STUDIES IN THE SURFACE CHEMISTRY OF BOUNDARY LUBRICATION

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by

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ABSTRACT

A general survey of the published literature on boundary lubrication is presented at the beginning of the thesis.

Physico-chemical phenomena at the metal/hydrocarbon solution interface have been studied in an investigation of the thickness of the "interfacial region", where the liquid is said to possess abnormal properties. Russian workers claim that this region is about 1000Å deep, and that the properties of solutions in it determine their efficiency as boundary lubricants.

Direct determination by a radio-tracer technique has shown that adsorption of octadecanoic acid on pure iron from hexadecane is irreversible and does not significantly exceed a monomolecular layer. Studies of the wettability at elevated temperature of stainless steel bearing adsorbed fatty acids suggest that participation of solvent molecules in the surface film is important when a proportion of the adsorbate molecules has been desorbed.

Suspensions of iron powder in hydrocarbons are only partially stabilised by dissolved fatty acids. Since aggregation of primary particles is not prevented, mutual approach to within not more than 300Å must still occur.

Determinations of the effect of long-chain fatty acids on the rate of flow of hexadecane through stainless steel capillaries have demonstrated the absence of immobilised wall layers more than 300Å deep.

Comparison of X-ray diffraction traces from films of octadecanoic acid-hexadecane solution on mild steel with those from Langmuir-Blodgett multilayers shows that vertical orientation of molecules (with respect to the metal surface) in the interfacial region extends through less than 5 molecular layers (125Å).

Almost all these findings are consistent with retention of normal ("bulk") properties by solution adjacent to a metal surface, itself bearing an adsorbed film only one molecule thick. Immobilised boundary layers more than 300Å deep were proved to be absent in the systems studied.

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CONTENTS

1. INTRODUCTION

This chapter contains a brief survey of the literature on boundary lubrication, outlining the background for the work described in this thesis. Detailed discussion of individual points is deferred until the appropriate sections of later chapters in order to avoid repetition.

1.1 Hydrodynamic, elastohydrodynamic, and boundary lubrication.

It has long been known that when "clean" solids rub together, seizure occurs at points of real contact and movement causes tearing of the bridges formed, with generation of high local temperatures. Under these conditions the sliding surfaces are severely damaged and friction is very high.

If, however, the surfaces of two solid bodies in sliding contact can be kept apart by a coherent oil film, practically no wear occurs and resistance to motion is due entirely to work done in shearing the oil. The "performance" of a lubricating oil under these purely hydrodynamic conditions is governed by its viscosity and is independent of its chemical properties and of the chemical nature of the solid surfaces. A load applied normal to the plane of contact causes lubricant to be squeezed out of the contact area. In "point" and "line" contacts under high loads this is opposed by an increase in contact area owing to elastic deformation of the solid surfaces, and by a rise in viscosity due to the high hydrostatic pressure in the contact region. This is the regime of elastohydrodynamic lubrication. It has been shown by Archard and Kirk[1] to enable loads of several kilograms to be supported by an oil film between crossed cylinders at sliding speeds of less than 1 cm/sec. Cameron has shown[2] that the oil film thickness between spheres in sliding contact may actually increase with load when elastic deformation and increase in viscosity with pressure are taken into account, and is in general only weakly dependent on load.

Under even higher loads and at lower sliding speeds a coherent oil film can no longer be maintained, contact of the surfaces occurs, and considerable wear ensues, with frictional heating, severe damage, and eventual seizure, unless a "boundary lubricant" is present. The effectiveness of boundary lubricants is governed by their ability to adsorb on the sliding surfaces and is independent of their viscosity. Coefficients of friction between dry metal surfaces are reduced from about 1.0 to 0.05-0.10 by a monomolecular layer of a good boundary lubricant such as stearic acid. It will be seen, however, in later sections that conditions intermediate between those of true boundary and elastohydrodynamic lubrication are frequently encountered. This occurs when the oil film thickness is comparable with the height of irregularities in the sliding surfaces. Friction and wear can then be considerably reduced by the presence of dissolved boundary additives although the viscosity of the oil is still an important factor.

1.2 True boundary lubrication : the Bowden-Leben apparatus[3,4].

Conditions of true boundary lubrication may be reached under very high loads and slow sliding speeds, or when the supply of lubricant is restricted. In the Bowden-Leben apparatus a hemispherical rider under loads of up to several kilograms is in sliding contact with a flat polished plate which is driven at speeds of the order of 0.01 cm/sec. by a variable speed hydraulic ram. Frictional heating is negligible at such low sliding speeds and deformation of the slider results in a normal pressure equal to the yield strength of the metal. This arrangement has been critised by Dacus[5] and Fein[6], who considered that a thick layer of lubricant could accumulate on the rider even if the film on the plate was only one molecule thick. It is true that Zisman[7] observed transfer of lubricant from the plate to an originally uncoated slider but there has been no evidence published of a multimolecular deposit being built up in this way. Conditions in the Bowden-Leben apparatus approximate closely to those of true boundary lubrication, and the next sub-sections will describe its use in studies of the action of boundary lubricants, which has been widespread.

1.2(1) Dependence of coefficient of friction on chain length of lubricant.

Bowden et al.[4] showed that smears of hydrocarbons, alcohols, or fatty acids reduce the coefficient of dynamic friction (μ) between clean steel surfaces from about 1.0 to less than 0.1. μ falls linearly as the homologous series are ascended, until a critical hydrocarbon chain length is reached above which there is no further reduction in friction. This chain length is 20 carbon atoms for paraffins, 12 for alcohols, and 6 for fatty acids. A similar proportionality had been reported earlier in Hardy's studies[8] of static friction, although limiting values were not reached.

1.2(2) Effect of temperature on boundary lubricants.

The protection afforded by a paraffin or alcohol is not impaired by an increase in temperature until its melting-point is reached. At this temperature both friction and surface damage rise markedly[4]. The behaviour of fatty acids is similar on inert metals, such as platinum, but on relatively reactive metals like mild steel or zinc the transition does not occur until a much higher temperature (about 70°C higher) is reached.[9,10,11.] This was originally considered to correspond unequivocally with the softening-point of the corresponding metal soap, formed by reaction of the fatty acid with the surface. Electron diffraction studies[12] by Menter and Tabor supported this view, but later investigations have revealed the existence of two distinct transitions.[13] These appeared to correspond with change of phase of the adsorbed film from solid to liquid, followed later by complete desorption of the film. Research by other workers has shown that the precise value of transition temperature may be affected by experimental conditions, such as the load used.[14,15,16.]

1.2(3) Mono- and multimolecular films as boundary lubricants.

Blodgett showed that monolayers of fatty acids or their salts spread on a water surface could be transferred to a solid by passing a specimen through the air/water interface containing the film.[17.] Repetition of the process enabled films hundreds of molecular layers thick to be deposited.[18] The technique has been used by several investigators[3,4,14,15,19,20,] to explore the effectiveness of a known number of molecular layers of a boundary lubricant such as calcium stearate deposited on a metal. A single molecular layer of calcium stearate was found to reduce μ to about 0.1, but it was worn away so quickly that repeated runs over the same track gave rapidly increasing values of μ. Increasing the number of layers in the film did not alter μ, but durability improved, and a film 53 layers deep survived repeated sliding indefinitely. Other authors have reported similar findings. Frewing[15] observed that the transition temperatures of films less than 40-50 molecular layers deep were lower than the bulk values. Built-up films, however, are artificial in nature and may not even follow the profile of a metal surface precisely unless it is perfectly smooth.[21] Furthermore, the improved durability of thicker films may be due merely to the presence of a reservoir of soap, from which breakages in the primary film can be repaired. The thickness of the actively engaged boundary layer may not necessarily be more than two or at most a few molecules thick.

1.2(4) Retracted monolayers and their durability.

Extensive studies of the composition, wettability, and durability of monolayers adsorbed from solution in alkanes have been made by W.A. Zisman.[7,22-26] The oleophobic nature of monolayers of long-chain polar molecules adsorbed on metal or glass surfaces enable a specimen to be withdrawn free from adhering liquid after immersion in such a solution or the molten compound itself.[22]

Coefficients of friction between a stainless steel slider and a glass plate coated with retracted films of lower amines and fatty acids were found to be inversely proportional to the molecular weight of the lubricant.[7] A limiting value of $\mu = 0.05$ was reached for compounds containing at least 14 carbon atoms. Durability was much greater than had been expected in the light of Bowden's experiments.

The composition of monolayers retracted from solutions in which the hydrocarbon chain lengths of the solute and solvent were closely matched was found to be a function of the time of immersion.[24] Contact angle and contact potential measurements[26] indicated that a significant proportion of solvent molecules were initially co-adsorbed with the solute, but were gradually replaced by polar solute molecules. Films[24] retracted on glass sliders which had been immersed for short periods in solutions of n-alkyl amines in n-alkanes of the same chain length showed very poor resistance to wear under heavy loads (5kg). Under lighter loads (1kg), however, durability was unimpaired, since under these conditions lateral van der Waals interactions were sufficient to hold adlineated solvent molecules in place and prevent break-up of the film.

Films of fatty acids, amines, and alcohols retracted on stainless steel from the melt were far less durable under a stainless steel slider than similar monolayers on glass.[25] Fatty acids were more effective lubricants than the corresponding amines, the reverse of the behaviour which had been observed in films adsorbed on glass. This was attributed to chemical attack of the stainless steel surface by the fatty acids, while the higher dipole moment of the amines had resulted in their being more strongly adsorbed on glass. Zisman deduced that the poor durability of monolayers adsorbed on stainless steel was due to the high mutual affinity of the surfaces. Breakages in the lubricant film would therefore be rapidly followed by cold welding and local seizure.

1.2(5) Lubrication by solutions of polar compounds in hydrocarbons.

Gregory used 1% solutions of fatty acids and metal soaps in mineral oil to show the divergence of transition temperature (T) on inert and reactive metals.[11,27]. Similar solutions were employed by Tingle in his studies of the importance of oxygen and moisture in lubrication of metals by fatty acids.[28] Transition temperatures were in both cases unchanged from the values for the bulk acids. Hughes and Whittingham[14] found that a 0.01% solution of oleic acid in a paraffin oil gave a transition temperature only 8°C below that observed for the pure acid, and considered that "very dilute solutions are able to saturate the surface as far as boundary lubrication at low speeds is concerned".

Other authors, however, have reported a marked dependence of transition temperatures of solutions on their concentration (C). Frewing found that graphs of log C versus $\frac{1}{T}$ for decanoic, dodecanoic, tetradecanoic, and octadecanoic acid on mild steel gave a set of parallel straight lines.[29] The slope of these lines was used to calculate the heat of adsorption (ΔH)

of the fatty acids, on the assumptions that adsorption was reversible, and that the transition to higher friction occurred when the monolayer had been depleted to a critical fractional coverage. Although ΔH appeared to be the same for all the acids studied, an increase in fatty acid chain length resulted in a higher transition temperature at a given concentration. Frewing considered that the reversibility of the transition and the low values of ΔH deduced in this way, namely, 13.5 k.cal/mole, were proof that adsorption of the fatty acids was entirely plysical in nature.

Coefficients of friction of various metal surfaces covered with fatty acid monolayers retracted from hexadecane solution have been studied by Shooter,[30] both dry and in the presence of a pool of the corresponding solution. There was usually a further fall in μ in the presence of excess solution. μ generally decreased to a limiting value with increasing fatty acid chain length, but in the case of iron surfaces the lowest values (0.06-0.13) were observed with stearic acid (C_{18}); a solution of octacosanoic acid (C_{28}) gave values of μ in the range 0.1 - 0.2. There is a hint here of the "chain matching" optimum which has been reported by Cameron and Grew.[31] These authors found that solutions of fatty acids with the same chain length as that of the n-alkane carrier gave higher transition temperatures than those of a similar concentration of either higher or lower acids in the same solvent. A solution of dodecanoic acid in dodecane gave a higher transition temperature than similar solutions in decane, tetradecane, or hexadecane. Furthermore, graphs of log C versus $\frac{1}{T}$ for dodecanoic acid solutions in a series of different alkanes had differing slopes, implying that the heat of adsorption altered with the solvent. The observation that the solvent influenced boundary layer properties in a very specific way confirmed earlier investigations by Askwith, Cameron, and Crouch[32] in the field of elastohydrodynamic lubrication (see section 1.4(1)).

1.3 The friction pendulum and durability of retracted monolayers.

The durability of films of tetradecanoic acid retracted from the melt, or from solutions in various media, on steel of an unspecified type was investigated by Tamai[33,34], with a "friction pendulum". Coefficients of friction were calculated from the damping. Strict comparison with Zisman's work is difficult since the sliding speed was not constant, but varied between zero and 3 mm/sec, and loads of only 100g were used.

In contrast with Zisman's observations[24], durability of tetradecanoic acid retracted from solution in hexadecane, after immersion for only three minutes, was greater than that of films retracted from the molten acid or from solution in benzene.[34] Films retracted from the melt or from benzene solution, however, showed a sharp fall in friction at the melting-point of the acid, while those from hexadecane solution gave a continuous increase in friction with temperature above the melting-point. Tamai considered that the superior "lubricity" of mixed tetradecanoic acid -

hexadecane films at temperatures below the melting-point of the acid was due to improved fluidity of the adsorbed layer, which allowed quick repair of breakages in the film. In view of the apparent conflict between the data reported by the two authors, it is important to note that Zisman did not check that the poor durability which had been found for mixed monolayers on glass, was also true of similar films on steel.[25] Tamai's results are, furthermore, in accord with those of Askwith, Cameron, and Crouch.[32]

1.4 Quasi - elastohydrodynamic lubrication.

1.4(1) The four-ball machine.

This consists basically of a single ball, usually $\frac{1}{2}$-inch in diameter, in loaded contact with three similar balls mounted in a cup whose torsional movement is restricted by a spring balance. The single ball is rotated by a variable-speed electric motor and frictional resistance measured directly by the spring balance; the cup also acts as an oil reservoir.

Beeck et al. found that friction in a four-ball machine lubricated by a hydrocarbon oil was reduced by fatty acids,[35] reaching a steady value of $\mu = 0.10$ at speeds below 0.3 r.p.s. Reduction of friction by dissolved fatty acids at higher speeds was attributed to a "wedging effect" on the lubricant film separating the balls, associated with their surface activity. This was most marked when the sliding surfaces were very smooth; a companion paper[36] reported the importance of incorporating a "chemical polishing" agent in lubricants for maximum reduction of wear. The existence of such a wedging effect would imply that dissolved fatty acids alter the structure or viscosity of a coherent liquid film, in addition to their conventional boundary lubrication properties.

Fein[6,37], reported that the critical surface temperature for "scuffing" (i.e. onset of severe wear), in a 4-ball machine lubricated by solutions of fatty acids in n-alkanes was proportional to log (sliding speed/$_{\text{load}}$). The proportionality held over a wide range of speed/$_{\text{load}}$ values up to 10^4x those encountered in the Bowden-Leben apparatus and showed that a hydrodynamic component was nearly always present. Equimolar solutions of octadecanoic acid in dodecane and hexadecane gave similar transition temperatures at low speed/$_{\text{load}}$ ratios, but an increasing divergence appeared at higher sliding speeds, when the higher viscosity of hexadecane (twice that of dodecane) became critical. Addition of octadecanoic acid to the more viscous hydrocarbon, squalane, actually resulted in a <u>lowering</u> of transition temperature at high speed/$_{\text{load}}$ values.

Askwith, Crouch, and Cameron[32] studied lubrication by equimolar solutions of fatty acids, amines, and alcohols in n-alkanes. Critical loads for onset of scuffing were determined and changes in the thickness of the oil film separating the balls were followed by a discharge voltage method,[2] although the geometry of the contact area did not allow precise calibration. For solutes of a given homologous series it was found that the scuffing load was a maximum when the chain length of the additive matched that of the paraffin carrier. Film thickness under a given load was also found to be greatest under this condition, indicating that the relationship between solvent and solute chain length influenced the properties of the oil film over a region extending far into the liquid phase. The scuffing load for a given fatty acid and carrier increased sharply with concentration until this reached about 0.001M, but showed only a slight dependence at higher concentrations. This contrasts with the uniform dependence of $\frac{I}{T}$ on log C which had been observed by Grew and Cameron[31] on the Bowden-Leben apparatus over the whole concentration range studied (up to 5.0%). Frewing[29] had observed linear behaviour right up to around 80% fatty acid in white oil.

1.4(2) The pin-on-disc apparatus.

In the pin-on-disc apparatus friction is measured between a flat - or hemispherical - ended rod pressed against a rotating, polished disc. Russell[38] has reported that the variation of friction with temperature of copper surfaces lubricated by solutions of 0.5, 1.0, or 5.0% octadecanoic acid in hexadecane is independent of concentration right up to the transition temperature. This is consistent with Cameron's observation on the 4-ball machine that scuffing loads were only slightly affected by increases in concentration above 0.001M.

Fein[6] obtained identical transition temperature: log $(\text{speed}/_{\text{load}})$ graphs for 0.43% octadecanoic acid/hexadecane solutions in the 4-ball and pin-on-disc machines, showing that they operate under equivalent conditions. Askwith, Cameron, and

Crouch[32] were able to reproduce the "chain matching" effect, which had been found on the four-ball machine, in durability measurements on the pin-on-disc machine. In both cases speeds of several hundred r.p.m. were used, which would be expected to result in a considerable hydrodynamic contribution to the load-carrying film in the light of Fein's investigations. Experiments on the Bowden-Leben apparatus, however, (section 1.2(5)), demonstrated that solutions containing matched additive and carrier also gave enhanced transition temperatures under conditions of exclusively boundary lubrication.[31]

1.5 The range of action of boundary lubricants.

Although there seems little doubt that under drastic conditions sliding surfaces are separated only by adsorbed, probably unimolecular, films, uncertainty remains about the depth and nature of the boundary zone under conditions of "mixed lubrication". The work of Fein appeared to demonstrate that the effect of the solvent was purely a function of its viscosity, but Cameron and his co-workers claimed to have observed the interaction of solute and solvent molecules to produce fairly thick films with modified rheological properties.[32] The latter view is supported by Fuks' studies[39] of the thinning of solutions of fatty acids in hydrocarbons between polished metal discs, which will be discussed in detail in Chapter (4). Fuks found evidence for the existence of a quasi-solid layer extending up to 1000 A from the surface into the bulk liquid. This zone was thickest when the molecular structures of the fatty acid and the hydrocarbon were not too different.

1.6 Summary.

The action of boundary lubricants has been correlated with their ability to form adsorbed films on metal surfaces. The protection afforded by such a film depends on the strength of the metal-adsorbate bond and on the lateral cohesion between the adsorbed molecules. Adsorbed films are apparently only effective lubricants at temperatures below their bulk melting-points. The increased transition temperatures of fatty acids on chemically reactive metals are probably related to the softening-points of the corresponding soaps. The difficulty of preparing soaps in a pure state, however, prevents accurate determination of melting-points for comparison. In any case it seems unlikely that the disorientation temperature of a compound adsorbed on a metal and subjected to shear under heavy loads will necessarily be identical with its bulk melting-point, in view of the difference in the environment of the polar head-groups and the effect of pressure.[4]

Differences in opinion exist on the effect of the concentration of solutions of boundary lubricants on friction transition temperatures. Bowden's school considered that dilution of fatty acids by mineral oil to 1% $^{w}/_{v}$ had little effect, whereas Frewing and Cameron have found a marked dependence of transition temperature on concentration.

Experiments carried out by Fein under conditions of elastohydrodynamic lubrication indicated that hydrocarbon solvents behaved as inert carriers in the presence of dissolved fatty acids. They only contributed to the load-bearing film at high sliding speeds, when hydrodynamic conditions predominated. Cameron, on the other hand, considered that interactions between structurally similar solute and solvent molecules led to formation of a comparatively thick, viscous or solid surface film even under static conditions.

1.7 Scope of research.

The work described in this thesis was undertaken to explore the extent and structure of "surface films" in solutions of boundary lubricants near metal surfaces, with particular attention to the part played by the solvent. Several surface chemical techniques have been used to investigate the effect of fatty acids (chosen as representative boundary lubricants) on interactions between metal surfaces immersed in hydrocarbons, and on the films separating them:

(i) The extent of adsorption of octadecanoic acid on iron from solution has been checked by the use of radio-tracers.

(ii) Molecular orientation in the interfacial zone has been studied directly by X-ray diffraction of oil films and built-up Langmuir-Blodgett multilayers on metal surfaces.

(iii) Measurements of flow-rates of solutions through fine pores have been used to establish whether a comparatively thick viscous surface layer is present at the solid-solution interface.

(iv) Stability and rheology of suspensions of finely-divided iron powder in hydrocarbons containing dissolved additives have been used to correlate adsorption of the additive with its affect on surface fields of force.

(v) Changes in the wettability of metal surfaces in contact with solutions of fatty acids at elevated temperatures have been compared with frictional transitions.

(vi) Solute-solvent interactions between homologous series of polar compounds and hydrocarbons have been studied by solubility measurements.

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2. ADSORPTION AND BOUNDARY LUBRICATION.

2.1 Introduction.

The action of boundary lubricants is associated with their ability to form cohesive adsorbed films, firmly bound to metal surfaces but able to slide easily over each other. Such a layer would be expected to possess quasi-solid properties and would constitute a deep cushion against contact between sliding surfaces, at least if it were several molecules deep.

Theoretical considerations, however, suggest that adsorption of multimolecular layers of polar compounds from hydrocarbon solutions is unlikely. The outer surface presented by the hydrocarbon "tails" of a single adsorbed layer of polar molecules oriented with their head-groups towards the metal surface, is chemically similar to the hydrocarbon solvent, and would not be expected to promote adsorption of a second layer. Further adsorbed layers could only be bound to the metal surface by weak van der Waals interactions which would be masked by the first adsorbed layer. The van der Waals attractive energy between the terminal methyl groups of the molecules in a vertically oriented monolayer and those of a hypothetical second layer have been calculated to be of the same order as their thermal energy.[1] Multimolecular adsorption therefore appears unlikely, except perhaps in almost saturated solutions, when it would have more of the character of premature crystallisation than adsorption. The non-formation of micelles in solutions of simple alcohols, amines, and fatty acids[2] is itself an indication of the unlikelihood of multilayer adsorption.

Solutions of metallic salts of fatty acids in hydrocarbons, i.e. soaps, have been shown to contain micellar species,[3] and even "set" to form quasi-solid gels.[4] It is possible, therefore, that if large amounts of soap were formed by reaction of dissolved fatty acid at the metal surface, multilayers of soap molecules could build up in the surface zone to form a "liquid-crystalline" structure.[5]

2.1(1) Adsorption of hydrocarbons on metals.

