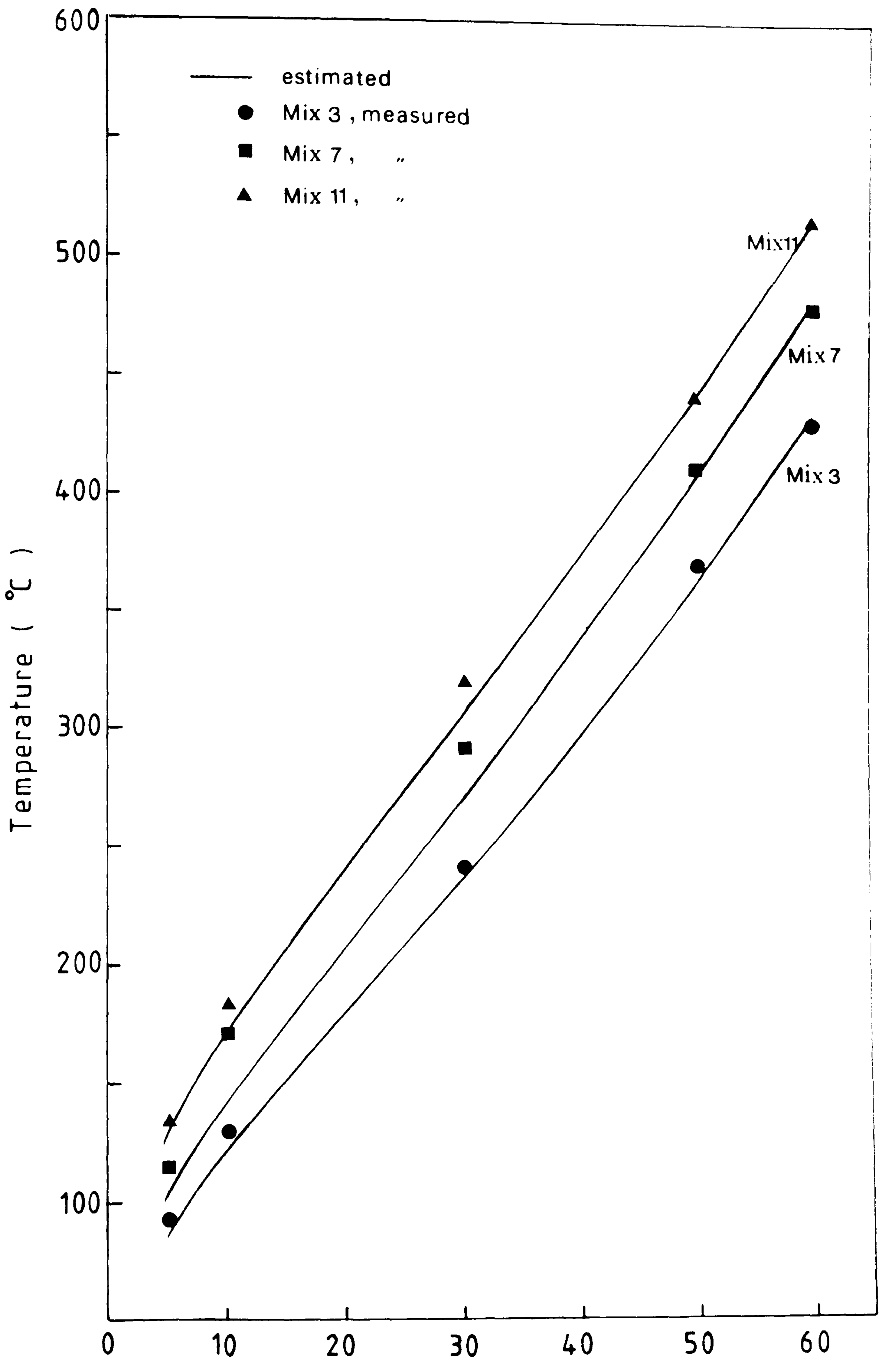


Figure 9.94 Estimated Distillation Curves, for Crude Oil Mixtures 3, 7 and 11, Using Figure 9.93

9.6 REID VAPOUR PRESSURE

The Reid vapour pressures of crude oil binary mixtures have been examined. The data obtained are summarised in Table 9.62 and presented graphically in Figure 9.95.

It is clear that Reid vapour pressure does not blend linearly. The RVP - composition diagram of the binary mixtures exhibited values less than those predicted if linearity is assumed.

However in Figure 9.96, the RVP data of crude oils have been drawn against the distillation data presented in Section 9.5, and smooth curves obtained. This may provide a good basis for correlating RVP with the distillation data in more detail, as has been done in an analogous manner for gasolines and light distillates (127, 128). Further work is needed in this area, as well as examining the effect of the blending on the RVP of selected petroleum products such as naphtha and gasolines.

GENERAL

All the correlations and behaviour described are limited to the range of parameters and typical compositions, from Kuwaiti crudes covered. A series of similar tests would be necessary before extrapolation.

Table 9.62 Reid Vapour Pressures of Crude Oils Binary Mixtures

Mixture Number	R.V.P. (psi)
light crude oil	14.0
medium crude oil	5.3
heavy crude oil	2.0
Mix 1	12.1
Mix 2	9.5
Mix 3	8.1
Mix 4	6.0
Mix 5	11.9
Mix 6	8.5
Mix 7	6.0
Mix 8	2.7
Mix 9	4.8
Mix 10	3.4
Mix 11	3.0
Mix 12	2.2