Zisman has shown by contact angle and contact potential measurements[6] that the surfaces of polished metal specimens withdrawn from immersion in liquid hydrocarbons are covered by an adsorbed monolayer. Contact angles of drops of several liquids on metal surfaces coated with adsorbed alkane films were found to be similar to those on polyethylene, which suggested that the outer surfaces of the films were compound of methylene ($-CH_2-$) groups. Hexadecane spread completely on these surfaces, but retracted into droplets on adsorbed films of amines or fatty acids on similar substrates. This indicated that alkanes were adsorbed with the axes of the molecules parallel with the metal surface, in contrast with the vertical orientation assumed by adsorbed polar molecules.

2.1(2) Adsorption of fatty acids on metals.

Bowden and Moore[7] immersed irradiated metal foils in a solution of octadecanoic acid in benzene and measured the radioactivity transferred to the solution. The foils were removed, extracted with benzene in a Soxhlet apparatus, and the amount of chemisorbed material which had been removed was estimated from the activity of the extract. Interpretation of the results was vitiated by extensive adsorption of the tagged metal stearate on the walls of the apparatus. With the metals Cd, Zn, and Cu, however, it was evident that the amount of soap formed greatly exceeded the equivalent of unimolecular coverage of the metal surface. No transfer of radio-active material to either the extract or the original solution was observed, however, in the cases of Pt and Au, showing that no removable chemisorbed layer had been formed.

Transfer of metal to the liquid phase from steel plates and iron powder immersed in solutions of long-chain fatty acids in hexadecane has been studied by Sakurai and Baba.[8,9.] After periods of 2-7 hours at 100°C appreciable concentrations of iron were detected in the solutions after filtration, by treatment with o.phenanthroline (complexing reagent). Evidence of micelle formation was shown by depolarisation of the fluorescence of Rhodamine B, a dye which has been shown by Singleterry[3] to be colourless in hydrocarbon solutions but coloured when solubilised in micelles. Very little dissolved iron could be detected in solutions which had been in contact with iron powder at only 50°C. These observations suggest that the adsorption measurements surveyed in this chapter, which were all carried out at or around 25°C, have only limited relevance to boundary lubrication. Even in lubricated sliding, frictional or external heating may result in generation of local temperatures well in excess of 100°C. "Boundary layers" of solutions of fatty acids in hydrocarbons, however, have also been reported to possess enhanced resistance to thinning under purely vertical stresses,[8,9,10,11] when no question of frictional heating arises. It seems worthwhile, therefore, to examine the results of adsorption determinations at near-ambient temperatures.

Adsorption of octadecanoic acid, apparently extending to several molecular layers, was observed by Hirst and Lancaster[12,13] on Zn, ZnO, Cu_2O, and CuO powders, the surface areas of which had been determined by water vapour adsorption. Adsorption from benzene was followed by spreading samples of the super~~natant~~ solution on a film balance and noting the decrease in film area under constant pressure. After rigorous degassing the powders adsorbed only the equivalent of a fraction of a monolayer of octadecanoic acid, but prior exposure to water vapour resulted in adsorption greatly in excess of a monolayer. The authors concluded that adsorption was a physical process under dry conditions, but that chemisorption frequently occurred in the presence of moisture. This conclusion was supported by the results of direct, calorimetric measurements of heats of adsorption by Lancaster and Rouse.[14]

Adsorption of radio-octadecanoic acid from hexadecane on evaporated iron films 1000-2000 Å thick vacuum-deposited on cleaved mica was studied by Cook and Ries.[15] The support formed the window of a Geiger-Muller counter so that adsorption could be followed continuously in situ. No details were given of pre-treatment of the metal films, which were presumably covered with at least a monolayer of adsorbed water molecules.[16] Adsorption on iron was still continuing after 180 hours immersion, when the equivalent of 1.8 monolayers had been deposited, whereas adsorption on a gold film had only reached 0.2 monolayer after 20 hours and showed little further change.

Smith and others[17,18], found that adsorption of non-adecanoic acid labelled with C-14 from cyclohexane on specimens of Cu, Ni, Fe, and Al which had been machined under air rose continuously over a period of 7 days. By this time the equivalent of up to 3 molecular layers had been deposited. Adsorption on specimens which had been freshly machined under the test solution rapidly reached a limiting value which did not exceed a monolayer. The surface areas of the specimens used in this investigation, however, like those used by Cook and Ries[15], were not accurately known. An increase in surface area due to oxidation may have accounted for the increased adsorption on the unprotected surfaces in both cases: the evidence for multilayer adsorption is therefore inconclusive.

The work of Gaines[19], like that of Smith, involved removal of metal plates for counting after immersion in a radio-active solution. Since the solution did not retract to leave a completely dry surface in either case, errors were inevitably introduced by attempts to remove, or allow for the presence of, adhering solution. Adsorption of C-14 - labelled octadecanoic acid on Al and Cu from hexadecane apparently reached the equivalent of six monolayers within 135 minutes. This high adsorption could again have been largely due to the presence of porous oxide films of increased surface area, although the author claimed that the retention of a high polish by the specimens showed that this was not the case.

Sherwood and Rybicka[20] demonstrated the influence of moisture on adsorption of radio-octadecanoic acid on rutile (TiO_2) of known specific surface area from benzene. The benzene was rigorously dried throughout, but the TiO_2 powder in parallel experiments was either dried at 150°C to constant weight before use or equilibrated at 60% R.H. Constant adsorption equivalent to slightly less than a close-packed monolayer was rapidly reached on "dry" powder, but on the "moist" powder adsorption was still increasing after 20 days, by which time the equivalent of 2-3 molecular layers had been sorbed.

While investigating the effect of thermal pre-treatment of metal substrates on the wettability of monolayers adsorbed thereon, Bascom[21] found that an adsorbed film of octadecanoic acid on iron which had been exposed to moisture contained microscopic solid particles. These were thought by the author to be iron stearate, and in support of this hypothesis he cited a contemporary paper by Timmons, Patterson, and Lockhart[22], which contained evidence of adsorption of stearic acid on iron in excess of a monolayer after prolonged immersion.

Adsorption of labelled octadecanoic acid from n-heptane on rutile under rigorously dry conditions has been shown not to exceed monolayer coverage by Ottewill and Tiffany.[23] These authors found, however, that unsaturated fatty acids gave adsorption isotherms which contained discontinuities indicative of phase changes in the adsorbed film, and tended to limiting adsorptions well in excess of a monolayer.

A direct weighing techinque was used by Cook and Hackerman[24] to show that decanoic and octadecanoic acids were adsorbed on mild steel powder from benzene in two stages, one reversible and the other irreversible. The amount of acid adsorbed irreversibly was the same for both acids, reaching a plateau at low concentrations, but the reversible component was higher for the longer chain acid and did not reach a limiting value. The surface area of the powder was known from krypton adsorption data, and showed that irreversible adsorption was the equivalent of about half a close-packed monolayer and that the total did not exceed the equivalent of 2 molecular layers over the range of concentration studied. Dobry[25] also used a weighing method to show that adsorption of octadecanoic acid on copper from benzene solution was approximately unimolecular, assuming a roughness factor of several times unity.

Adsorption of octadecanoic acid from benzene was investigated by Greenhill[26] and Daniel[27] on Cu, Ni, Ag, Fe, Pb, Al, and Cr powders which had previously been stored in a vacuum desiccator. A surface balance was used to follow changes in the concentration of the supernatant solution during adsorption. For all the metals except Cu adsorption isotherms measured after 4 hours immersion gave smooth curves which reached limiting values at high concentrations. This was interpreted as indicating that adsorption ceased when a saturated, close-packed monolayer had been formed. Direct confirmation of this was not possible as the surface areas of the powders were not accurately known.

Walker and Ries[28] measured adsorption of radio-octadecanoic acid from hexadecane solution on 100 Å thick films of evaporated metals on mild sheets. In contrast with the earlier work of Ries,[15] adsorption on iron films under dry conditions did not exceed monomolecular coverage at the single concentration used (0.0005 molal).

Doyle and Ellison[29] attempted to follow co-adsorption of solute and solvent molecules on polished metal plates from solutions of C-14-tagged octadecanoic acid in H-3-tagged hexadecane. Use of a rinsing technique to remove adhering solution from the plates vitiated the results, particularly in respect of co-adsorbed solvent. Adsorption of octadecanoic acid on Cu, Ag, Pt, and Fe, however, did not appear to exceed one monolayer significantly.

The monomolecular nature of "retracted" films has been confirmed by optical interferometry[30] and ellipsometry.[31,32,33] The thickness of depleted monolayers calculated from ellipsometry measurements have been found consistent with adsorption density followed by radiotracers.[33]

2.1(3) Adsorption of other polar compounds on metals.

The literature on adsorption of amines, alcohols, and esters on metals will not be discussed in detail. These compounds are almost always less strongly adsorbed than the fatty acids, although when attachment is mainly physical, as on glass or platinum, the greater dipole moment of the amines results in their being adsorbed more strongly than the fatty acids.[34] Adsorption of polar compounds other than fatty acids on metals from hydrocarbon solutions has been studied by Greenhill,[26] Daniel,[27] Bowden,[7] Cook,[15] Hackerman[24], Crisp,[35] Haydon,[36] Parfitt,[37] Sherwood,[20] and Block,[34] to name a few. Parfitt reports the interesting finding that adsorption of octanol on rutile from p-xylene or n-heptane is greater than that of either ethanol or dodecanol from solution of the same concentration.

2.1(4) Reversibility of adsorption and nature of adsorption bond.

Daniel observed that adsorption of octadecanoic acid on nickel from benzene was at least partially reversible[27]; desorption could be achieved either by dilution or at increased temperature. Adsorption isotherms for dodecanoic, hexadecanoic, and octadecanoic acids became almost superimposable when plotted as a function of $(\text{concentration}/_{\text{saturation concentration}})$. This suggested that adsorption was a physical process, controlled by the solubility of the acids.

It has been established, however, by Cook and Hackerman[24] that adsorption of amines, alcohols, and esters as well as fatty acids is only partially reversible. The irreversibly held component reaches its maximum adsorption at low concentrations, which suggests that chemisorption occurs initially, followed at higher concentrations by a physically held component which does not reach a limiting level. Young[38], Timmons[22], and Beischer[39] have confirmed that adsorption of C-14-labelled octadecanoic acid on oxide surfaces is only partially removed by dilution or heating, and Dobry[25] considered that only one-quarter of the total adsorption of octadecanoic acid on copper from benzene was chemisorbed. Timmons and Zisman[40] found that the contact angle of methylene iodide on octadecanoic acid monolayers on platinum reverted to the value which had been observed on the bare metal after the specimen had been heated to 130°C. Contact angles on monolayer-covered nickel substrates, however, showed only comparatively small changes after the specimens had been heated to 150°C. Desorption by solvents resulted in similar differences in behaviour.

Block and Simms[34] studied desorption and exchange of C-14-tagged octadecanoic acid and octadecylamine from mild steel and borosilicate glass surfaces immersed in dicyclohexyl. Adsorption of both compounds on mild steel from 0.003% solution did not exceed the equivalent of 0.54 close-packed monolayers even after immersion for 7 days. Adsorption of octadecylamine on glass reached 0.86 monolayers but that of octadecanoic acid was only

0.03 monolayers after 8 days, which explains why oleophobic fatty acid films cannot be prepared on "Pyrex" surfaces. Desorption of octadecanoic acid from mild steel by dilution reduced the coverage by about 60%. Exchange with a solution of inactive acid also removed the same proportion of adsorbate, showing that the remainder was irreversibly bound to the surface. Over 90% of octadecylamine adsorbed on steel or glass could be exchanged, however, although solvent desorption only removed about 60% in both cases.

The "irreversible adsorption" observed by Cook and Hackerman[24] must therefore be sub-divided into two components, chemically and physically bound, since a large fraction of the apparently non-desorbable amine molecules were sufficiently mobile to exchange with those in solution.

Smith and Fuzek[41] found that adsorption of hexadecanoic acid from benzene on Adam's platinum catalyst was independent of concentration. This is taken[42] as an indication of the presence of an entirely chemisorbed layer. Corrosion of metals by solutions of fatty acids in hydrocarbons, especially at temperatures above 80°C and in the presence of molecular oxygen, was demonstrated by Prutton[43] . The work of Bowden and Moore[7], and Sakurai and Baba[8,9], mentioned earlier, also demonstrated extensive reaction of fatty acids with metals. Infra-red spectroscopy was used by Sherwood and Rybicka [20] to demonstrate the presence of carboxylate ions on rutile surfaces which had been immersed in solutions of octadecanoic acid in benzene. These authors also confirmed the presence of strongly held adsorbate molecules in radiotracer exchange experiments. Adsorption of octadecanoic acid on titanium dioxide surfaces from benzene has also been studied by infra-red spectroscopy by Smith.[44] Evidence was obtained for the existence of both hydrogen-bonded, physically adsorbed carboxylic acid molecules and chemisorbed carboxylate ions in the adsorbed film. Dawson, Haydon, and Rich[45] reported that formic and octadecanoic acid adsorbed on rutile from benzene irreversibly, but found that, although the limiting coverage by formic acid approximated to a close-packed monolayer, considerably lower coverages were reached by octadecanoic acid. The discrepancy was greatest for rutile powders of finest particle size, and was attributed to presence of voids between adjacent particles which could be penetrated by formic acid molecules but not by the larger, octadecanoic acid molecules.

2.1(5) Summary.

There is little evidence which suggests that adsorption of simple polar compounds on metals from hydrocarbon solutions exceeds a monomolecular layer. Adsorptions carried out on metal plates the surface areas of which were not accurately known are useless for the purpose of determining the limiting extent of the adsorbed layer. The high adsorption of fatty acids reported to occur on reactive metals may be due to extensive chemical attack, followed by separation of the relatively insoluble metal soap, possibly as a liquid crystalline interfacial layer. This may occur with less reactive, e.g. ferrous metals at elevated temperatures.

2.2 Aim and method of investigation.

The conclusion drawn from the analysis of the literature in section 2.1 was that adsorption of fatty acids on metals from solutions in hydrocarbons rarely exceeds a monomolecular layer, although some investigators have claimed "adsorption" in excess of a monolayer on reactive surfaces after long periods of immersion. This section describes studies of adsorption of C-14-labelled octadecanoic acid on a spheroidal iron powder from solution in hexadecane. Since the powder consisted of smooth spherical particles their surface area could be found accurately and unambiguously from gas adsorption measurements. Routine analysis by the manufacturers showed that the iron content of the powder was around 99.5%. Such a powder would be expected to be quite reactive chemically, and might promote multilayer adsorption if this occurs at all on the surfaces of ferrous metals.

Materials and apparatus.

The iron powder, designated type HP, was manufactured by the General Aniline and Film Corporation, U.S.A. by reduction of the carbonyl. Typical average particle diameter was stated by the manufacturers to be 6-8 microns. Hexadecane was supplied by Newton Maine Limited, and was stated to be 99% pure and olefin-free. Its freedom from surface-active impurities was checked by interfacial tension determination against surfactant-free distilled water. More importance was attached to absence of "ageing" than to the absolute magnitude of the interfacial tension. Octadecanoic acid of Puriss grade was supplied by Koch-Light Ltd. and was used without further treatment. C-14-tagged octadecanoic acid of activity 30mC/mM was obtained in benzene solution from the U.K. Radiochemical Centre, Amersham.

Counting was carried out with a Panax type SC/LP scintillation counter, using a liquid scintillator prepared by dissolving 5g 2,5 diphenyloxazole + 1g 1,4-bis-2-(5 phenyloxazolyl) benzene in 1 litre of AR toluene. Samples for counting were pipetted direct into glass phials containing 10ml of this solution.

The adsorbent and adsorbate solution were contained in a non-plasticised polypropylene flask placed inside a wide-necked 2 litre culture vessel. This was fitted with a detachable lid which was equipped with several ground glass sockets. The adsorption mixture was agitated by a simple two-bladed glass stirrer driven by an electric motor via a mercury seal gland.

Procedure.

A relatively concentrated (10^{-3} mole fraction) solution of radio-octadecanoic acid in hexadecane was made up by adding a suitable (very small) amount of C-14-tagged material to a solution of the inactive acid. The activity of this solution was about 100 times the most convenient level for counting. Count rates exceeding 10,000 cpm were not normally used, in order to avoid changes in counter sensitivity, and the size of samples was adjusted in order to achieve this. 0.5 ml of this solution were diluted to 50ml with hexadecane and placed in the polypropylene adsorption flask inside the culture vessel. This was purged for 15 minutes with air which had passed through a train of $MgCl_2$ bubblers to control the relative humidity at 30%, and finally through a tube filled with cotton-wool in order to remove entrained liquid droplets. The solution was stirred mechanically and at intervals samples of 0.02 - 0.05 ml of solution were withdrawn with an Agla micrometer syringe for assessment of its radioactivity. After each sample had been taken, the assembly was purged once more before re-stirring. Temperature was not controlled, but remained in the range $21 \pm 1^{\circ}C$. When readings of the activity of the solution had become constant, 5g of iron powder were added and stirring was resumed. The activity of the supernatant liquid was determined at intervals until it was constant once more. The stirrer was stopped 5 minutes before a sample was taken in order to allow the powder to settle. The extent of adsorption and the equilibrium concentration of octadecanoic acid were calculated from the original concentration and activity and the final activity, allowance being made for solution removed in sampling. A further point higher on the adsorption isotherm was obtained by adding, say, 0.5ml of the 10^{-3} mole fraction stock solution to the mixture after the first adsorption, and determining the new equilibrium activity and concentration. By repeating this process a series of points on the adsorption isotherm were obtained, although in later stages the accuracy was reduced owing to the smaller relative changes in concentration, and was dependent on accurate allowance having been made for solution removed during sampling.

Two series of points on the adsorption isotherm were obtained in this way, and a further point was determined from a single adsorption measurement from a concentrated solution.

In order to test the time-dependence of adsorption, a further series of measurements was made after adsorbent and solution had been in contact for only 5 minutes. 4-10g lots of type HP iron were weighed out from an air-tight tin without further conditioning, and were added to five 10ml samples of radio-octadecanoic acid/hexadecane solution contained in test tubes fitted with ground-glass stoppers. Samples of the supernatant liquid were withdrawn for determination of the change in activity after 5 minutes shaking by hand. The initial concentrations of the solutions were chosen so as to give a spread of adsorption values extending over the whole of the upper part of the isotherm.

2.3 Results.

Adsorption values and corresponding equilibrium concentrations of octadecanoic acid for the two series and the single determination are listed in table (2.1) and shown graphically in fig.(2.1). The specific surface area of the iron powder calculated by the BET method from krypton adsorption was 0.291 m^2/g. Examination of the particles under the electron microscope at 2500x magnification confirmed that the powder contained smooth, spherical particles most of which appeared to lie in a fairly narrow size range (1-3 microns), but really good photomicrographs suitable for reproduction were not obtained owing to aggregation of the particles.

Fig. (2.1) Adsorption of octadecanoic acid from hexadecane on type "HP" carbonyl iron powder.

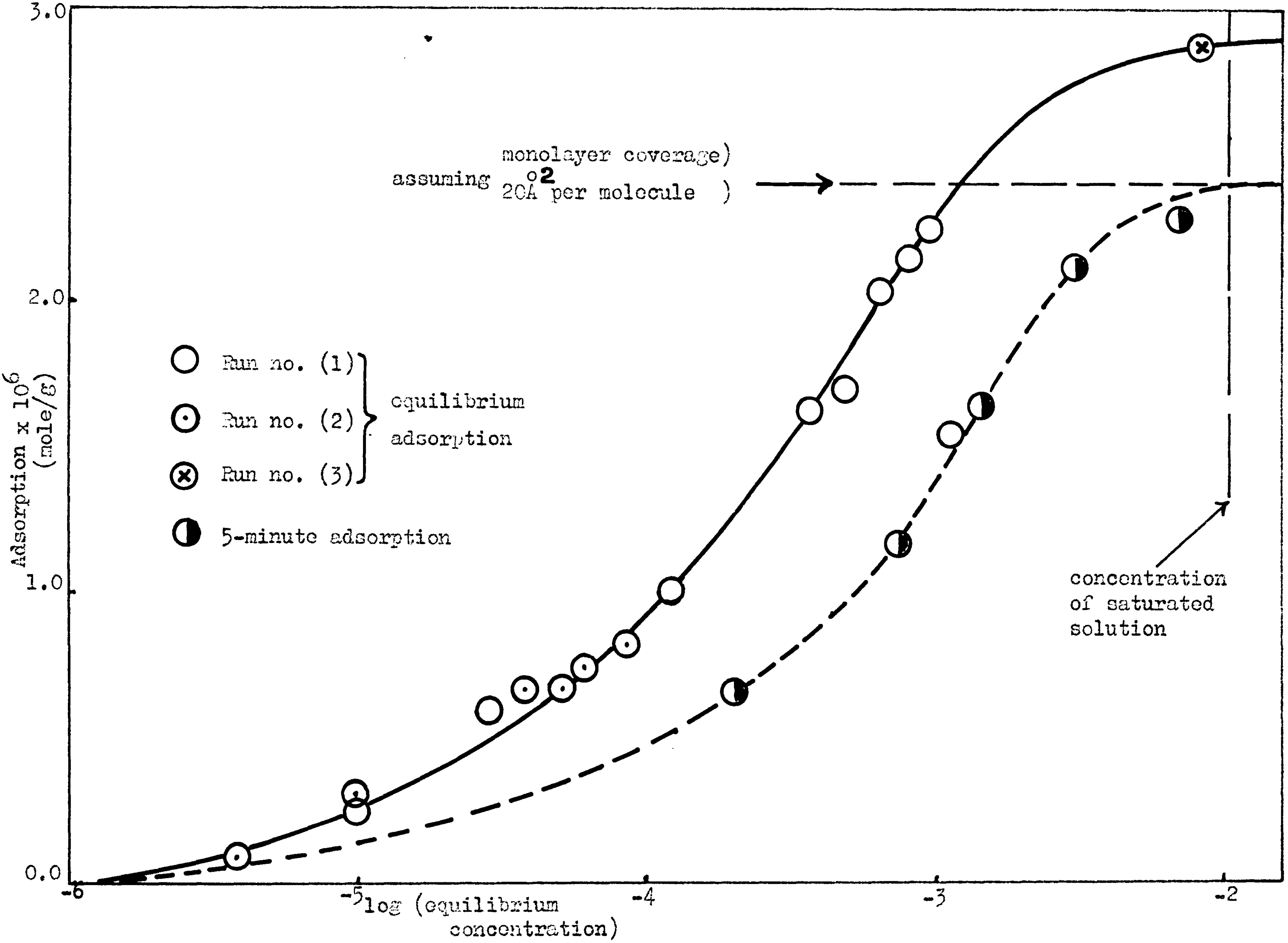

Table 2.1. Adsorption and equilibrium concentration of octadecanoic acid.

Run number	Equilibrium concn. x 10^{-4}, mole/l (c)	Adsorption x 10^{-6}, mole/g(n_1^s)	$^c/_{n_1^s}$
1	0.098	0.24	40.8
"	0.281	0.59	47.7
"	1.23	1.00	123
"	3.68	1.63	226
"	4.94	1.69	292
"	6.35	2.03	313
"	8.04	2.15	374
"	9.48	2.13	445
"	11.5	1.54	747
2	0.039	0.09	43.4
"	0.098	0.30	32.7
"	0.37	0.66	56.1
"	0.51	0.67	76.1
"	0.60	0.74	81.0
"	0.84	0.82	102.4
3	84.3	2.87	3080

Adsorption equivalent to coverage of the surface by a monomolecular layer has been calculated on the assumption that each molecule occupies 20.5Å^2 of surface. Vold[46] has shown that this is the smallest area per molecule which can be achieved by close packing of vertically oriented carboxylic acids. From fig.(2.1) it appears that adsorption exceeded saturated monolayer coverage at high concentrations by 20%. This conclusion is still valid even if the point corresponding to the highest concentration is rejected as being subject to excessive uncertainty. If a Langmuir-type equation[47] is fitted to the 5 points lying in the concentration range $3x10^{4}$ - $1x10^{3}$M, it can be calculated that the limiting value of adsorption would be $2.83x10^{-6}$ moles/g, which is in agreement with the experimental adsorption at the highest concentration studied. The apparent divergence from monomolecular coverage may be due to breakdown of particles and creation of new surface area during prolonged stirring. Results of the studies of wettability of stability of dispersions reported in chapters (5) and (6) are entirely consistant with adsorption limited to one molecular layer.

Everett[48] has shown that the Langmuir isotherm can be applied to adsorption on solids from dilute solutions under certain conditions. It may be written in the form

$$\frac{c}{n_1{}^s} = \frac{1}{Kk_1N_s} + \frac{(K-1)c}{KN_s}$$

where c = equilibrium concentration, molar.

$n_1{}^s$ = adsorption, moles/g.

where K = a surface equilibrium constant.

k_1 = conversion factor to bring concentration to mole fractions.

N_s = moles acid/g. required to form close-packed monolayer.

If adsorption obeys the Langmuir isotherm, therefore, a graph of $\frac{c}{n_1}s$ against c should be linear. It is evident from fig.(2.2) that the experimental data do not all lie on a straight line - in fact there is a strong indication that they lie on two straight lines of different slopes. The presence of two linear regions suggests that adsorption obeys different Langmuir equations over the corresponding ranges of coverage. Values of K can be calculated for each region from the ratio gradient/intercept, which is equal to $(K-1)k_1$, and the standard free energy of adsorption found from the relation $-\Delta G^o = 2.303RT \log_{10}K$.
ΔG^o values calculated in this way are -7.0k.cal/mole for adsorption at low concentrations and -5.6k.cal/mole for the central part of the isotherm. The significance of these figures will be discussed in section 2.4.

Adsorption values observed after only 5 minutes are shown by a dashed line in fig.(2.1) and are listed in the table below:

Sample no.	Equilibrium concn. mM/l	Adsorption $\times 10^{-6}$,mole/g
1	0.21	0.65
2	0.75	1.17
3	1.5	1.65
4	3.1	2.13
5	7.0	2.28

Fig. (2.2) Adsorption of octadecanoic acid on grade HP iron powder from hexadecane

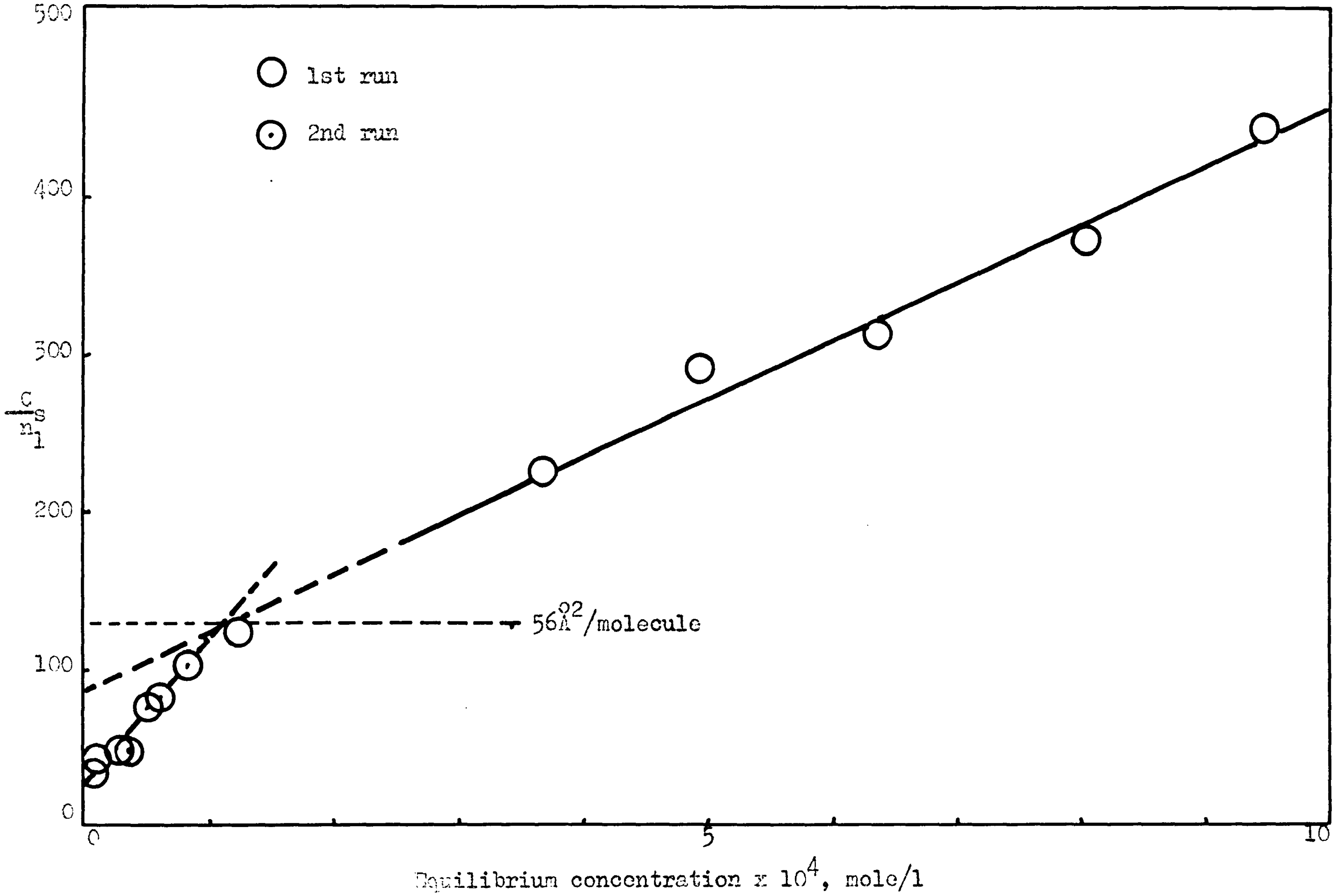

Fig.(2.1) shows that even at quite low concentrations adsorption after 5 minutes reached about 50% of the equilibrium value, and that at higher concentrations an even higher proportion was reached. The limiting value at high concentrations lies close to that of a close-packed monolayer, which supports the suggestion made earlier that the apparent excess of equilibrium adsorption over monolayer coverage at high concentrations may have been due to particle breakdown.

2.4 Conclusion and discussion.

Even after prolonged stirring for up to 24 hours, adsorption of octadecanoic acid on iron powder from hexadecane hardly exceeded the equivalent of a close-packed monolayer over the whole range of concentration studied. It is improbable that the slight excess (20%) over monomolecular coverage is significant.

Analysis of adsorption data in terms of the Langmuir isotherm is invalidated if the activity coefficient of the adsorbate varies greatly with concentration, either on the surface or in solution. It is well known that fatty acids dimerise strongly in hydrocarbons,[49,50] but data on the concentration dependence of the equilibrium between monomer and dimer is scarce. Attempts by Ottewill and Tiffany[23] to determine the extent of dimerisation at different concentrations in n-heptane by infra-red spectroscopy were only qualitatively successful. They found, however, that the percentage of acid in the monomeric form was considerably increased at concentrations below 5×10^{-4}M, which is in the same range as the discontinuity reported in the present work. Ottewill and Tiffany did not observe a discontinuity in isotherms for adsorption of stearic acid, but pronounced changes of gradient were evident in those for unsaturated acids of similar chain length. Daniel[27] reported that a graph of $\frac{c}{n_1}$s against c for adsorption of laurio acid on nickel from benzene contained two linear regions with different slopes. Similar graphs for adsorption of hexadecanoic and octadecanoic acid, however, showed no change of slope.

Discontinuities in the adsorption isotherms of unsaturated fatty acids were explained by Ottewill and Tiffany[23] on the basis of changes in the orientation of the adsorbed molecules. Saturated fatty acid molecules adsorbed on a surface would be expected to lie completely flat on the surface or to be attached at the head-group only. If octadecanoic acid molecules were adsorbed horizontally at low coverages, the area per molecule at saturation of the surface would be $92.5\mathring{A}^2$. If a transition to head-group attachment occurred above a certain concentration, a discontinuity might be visible on the adsorption isotherm at a point corresponding to coverage of one molecule/$92.5\mathring{A}^2$. The change in slope in fig.(2.2), however, occurs at about $56\mathring{A}^2$/molecule, and therefore appears unlikely to be associated with a transition of the orientation of the adsorbate molecules from horizontal to single-point attachment.

The discontinuity in the isotherm may, of course, be due to inhomogeneity of the iron surface resulting in areas of preferential adsorption, or to a rapid change in the octadecanoic acid monomer-dimer equilibrium. There is a further possibility, however;

Cook and Ries[15] found that the fractional coverage of the surface by adsorbate during adsorption of octadecanoic acid or octadecanol on iron from hexadecane increased rapidly to around 0.3 during the first 10 minutes, but that further adsorption occurred at a greatly reduced rate. In the light of the results of solvent desorption experiments on mixed monolayers and the ease of spreading of mixtures of octadecanoic acid and hexadecane on water, the authors put forward the following hypothesis in order to explain their observations: It was assumed that the adsorbed layer contained a mixture of vertically oriented acid and solvent molecules; differences in the cross-sectional area of the hydrocarbon chains and the carboxyl groups were neglected, and the molecules were treated as vertically oriented cylinders. Using this model, it was shown that if $\frac{1}{3}$ of the adsorbed molecules were octadecanoic acid, each of the "adlineated" hexadecane molecules would be in contact with three acid molecules if the arrangement was symmetrical. The stability of a monolayer of this composition to further adsorption or to desorption was attributed to the binding effect of three adjacent, strongly adsorbed acid molecules on each hexadecane molecule. The form of fig. (2.2) is consistent with this hypothesis, since the change of slope occurs at a coverage equivalent to about 56Å^2/molecule, which corresponds well with the postulate of one stearic acid (cross-sectional area 20.5Å^2) molecule adsorbed for every two adlineated solvent molecules (cross-sectional area taken as 17.5Å^2).

The experimental values of ΔG^o, -5.6 and -7.0k.cal/mole, are in fair agreement with those deduced by Daniel[27] and Ottewill and Tiffany[23] from adsorption measurements. Daniel found that ΔG^o for adsorption of octadecanoic acid on nickel from benzene was about -6.0 k.cal/mole, and Ottewill and Tiffany obtained a value of -6.16 k.cal/mole for adsorption of the same acid on rutile from n-heptane.

Since changes in standard free energy are obtained from equilibrium constants, they are meaningless unless the corresponding standard states of the adsorbate are defined. Ottewill and Tiffany did not even mention that it was the standard free energy change which had been evaluated, while Daniel did not specify the standard states applicable to his system. The coincidence of the ΔG^o values reported by these authors is probably fortuitous, as considerably different assumptions were made in their calculations. In Everett's statistical treatment, which was followed by Ottewill and Tiffany, adsorbed molecules of both solute and solvent are assumed to occupy a number of equivalent "lattice sites". Daniel, however, assigned to the adsorbed film a finite depth (5Å), from which a volume concentration of adsorbed octadecanoic acid molecules could be calculated and a standard "law of mass action" equation set up. Definitions of the standard state of compounds in solution are arbitrary and great difficulty is encountered in attempts to designate a standard state for adsorbed films. In addition to this, the conditions of reversible adsorption, non-interaction of adsorbate molecules, and ideality of the supernatant solution, which must be made before the Langmuir isotherm is obeyed, are not fulfilled in the present system. Little quantitative significance can therefore be attached to the ΔG^{o} values reported in section 2.3, and the change of slope in fig. (2.2) is probably best regarded as merely a qualitative indication of a change in the average energy of adsorption.

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3. MOLECULAR ORIENTATION IN HYDROCARBON SOLUTIONS NEAR METAL SURFACES.

3.1 Introduction.

The effective range of action of "surface forces" has been in dispute for many years.[1] Even in the absence of multimolecular adsorbed layers, it is not inconceivable that the influence of a metal surface in contact with a solution could exert an orienting effect on long-chain polar molecules some distance from the surface. X-ray diffraction is an appropriate technique for studying such effects, since the high penetrating power of X-rays enables thick films of oil to be examined. It is not necessary to work in vacuo, as is the case with electron diffraction, so that evaporation problems do not arise. The chief drawback of X-ray diffraction is that the long spacings to be expected in oriented layers of long-chain molecules, 20-50Å, are large compared with the wavelength of X-rays, so that diffraction features may then appear at very small angles of reflection (less than 1°), where resolution from the main, undiffracted beam is difficult.

The detection of oriented molecular layers in the interfacial region by X-ray diffraction depends on the presence of planes of high electron density parallel to the surface, with constant spacings between adjacent layers. Such planes would be provided by the oxygen atoms of the carboxyl group in successive layers of long-chain fatty acids oriented normal to the surface, or by the metal atoms in soaps derived from these acids. The classical work of Trillat[2] demonstrated that the principal spacings revealed by X-ray diffraction of fatty acids crystallised from the melt on glass and metal surfaces correspond to a bimolecular repeating unit. This is due to hydrogen-bonding between adjacent headgroups, leading to head-to-head, tail-to-tail configurations in alternate molecular layers. Trillat also considered that glass and metal surfaces caused orientation of fatty acid molecules up to 5 microns distant from the surface. It is not clear in the original paper whether the fatty acid was molten or solid in this case, but in other work[3] Trillat stated categorically that a film of a <u>molten</u> fatty acid on a mercury drop gave a diffraction pattern showing perfect orientation of molecules at the interface which persisted even at temperatures of 100°C.

Clark and co-workers[4,5] carried out an extensive investigation of orientation in thick layers, built-up Langmuir-Blodgett multilayers,[6] and smears of solutions of fatty acids and esters deposited on a metal substrate. The use of cylindrical metal specimens coated with the test material enabled a complete diffraction pattern to be obtained without rotation of the specimen. Oriented layers of molecules gave rise to diffraction arcs, the length of which was an inverse function of the degree of orientation. The number of orders visible increased with the number of oriented layers present and varied with the nature of the metal substrate and the polarity of the lubricant. Diffraction arcs were observed from built-up films of octadecanoic acid transferred from the surface of a pure water substrate, provided these contained more than about 25 molecular layers (a thickness of about 500Å). A further diffraction order was visible for each increment of 25 molecular layers in film thickness. A specimen coated with a film of a dilute solution of ethyl dichlorostearate in a mineral oil gave a diffuse halo due to the oil, within which arcs corresponding to seven diffraction orders were visible. The authors concluded[5] that "polar compounds in dilute hydrocarbon-oil solution such as is used in practical lubrication, orient on metal surfaces more or less completely as they do in the pure state". The depth of orientation was estimated as more than 3000Å.

A search of the literature has not revealed any other studies by X-ray diffraction of the effect of metal surfaces on the orientation of polar compounds in solution. Since the deep orientation reported by Clark might explain phenomena observed by Deryagin,[1] Fuks,[7] and Cameron,[8] it was decided to check Clark's investigations. It was anticipated that the use of modern instruments with higher resolving power and greater sensitivity would allow detection of even thinner oriented layers.

3.2 Experimental procedure

3.2(1) Specimen preparation.

1" x 1^{3}/16" x ^{1}/16" pieces were cut from mild steel or nickel sheets, and both sides were ground under distilled water with 600-grade silicon carbide paper. The specimens were dried by evacuation as it had been found that heating in an oven or even exposure to the atmosphere at room temperature caused the clean, hydrophylic metal surfaces to become coated with a hydrophobic film within a few minutes. An oleophobic monolayer was next deposited on the specimens by polishing alumina on a "Hyprocel" disc under a lg/l solution of octadecanoic acid in hexadecane. After the specimens had been polished they were washed thoroughly with distilled water in order to remove adhering alumina particles. Whenever it was subsequently desired to remove dust or contamination from the film-covered surfaces, it was found that repeated quick dips in AR benzene were effective and did not destroy their oleophobic nature.

In order to explore the possible existence of extensive orientated layers of molecules in the interfacial region, a drop of a solution of lg/l octadecanoic acid in hexadecane was placed on each specimen and covered with a 1" x $\frac{1}{2}$" piece of non-waterproofed "Cellophane". (The latter was applied in order to prevent retraction of the oil layer.) With practice air bubbles could be excluded and a fairly uniform "sandwich" of solution was produced; surface tension was sufficient to hold the "Cellophane" in place and prevent leakage even if the specimen was left in a vertical position. In the absence of a film of solution the "Cellophane" gave no diffraction pattern.

In order to provide "control" samples so that the sensitivity of the technique could be established, multimolecular layers were deposited on monolayer-coated specimens by the method of Langmuir and Blodgett.[9,10] In this method successive monomolecular films are transferred from an aqueous substrate to a metal specimen by repeatedly raising and lowering the specimen through the surface of the water. In order to obtain reliable transfers it was essential to verify that the area of the surface film did not shrink owing to leakage before immersion of the specimen, and that the reduction in film area after each "trip" was equal to the total surface area of the specimen. For this reason, both sides of the specimens and their edges were treated in order to render them oleophobic, so that all surfaces would accept deposited layers.

In preliminary trials, a flat-rimmed glass container was filled to the brim with distilled water after the rim had been waxed, and a mobile floating barrier consisting of a "Vaseline"-impregnated thread was attached to the rim at two places with paraffin wax. The surface of the water was cleaned by "sweeping" with glass barriers which had been waxed to make them hydrophobic, and by sucking off contamination with a finely drawn-out glass tube just touching the surface and connected to a vacuum pump. The surface was not considered clean until approach of the glass barriers on either side of the thread caused no movement of the thread. A dilute solution of octadecanoic acid in 40/60 petroleum ether was added dropwise on one side of the thread until its rate of spreading and evaporation became slow. It was found by experience that addition of a further drop resulted in the appearance of solid acid in the surface. The octadecanoic acid monolayer was compressed by deposition of a drop of oleic acid on the other side of the thread. This acted as a "piston oil",[10] exerting a constant surface pressure of about 30 dynes cm^{-1}. During investigation of the reasons for the irreproducible X-ray diffraction features of early built-up films, it was discovered that reduction in the film-covered area of the water tended to occur even before deposition had been started. It was also found that the changes in film area during passage of the specimen through the surface were variable and often much less than its surface area. The cause was traced to leakage of the film part the barrier, especially near the points where the thread was attached to the rim.

This difficulty was avoided by use of a flat-bottomed, parallel-sided container which was not filled to the brim. The octadecanoic acid monolayer was enclosed completely in a circular loop of thread which was not directly attached to the walls, but was loosely tethered to them by two further threads. This eliminated the chief source of leaks and also removed the necessity of keeping the vessel filled to the brim (or to any set level). The vessel was stood over graph paper and the co-ordinates of a series of points along the loop could be read off, enabling its area to be calculated. This was normally done by re-plotting the outline of the loop, and comparing the weight of graph-paper enclosed with that of a figure of known area. Changes in the film area after successive depositions were determined similarly.

Before deposition of a built-up film, the size of the loop and the amount of acid spread on the water surface were adjusted to give enough acid for the desired number of layers, but with sufficient movement of the thread after each deposition to give a measurable change in area. The area of the film was checked 15 minutes after it had been spread and deposition was not commenced if there was any sign of leakage. Each specimen was supported above the film by a thread passing through two holes drilled at one end of the specimen, and wound on a roller. The first deposition was made by turning the roller by hand slowly and steadily, lowering the specimen through the surface at about 5cm/minute until it was completely submerged. The change in film area which had occurred was measured and the process reversed to withdraw the specimen slowly but completely from the film-covered water. Repetition of this technique enabled up to 14 molecular layers to be deposited in succession from a single spread monolayer. Specimens emerged dry on upward trips if the rate of removal was sufficiently slow, and the average change in film area per trip was close to the surface area of the specimen, showing that 100% transfer was achieved.

It was found that transference of octadecanoic acid monolayers from distilled water (acidic due to CO_2) or tap water (alkaline) to steel surfaces was equally satisfactory. Deposition occurred on both upward and downward trips of the specimen through the surface. Blodgett,[9] however, considered that it was essential to use an alkaline substrate in order to obtain clean withdrawal of water from the film-coated specimen on upward trips, and as a result, much of the published work on built-up films has been carried out either on tap water or in the presence of deliberately added calcium carbonate.[6,11,12] Films prepared in this way consist at least partially of layers of metal soap molecules, rather than of the pure fatty acid.[13] Since only a single chemisorbed soap layer is likely to exist at the interface between a steel specimen and a solution of octadecanoic acid in hexadecane, any extensive oriented layers would consist almost entirely of acid, rather than soap, molecules. It is desirable, therefore, that built-up films used in comparative X-ray diffraction studies should also contain only fatty acid molecules. In view of this all transfers were made from distilled water without addition of metal salts.

This also avoided possible complications arising from the uncertain structure of multilayers deposited from alkaline substrates.[2,9,14,15,16,17,18,19.] Since deposition at high pH has been reported to occur only on downward trips,[10] it might be expected that successive molecular layers would be oriented in the same direction. X-ray diffraction studies,[2,14,15,16] however, have indicated that the orientation alternates in successive layers, and studies of the wettability[9,17,18] of built-up films have given conflicting results.

3.2(2). Examination of specimens by X-ray diffraction.

The dimensions of the metal specimens were chosen so that they were identical with those of the sample holders in a General Electric type XRD 6 powder diffractometer. (This instrument was kindly made available by Professor D. Rogers, of the Department of Chemistry, Imperial College). The specimens were thus easily mounted on the diffractometer in place of the sample holders.