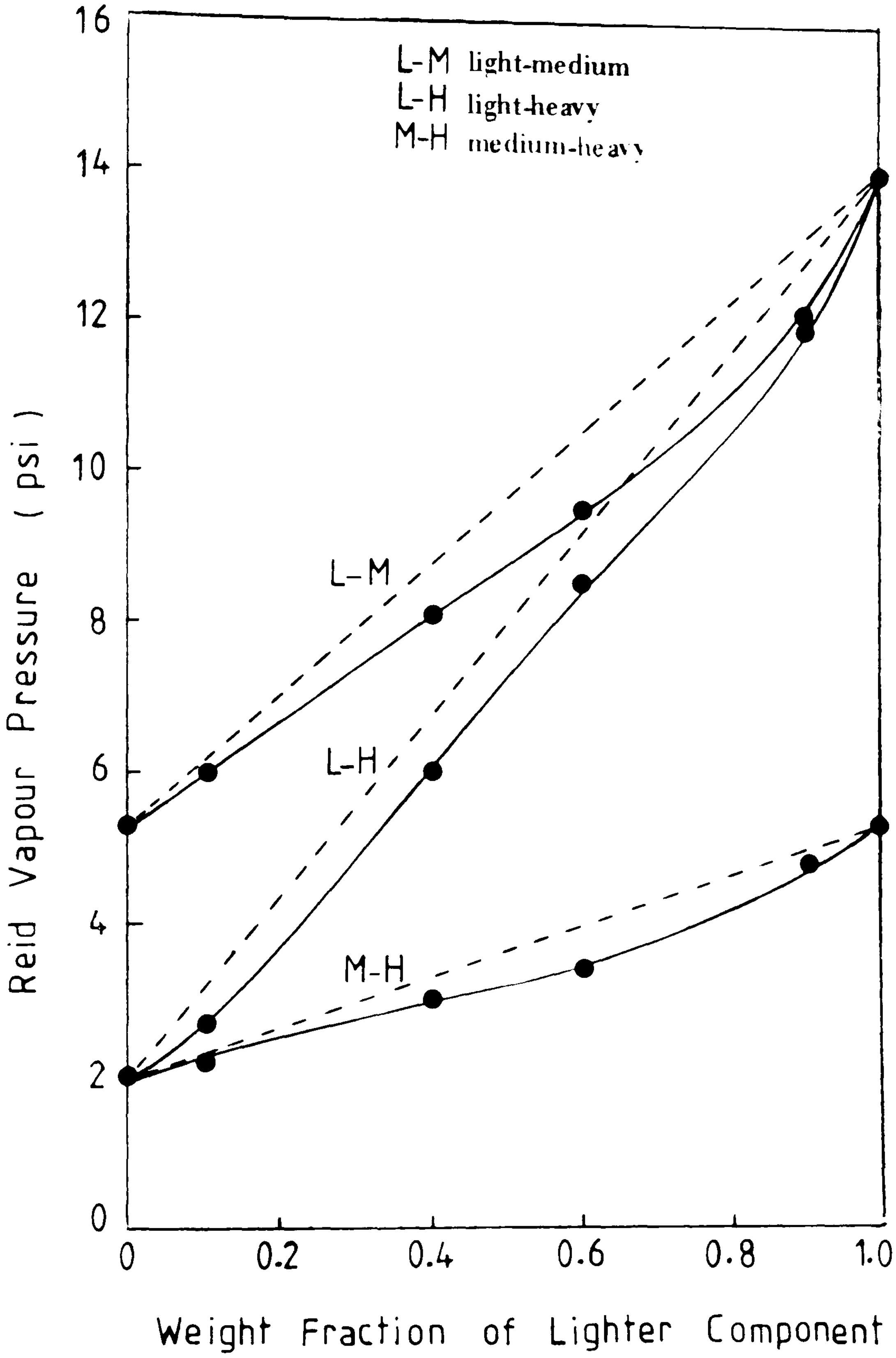


Figure 9.95 Reid Vapour Pressures of Crude Oils Binary Mixtures

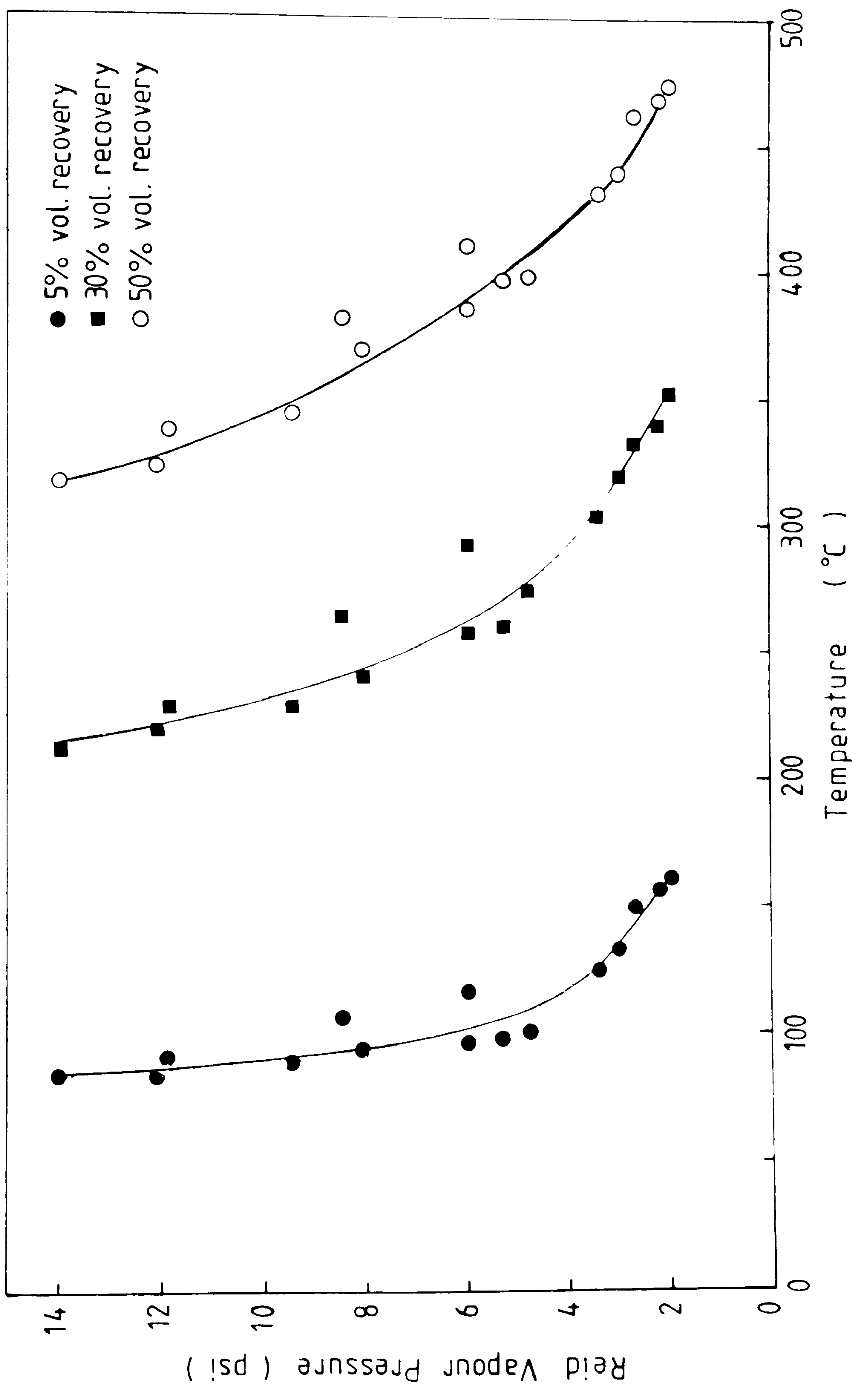


Figure 9.96 Relationship Between the Distillation Temperatures and RVP of Crude Oils

9.7 STABILITY OF CRUDE OILS

The validity of all the correlations developed in this project for the prediction of the viscosity of crude oil mixtures, and the proposed mechanisms for the non-ideal behaviour of the viscosity and pour point of such mixtures is strongly influenced by the stability of the mixtures against stratification (layering) during storage. Tests were, therefore, performed on the stability of crude oil mixtures.

Samples of light, medium, heavy crude oil, mixture 3 (40% light - 60% medium), mixture 7 (40% light - 60% heavy) and mixture 11 (40% medium - 60% heavy) were kept at three different temperatures (1°C, 16°C and 30°C) for 12 weeks as described in Section 8.13.

Crude oil binary mixtures 3, 7 and 11 were selected because they demonstrated the highest non-ideal viscosity characteristics among the mixtures examined as described in Section 9.3.3. It was also anticipated that mixtures of these particular compositions would be, thermodynamically, the least stable.

Top and bottom representative samples were withdrawn by means of a syringe (as described in Section 8.13) from each crude oil and the three binary mixtures. This was repeated at fixed intervals as shown in Tables 9.63, 9.64 and 9.65. The kinematic viscosities at 10°C were determined for all the samples stored at different temperatures (1°C, 16°C, 30°C), and the data obtained are summarised in Tables 9.63, 9.64 and 9.65.

An arbitrary stability factor (K), whose value indicates the degree of stability of a mixture; was defined as:

$$K = \frac{v_{\text{bottom}}}{v_{\text{origin}}} - \frac{v_{\text{top}}}{v_{\text{origin}}} \qquad 9.41$$

Values of K were calculated for all samples at 1°C, 16°C and 30°C and are summarised in Tables **9.63, 9.64 and 9.65** The K-values of the three mixtures (light-medium, light-heavy and medium-heavy) are presented graphically in Figures 9.97, 9.98 and 9.99 .

The calculated K values indicated that the component crude oils and their mixtures were fairly stable over a temperature range 1°C - 30°C and time period up to 12 weeks. As expected, the crude oil mixtures exhibited less stability than the crude oil components. Mixture 7 (light-heavy crude oil mixture) was the least stable, i.e. it had the highest K-value.

The mixtures exhibited less stability at lower temperature (1°C) than at higher temperatures (16°C and 30°C), i.e. the mixtures were more homogenous when stored for long periods at the higher temperatures providing vaporisation of light ends was avoided. This could be attributed to the fact that each crude oil responds differently to an increase or decrease in temperature as discussed in Section 9.3.1, i.e. the viscosity difference between the crude components decreases as the temperature increases. Therefore in terms of viscosity the tendency of a crude oil mixture to stratify would tend to increase at lower temperatures. However this may not be the case for heterogenous liquid mixtures, e.g. a suspended aqueous phase in crude oil.

Although precautions were taken to avoid the problem, the irregularity observed for K-values of mixtures at 30°C could be attributed to some evaporative loss of light ends of mixtures leading to an increase in viscosity over a long period.

Table 9.63 The Effect of Storage at 1°C on the Stability of Crude Oil Components, Mixture 3, Mixture 7 and Mixture 11 in terms of Kinematic Viscosity @ 10°C

Mix	$\nu_{10°C}$ (cSt) original	Sample	$\nu_{10°C}$ (c St.) after			
			2 weeks	4 weeks	8 weeks	12 weeks
L	14.22	T	14.20	14.16	14.19	14.10
		B	15.02	15.10	15.05	15.21
		K	0.058	0.066	0.060	0.078
M	163.4	T	162.2	161.0	160.1	161.3
		B	165.1	165.0	165.9	166.4
		K	0.018	0.025	0.036	0.031
H	2193	T	2190	2192	2190	2189
		B	2198	2199	2198	2199
		K	0.004	0.003	0.004	0.005
Mix 3	49.86	T	48.15	48.18	48.16	47.91
		B	50.78	51.20	51.65	52.59
		K	0.053	0.061	0.07	0.094
Mix 7	146.12	T	141.2	138.6	136.2	135.4
		B	150.3	155.1	157.7	159.1
		K	0.062	0.113	0.147	0.162
Mix 11	643.1	T	639.4	639.2	636.9	635.7
		B	645.3	649.3	651.9	653.3
		K	0.009	0.016	0.023	0.027

L = light crude oil,
M = medium crude oil
H = heavy crude oil,
K = arbitrary stability factor
T = top sample
B = bottom sample

Table 9.64 The Effect of Storage at 16°C on the Stability of Crude Oil Components. Mixture 3, Mixture 7 and Mixture 11 in terms of Kinematic Viscosity @ 10°C

Mix	$\nu_{10°C}$ (cSt) original	Sample	$\nu_{10°C}$ (cSt.) after			
			2 weeks	4 weeks	8 weeks	12 weeks
L	14.22	T	14.20	14.13	14.27	14.25
		B	14.34	14.40	14.72	15.
		K	0.010	0.019	0.032	0.053
M	163.4	T	162.0	162.5	161.5	161.5
		B	165.8	165.9	166.1	166.4
		K	0.023	0.021	0.028	0.03
H	2193	T	2190	2194	2189	2188
		B	2198	2199	2198	2198
		K	0.044	0.002	0.004	0.005
Mix 3	49.86	T	48.50	48.50	48.19	47.82
		B	50.70	51.10	52.22	52.17
		K	0.044	0.052	0.081	0.087
Mix 7	146.1	T	142.5	141.1	139.4	136.6
		B	150.1	153.9	156.2	158.3
		K	0.052	0.088	0.115	0.149
Mix 11	643.1	T	640.3	641.1	639.8	639.0
		B	645.6	647.4	648.7	649.8
		K	0.008	0.010	0.014	0.017

L = light crude oil,
M = medium crude oil
H = heavy crude oil,
K = arbitrary stability factor
T = top sample
B = bottom sample

Table 9.65 The Effect of storage at 30°C on the stability of crude oil components, Mixture 3, Mixture 7, and Mixture 11, in terms of kinematic viscosity @ 10°C

Mix	$\nu_{10^{\circ}C}$ (cSt) original	Sample	$\nu_{10^{\circ}C}$ (cSt.) after			
			2 weeks	4 weeks	8 weeks	12 weeks
L	14.22	T	15.08	15.31	15.92	16.13
		B	15.17	15.58	16.04	16.19
		K	0.006	0.019	0.008	0.004
M	163.4	T	164.1	165.8	166.4	168.0
		B	166.3	167.5	169.1	169.9
		K	0.013	0.010	0.017	0.012
H	2193.1	T	2199	2207	2211	2219
		B	2204	2210	2213	2223
		K	0.002	0.001	0.001	0.002
Mix 3	49.86	T	50.42	52.00	52.68	53.17
		B	50.96	52.37	53.09	53.81
		K	0.011	0.007	0.008	0.013
Mix 7	146.1	T	145.7	147.9	148.1	149.8
		B	147.6	153.0	155.3	158.0
		K	0.013	0.023	0.049	0.056
Mix 11	643.1	T	645.5	647.0	649.8	653.7
		B	649.1	656.8	657.4	660.2
		K	0.006	0.015	0.012	0.010

L = light crude oil, M = medium crude oil
H = heavy crude oil, K = cubitrary stability factor
T = top sample B = bottom sample

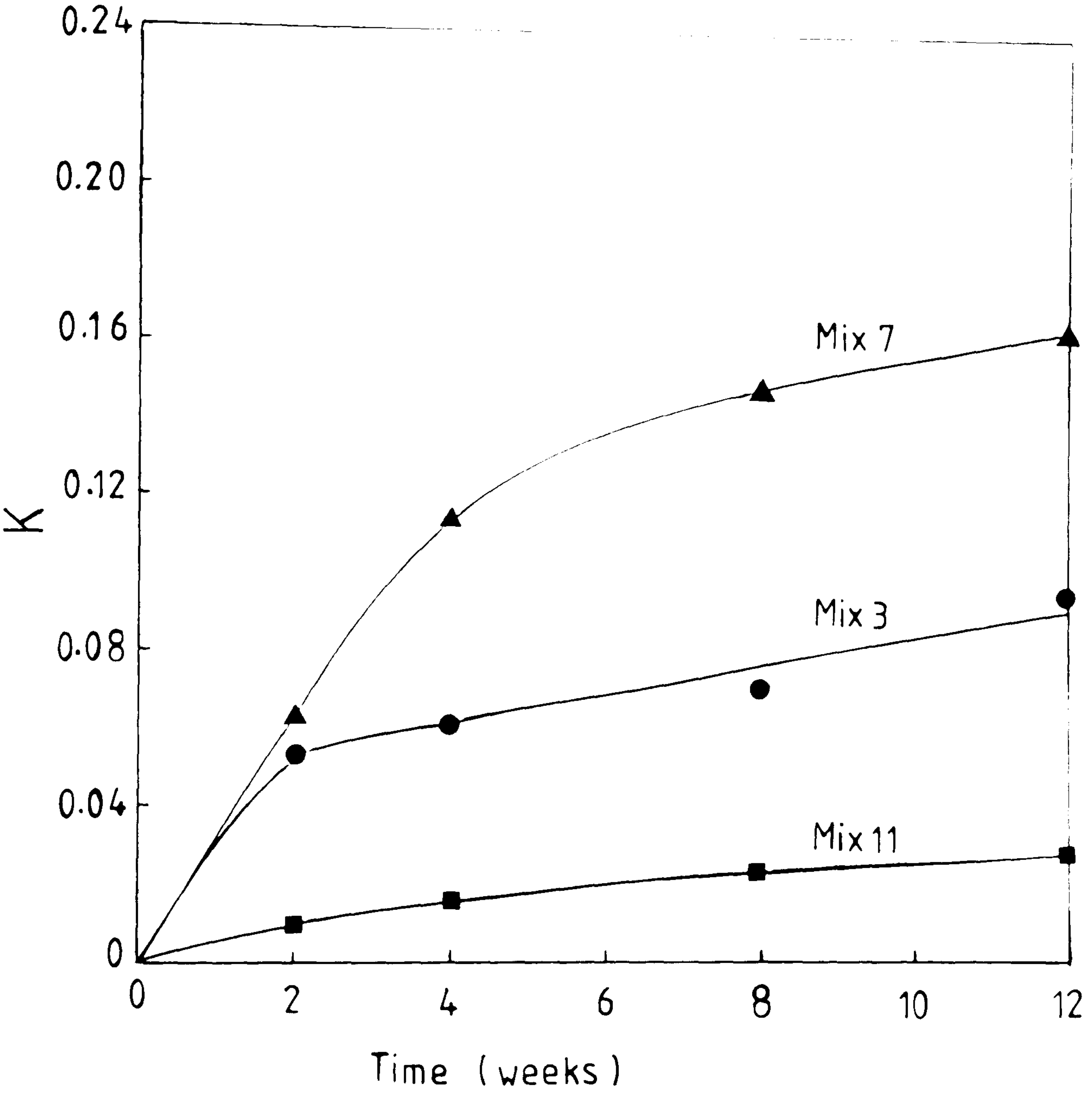


Figure 9.97 K-Values at 1°C, Calculated from equation 9.41, for Crude Oil Mixtures