The diffracted beam is monitored in this instrument by a proportional counter which is initially aligned with a collimated beam of X-rays parallel with the surface of the specimen. The diffraction pattern is scanned by slow mechanical rotation of the specimen, accompanied by movement of the counter on a circular traverse at twice the velocity of rotation of the specimen, thus maintaining equality of the angles made by the incident and reflected beams with the surface of the specimen, as illustrated in fig.(3.1). Copper K_α radiation (wavelength 1.54$\mathring{A}$) was used, with the highest amplification of the ionisation chamber output which permitted the diffraction peaks to be completely displayed on a pen recorder chart. Scanning speed was 0.2°/minute, the slowest available. Two or three complete scans were carried out on each film-covered specimen. The Author is indebted to Miss. R. S. Osborne for operating the diffractometer.

If layers of octadecanoic acid molecules oriented vertically with respect to the metal surface are present, as is suggested in fig.(3.2), the spacing between repeating units, d, is given by the Bragg equation, $n\lambda = 2d \sin\theta$, where n = number of diffraction order, λ = wavelength of X-rays, and θ = angle made by the incident beam with the surface of the specimen.

3.3 Results.

3.3(1) Built-up films.

Diffraction traces from mild steel specimens which had initially been rendered oleophobic by deposition of an adsorbed monolayer of octadecanoic acid and then coated with a further 4, 8, Fig.(3.1) Diagrammatic representation of incident beam specimen, and diffracted beam

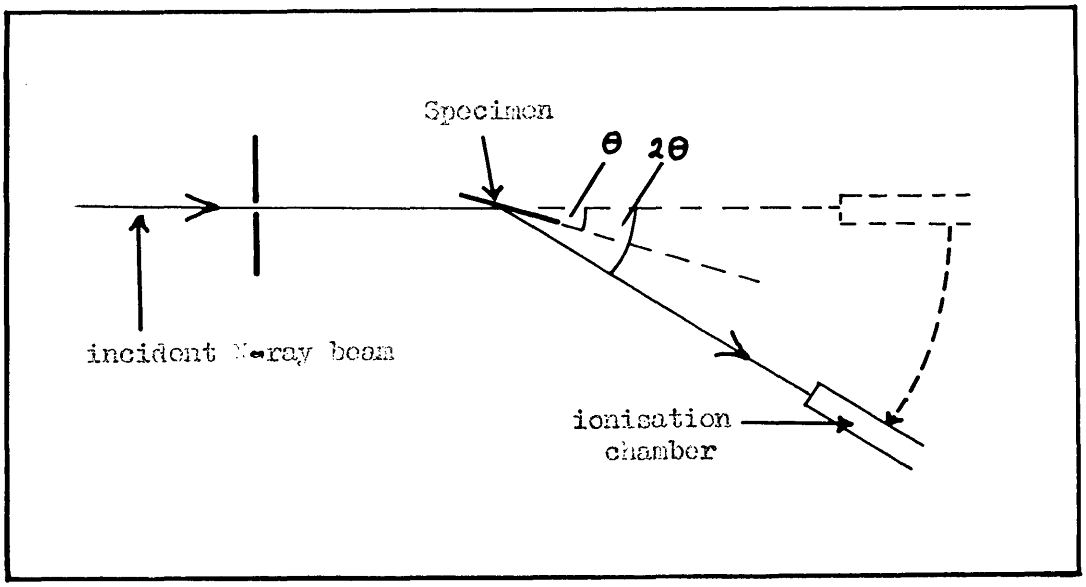
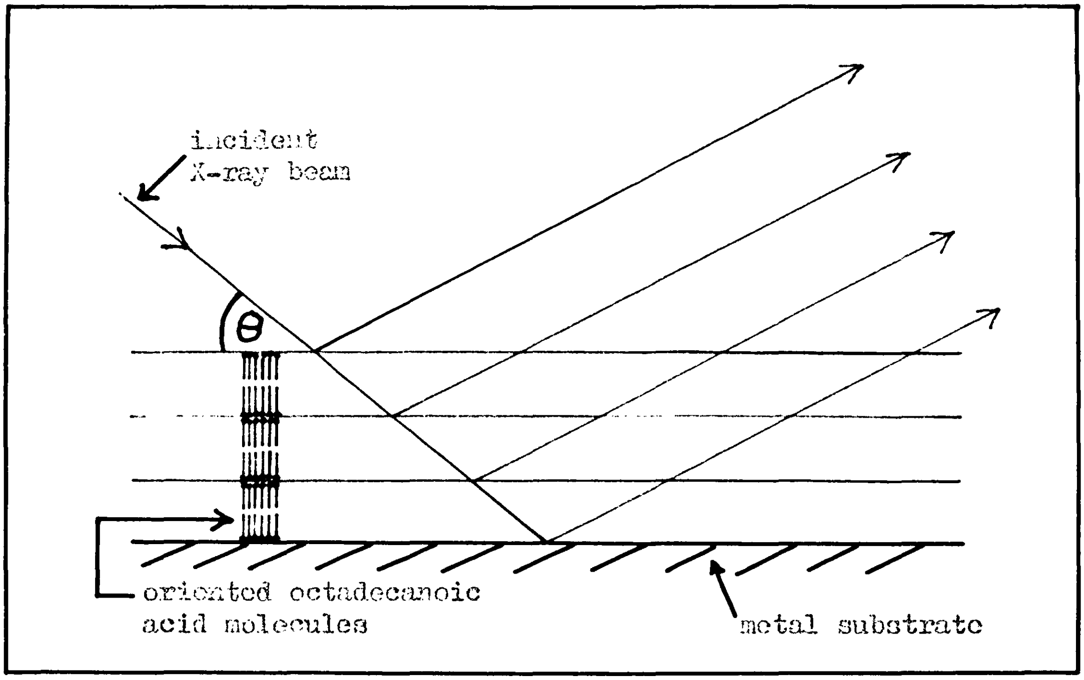


Fig. (3.2) Diffraction of X-rays by layers of oriented molecules



or 14 molecular layers (i.e. a total of 5, 9, and 15 layers) are shown in figs. (3.3), (3.4), and (3.5) respectively. Only a single diffraction peak is visible in traces from specimens bearing 5 or 9 molecular layers but the trace from the one coated with 15 layers contains one large peak and two smaller ones at diffraction angles which suggest that they are the second and third orders corresponding to the main peak. Spacings corresponding to the positions of the peaks are 41, 52, and 52Å respectively for the films containing 5, 9, and 15 molecular layers. The significance of these values will be discussed in section 3.4(1). The average reduction in film area during each trip through the monolayer-covered water surface during deposition was 17.5cm^2 for the first (5 layers) specimen, 18.6cm^2 for the second, and 17.5cm^2 for the third. The total apparent surface area of the specimens was 17.2cm^2, which confirmed that a complete monomolecular film was transferred to the specimen during each deposition.

A specimen nominally coated with 9 molecular layers earlier in the program also gave a peak which corresponded to a spacing of 52Å, but others gave inconsistent X-ray patterns. It has already been mentioned in section 3.2(1) that the cause of this was traced to incomplete transfer of the films to the metal surface. Multilayers prepared more recently were a uniform pale straw colour, which became darker with increasing thickness. This is in agreement with the experience of Langmuir,[10] who observed "interference colours" in built-up films which contained more than nine molecular

Fig. (3.3) Diffraction trace from mild steel + 5 monolayers octadecanoic acid.

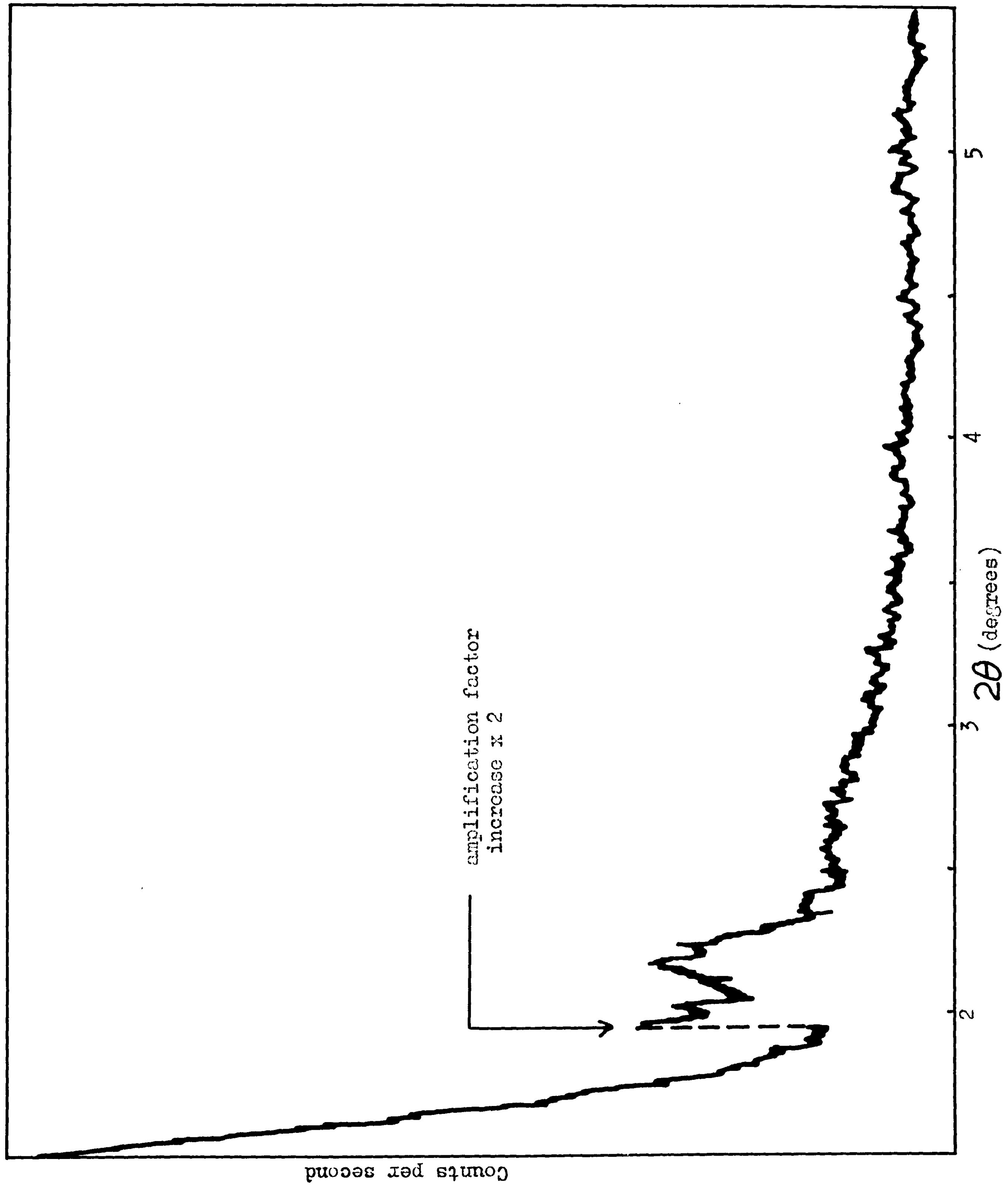


Fig. (3.4) Diffraction trace from mild steel + 9 monolayers octadecanoic acid.

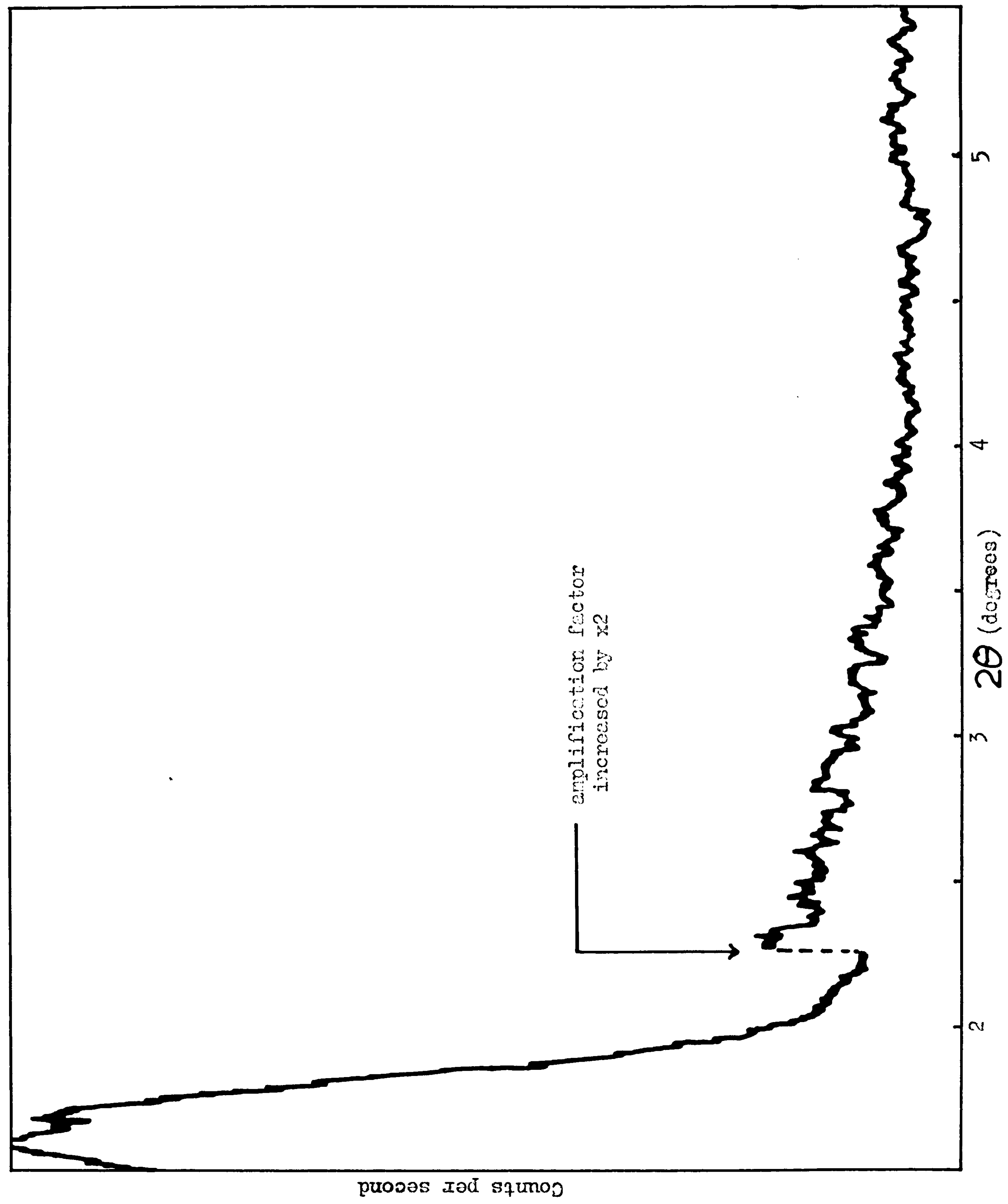
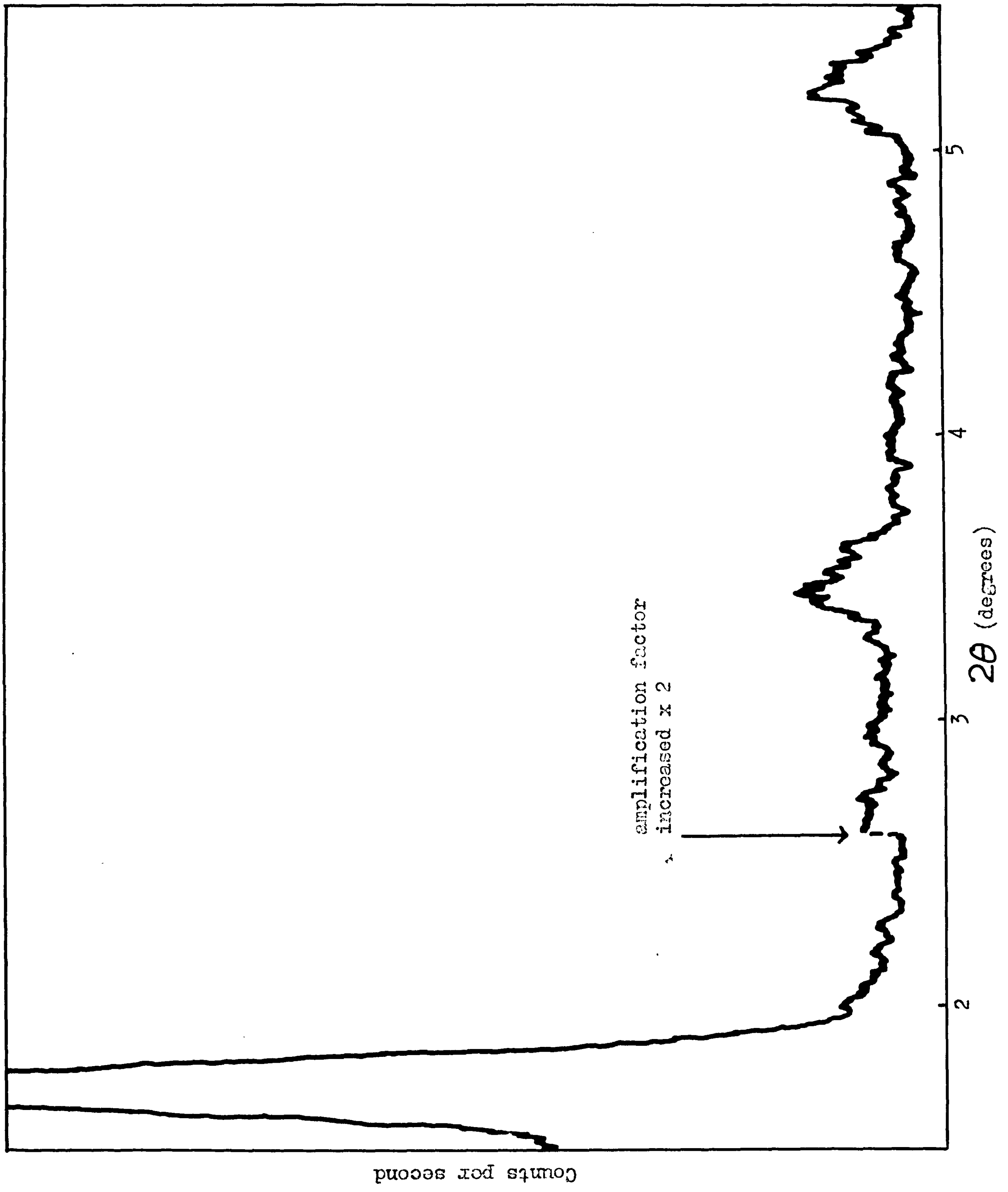


Fig. (3.5) Diffraction trace from mild steel + 15 monolayers octadecanoic acid.



layers. The early, faulty films showed less uniform, patchy interference colours.

Since films only 5 molecular layers deep (about 125Å) gave unmistakable diffraction peaks, the technique should be capable of detecting orientation to a similar depth, if present, in a solution of octadecanoic acid in an oil.

3.3(2) Solution of octadecanoic acid in hexadecane.

Each of three mild steel specimens coated with a film of octadecanoic acid solution as described in section 3.2(1) gave a diffraction trace containing a broad "hump" over the range $2\theta = 1.6^{\circ} - 3.3^{\circ}$, corresponding to spacings in the range 27-55Å. A nickel specimen, which had originally been considered as an alternative substrate in case of excessive interference of the steel with diffraction patterns, gave a similar plateau region. A specimen covered with a film of pure hexadecane also gave a similar "hump". It was verified that one covered only by "Cellophane" gave a trace (fig.3.6) which showed a smooth decline in intensity from the main undiffracted beam and contained no features at all. The "hump" was therefore due to the film of paraffin. Fig. (3.7) shows a typical trace from a specimen bearing a film of octadecanoic acid solution; it contains the usual plateau but no individual peaks comparable with those in figs. (3.3), (3.4), and (3.5).

Thus, it is evident that X-ray diffraction has not yielded evidence of orientation in the metal/solution interfacial region comparable with that found in built-up multilayers only five

Fig.(3.6) Diffraction trace from nickel specimen covered only by Cellophane sheet.