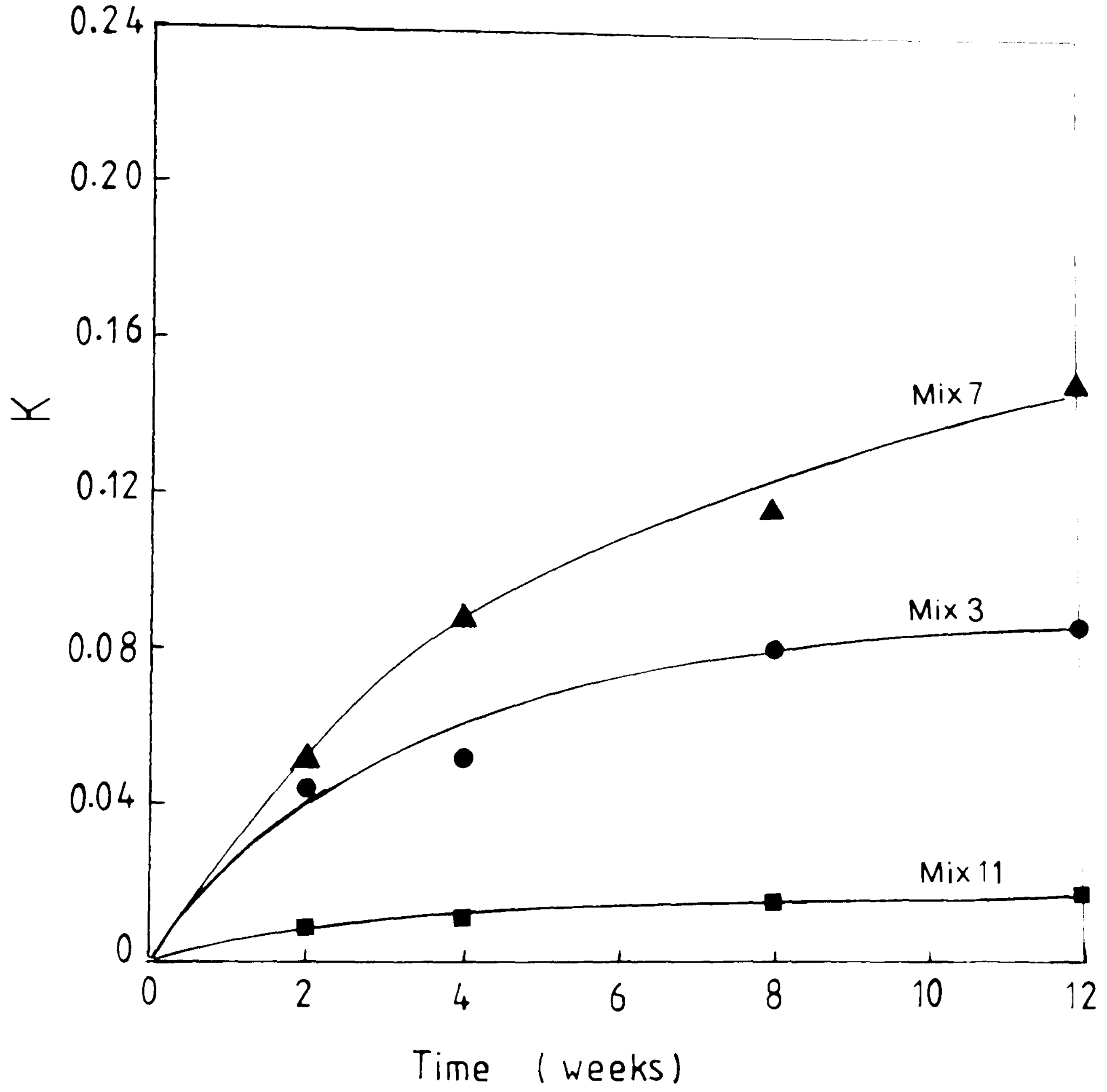


Figure 9.98 K-Values at 16°C, Calculated from equation 9.41, for Crude Oil Mixtures

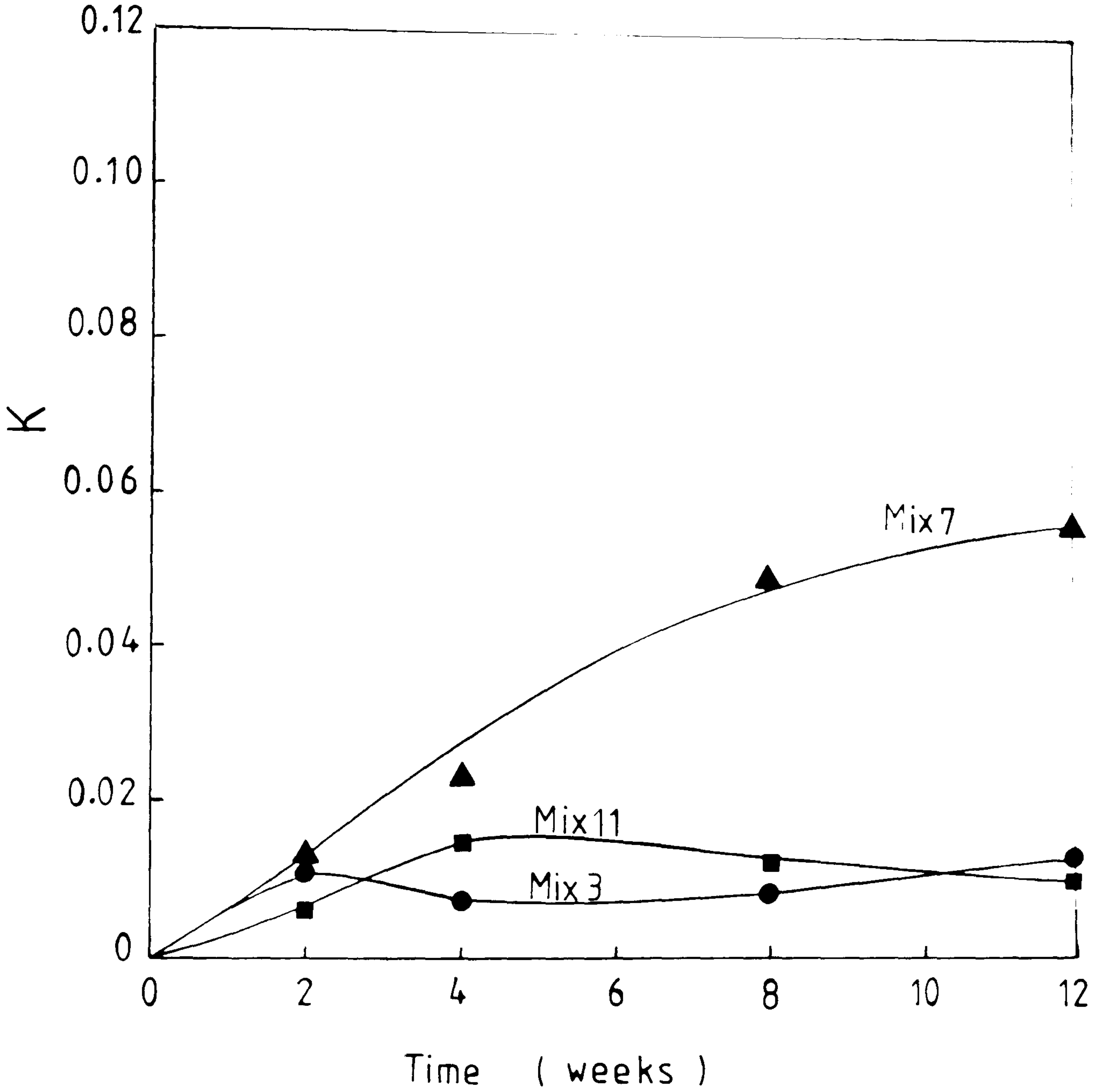


Figure 9.99 K-Values at 30°C, Calculated from equation 9.41, for Crude Oil Mixtures

CHAPTER 10

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

The effect of blending on selected physical properties, ie. kinematic viscosity, pour point, boiling points and Reid vapour pressure, of crude oils and their products was studied using three main systems of binary mixtures.

10.1 CONCLUSIONS

The following conclusions arise from this work.

1- The densities of crude oils,base oils and petroleum products blended non-idealy, with minima in their density-composition curves. However, the divergence from ideality was relatively small in the cases of crude oil (average deviation = 0.13%) and of base oil (average deviation = 0.06%), mixtures, but increased for the petroleum products binary mixtures (average deviation = 0.57%).

2- Since molecular weight is an additive property when subjected to mixing, as a consequence of the density behaviour, the molar volumes of the binary mixtures also exhibited non-ideal behaviour with maxima in their molar volume-composition curves.

3- The kinematic viscosities of the crude oils and their products decreased exponentially with an increase in the temperature. The rate of decrease in the viscosity varied with the density of oil, where it increased as the density of the oil fraction increased.

4- The effect of pressure, in the range 14.7 psi to 8000 psi, on the viscosities of crude oils and their binary and ternary mixtures was studied over the temperature range of 25°C to 50°C. The viscosities increased as the pressure of the oils increased. The rate of increase in the viscosity with pressure increased as the density of the crude oil increased.

A general method was developed to predict the kinematic viscosity of crude oils and their mixtures at high pressure, ie. 14.7 psi - 8000 psi. The proposed equations,

$$v_p - v_o\, e^{R(P-14.7)} \tag{9.8}$$

$$R = -4.65521 \times 10^{-4} + (6.66906 \times 10^{-4} \times \rho r) \tag{9.5}$$

resulted in absolute average deviations ≤ 5.2% and ≤ 6.0% for the binary and ternary mixtures, respectively. The kinematic viscosities, predicted by the proposed method, showed significantly better agreement with the experimental values than those obtained using the method (Kouzel equation, 5.61) currently adopted by the American Petroleum Institute, which resulted in deviations of <34.7% and <27.7% for the same binary and ternary mixtures (Tables 9.19 and 9.20). A similar approach can be followed to predict the kinematic viscosity of petroleum products and base oils at high pressures. It can also be followed to predict the kinematic viscosity of live crude (rich in associated light gases), provided an allowance is included for the effect of dissolved gas concentration. Empirical correlation of such correction factors would need to be based upon experimental data obtained in a similar way to that described in Section 8.5.2.

5 - The effect of mixing on the kinematic viscosity of crude oils was studied over a temperature range of 10°C-50°C and a pressure range of 14.7-8000 psi (Tables 9.10, 9.15 and 9.16).

Viscosity was found to blend non-linearly. The viscosity-composition diagrams (Figures 9.21, 9.22 and 9.23) exhibited non-ideal behaviour, the viscosities of binary mixtures of crude oils being always less than the ideal values. The divergence from ideality, represented by the excess viscosity function v^E

composition plots (Figures 9.24, 9.25 and 9.26), showed minima at any temperature and pressure, and was always of negative sign. For the three binary mixture systems tested, the minima of excess viscosity function-composition diagrams (i.e. the maximum deviations) were in all cases in a similar region (0.2-0.4 weight fraction of a lighter component), but shifted slightly with changes in temperature or pressure.

The effect on viscosity of adding the lighter component to a mixture was greater at low temperature, e.g. 10^oC or higher pressures, eg. 8000 psi than at high temperature or low temperature, i.e. the rate of decrease in viscosity with added lighter component deviated most from ideality at low temperature or high pressure.

6 - The effect of mixing on the kinematic viscosities, of petroleum products and base oils, was studied over a temperature range of 20-100^oC (Table 9.21 and 9.22).

The binary mixtures of petroleum products or base oils, did not exhibit ideal viscosity characteristics. As with crude oil mixtures, the viscosities of the mixtures were always less than the ideal case (Figures 9.33, 9.34, 9.35, 9.39, 9.40, 9.41, 9.42 and 9.43). The divergence from ideality, exhibited by the excess viscosity function v^E-composition diagrams (Figures 9.36, 9.37, 9.38, 9.44, 9.45, 9.46, 9.47 and 9.48) showed minima, and was always of negative sign. For the two binary mixtures systems tested, the minima of excess viscosity function - composition diagrams (i.e. the maximum deviations) were in all cases in a similar region (0.2 to 0.4 weight fraction of lighter component), but shifted slightly with changes in temperature.

The non-ideal behaviour of viscosity was strongly dependent upon the nature of the mixture components. Mixtures of components of hydrocarbons of different nature (e.g. kerosene-residue mixtures) exhibited a much greater divergence from ideality than mixtures in which the components were of similar nature (e.g. base oils mixtures).

The deviation of the viscosity from ideality decreased as the temperature increased, and hence v^E decreased also.

7 - Since the non-ideal viscosity behaviour of the binary mixtures of crude oils, base oils and of petroleum products, increased with an increase in the difference between the densities (or API gravities) of the components, the Grunberg equation (equation 9.13) for the calculation of the viscosities of binary mixtures was modified, with G expressed as a function of $(\Delta API)^2$. The proposed equation

$$\ln v_{mix} = \Sigma x_i \ln v_i - 4.976 \times 10^{-3} x_1 x_2 (\Delta API)^2 \qquad 9.15$$

fitted the experimentally determined viscosity data of crude oil binary mixtures, with absolute average deviations of 3.3% to 8.3%. It also fitted the experimentally-determined viscosity data of base oils binary mixtures, with absolute average deviations of 1.4% - 4.7%. This should enable the viscosity of binary mixtures of crude oils or of base oils, at any fixed temperature, to be predicted with a high degree of accuracy from the API gravity and viscosity of each component at that temperature. However absolute average deviations of 6.3%-26.0% were obtained for the viscosity of the binary mixtures of petroleum products.

8 - A mechanism has been postulated to explain the non-ideal behaviour of viscosity. This non-ideal behaviour is attributed to an increase in the average molar volume due to mixing. Two types of accompanying mechanism have been suggested:

(a) Small molecules of lighter components are captured into the lattice of larger molecules of heavy components, resulting in an increase in the average molar volume and hence an increase in the free-volume. This facilitates movements of the liquid molecules, and hence decreases its viscosity, causing the 'non-ideal' behaviour. This mechanism is considered to be enhanced by the presence of asphaltenes, which are very polar compounds, in any one of the components.

(b) The formation of a solvated shell by the small molecules, of lighter component, surrounding the larger molecules of heavier component. This leads to the formation of a micro cluster-like structure of enlarged molar volumes. This will increase the free volume of the liquid mixture, and hence facilitate movement of the molecules. Consequently, the viscosity decreases causing the 'non-ideal' behaviour. This mechanism is also promoted by the presence of asphaltenes.

9 - The non-ideal viscosity behaviour, of petroleum oil binary mixtures is highly influenced by the polarity of one or more of the mixture components. The greater the polarity of the liquids, the greater the non-ideal behaviour. Thus, the rate of decrease in the viscosity of heavy crude oil increased as the dipole moment of the chemical solvent mixed with it increased (Section 9.3).

10 - From the evaluation (Section 9.3) of Eyring's theory for viscous flow, it may be concluded that:

(a) Eyring's theory of viscous flow, is an approximate theory, based on assumptions of the molecular interactions influencing the movement of liquid molecules. Whilst the equation (9.17) is useful for calculating the viscosity of pure liquids, it cannot be used in its present form for the prediction of the viscosity of complex liquids, e.g. crude oils or petroleum products. This is due to the inavailability of ΔF (the activation energy of viscous flow) values for such complex liquid mixtures.

(b) A modification of Eyring's equation has been proposed, which enables ΔF values to be calculated for crude oils and petroleum products, from values of other measured properties, i.e. boiling points and densities. The equations proposed are:

$$\ln \ln (\Delta F) = 0.0075 (d)^{-0.0180} (T)^{0.7179} \qquad 9.26$$

$$\ln (\Delta F) = \frac{0.0559}{T^{-0.5664}} \qquad 9.27$$

and, for crude oils and petroleum products,

$$\Delta F = -12073 + 23422\, d \qquad 9.28$$

for base oils,

$$\Delta F = 21390 \times (d)^{5.928} \qquad 9.29$$

Use of equation 9.17 with equation 9.26 to predict the kinematic viscosities of crude oils and their products, resulted in a reasonable accuracy. Absolute average deviations were 17.3% to 35.2% (Table 9.30), 20.3% to 26.5% (Table 9.31) and 29.5% to 84.3% (Table 9.32) for crude oils, base oils and petroleum products respectively, over a temperature ranges of 10°C-50°C for crude oils, and 20°C-100°C for base oils and petroleum products.

Use of equation 9.17 with equation 9.27, to predict the kinematic viscosities of crude oils and their products, resulted in absolute average deviations of 18.3% to 38.1% (Table 9.33), 22.3% to 28.9% (Table 9.34) and 36.4% to 78.2% (Table 9.35) for crude oils, base oils and petroleum products, respectively, over a temperature ranges of 10°C-50°C for crude oils, and 20°C-100°C for base oils and petroleum products.

Use of equations 9.17 and 9.28 to predict the kinematic viscosity of crude oils resulted in absolute average deviations of 12.5% to 21.1% (Table 9.39) over the temperature ranges of 10°C-50°C for crude oils, and 20°C-100°C for base oils and petroleum products. However, high deviations (40.2% to 128%) were obtained when using the same equations to predict the kinematic viscosity of petroleum products.

Lastly, use of equation 9.17 with equation 9.29, to predict the kinematic viscosity of base oils, resulted in absolute average deviations of 21.3% to 29.9% (Table 9.40) over the temperature range.

In summary, whilst the appropriate combination of equation 9.17 with equations 9.26, 9.27, 9.28 or 9.29 are satisfactory for prediction of the viscosity of crude oils and base oils, they failed to give acceptable accuracy for petroleum products.

11 - The kinematic viscosity of ternary mixtures of crude oils can be estimated by the developed equation,

$$\ln \nu_{mix} = \Sigma x_i \ln \nu_i \pm \ln \nu^E \qquad 9.34$$

$$\ln \nu^E = a_{12} x_1 x_2 + a_{23} x_2 x_3 + a_{13} x_1 x_3 + a_{123} x_1 x_2 x_3 \qquad 9.36$$

Values of kinematic viscosity of crude oils ternary mixtures calculated by this method, showed good agreement with the experimental results, with deviations in most cases <6% (Table 9.48). This method provided a better fit for experimental results for crude oils, than the currently used methods, ASTM D341 and Refutas Index (Table 9.50).