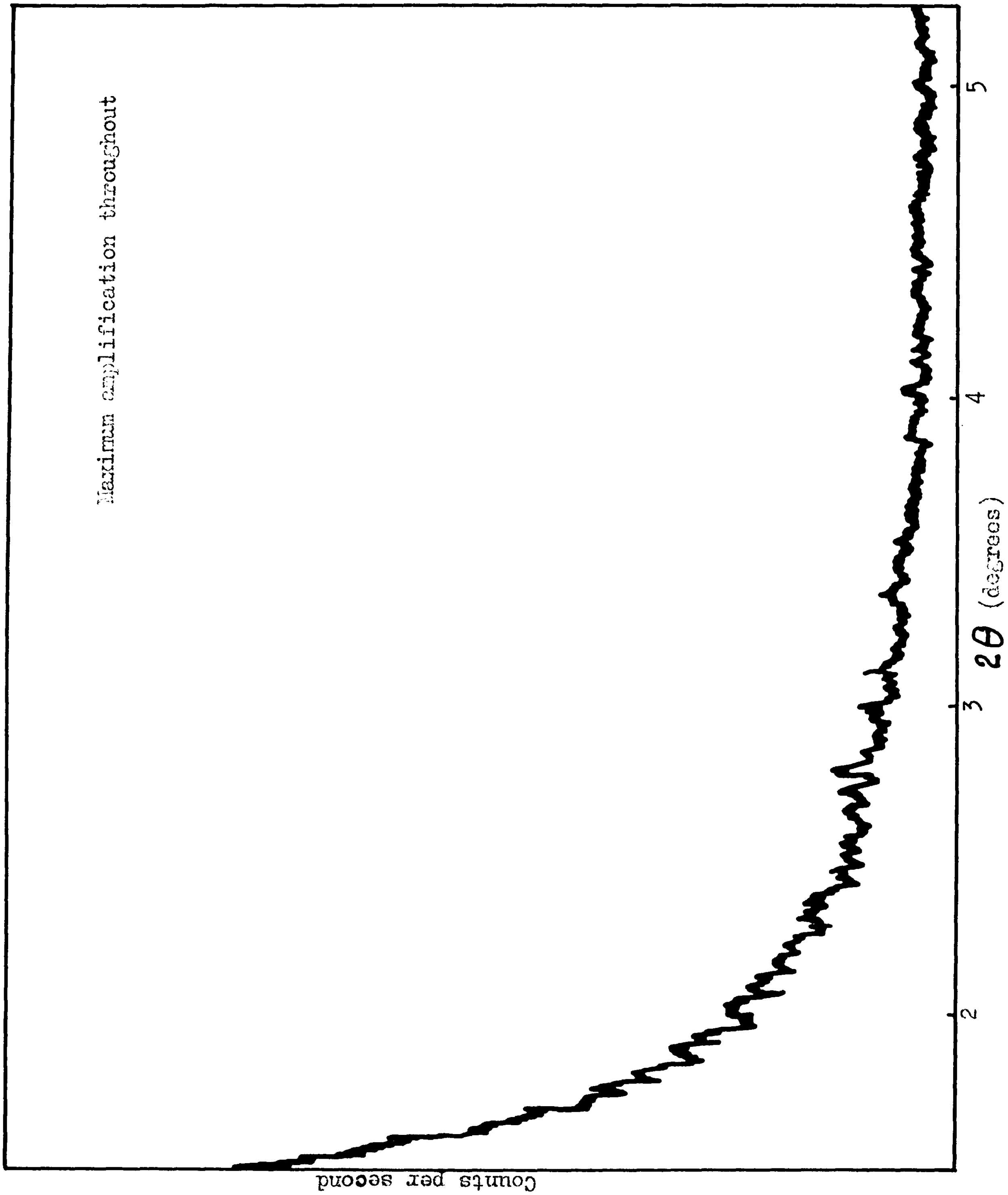
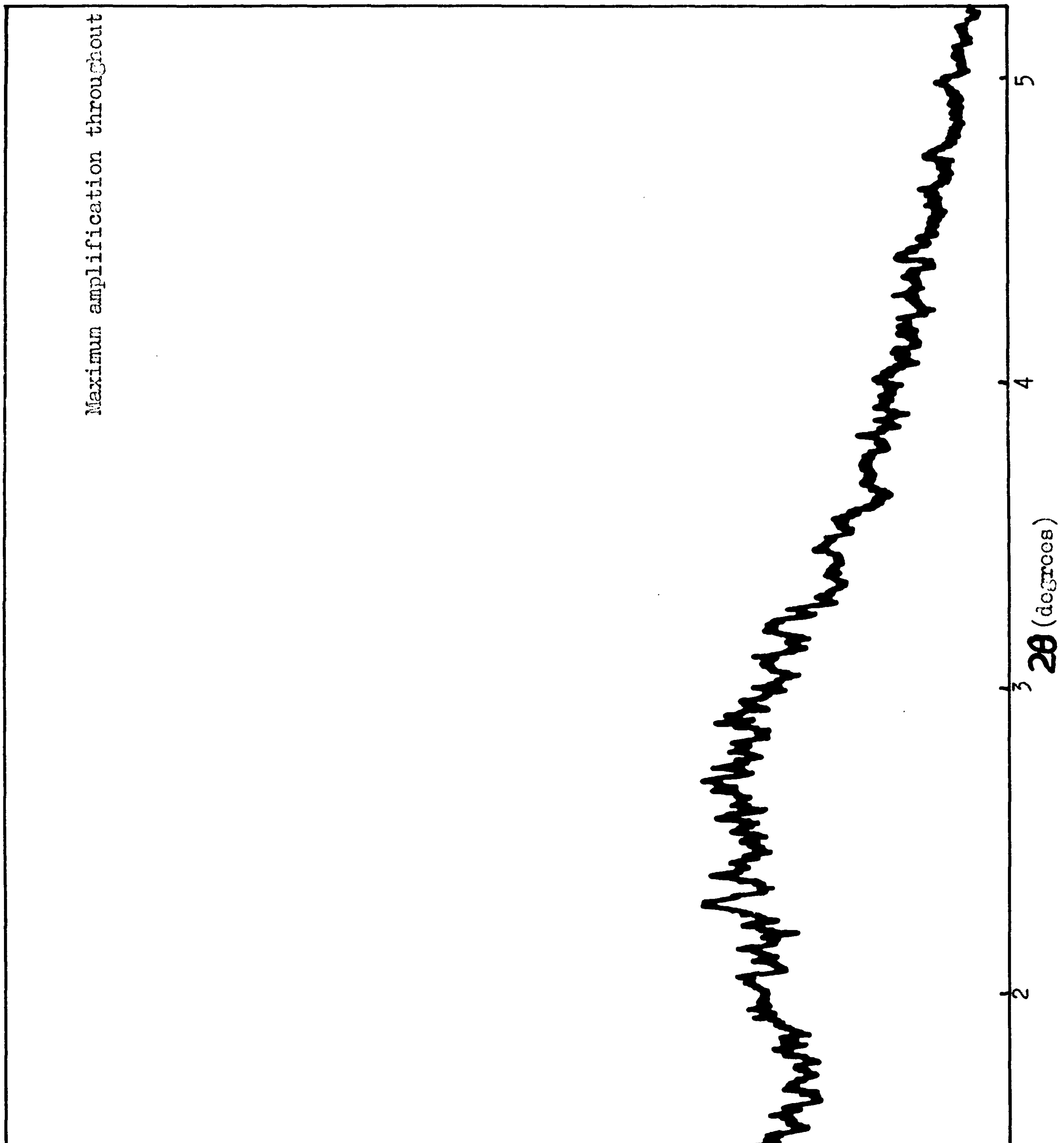


Fig.(3.7) Diffraction trace from mild steel specimen covered with 1g/1 solution of octadecanoic acid in hexadecane.



molecules (125Å) thick. Implications of these results will be examined in section 3.4.

3.4 Discussion.

3.4(1) Built-up films.

Interferometric measurements by Langmuir[20] of the thickness of barium octadecanoate films on chromium containing a known number of molecular layers showed that the increment per molecular layer was 24.4Å for films which had been deposited on both up- and down-trips, and 26-28Å for those which had been deposited on down-trips only. The thickness of barium octadecanoate multilayers deposited on metal substrates, which were studied by Mertens, Theroux, and Plumb[12,21] with ellipsometry, gave values of 25±1Å per molecular layer. Neither of these measurements, however, yielded direct information about the orientation of the molecules in successive layers. Clark et al.[4,5,15] observed by X-ray diffraction a "long spacing" of 46.5Å for octadecanoic acid and 47.5Å for calcium octadecanoate films deposited on metal rods. In a comparative study by Holley[16] of built-up films of mixed barium/copper octadecanoate on glass, X-ray diffraction revealed a principal spacing of 50.43Å and optical interferometry an increment of 24.2Å per molecular layer. It is evident from the latter observations that the principal X-ray scattering planes are separated by a distance approximately twice that of the depth of a single molecular layer. It is interesting to compare the spacings which have been reported for films built-up by the Langmuir-Blodgett technique with values published for the bulk solid.

Long spacings in thin films of octadecanoic acid prepared by crystallisation from the melt on glass and metal surfaces were found by Müller[14] and Clark[4] to be 38.7 and 39.5Å respectively. Trillat[2] observed that films of octadecanoic acid on glass prepared by evaporation of a solution in a volatile solvent contained a similar spacing (39.1Å). Piper[22] and Thibaud,[23] however, found that films of a series of fatty acids prepared by these two techniques were polymorphic and did not have the same long spacing. Octadecanoic acid films crystallised from the melt showed a spacing of 39.9Å, but similar films prepared by evaporation of a solution gave a value of 43.95Å. The theoretical length of an octadecanoic acid molecule, calculated from accepted covalent bond length data,[24] is 21.4Å. The length of a hydrogen-bonded dimer unit would be expected to be rather more than double this figure (i.e. 42.8Å), which is, however, rather greater than most values reported for the long spacing in the bulk acid, but lower than those for built-up films. The divergence in spacings observed in fatty acid crystals and built-up films is largely due to differences in the orientation of molecules in each layer. Verma[1(ii),25] has shown that molecules in a single crystal of hexadecanoic acid are oriented at an angle of 62° (28° from the vertical) to their basal plane. Electron diffraction studies by Germer and Storks[26], have shown, however, that in built-up films of barium octadecanoate and octadecanoic acid the molecules are almost vertical to the surface of the substrate.

In this investigation, features arising from spacings greater than about 40Å coincided with the fall-off in intensity of the undiffracted main beam. Small peaks therefore tended to appear only as shoulders on a steeply-falling curve, the precise position of which was a function of the surface preparation and varied somewhat from one specimen to another. The traces contained considerable fluctuations at the high amplification which was required for observation of peaks arising from only a few layers of ordered molecules. Fig. 3.3 shows, however, that a film only 5 layers deep gave an unmistakable peak, while large diffraction features were observed in traces from films containing 9 and 15 layers even at reduced amplification. Spacings for the thicker films (52Å) showed fair agreement with values reported by Clark[4,15] and Holley.[16] The reason for the low figure (41Å) for the 5-layer film is not known; this value is close to twice the length of the octadecanoic acid molecule, and is in closer agreement with figures quoted in the literature for the bulk acid than those for built-up films. The object of the investigation, however, was to establish the limit of detection of oriented layers, and the precise position of the peak is of secondary importance. Since only built-up films containing an odd number of molecular layers can be prepared, the next thinnest film which could be tested would contain only 3 layers of molecules. Such a film was not prepared because it was considered that a peak much smaller than the one which had been obtained with a film 5 layers thick would not have been outside random fluctuations of the diffractometer trace.

The sensitivity of the technique employed by Clark et al. was only good enough to detect orientation in built-up films which contained at least 25 molecular layers of octadecanoic acid,[5] i.e. were about 525Å thick. The sensitivity achieved in the present investigation was much higher, for diffraction peaks from the thickest built-up film that was studied would have been undetectable in Clark's apparatus.

3.4(2) Solutions of octadecanoic acid in hexadecane.

Traces from specimens covered with a film of solution contained larger irregularities than those coated with built-up films. This may be due to "smoothing out" of the surface by transferred monolayers; Bikerman[18] has shown that a monolayer deposited on a metal from the surface of an aqueous substrate is unlikely to follow the profile of sub-microscopic asperities closely.

In contrast with the results of Clark's investigation[5], no diffraction peaks were observed on traces from specimens coated with a film of solution, in spite of the greatly improved sensitivity. The ingredients of the solution had been chosen so that the solute had a high molecular weight and a hydrocarbon chain length close to that of the solvent, resulting in conditions which should be favourable for formation of the plastic boundary layer reported by Cameron.[8] The concentration was restricted to 1.0g/l, about 30% of saturation concentration, in order to avoid spurious results due to crystallisation of octadecanoic acid. Although the concentration was near the maximum which could have been used legitimately, diffraction peaks comparable even with those which had been obtained with the 5-layer film were not observed. However, this did not prove that the surface had no orienting effect at all, merely that, if orientation occurred, it was not sufficiently complete to give a detectable diffraction peak. It is possible that the plateau region was more pronounced in the presence of octadecanoic acid, but this could not be checked because the thickness of the film could not be controlled.

Since the plateau or "hump" was shown by pure hexadecane even when it was insulated from actual contact with the steel surface by a lining of "Cellophane", it was almost certainly due to the "halo" from the bulk liquid and not associated with any orienting effect of the metal surface. Stewart[27] found that liquid alcohols and fatty acids gave X-ray diffraction haloes which contained two maxima, the principal one corresponding to the molecular "diameter" and the other to a multiple of the length of the molecule. Liquid hydrocarbons had a halo which contained only one maximum, the one related to the molecular diameter. The plateaux observed in the present study, however, correspond to spacings in the range of 22-60Å, which is from one to three times the length of the hexadecane molecule.

3.5 Conclusion.

Orientation in built-up films of octadecanoic acid on steel only 5 molecular layers deep was detectable by X-ray diffraction. No comparable diffraction peaks were observed when steel specimens were covered by films of a solution of 1.0g/l octadecanoic acid in hexadecane, showing that orientation due to the field of force of the metal surface was either restricted to a depth of less than 5 molecular layers (about 125Å) or was too weak to give a well-defined peak.

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4. ANOMALOUS VISCOSITY IN INTERFACIAL REGIONS.

4.1 Introduction.

Reported anomalies in the rheological properties of liquids in regions close to metal surfaces have already been mentioned in chapter (1). Claims of direct observation of viscous anomalies in solutions of polar compounds in hydrocarbons near metal or metal oxide surfaces will be reviewed in this section. Studies of the flow properties of thin films of liquids are extremely vulnerable to the effect of dirt and suspended colloidal matter, as entirely spurious phenomena may obliterate any genuine manifestation of long-range surface forces.

It was claimed, for instance, by Hardy[1] and Watson[2] that polished steel surfaces allowed to approach each other under gravity through an oil- or air-filled space were separated by a residual gap of 4 microns when equilibrium had been reached. Bastow and Bowden[3], however, used optical interference measurements to show that polished glass surfaces could approach to within a mutual separation of less than 0.3 microns providing that the surfaces were kept scrupulously dust-free. Studies of the rate of approach and equilibrium separation of polished steel discs, containing surface irregularities of not greater than 254Å, through oil films, have been reported by Needs.[4] Poor reproducibility was obtained, however, and the importance of filtration seems to have been overlooked. The rate of approach of the discs when separated by castor oil apparently adhered closely to the theoretical value calculated from classical hydrodynamics, (Stefan-Reynolds equation), but the thinning of a mineral oil took place at a reduced rate. (Anomalies might have been anticipated, however, with the highly polar, well known boundary lubricant, castor oil rather than with (presumably) non-polar mineral oil).

Extensive investigations have been made by G.I.Fuks[5,6,7] on the kinetics of approach and equilibrium separation of plane-parallel quartz and steel discs separated by films of solutions in both aqueous and hydrocarbon media. Thinning of aqueous films and the effect of dissolved electrolytes could be correlated with "disjoining pressure", the resultant of electrostatic repulsive and London-van der Waals attractive interactions, although experimental equilibrium thicknesses greatly exceeded the theoretically calculated values.[5] Pure hydrocarbons of low-molecular-weight did not form equilibrium films after dust and surface-active contamination had been carefully excluded, but solutions of fatty acids in hydrocarbons gave equilibrium films the thickness of which conformed to the equation $h_{min} = k_1+k_2c_n$, where h_{min} = equilibrium thickness under a given load.

k_1 and k_2 are constant for a particular hydrocarbon,

and c_n = number of carbon atoms in fatty acid molecule.

h_{min} values lay in the range 200 - 2000Å, becoming less under higher normal loads.[6] Fuks[8] has also recently studied the rate of <u>separation</u> of steel discs immersed in iso-octane, after removal of a load of 0.12 kg/mm^2 which had been applied for 15 minutes. The initial rate of thickening of the residual interfacial film was increased markedly by the presence of 0.05% octadecanoic acid, demonstrating that an elastic polymolecular layer was present.

A simplified form of Fuks's apparatus was used by Askwith, Crouch, and Cameron[9] to show that the viscous anomaly was greatest when the fatty acid and hydrocarbon solvent contained the same number of carbon atoms. An important departure from Fuks's results was that the equilibrium gap was the same for all the solutions and for the pure hexadecane solvent (20,000 Å). Differences were observed only in the rate of approach to the equilibrium position. Anomalous rates of thinning were observed at gaps of greater than 90,000 Å. The enormous range apparently shown by surface effects is not necessarily inconsistent with Fuks's results since much lower loads were used, although it is not clear whether adequate precautions were taken to exclude dust.

An apparatus for measurement of attractive and repulsive forces between macroscopic parallel metal surfaces was described by Sonntag[10] in 1964, but no experimental results appear to have been published yet. However, Sonntag[11,12] has carried out extensive investigations into the thinning of oil and water films between coalescing mercury surfaces. Films of xylene stabilised by fatty acids either collapsed within one minute or reached a constant thickness of less than 100 Å in a similar time. Residual films with thicknesses comparable with those reported by Fuks were not observed in the presence of either fatty acids or heavy metal soaps, although both positive and negative deviations from the Stephan-Reynolds equation occurred in films less than 500Å thick. These were correlated with "disjoining pressure",[13,14] which governs the equilibrium thickness of liquid films, and may not necessarily have reflected divergences from bulk viscosity.

Investigations by Cameron and Smith on the thinning of oil films between the surfaces of mercury and evaporated metal films deposited on glass are in progress at Imperial College. Preliminary results indicate that the rate of thinning of a hexadecane film is greatly reduced by the presence of dissolved octadecanoic acid, but quantitative studies await refinement of the capacitance measurement technique which is used for determination of film thickness.

Determination of flow rates through capillaries has been used by Henniker,[15] Deryagin,[16] and Eirich,[17] to demonstrate the existance of regions of anomalous flow close to the walls. Wilson and Barnard[18] found that 1% oleic acid, p-cresol, or octadecanoic acid added to a refined mineral oil caused a great reduction in the rate of flow through a glass capillary as large as 0.3mm in diameter. The flow of less highly refined mineral oil through magnesium, brass, iron, and steel capillaries of the same diameter occurred at a rate which decreased with time and eventually became almost negligible. This "clogging" of capillaries by oils which had been pre-filtered through 200-mesh gauze was attributed by the authors to adsorption of materials present in small concentrations. When this work was repeated by Buckley,[19] however, with glass and platinum tubes of microscopic diameters, no plugging was observed even in the presence of 1% oleic acid, provided that the solution had been pre-filtered through cotton wool (!). Experiments with platinum capillaries 9.35 microns in radius showed that no stationary adsorbed layers extending more than 300Å from the walls were present.

The flow-rates of cyclohexane, propyl alcohol, and water through a gap between polished glass or stainless steel discs were compared by Bastow and Bowden[20] with that of a 1% solution of ammonium oleate (a compound known to form "liquid crystals" in aqueous solution). The width of the gap was usually at least 2 microns, although in some of the experiments on water separations of only 2000Å were used. Anomalous flow was not observed with any of the liquids tested except the ammonium oleate solution. Rates of flow were directly proportional to the pressure gradient across the constriction and were consistent with values calculated from optical determinations of the width of the gap on the assumption that flow was Newtonian. It was concluded that if stationary zones existed in liquid adjacent to the walls they were less than 1000Å deep. The behaviour of long-chain polar compounds dissolved in hydrocarbons was not, however, investigated.

Deryagin[21,22] and his collaborators have studied the variation of viscosity with distance from the surface in thin layers of solutions on polished metal substrates. Changes in viscosity were deduced from observations of the profile of a liquid drop placed on a metal specimen and subjected to a tangential air blast - a technique known as the "blow-off" method. Study of the profile of polymer solutions by optical interference measurements revealed continuous variations in viscosity in films up to 2 microns in thickness. Although Deryagin claimed that ellipsometric studies of films of stearic acid/hexadecane solution confirmed the existence of a structured, but heterogeneous boundary layer 100 to 1000Å deep, the evidence is less convincing in this case. It was not possible to use solutions containing concentrations of octadecanoic acid comparable with those normally used in lubrication (about 1%) because such solutions are autophobic and do not wet metal surfaces.

A coherent drop with a stable leading edge could therefore not be obtained. Observations were made instead on drops of a solution of 0.00054% octadecanoic acid in vaseline oil, which wetted the steel surface satisfactorily. No continuous deviations from the wedge-like form predicted for Newtonian flow were noted in the profile of these drops; the profiles were jagged, however, in contrast with the smooth ones which had been observed with pure vaseline oil. The "jaggedness" was interpreted by Deryagin as evidence of a heterogeneous, structured region, although no continuous deviation from the bulk viscosity was evident. In assessing the validity of this conclusion it should be remembered that the concentration of octadecanoic acid was so low that a layer of solution 1mm deep would contain only just enough to cover the metal surface with a close-packed monolayer if the whole of the acid were adsorbed. The jagged profile might well arise from unequal adsorption of the acid due to heterogeneity of the surface.

To summarise, early claims of evidence to support the existence of stationary or viscous layers extending a micron or more from solid surfaces into bulk solution have been discredited and more recently reported deviations from bulk rheological properties in zones extending to similar distances from surface must be viewed with scepticism. There is, however, considerable experimental evidence which suggests that the properties of liquids may differ from bulk values in regions up to 1000Å from metal surfaces.

4.2 Aim and method of investigation.

Reduction of the flow-rate of hydrocarbons through fine capillaries in the presence of dissolved long-chain fatty acids has been investigated. If deviations from the bulk viscosity occur in boundary layers to the extent reported by Askwith, Cameron, and Crouch, there should be detectable differences in rates of flow through capillaries many microns in diameter. Even if the effect of fatty acids was restricted to formation of an immobilised zone 100Å deep, application of the Poiseuille equation shows that a reduction in rate of flow of 3.6% would occur in a capillary of 1 micron radius, assuming stream-lined flow. A stationary layer 500Å deep would reduce the flow rate through capillaries of this radius by 18%.

It was decided to limit the investigation to studies of the flow of solutions through metal capillaries so that the solid/liquid interfaces resembled those encountered in most boundary lubrication applications. It is experimentally much more convenient to measure flow-rates through collections of capillaries, as in sintered filters or beds of powder, than through a single capillary. The fragility and inconvenience of handling of single capillaries of microscopic bore, coupled with the difficulty of measuring movements of minute volumes of liquid, pose formidable problems.

In preliminary experiments flow-rates were determined through beds of electrolytic iron powder. The specific surface of the powder was found by krypton adsorption to be $0.105 m^2/g$, equivalent to an average particle radius of 3.7 microns. Microscopic examination showed, however, that the particles were irregularly shaped and lay in a wide range of sizes. Other investigations were carried out with commercially produced sintered stainless steel discs which were claimed by the manufacturers to contain pores not greater than 3 microns in size.

4.3. Experimental procedure.

4.3(1) Flow-rates through powdered iron beds.

Materials.

Solvents and solutions were pre-filtered through no. 5 porosity (1-2 microns) sintered glass filters. (Passage through Membranfilter MF10 membrane filters which had been Soxhlet extracted for 80 hours in iso-octane in order to remove oil-soluble surface-active material nevertheless gave filtrates which foamed, indicating the presence of leached impurities). The filtered solutions did not show a visible Tyndall effect when illuminated by a powerful beam of light in a darkroom, and there was no significant difference in the scattering by pure hexadecane and solutions of dodecanoic, tetradecanoic, and octadecanoic acid in the same solvent when these were tested in a sensitive nephelometer.

Fatty acids used in these preliminary investigations were laboratory reagent grade; no further purification was attempted. Hydrocarbons were checked for freedom from surface-active contamination by measurement of their interfacial tension with high purity distilled water, which itself did not foam on shaking. The drop-volume method was employed, giving values within the range quoted in the literature; the fall in interfacial tension after 30 minutes ageing was less than 0.2 dyne cm^{-1}.

The iron powder was "Sintrex 300 mesh" unannealed material supplied by George Cohen & Son, Ltd., which was ground further on a steel-lined vibratory mill. It has been mentioned earlier that krypton adsorption measurements gave a surface area equivalent to an average particle radius of 3.7 microns for this powder, although a wide range of particle shapes and sizes were known to be present. The powder was kept in an air-tight tin without further conditioning, and showed no discolouration or detioration in flow properties after prolonged storage. It had not been realised at this time that spheroidal carbonyl iron powder with a fairly narrow size distribution around 1 micron was available, which would probably have been more suitable.

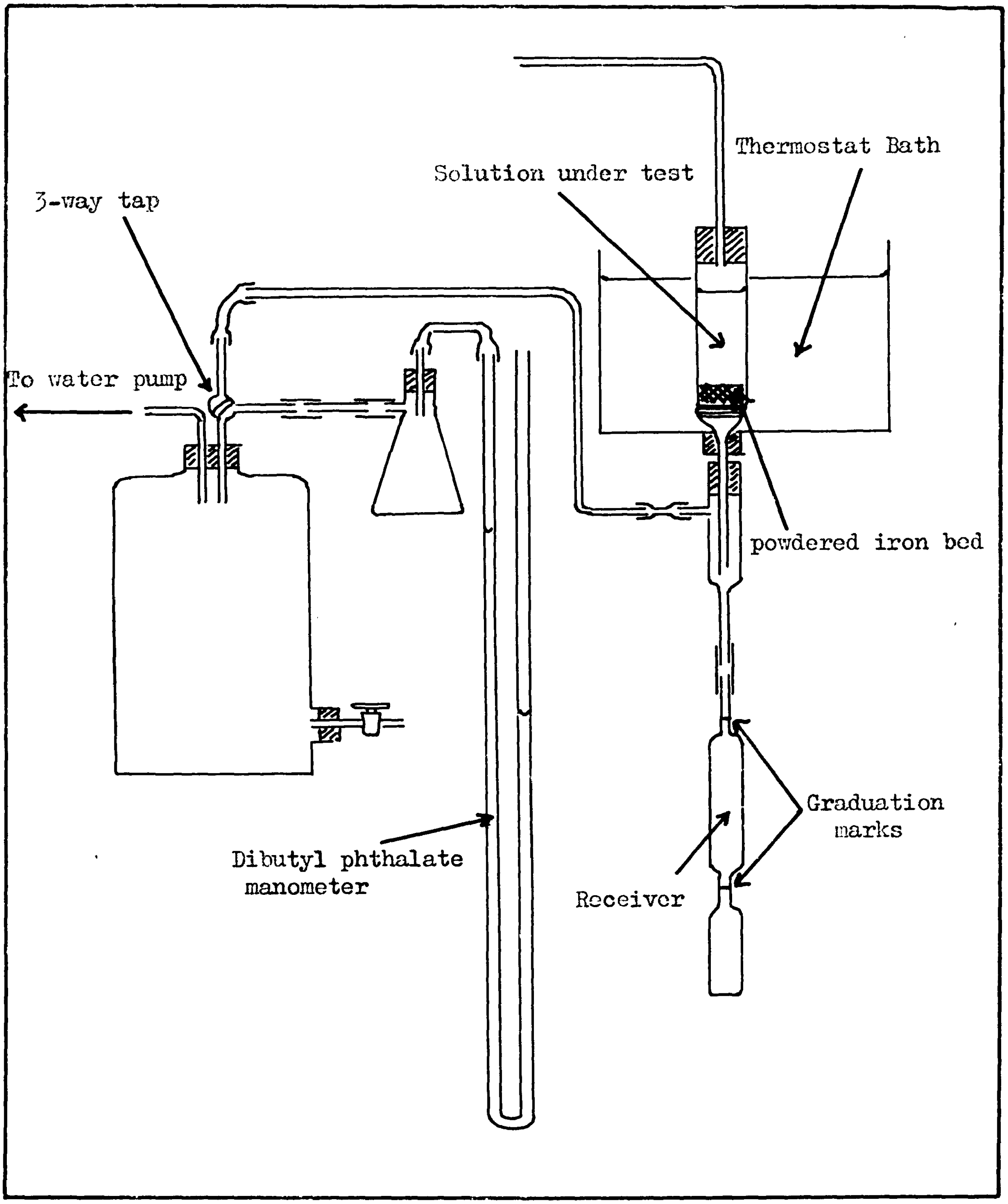
Procedure.

The simple apparatus shown in fig.(4.1) was set up after all glassware had been cleaned by prolonged soaking in chromic acid, washed thoroughly in distilled water, and dried in an oven. It sonsisted of a 2 cm diameter funnel containing a number 4 porosity (5-10 microns) sintered glass disc, which acted as a support for the powdered iron bed. The funnel, which was surrounded by a thermostat bath, drained into a detachable receiver under a partial vacuum measured by a dibutyl phthalate manometer and maintained in a large air reservoir.

The bed was prepared by allowing 10g of iron powder to settle from a slurry in the test liquid hydrocarbon onto a glass-paper disc placed on the fritted glass disc. In a check experiment, it was found that the flow-rate of a given solution through the sintered glass support alone was five times that when the powder bed was in position, confirming that the support was not the rate-determining element.

The liquid reservoir was filled to an arbitrary level, care being taken not to disturb the bed. Flow-rates were determined by developing a steady vacuum in the large air reservoir, opening the 3-way tap, and observing the time taken for the liquid level in the receiver to rise from the lower to the upper graduation mark. After each determination it was necessary to empty

Fig. (4.1) Apparatus for measurement of rate of flow of fatty acid/ hexadecane solution through a bed of finely divided iron.



the receiver into the liquid reservoir to the mark, topping up with stock solution to the original level when this was required. A vacuum of 85-90 cm dibutyl phthalate gave convenient times of flow; slight differences in the vacuum were allowed for by converting all flow-times to 85 cm of dibutyl phthalate.

The procedure was repeated until the flow-times of pure solvent through the bed either became constant or developed a constant change between successive determinations. The bed was drained until it was only just covered by liquid, and the filtrate discarded. 3ml of acid solution were added, being allowed to drain down the sides of the funnel in order to disturb the bed as little as possible. The filtrate was discarded after drainage, as before, and the procedure was repeated twice before the funnel was filled to the original level with acid solution, fairly complete replacement of solvent by solution having been achieved without disturbance of the bed. Measurements of flow-time were taken once more until these became constant or showed a constant rate of drift with further readings.

4.3(2) Flow-rates through sintered stainless steel discs.

Materials.

Sintered stainless steel discs 2cm in diameter and stated to have a maximum pore size of 3 microns were obtained from Bound Brook Ltd. Long-chain fatty acids of Puriss grade (99% purity) were supplied by Koch-Light Ltd., and high purity hydrocarbons from Newton Maine Ltd. The hydrocarbons were checked for freedom from surface-active contamination by determination of their interfacial tension with surfactant-free distilled water, and were filtered as before.

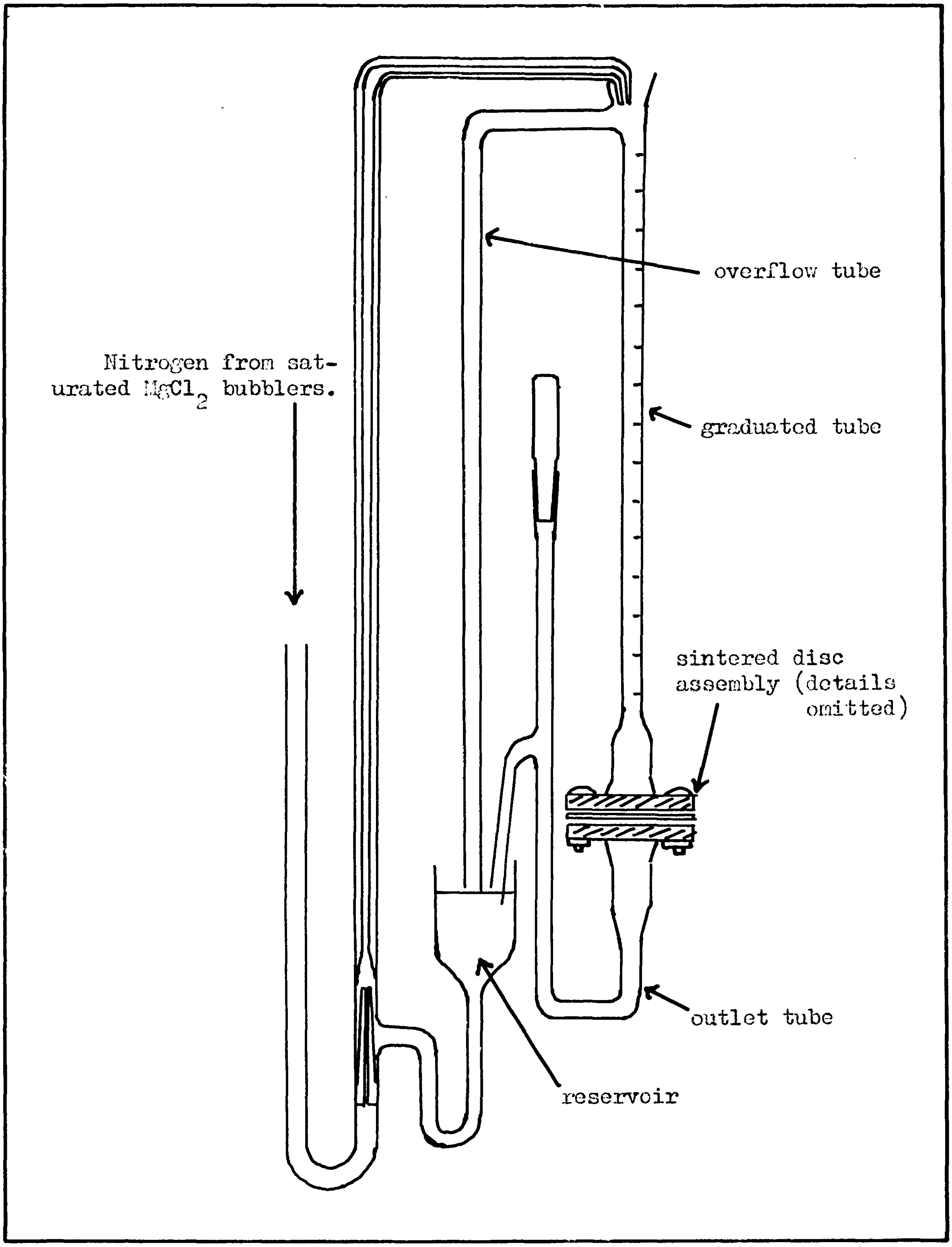
Apparatus.

The apparatus shown in fig.(4.2) was designed to maintain continuous circulation of the test liquid through the porous disc under controlled conditions. This was accomplished with a "nitrogen lift", in which oxygen-free nitrogen which had been passed through a train of saturated $MgCl_2$ bubblers and through a cotton-wool filled tube to remove entrained liquid droplets, was used to produce a stream of gas bubbles which carried liquid to the top of the capillary. An overflow tube allowed a constant hydrostatic head to be maintained above the disc.

The outermost 4mm of the porous disc was compressed on a 20 ton hydraulic press to give a smooth peripheral ring which was effectively non-porous and facilitated mounting of the disc. This was "sandwiched" in a QVF tapered butt-joint by insertion of a central asbestos template which located the disc. All washers in the assembly were protected by PTFE inserts.

The entire rig was mounted on a heavy metal stand and enclosed in a glass container with a detachable lid. This, together with the nitrogen train, stood in a thermostat bath maintained at $25.0 \pm 0.1^\circ C$. The nitrogen lift enabled the humidity of the enclosure to be controlled at 30% r.h.

Fig. (4.2) Apparatus for measurement of flow rates of solutions during continuous circulation through steel disc.



Procedure.

Before use the stainless steel disc was Soxhlet extracted with iso-octane in order to remove loose particulate matter and soluble surface-active contamination. Maximum pore size was checked by determination of the air pressure required to displace liquid of known surface tension from the largest pores (B.S.1752). This technique was modified in order to obtain information about the pore size distribution: the flow-rate of air through a disc covered with a layer of liquid was measured as a function of pressure. After the first bubble (which corresponded to penetration of the largest pore) had appeared, the flow rate increased only gradually with pressure. Above a certain pressure (p_1), however, the flow-rate began to increase much more rapidly until at pressures greater than p_2, flow-rate was directly proportional to pressure and the graph became superimposable on one obtained in the absence of liquid. The size of the rate-controlling pores therefore lay within a range of diameters limited by those corresponding to p_1 and p_2.

It was necessary to remove the apparatus from its thermostatted enclosure for the purpose of changing the circulating liquid. The outlet tube was first filled with pure hydrocarbon solvent until the pores of the disc were completely penetrated from below - this required careful manipulation. The graduated tube was then filled, and both sides of the disc checked for the presence of air bubbles. After a suitable volume of solvent had been placed in the reservoir, the apparatus was reassembled, care being taken that the graduated tube was vertical. It was replaced in the thermostatted chamber and circulation was commenced by applying a suitable nitrogen pressure through a reducing valve. The flow-rate through the disc was determined by closing the gas supply, thus temporarily stopping the circulation, and timing the descent of the liquid meniscus between selected marks in the graduated tube. When successive determinations gave results which were the same within experimental error, the apparatus was removed, emptied, and both assemblies washed with six aliquots of fatty acid solution, before refilling with acid solution using the same procedure as before to prevent formation of air bubbles. Circulation was recommenced and continued until readings of flow-rate became constant once more.

4.4 Results.

4.4(1) Flow-rates through powdered iron beds.

The effect on flow-rate of replacing pure hexadecane with solutions containing $^1/300$ mole fraction of dodecanoic, tetradecanoic, hexadecanoic, and octadecanoic acid are shown in figs. (4.3), (4.4), (4.5), and (4.6) respectively. (This concentration was chosen so as to permit direct comparison with the work of Askwith, Cameron, and Crouch.[8]). The dodecanoic acid run was carried out at 20.0±0.1°C, but solubility measurements had shown that solutions of octadecanoic and docosanoic acids precipitated at this concentration and temperature. Runs with the other acids were therefore carried out at 40.0±0.1°C, but docosanoic acid solution was almost saturated even at this temperature and precipitation

Fig. (4.3) Flow-times of hexadecane and dodecanoic acid/hexadecane solution through powdered iron bed.

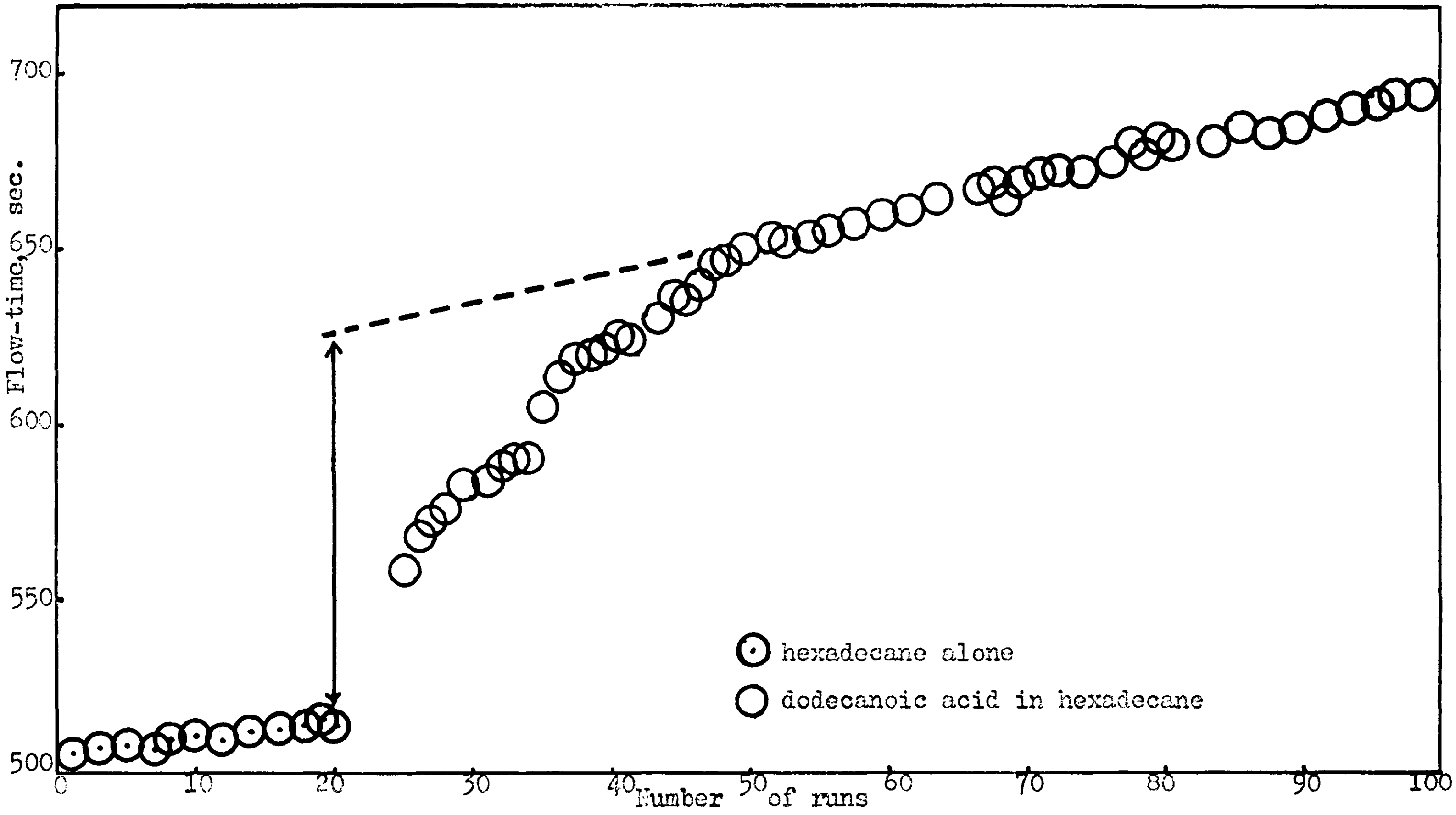


Fig.(4.4) Flow-times of hexadecane and tetradecanoic acid/hexadecane solution through powdered iron bed.

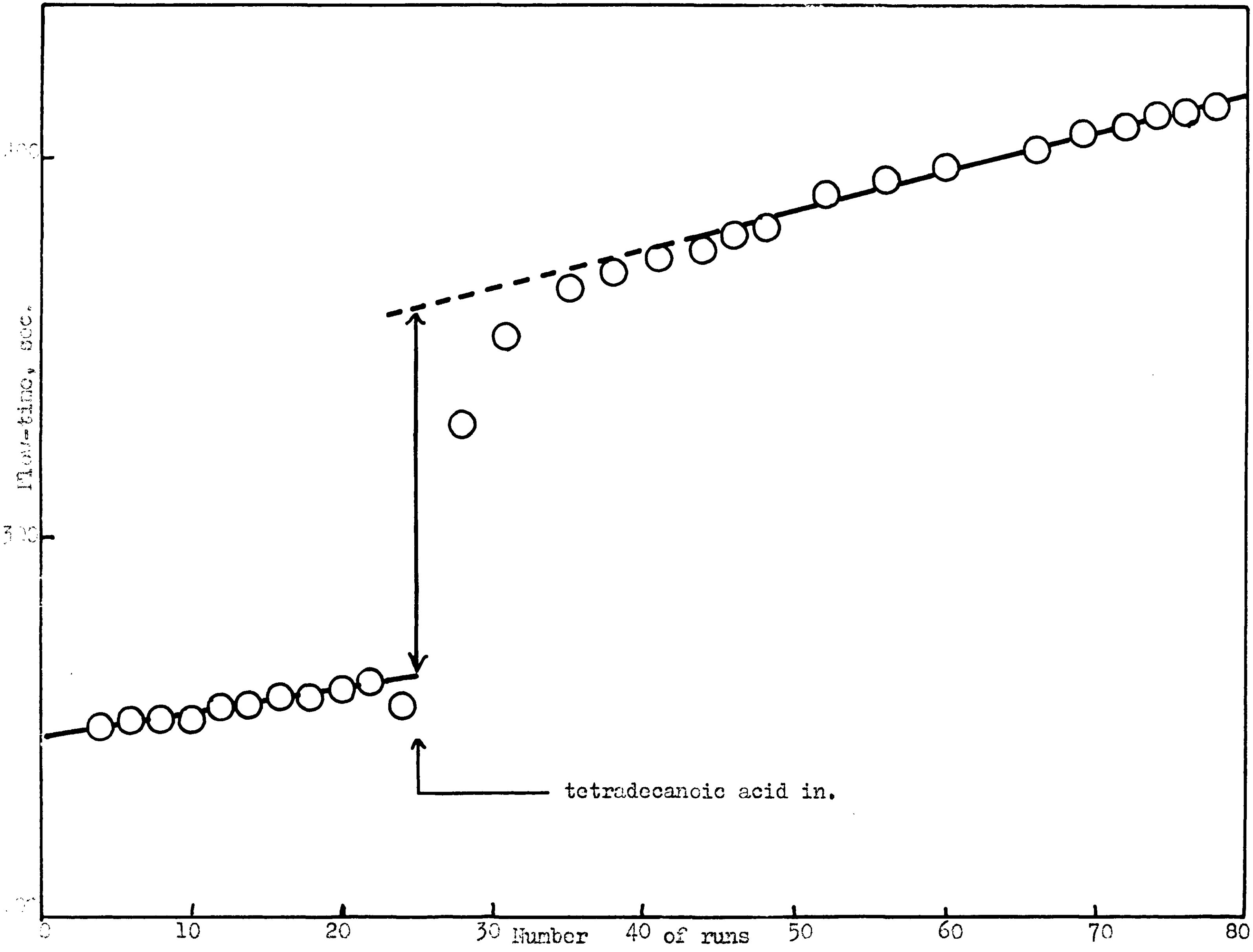


Fig.(4.5) Flow-time of hexadecane and hexadecanoic acid/hexadecane solution through powdered iron bed.