Equations 9.34 and 9.36 were also used to calculate the kinematic viscosities of newly-prepared ternary mixtures of base oils. Very good agreement was obtained with experimental results with absolute average deviations ~2.0%, within a temperature range of 20°C to 100°C (Table 9.53). The predictions obtained by this method were significantly better than those obtained by the standard methods, ASTM-D341 and Refutas (Table 9.53).

12 - The effect of blending on the pour points of the binary mixtures was studied for crude oil-crude oil, base oil-base oil and base oil-petroleum products mixtures.

Depressions of the pour points were always obtained with crude oil-binary mixtures. Conversely, slight elevations of the pour point were obtained with the base oil-base oil binary mixtures.

13 - From a study of the effect of wax formation on the pour point of crude oil mixtures, it can be concluded that the pour point increases linearly with the wax content. The pour point is attributed to the formation of a network of wax, resulting in total hinderance to the liquid movement. Wax content is considered an additive property which blends linearly.

The effect of the presence of asphaltenes upon the pour points of petroleum oils in general, when subjected to blending, was also studied. It can be concluded that the asphaltenes act as a pour point depressant, resulting in an improvement in the flow property of the oil mixture.

Binary mixtures of wax bearing and asphaltenes-free base oils components, exhibited a slight elevation in their pour points.

A mechanism of the pour point behaviour was proposed for the different binary mixtures systems (Section 9.4), based on the assumptions made to explain the non-ideal behaviour of the viscosity of binary mixtures. The presence of asphaltenes was considered a predominant factor.

14 - From a study of the effect of blending on the boiling point ranges of the crude oils, base oils and petroleum products (Section 9.5), it may be concluded that boiling point ranges are additive properties, and blend almost linearly (Tables 9.59, 9.60 and 9.61). The distillation data, particularly $T_{50\%}$, exhibited smooth curves when plotted against other properties such as density, molecular weight and viscosity (Figures 9.90, 9.91 and 9.92). This might be used for prediction purposes, but more detailed investigation is needed to assess this possibility.

15 - The Reid vapour pressure did not blend linearly, and exhibited non-ideal behaviour (Section 9.6). The RVP values of the crude oils binary mixtures, in the RVP-composition diagrams (Figure 9.95), were less than the ideal cases represented by dashed straight lines on the same diagram. However, the RVP's of the crude oils and their binary mixtures exhibited smooth curves with the corresponding distillation data (Figure 9.96). More detailed study is needed in this particular area to develop a predictive method for RVP of crude oils based on the distillation data.

16 - In terms of viscosity, the light, medium and heavy crude oils, and their

binary mixtures were found to be fairly stable, against stratification over a temperature range 1°C-30°C, and time period up to 12 weeks. However, the crude oil mixtures exhibited less stability than the crude oil components.

The crude oil binary mixtures were, generally, less stable at lower temperature (1°C) than at higher temperature (16°C and 30°C).

17 - A technique for molecular weight determinations of crude oils was developed (Section 8.10).

In conclusion, the study of the effect of blending on selected physical properties of petroleum oils, particularly for crude oils, base oils and petroleum products, should assist in the understanding of changes which occur on blending, and the correlations proposed in Section 9.3 should facilitate more scientific and economic mixing to attain the objectives outlined in Section 1.3.

10.2 RECOMMENDATIONS FOR FURTHER WORK

Several suggestions for future work are presented in this section.

1 - Consideration should be given to the possible extension of this work to cover other physical and transport properties of potential scientific and industrial importance, such as diffusivity, thermal conductivity and Octane Number blending of petroleum oils. Such an investigation should concentrate on the behaviour of these properties upon blending, for the purpose of improving the quality of petroleum oils under different operating conditions. It must also develop predictive correlations of the tested properties.

2 - The present work can be considered as a first step for a long term research project, aimed at providing a better understanding of the chemistry

governing the interactions between different groups of molecules or chemical species present in petroleum oils.

Such a project may provide solutions to the many problems that arise due to the introduction of highly-sophisticated technology into refining, particularly those associated with blending, and which may result in off-specification products and consequently, high quality give away-values. For such a project, the following tasks should be considered.

(a) Initially, qualitative and quantitative analyses are required of the major chemical groups most likely to be present in typical crude oils or their fractions. Subsequently, it will be necessary to develop/modify advanced analytical techniques such as HPLC, glc/mass spectrometry, IR, C^{13} NMR and x-ray defraction spectroscopy, for the analysis of very complex mixtures of hydrocarbons such as petroleum oils.

(b) The crude oils should be classified and categorised according to their major chemical constituents, e.g. paraffins, naphthenes etc. The use of US Bureau of Mines classification (Section 2.1.2) is therefore recommended.

(c) Crude oils can, on the bases of their distillation curves be divided theoretically into fractions of narrow boiling point range, e.g. 20°C. The crude oils can then be distilled to produce the requisite fractions.

(d) Using the analytical techniques mentioned above, together with conventional analytical methods, the narrow boiling point range fractions can be analysed to determine the major chemical compounds present in each, which may be considered as representative compounds or "model compounds" for each fraction.

(e) The different properties of each narrow boiling point fraction can then be easily deduced from the chemical and physical properties of corresponding model compounds.

3 - Using the analytical techniques mentioned earlier, the chemical functional groups can be determined for each narrow boiling point range fraction, and hence for any wide boiling point range fraction produced by back-blending the narrow ones. The application of a group contribution method for the prediction of the viscosity and other properties of crude oils and their products is very promising, since Diab and Maddox(25) obtained very good results for pure hydrocarbon mixtures.

4 - The Corresponding States Principle (CSP) has been used by Johnson(56), to predict the viscosity of Athabasca bitumen, and by Pedersen et al(60) to predict the viscosity of North Sea crude oil. In this method, the pseudo component concept is usually used to characterise the oil in question, with methane as reference fluid. Johnson(56) reported that methane is an inadequate reference fluid for the prediction of bitumen properties. However, it is recommended that this area should be investigated in more detail.

5 - Since the method developed for the prediction of the crude oils viscosities at high pressure (equation 9.8) gave very good agreement with the measured values, it is recommended for testing and validation to predict viscosities of petroleum products and base oils at high pressure.

6 - Because of the initial success in correlating the activation energy of viscous flow, ΔF, used in Eyring's equation of viscosity, with the boiling points, $T_{50\%}$, and densities of petroleum oils, further work in this area is to be encouraged.

Consideration should be given to the effect of temperature upon the ΔF over a wide range of temperature. This may result in improved accuracy for the correlations presented in this work, and therefore modify the applicability of Eyring's equation.

7 - The $T_{50\%}$ of the residue >360°C, obtained by extrapolating the corresponding distillation curve in Figure 9.87, appears to be over estimated. This resulted in inconsistencies in the calculated viscosities by the modified Eyring's equation, and resulted in points off the curves in Figures 9.90, 9.91 and 9.92. Duplicate measurements are therefore required to check this, and may improve the accuracy of the modified Eyring's equation.

8 - Although the distillation curves of the crude oils, petroleum products and base oils were found to be additive, the addition of some chemical solvents, or narrow boiling point fractions, of relatively low boiling point, may improve the distilled yield of crude oils (particularly heavy ones) and residues. This phenomenon could be much more effective if the additives possess high solvation characteristics. This area should, therefore, be explored in detail.

9 - Based on the distillation data of petroleum oils, it would appear worthwhile to investigate the possibility of predicting selected physical and transport properties, particularly those which are not usually available in the literature such as thermodynamic properties.

APPENDICES

Appendix A

DEFINITIONS AND SUMMARIES OF SOME IMPORTANT TEST METHODS OF PETROLEUM

Definitions and summaries of some important test methods of petroleum properties, explained previously are given below alphabetically. For completeness, a list of all common methods of test is also included as A-11.

A-1 Asphaltenes Content (IP 143):

The asphaltenes content of a petroleum oil is the percentage by weight of wax-free material insoluble in n-heptane but soluble in hot toluene.

A known quantity of the sample is dissolved in n-heptane and the insoluble material, consisting of asphaltenes and waxy substances, is separated under hot reflux with n-heptane, and the asphaltenes are isolated by extraction with toluene or benzene.

A-2 Cetane Number (ASTM D613-86 / IP 41 - 81)

The Cetane Number is a measure of the ignition performance of a diesel fuel obtained by comparing it to reference fuels (n-cetane and heptamethyl nonane) in a standardized engine test. The Cetane method provides a means of determining the compression - ignition characteristics of diesel fuels. The method utilizes a single - cylinder engine of continuously variable compression ratio, with suitable loading and accessory equipment and instruments, mounted on a stationary base.

A.3 Cloud Point:

Cloud point of a transparent petroleum oil is the temperature, expressed as a multiple of 1°C, at which a cloud or haze of wax crystals appears at the bottom of the test jar when the oil is cooled under prescribed conditions. The cloud point of a petroleum oil is an index of the lowest temperature of its utility for certain applications.

A.4 Conradson Carbon Residue (ASTM D189-81 / IP 13-82)

The carbon residue is the percentage by weight of the carbonaceous residue formed after evaporation and pyrolysis of a petroleum product in a special crucible. The residue is not entirely composed of carbon, but is a coke which can be further changed by pyrolysis.

The carbon residue value of burner fuel serves as a rough approximation of the tendency of the fuel to form deposits in the burners.

The carbon residue value of motor oil is regarded as indicative of the amount of carbonaceous deposits a motor oil would form in the combustion chamber of an engine.

A knowledge of the carbon residue values of crude oil residuums and bright stocks is useful in the manufacture of lubricants.

A.5 Freezing Point (ASTM D2386-77 / IP 16-83)

The freezing point is that temperature at which crystals of hydro-carbons formed on cooling disappear when the temperature of a transparent fuel is allowed to rise.

The determination of freezing point of a fuel provides a method for the detection of separated solids in engines at any temperature likely to be encountered during operation.

A-6 Octane Number of Motor Fuels by the Research Method (ASTM D2699 - 86 / IP 237-69), and Motor Method (ASTM D 2700-86 / IP 236-69):

This test method covers the determination of the knock characteristics of motor gasolines intended for use in spark-ignition engines, in terms of Octane Number.

Octane Number is defined as the measure of the resistance of a fuel to knock, determined by comparing its knocking tendency with those for blends of reference fuels, of known Octane Number, under standard operating conditions.

This is done by varying the compression ratio, of a single-cylinder engine of continuously-variable compression ratio, for the fuel sample to obtain standard knock intensity as measured by an electronic detonation meter.

A-7 Penetration of Bituminous Materials (ASTM D5 / IP 49-86):

The penetration of a bituminous material is its consistency expressed as the distance in tenths of a millimeter that a standard needle penetrates vertically into a specimen of the material under specified conditions of temperature, load and duration of loading. The usual test temperature, applied load and duration of loading are 25°C, 100gm and 5 seconds, respectively. For special purposes, other conditions may be used. The penetration of bituminous materials is considered to be a measure of their hardness.

A-8 Smoke Point (ASTM D1322 / IP 57-55):

The smoke point is defined as the maximum flame height in millimetres at which a kerosene will burn without smoke. This is determined by burning the fuel sample in a standard lamp in which flame height can be varied against a background of a graduated millimetre scale. The smoke point is measured by raising the wick until a smokey flame is produced and then lowering it to the point where the smokey tail just disappears. This flame height, measured to the nearest millimetre, is the smoke point of the sample.

A-9 Softening Point of Bitumen, Ring and Ball (IP 58-86):

The softening point is the temperature at which a substance attains a particular degree of softness under specified conditions of test.

A steel ball of specified mass is placed upon a disk of bitumen contained within a metal ring of specified dimensions. The assembled apparatus is placed in a bath of liquid, and the temperature of the liquid is raised at a specified rate. The softening point is the temperature at which the bitumen surrounding the steel ball just touches the base plate of the apparatus.

A-10 Viscosity Index (ASTM D2270 / IP 226-84)

The viscosity index (V.I.) is an arbitrary number indicating the effect of change of temperature on the kinematic viscosity of an oil. A high viscosity index signifies relatively small change of kinematic viscosity with temperature.

Viscosity index for the range 0 to 100, for oils whose kinematic viscosity at 100°C is ≥ 2 cSt. and ≤ 70 cSt, is calculated via the equation,

$$\text{Viscosity Index} = \frac{L - U}{L - H} \times 100 \qquad (A.1)$$

where,

U = Kinematic viscosity at 40°C of the oil whose viscosity index is to be calculated.

L = Kinematic viscosity at 40°C of an oil of 0 viscosity index having the same viscosity at 100°C as the oil whose viscosity index is to be calculated.

H Kinematic viscosity at 40°C of an oil of 100 viscosity index having the same viscosity at 100°C as the oil whose viscosity index is to be calculated.

The values, in cSt , for L and H are read from a special table.

If the kinematic viscosity of the oil at 100°C is > 70.0 cSt., then the values for L and H are obtained via equations,

$$L = 0.8353\ Y^2 + 14.67\ Y - 216.25 \qquad (A.2)$$

$$H = 0.1684\ Y^2 + 11.85\ Y - 96.95 \qquad (A.3)$$

where,

Y = Kinematic viscosity at 100°C, cST.

A.11 Test Methods for Petroleum

Parameter	Units	Method Reference*
Aniline Point	°C	D 611 / IP 2
Ash Content - straight	% wt	D 482/ IP 4
- sulphated for metals	% wt	D 3327
Ashphaltenes	% wt.	IP 143
Breaking Point -Fraas	°C	IP 80
Cetane Index	-	D 976 / IP 218
Cloud Point	°C	D 2500 / IP 219
Cold Filter Plugging Point (CFPP)	°C	IP 309
Colour - ASTM	-	D1500 / IP 196
Congealing Point of Wax	°C	D 938 / IP 76
Conradson Carbon Residue	% wt	D 189 / IP 13
Copper Corrosion	-	D 130 / IP 154
Density - Hydrometer	g/ml	D 1298 / IP 160
- Pyknometer	g/ml	IP 190
Diesel Index	-	IP 21
Flash Point:		
- Abel	°C	IP 170
- Pensky Martens Closed Cup	°C	D 93 / IP 34
- Pensky Martens Open Cup	°C	IP 35
Freezing Point	°C	D 2386 / IP 16
Gravity - API	°API	D 1250 / IP 200
Heat of Combustion - Gross and Net	cal/g	US Bureau of Standards

Parameter		Units	Method Reference*
Hydrocarbon Type Analysis:			
	- Saturates/Aromatics / Olefins	% vol	D 1319 / IP 156
	- Saturates/Aromatics/Resins	% wt	BAM 74
Hydrogen Content		% wt	Elemental Analyser
Hydrogen Sulphide		ppm	by UOP 35780 titration
Loss on Heating		% wt	D 6
Mercaptan Sulphur		% wt	IP 104
Metals		µ/g	ICAP spectrophotometry on solution from D 3327 ash
Neutralisation Number - TAN and TBN		mg KOH/g	D 664/ IP 177
Nitrogen Content		% wt	D 3228
Octane Number	- Motor	O.N.	D2699
	- Research	O.N.	D 2700
Penetration at 25°C		0.1 mm	D 5/ IP 49
Pour Point		°C	D 97/ IP 15
Refractive Index		-	D 1218 or D 1747
Reid Vapour Pressure		psi	D 323/ IP 69
Salt Content		% wt	IP 77
Sediment		% wt	D 473/ IP 53
Smoke Point		mm	D 1322/ IP 57
Softening Point		°C	IP 58
Sulphur Content		% wt	Microcoulometer UOP Raney Nickel IP 336
Viscosity	- Kinematic	cSt	D 445/ IP 71
	- Saybolt	SUS	D 2161