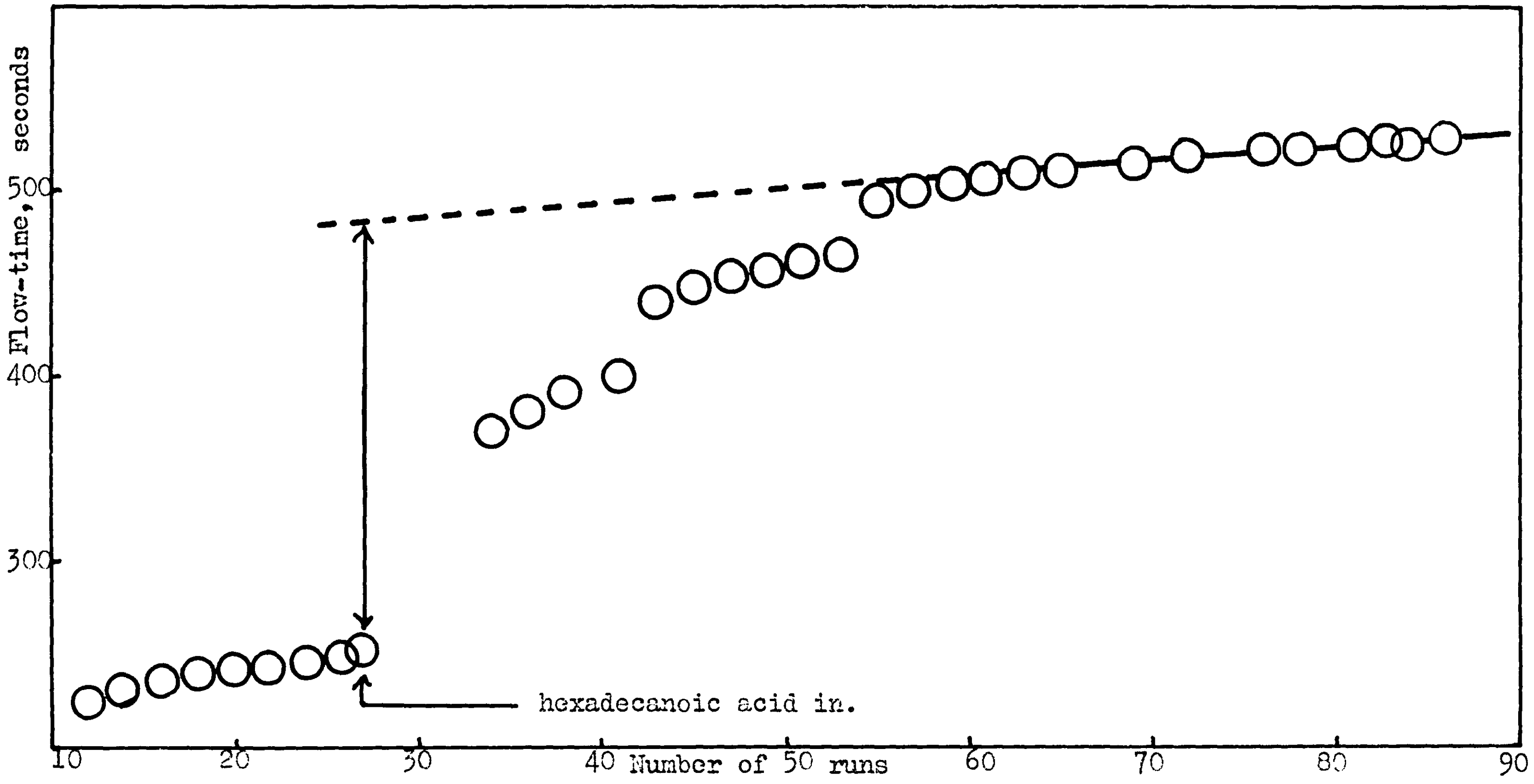
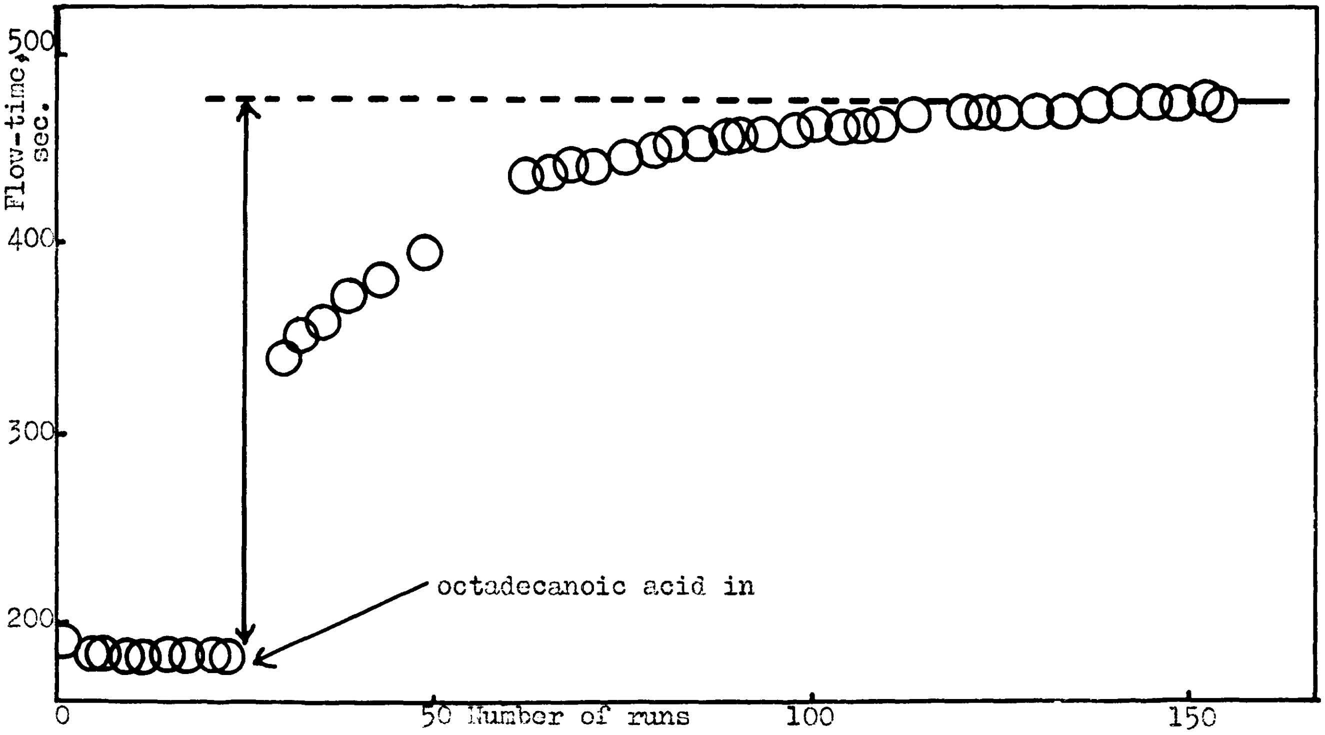


Fig.(4.6) Flow-time of hexadecane and octadecanoic acid/hexadecane solution through powdered iron bed.



of solid occurred, invalidating the results of this run.

It is evident from the figures that constant flow-rates were not observed (in three of the runs) either before or after replacement of pure solvent by fatty acid solution. The curves do not even have uniform shapes. These divergences will be discussed in a later section, but from table (4.1) and fig. (4.7) it is apparent that the percentage reduction in flow-rate by the different acids shows a clearer trend.

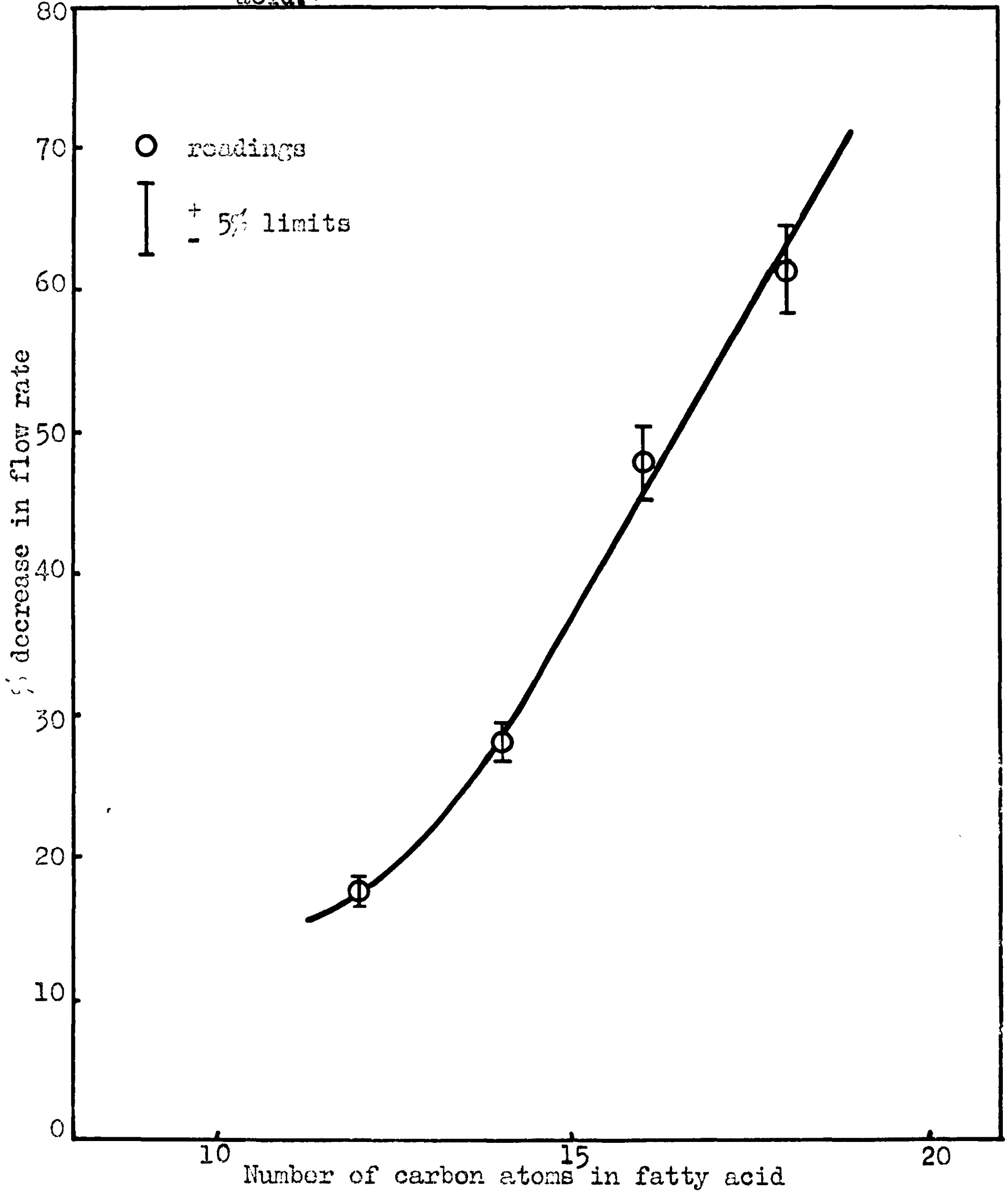
Table 4.1 Reduction of flow-rate of hexadecane through powdered iron bed in presence of $^1/300$ mole fraction of fatty acid

Acid	Reduction in flow-rate(%)
Dodecanoic	17.7
Tetradecanoic	27.9
Hexadecanoic	47.8
Octadecanoic	61.8

The changes were measured by extrapolation of the flow-time after addition of fatty acid to the changeover point. Even the change for dodecanoic acid, which was observed at a lower temperature, lies on a smooth curve relating the decrease in flow-rate with increasing fatty acid chain length.

When a constant flow-rate, or at least a constant drift of flow-rate, had been reached after addition of fatty acid, further determinations were made at a series of temperatures between 20° and 80°C after 30 minutes had been allowed for equilibration at

Fig. (4.7) Dependence of decrease in flow rate of hexadecane through iron bed on number of carbon atoms in fatty acid.



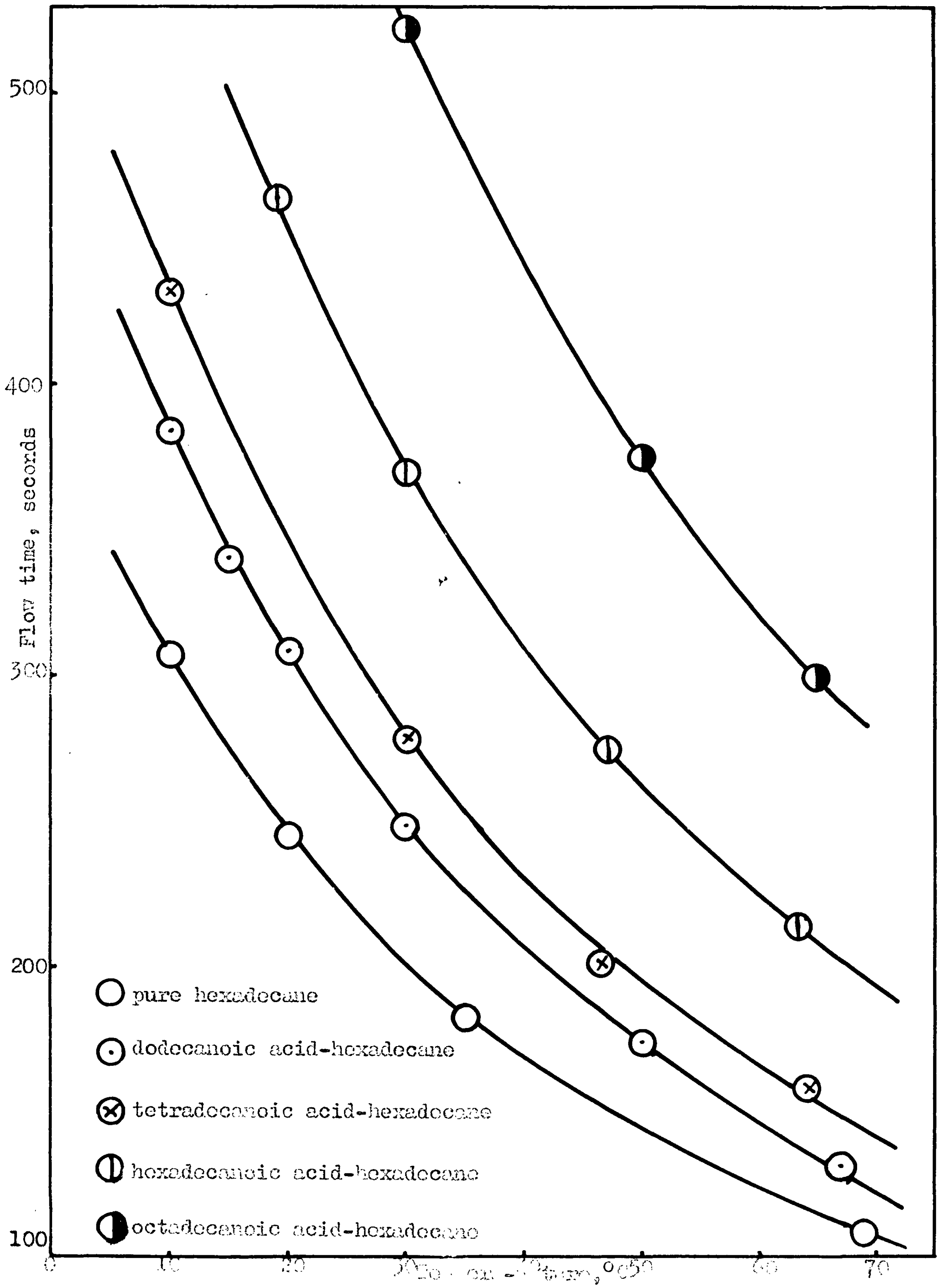
the new temperature. The variation of flow-time with temperature for solutions of the various fatty acids is shown in fig.(4.8), the flow-times of hexadecane in each bed being brought to superposition and the flow-times of the acid solution multiplied by the appropriate conversion factor.

At the end of the first run, dodecanoic acid solution was finally replaced by pure hexadecane once more. No change in flow-time, or at least in its rate of drift, was observed, showing that the decrease in flow-rate which had resulted in the presence of the acid was irreversible.

Changes in the rate of flow of pure n-octane which had been replaced with $^1/300$ mole fraction solutions of fatty acids were also studied. In this system, behaviour was very irreproducible, with varying, usually rapid, drifting of flow-times. Runs with octanoic and decanoic acids at 20°C gave reductions in flow-rate of around 14% and a hexadecanoic run showed a reduction of 25%; but behaviour was so haphazard that these data have doubtful quantitative significance.

In an attempt to obtain information about the effect of replacement of pure hexadecane by fatty acid solution on the <u>packing</u> of the bed, the influence of dissolved hexadecanoic acid on the stability of dispersions of iron powder in hexadecane was studied. It was realised that all or part of the observed decrease in flow-rate in the presence of fatty acids might have been due, not to the presence of boundary layers with enhanced viscosity, but to

Fig. (4.8) Flow times of fatty acid/hexadecane solutions through powdered iron bed as a function of temperature.



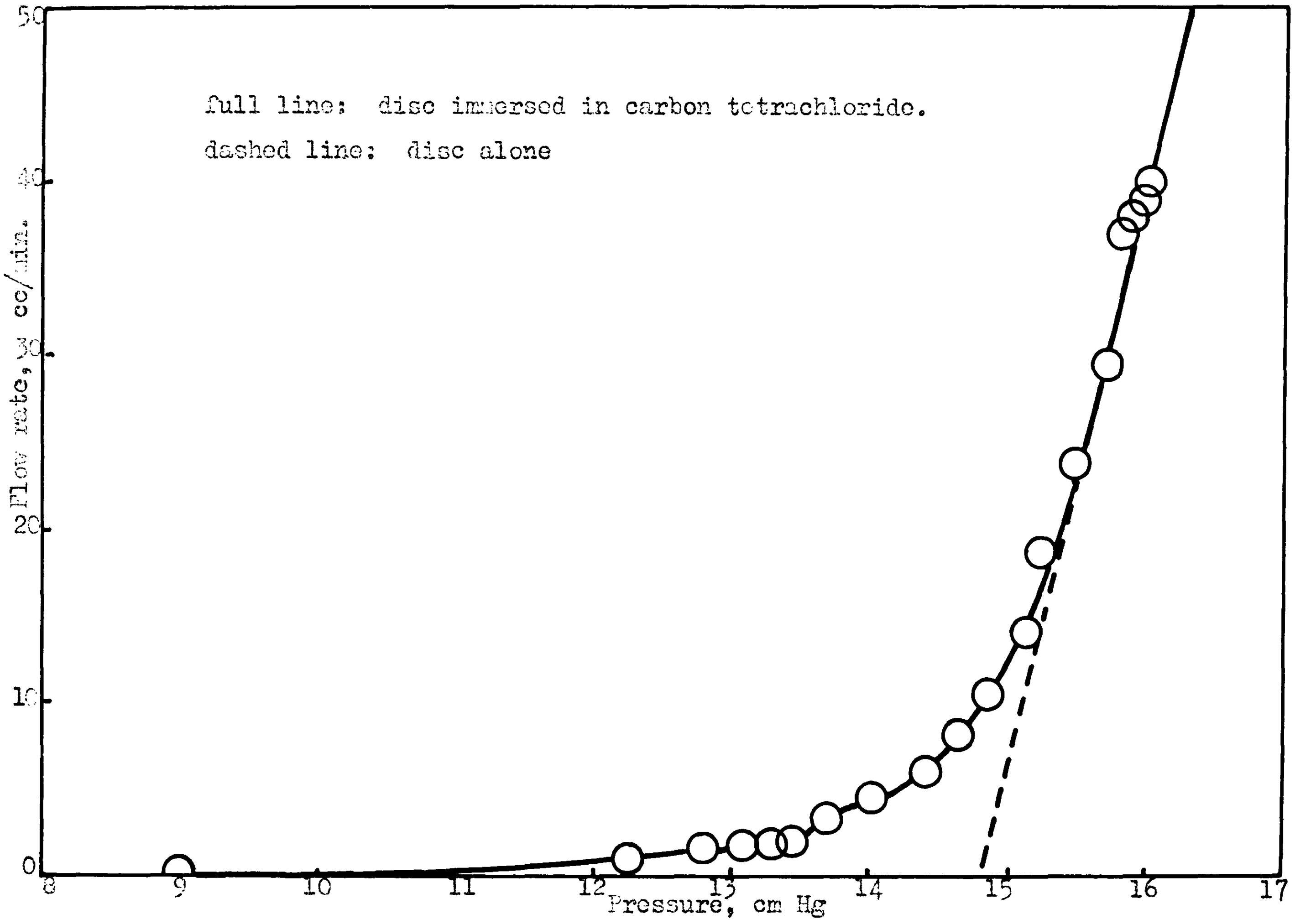
the detergent action of adsorbed acid, which, combined with flow of liquid through the bed, might have caused detachment of fine particles from the upper parts of the bed and accumulation of a more closely packed layer on the support. In order to assess the probability of this, two suspensions containing 0.6g iron powder per 100ml hexadecane were prepared, one of which contained 0.2g dissolved hexadecanoic acid. These were shaken manually for two minutes and the rates of settling were followed by measurement of changes in optical density on an "EEL" absorptiometer. Settling rates of the two suspensions were not significantly different and there was no evidence to suggest that inter-particle adhesion had been altered by the presence of adsorbed hexadecanoic acid. Sedimentation was assumed to be complete when no further change in optical density occurred - about 80 minutes after dispersing. This corresponded to a Stokes radius of about ·1 micron. Since adsorbed hexadecanoic acid apparently had no effect on interparticle adhesion, it was concluded, at first, that reduction in flow-rate in the presence of fatty acids was unlikely to be due to increased rearrangement of the bed as a result of detergent action. It will be seen in section 4.5, however, that this opinion has been revised in the light of observations of the settling characteristics of more concentrated suspensions.

4.4(2) Flow-rate through sintered stainless steel discs.

Pore size measurements.

Fig. (4.9) is typical of the air flow-rate: pressure curves obtained with all the discs used. The greatest change in

Fig. (4.9) Flow rate of air through sintered stainless steel disc.



flow-rate not solely attributable to an increase in the rate of viscous flow occurred over the pressure range 13.5-15.5cm Hg. The diameter of the smallest pores penetrated by the air is given by the equation $d = \frac{30\gamma}{p}$, where d = diameter in microns, γ = surface tension of the test liquid, and p = air pressure in mm Hg. It can be deduced, therefore, that the pores which determined the rate of flow had diameters within the range 5 - 6 microns, although a few up to 9 microns in diameter were present.

Rates of flow through discs.