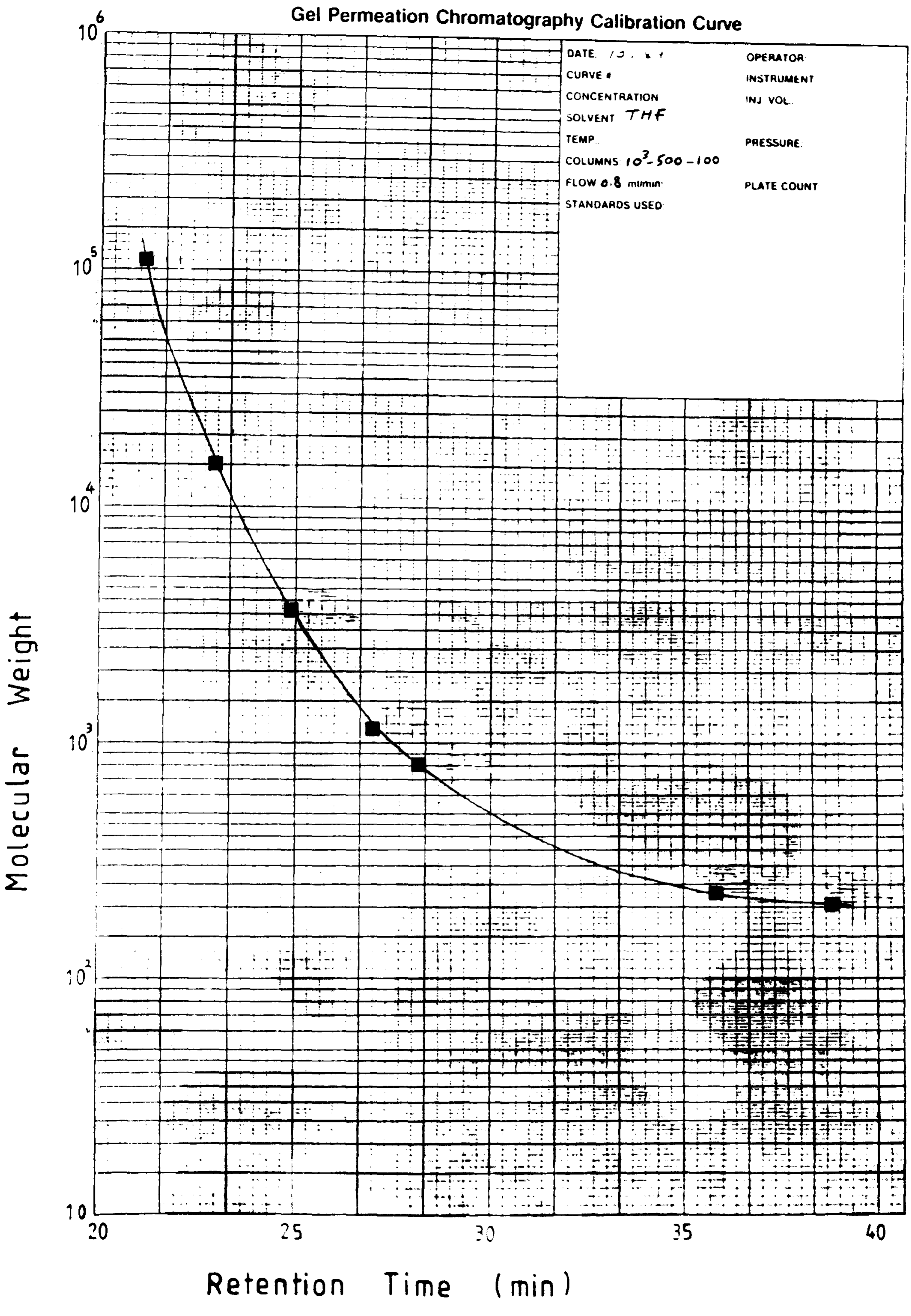
Parameter	Units	Method Reference*
Viscosity Index	-	D 2270/ IP 226
Water Content	% vol	D 95/ IP 74
Wax Content	% wt	BP 237

* Initials define the sources of the test methods utilised:

D	-	A.S.T.M.
IP	-	Institute of Petroleum
BAM	-	Burmah Oil Analytical Method
BP	-	British Petroleum Analytical Series
UOP	-	Universal Oil Products Analytical Series.

Appendix B

Gel Permeation Chromatography Calibration Curve



DATE: [illegible]
CURVE #
CONCENTRATION
SOLVENT THF
TEMP.
COLUMNS 10^3-500-100
FLOW 0.8 ml/min
STANDARDS USED

OPERATOR
INSTRUMENT
INJ VOL.
PRESSURE
PLATE COUNT

Appendix C

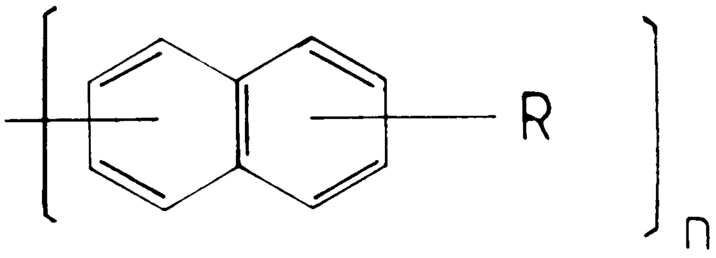
CHARACTERISTICS OF SHORT RESIDUE > 530°C

Parameter	Units	Results
Density @ 65°C	g/ml	1.078
Density @ 15°C	g/ml	1.110
Gravity	°API	-4.0
Total Sulphur	%wt	6.0
Total Nitrogen	% wt	0.50
Kinematic Viscosity		
at 100°C	cSt	11700
Pour Point	°C	>60
Flash Point	°C	351
Asphaltenes Content	%wt	18.6
Hydrocarbon Type		
Distribution:		
Saturates	%wt	11.2
Aromatics	%wt	60.0
Resins	%wt	5.4
Asphaltics	%wt	23.4
Conradson Carbon Residue	%wt	24.6
Penetration (100g @ 25°C)	1/10 mm	16
Softening Point	°C	60
Loss on Heating	%wt	0.02

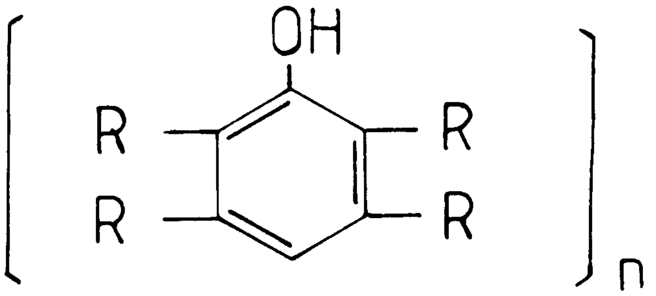
Appendix D

Chemical Structures of Some Pour Point Depressants (102):

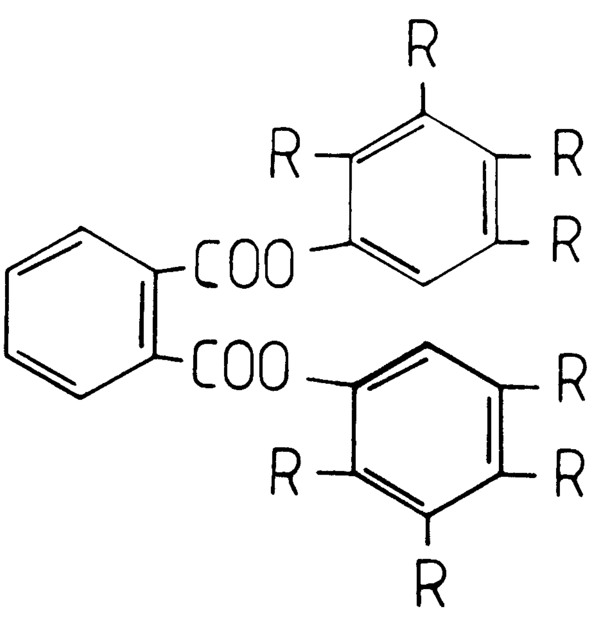
1. Condensation product of a chlorinated paraffin wax with naphthalene:



2. Condensation Products of tetra paraffin phenol:



3. Di(tetra paraffin - phenol) - phthalate:

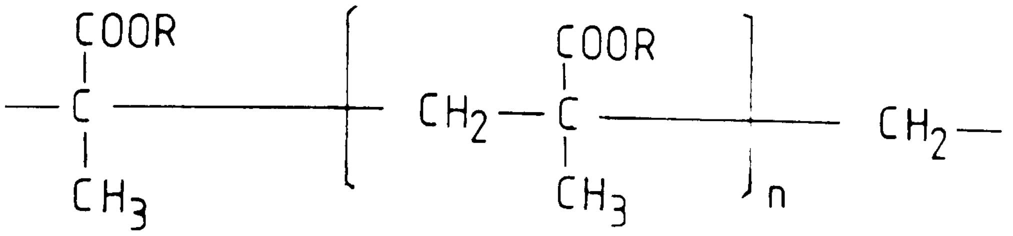


where,

R = alkyl group

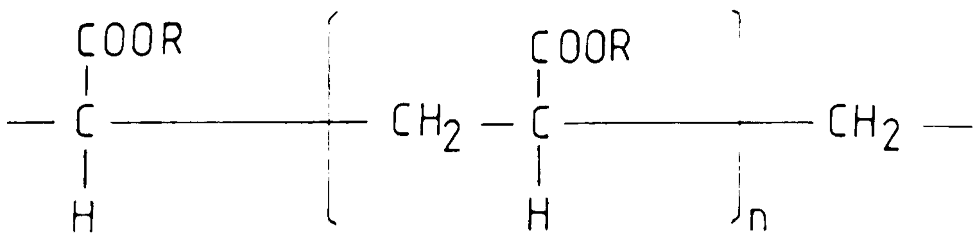
Appendix D. (continued)

4. Polymethacrylates:



$$-\underset{CH_3}{\overset{COOR}{C}}-\left[CH_2-\underset{CH_3}{\overset{COOR}{C}}-\right]_n-CH_2-$$

5. Polyacrylates:



$$-\underset{H}{\overset{COOR}{C}}-\left[CH_2-\underset{H}{\overset{COOR}{C}}-\right]_n-CH_2-$$

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