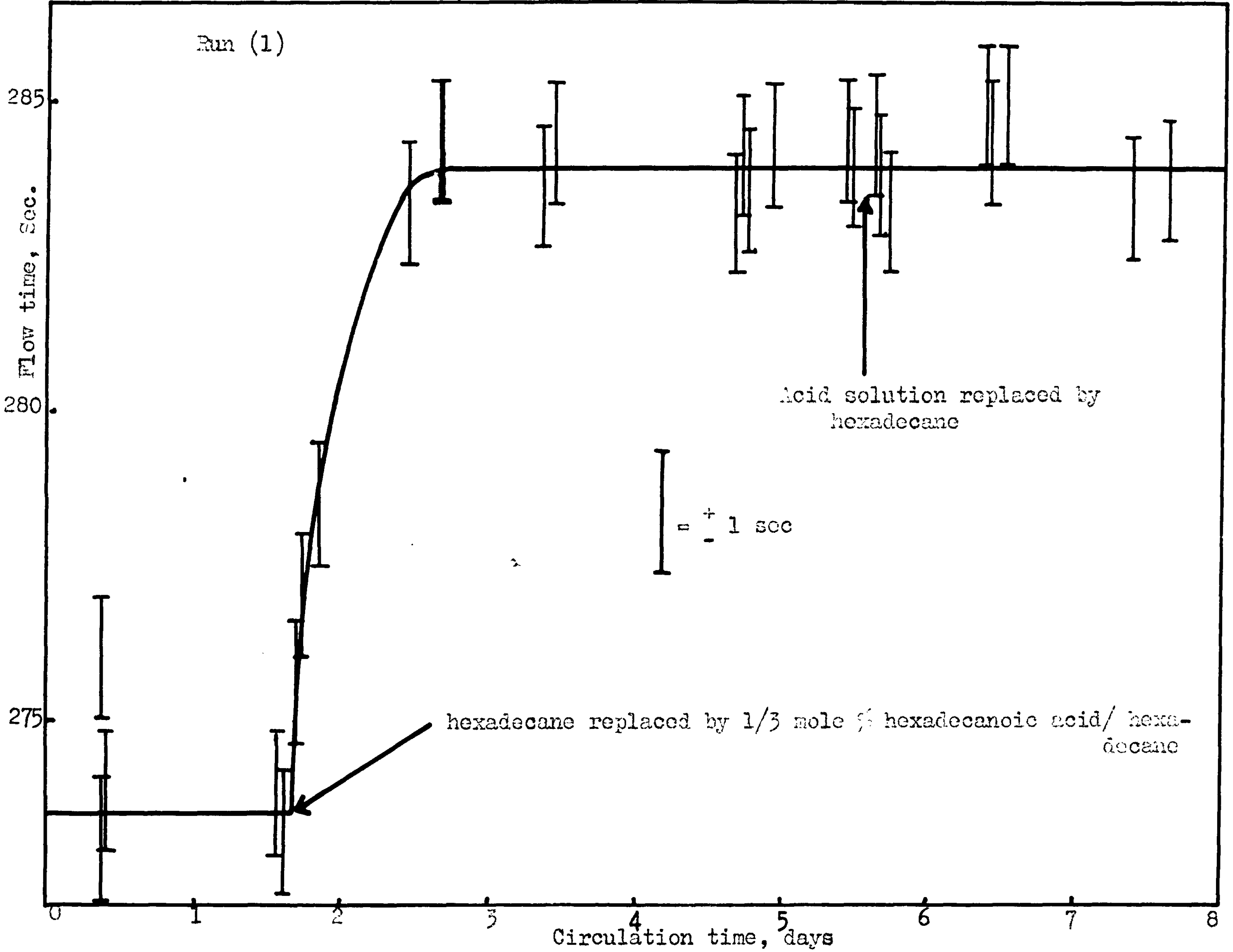
In the first experiment tetradecane, which had a flow-time of 335±1 seconds for descent of the meniscus between selected graduation marks corresponding to the passage of 0.5ml, was replaced by a $^{1}/300$ mole fraction solution of tetradecanoic acid in the same solvent. The flow-time remained unaltered during eight hours of continuous circulation after the change had been made, but the following day the flow-time actually fell to 327 seconds. There was thus not only no reduction in flow-rate in the presence of acid, but apparently a delayed increase, for which no satisfactory explanation could be found. After this run the porous disc was more positively located (as described in section 4.3(2)), in order to eliminate the possibility of movement and consequent alterations in the flow pattern, when the test liquid was being changed.

Further runs were carried out with hexadecane and a similar concentration of hexadecanoic acid. Flow-times are plotted in figs. (4.10) and(4.11) as a function of circulation time. The rate of flow during continuous circulation was not known precisely, but took place under only a slightly greater hydrostatic head, and is unlikely to have been significantly different. It is evident from the figures that flow-rates both before and after replacement of the pure hydrocarbon with fatty acid solution were constant to within ±1 second, and that the changes in flow-rate were complete within 24 hours. The reduction in flow-rate as a result of adding the acid was 3.8% in run (1) and 5.4% in run (2).

The disc from run (2) was next removed, Soxhlet extracted for 4 hours with iso-octane, and replaced in the apparatus. Hexadecane was circulated once more and flow-times of 226±1 seconds were obtained, only slightly higher than the original value (224 seconds) which had been observed before addition of hexadecanoic acid. In spite of uncertainties introduced during dismantling and reassembly of the apparatus, and the possibility of removal of further loose, particulate matter during extraction, the flow-time had been restored almost exactly to its original value.

The disc was returned to the Soxhlet extraction apparatus for a further 4 hours in order to check whether a further reduction in flow-time would occur. After this, however, the hexadecane flow-time had risen to 237 seconds. Replacement of the pure solvent by hexadecanoic acid solution which had been circulated through the disc earlier caused an increase in flow-time to 277 seconds, equivalent to a decrease of 14.4% in flow-rate. After

Fig.(4.10) Flow times of hexadecane and hexadecanoic acid/hexadecane solution through stainless steel disc.



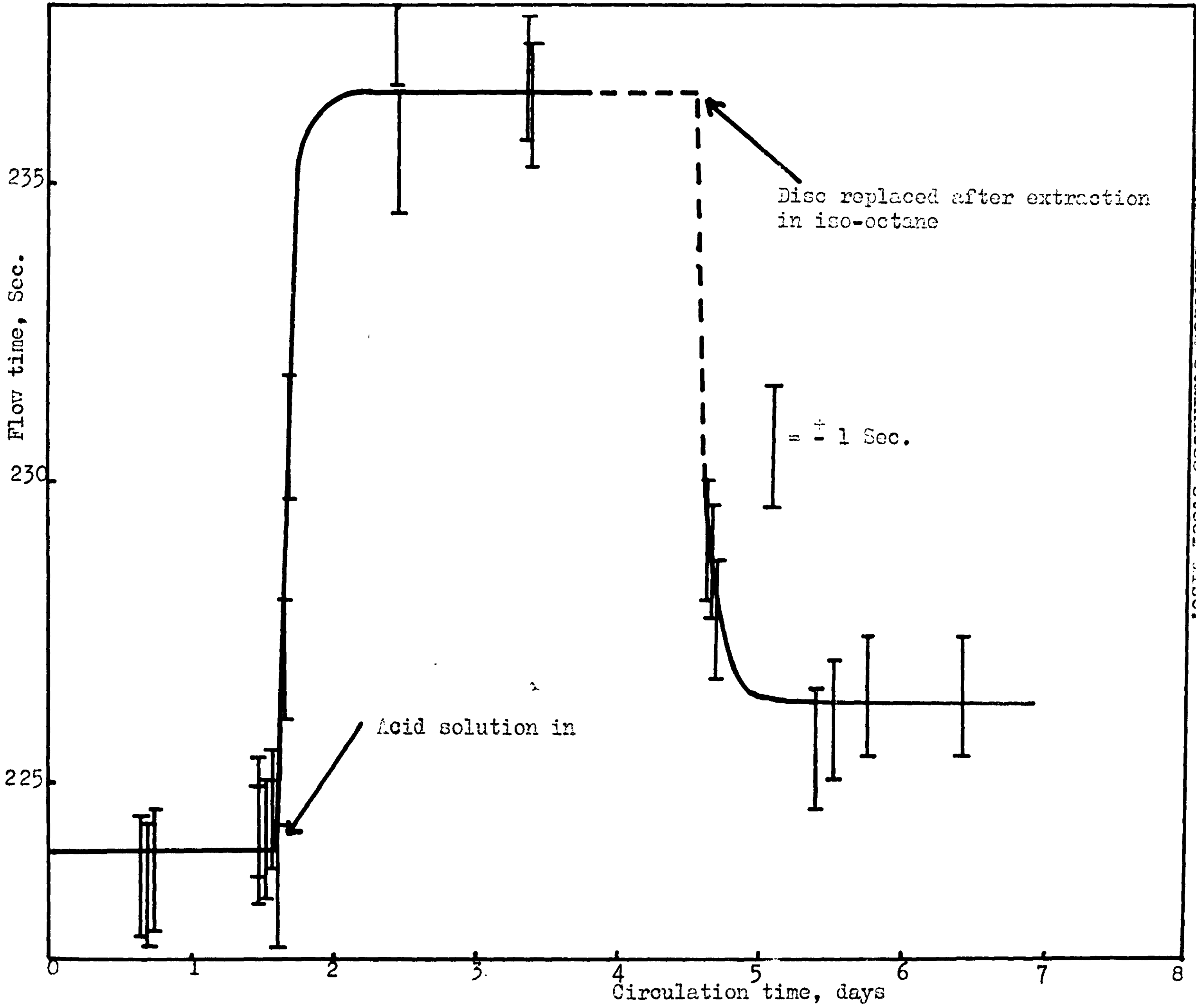


Fig.(4.11) Flow times of hexadecane and palmitic acid/hexadecane solution through sintered stainless steel disc.

3 hours Soxhlet extraction in iso-octane, the flow time of hexadecane through the disc was reduced to 240 seconds, close to the rate observed before the final addition of acid.

4.5 Discussion.

The usefulness of non-sintered beds of powder for observations of changes in rates of flow due to the presence of immobilised boundary layers is unfortunately limited by the unknown and irreproducible geometry of the flow passages, and the possibility of changes in the stacking of the bed occurring during determination of flow-rate. It has been shown by Graton and Fraser[23] that a bed of smooth, uniform spheres prepared by being tamped in a cylinder will contain localised colonies of close-packed particles scattered in a randomly-packed network. The irregularly shaped particles used in the present investigation would be stacked in an even more disordered manner since they would be unable to move over each other as easily during settling and compaction. Flow of liquid through such an array would occur preferentially through packing faults since the channels between particles in close-packed regions would be smaller. Since the number, cross-sectional area, and tortuosity of packing faults is likely to change from one bed to another, even of an identical sample, quantitative expression of the flow-rate in terms of individual channel cross-sectional areas is not possible and the depth of an immobilised wall layer consistant with a given decrease in flow-rate cannot be estimated with accuracy.

Many attempts have been made to relate the flow-rate of liquids through powder beds to the overall dimensions of the bed and its porosity. An example is Kozeny's modification of the Darcy equation[24]:

$$Q = \frac{CP^3}{TS^2} \frac{A}{\eta H} . p$$

where Q = rate of flow of liquid through bed

C = geometrical constant depending on shape of pore

P = porosity

A = cross-sectional area of bed

T = "tortuosity factor"

S = specific surface area of powder

η = coefficient of dynamic viscosity of liquid

H = depth of bed

p = pressure difference across column

This equation was derived by considering the bed as a collection of parallel capillaries of equal length but differing radii. The divergence of this model from the actual conditions in a powdered bed is reflected in the empirical nature of the "tortuosity factor". The Kozeny equation is therefore of no value for the purpose of relating changes in flow-rate to the actual dimensions of the channels in the bed.

The continuous drift of flow-rates which was observed in nearly every run both before and after replacement of pure solvent by fatty acid solution suggested that flow of liquid through the bed caused changes in the packing of the particles. Adsorption of polymeric oxidation products of hexadecane is another possible explanation for the drifting of flow times. Groszek and Palmer[25] have shown that an acidic compound of high molecular weight is formed in mineral oils which have been heated in air; such a reaction might be catalysed by the iron powder sufficiently to cause appreciable reaction even at ambient temperature. Since no drift of flow times was observed with the porous discs, however, adsorption of oxidation products had had no visible effect in that case. It therefore seems unlikely to have been the cause of the drift in flow times in the runs through beds of powder unless much greater catalytic activity occurred on the iron surface than on that of the stainless steel discs. Subsequent investigations (Chapt.5), however, showed that in concentrated suspensions of iron powder in hydrocarbons aggregates of 200 microns or more in size are formed, but that in the presence of fatty acids aggregation is greatly reduced. Since the drift in flow-rate indicated that not all the particles are firmly held in their position in the network, it is probable that adsorption of fatty acid on weakly held particles would increase their mobility by preventing further aggregation. Small particles or aggregates, able to move through the interstices between larger particles, would therefore be carried towards the bottom of the bed with less likelihood of deposition and adhesion en route. A layer of more tightly packed, smaller aggregates would accumulate at the bottom of the bed, and this may have been responsible for most of the decrease in flow-rate which was observed in the presence of fatty acids.

For the moment, however, it will be assumed that changes in the structure of the bed were <u>not</u> responsible, and an attempt will be made to estimate the depth of an immobilised surface zone of liquid which would be consistent with the observed decrease in flow-rate if this were the case. For the sake of simplicity the particles are considered to be uniform spheres 3.7 microns in radius, the equivalent figure calculated from the BET specific surface area. The rate-determining cross-section in a channel will be that of its smallest constriction. It is provisionally assumed that this is formed by the void between three mutually touching spheres. Flow is assumed to occur only within the largest circle which can be inscribed within this roughly triangular constriction. In the absence of turbulence and neglecting complications associated with the fluctuating cross-sectioned area of a passage, the flow-rate is taken as being proportional to the fourth power of the radius of this circle (as in Poiseuille's law), and the thickness of an immobilised wall layer consistent with a given decrease in flow-rate can be calculated. Values obtained from the data in table (4.1) are as follows:

Acid	Reduction in flow rate (%)	Depth of immobilised layer (Å)
dodecanoic	4.5	260
tetradecanoic	8	460
hexadecanoic	15	860
octadecanoic	21	1200

These figures must be regarded as minimum values, since flow probably occurs predominantly through packing faults, avoiding close-packed regions altogether. An estimate of the probable upper limit of the depth of stationary layers can be obtained if it is assumed that such faults will have one dimension comparable with the radius of the particles. A continuous fault through the bed with both its cross-sectional dimensions larger than this would almost certainly collapse. Depths of the boundary zones calculated for a channel containing a constriction equal in radius to the spheres are 1700, 3000, 5600, and 7800 Å for the fatty acids in order of ascending molecular weight. The actual depth of the immobilised region would probably lie between the values in the two series if the reduction in flow-rate could definitely be attributed to this cause alone.

Flow-rates measured through sintered discs are not subject to changes in pore geometry provided that any loose, particulate matter has been removed. The data presented in section 4.4(2) have been analysed on the assumption that the rate of flow was controlled by Poiseuille flow through pores 5.5 microns in diameter. Rough calculations confirmed that the velocity of flow was well below the critical Reynolds number for onset of turbulence, although the irregular, tortuous nature of the channels must inevitably have resulted in local eddying.

Falls in the flow-rate of hexadecane of 3.8% and 5.4% were observed in two runs when the pure solvent was replaced by a $^1/_{300}$ mole fraction solution of hexadecanoic acid. These decreases are consistent with formation of immobilised wall layers about 200 and 300Å deep respectively, which contrast with the tentative estimate of 860-5600Å inferred from runs in a powdered iron bed. The difference in the chemical reactivity of the iron and stainless steel substrates cannot be ignored, but wettability studies (Chapt.6) have shown that films of fatty acids adsorbed on stainless steel may not be significantly desorbed at temperatures well above their melting-points. The irreversibility of adsorption of octadecanoic acid on iron powder has been demonstrated in dispersion stabilisation experiments (Chapt.5), so the two surfaces are similar in so far as they would both be coated with a strongly-held monomolecular adsorbed film. The "squeeze film" investigations of Fuks[5,6,7] and Askwith, Cameron, and Crouch[9] were of limited duration and there was no possibility of extensive chemical reaction at the metal surface, resulting in formation of multi-molecular layers of the metal soap. The influence of the metal surface on molecules beyond the first, adsorbed monolayer would presumably arise solely from dispersion forces in the absence of an electrical double layer. The only large difference in dispersion forces from stainless steel and iron surfaces is likely to originate from differences in the depth of oxide films with which the surfaces are covered. Since stainless steel is likely to be coated with a thinner, more close-packed film of oxide its dispersion force interactions with molecules in a layer of liquid on the surface would probably be at least as great as those of pure iron.

It is therefore extremely doubtful whether a region of anomalous viscous properties extends *more than 200 or 300Å* into the liquid phase from either surface. The experiments with stainless steel discs showed poor reproducibility, no change in flow-rate at all being observed in the presence of 1/300 mole fraction of tetradecanoic acid. The pores in the stainless steel discs were too large to give the sensitivity required for study of immobilised wall zones only 200-300Å deep and their dependence on molecular weight and concentration of fatty acid, temperature, nature of solvent, etc. However, the technique was sufficiently sensitive to demonstrate conclusively that immobilised layers of the depth reported by Askwith, Cameron, and Crouch[9] (10,000Å) and Fuks[5,6,7] (1,000Å under light loads) were not present in this system under the conditions used. A stationary layer 1000Å deep would have reduced the rate of flow through the 5.5 micron diameter pores of the stainless steel disc by 17%. A reduction even approaching this magnitude was only observed in an isolated run, while two earlier trials with same solvent/solute combination had only shown reductions in flow-rate of around 5%.

Further note on comparison of flow-rates through powdered beds: effects attributed by Deryagin et al.[16] to "orientation of water molecules in the neighbourhood of oriented surface films" might alternatively have been due to differences in aggregation. Possible changes in porosity arising from this cause were not, apparently, considered.

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5. STABILISATION OF SUSPENSIONS OF IRON POWDER IN HYDROCARBONS BY FATTY ACIDS.

5.1. Introduction.

The influence of dissolved fatty acids on the stability of dispersions of metal or metal oxide powders in oils should yield information about their effect on the forces acting between metal surfaces in a hydrocarbon environment. The dispersing action of fatty acids may itself play an important role in boundary lubrication by limiting growth of wear debris.[1]

The extent of aggregation in coarse suspensions (particle size around 1 micron) can be studied by measurement of either their rate of settling or the volume of the sediment after settling is complete.[2] Unless the dispersed particles lie in a narrow size range the first method may not give a well-defined boundary between settling material and clear supernatant liquid. Under these conditions direct, visual observation of the settling rate is not practicable and it is more convenient to measure changes in optical density during sedimentation at a selected level instrumentally. Use of more concentrated suspensions may result in formation of a better-defined boundary, the descent of which can be observed easily; but under these conditions settling no longer obeys Stokes's law[3] and sedimentation rates cannot be correlated with particle and aggregate sizes except by the use of semi-empirical correction factors of doubtful validity.[4,5,6.] Comparative studies of the extent of aggregation are more conveniently made by measuring the volume of the sediment, since the randomly-formed aggregates of flocculated material contain larger, liquid-filled voids than do individually-settled particles.[7,8.]

A survey of the literature has revealed only two systematic investigations of the effect of fatty acids on the stability of dispersions of metal oxides in liquid hydrocarbons, and none on the stabilisation of metals. Dawson and Haydon[9] studied the stabilisation of outgassed rutile (average particle diameter 50Å) in dry benzene by a series of n.alkyl carboxylic acids containing from 2 to 18 carbon atoms, present in about 1M concentration. Dispersions in the presence of fatty acids containing from 12 to 18 carbon atoms did not settle completely in one month. Those stabilised by fatty acids containing 8 or 10 carbon atoms took more than a day to settle completely, and those containing 6 or 7 carbon atoms had settled completely in about one hour.

Adsorption experiments had shown that coverage of the rutile surface by long chain fatty acids did not exceed 40% at high concentrations, the adsorption being irreversible. The low limiting coverage was attributed to inability of the large adsorbate molecules to penetrate constrictions between aggregated primary particles. This explanation was supported by the fact that adsorption of formic acid approached a complete monolayer.[10] Suspensions prepared in solutions of octadecanoic acid which gave coverages below 25-30% settled within 30 minutes of dispersion. The results were explained by a modification of the "entropic repulsion" mechanism proposed by Mackor and van der Waals,[11,12] but light-scattering experiments indicated that the "stable" suspensions contained mainly particles of 800, not 25Å, radius. Such large particles were not expected to be stabilised by entropic repulsion, but measurements of the specific conductivity of the dispersions (about 10^{-15} ohm^{-1} cm^{-1}) indicated that electrostatic double layer effects were unlikely to be important. The explanation proposed by the authors was that, although the aggregates were about 800Å in radius, their structure was so loose that upon collision contact would occur only at one or two points, and the attractive energy would be only of the order of that for the interaction of particles 25Å in radius.

Stabilisation of suspensions of Fe_2O_3 and Al_2O_3 particles (average size 1 micron) in xylene by C_6, C_8, C_{10}, C_{14}, and C_{18} n-alkyl saturated fatty acids and oleic acid was investigated by Koelmans and Overbeek.[13] Settling times were increased by the presence of dissolved fatty acids, the greatest increase occurring with acids of longest chain length. Graphs of settling time versus adsorption, however, showed maxima beyond which further adsorption resulted in a rapid <u>reduction</u> in settling time, so that at high levels of adsorption all the saturated acids investigated gave comparable settling times. The specific conductivity of the acid solutions was about 10^{-14} $ohm^{-1}cm^{-1}$, but this was increased by a factor of 10^4 by the addition of 2-4% methanol. Suspensions containing dissolved fatty acids became stable for an indefinite period, irrespective of their chain length, in the presence of 2.25% methanol.

Koelmans and Overbeek correlated the stability of dispersions containing methanol with zeta potentials which had been determined by electrophoresis measurements. Stabilisation by fatty acids in pure xylene was attributed to prevention by steric hindrance of close approach of colliding particles, reducing the size of the attractive van der Waals interaction. The reduction in stability with increasing adsorption at high surface coverages was ascribed to adsorption of a second layer of fatty acid molecules oriented with their polar head-groups outwards. The surface areas of the powders had not been determined, so that accurate interpretation of adsorption values in terms of fractional coverage of the surface was not possible. Adsorption of a further, single layer of reversed polarity seems unlikely in view of the well-known dimerisation of fatty acids in non-polar solutions.[14] Further molecules would be expected to be adsorbed into a second layer as dimer units if at all. This would increase the depth of the steric barrier and lead to increased, rather than decreased, stability. It has been seen, however, in chapter 2, that the more carefully determined values of adsorption of fatty acids on well characterised metal surfaces strongly indicate that monomolecular coverage is never exceeded.

It is difficult to explain even the slight stabilisation observed by Koelmans and Overbeek[13] with fatty acids by a reduction in the attractive energy on collision. Koelmans himself gave the attractive energy for particles of 1 micron radius separated by a gap of 40Å as 510kT, assuming a Hamaker constant of 10^{-12}erg (which is below the figure deduced by Dawson and Haydon[9] from their studies), or 51kT, assuming a value of 10^{-13}erg. Furthermore, the apparent reversal of the increase in stability with adsorption reported by Koelmans and Overbeek still lacks a satisfactory explanation. As it was clearly impossible to reach a satisfactory understanding of inter-particle forces in non-polar media from the information available in the literature, a limited experimental investigation was carried out.

5.2 Materials.

Carbonyl iron powder (manufactured by General Aniline and Film Corporation) was used in most of the work described in this chapter, although Sintrex 300 electrolytic iron was employed in some preliminary experiments. The powder was used directly from the air-tight tins in which it was supplied without further conditioning. Fatty acids were adsorbed irreversibly on this untreated material, and pre-exposure to a moist atmosphere was not required to promote chemisorption. (Samples of "grade HP powder" taken at intervals of several weeks after conditioning at 30% r.h. over a saturated solution of magnesium chloride showed evidence of a decreasing tendency to form aggregates. This reduced the effect of deliberately added stabilisers on settling characteristics and would have vitiated comparisons of the behaviour of suspensions prepared on different occasions).

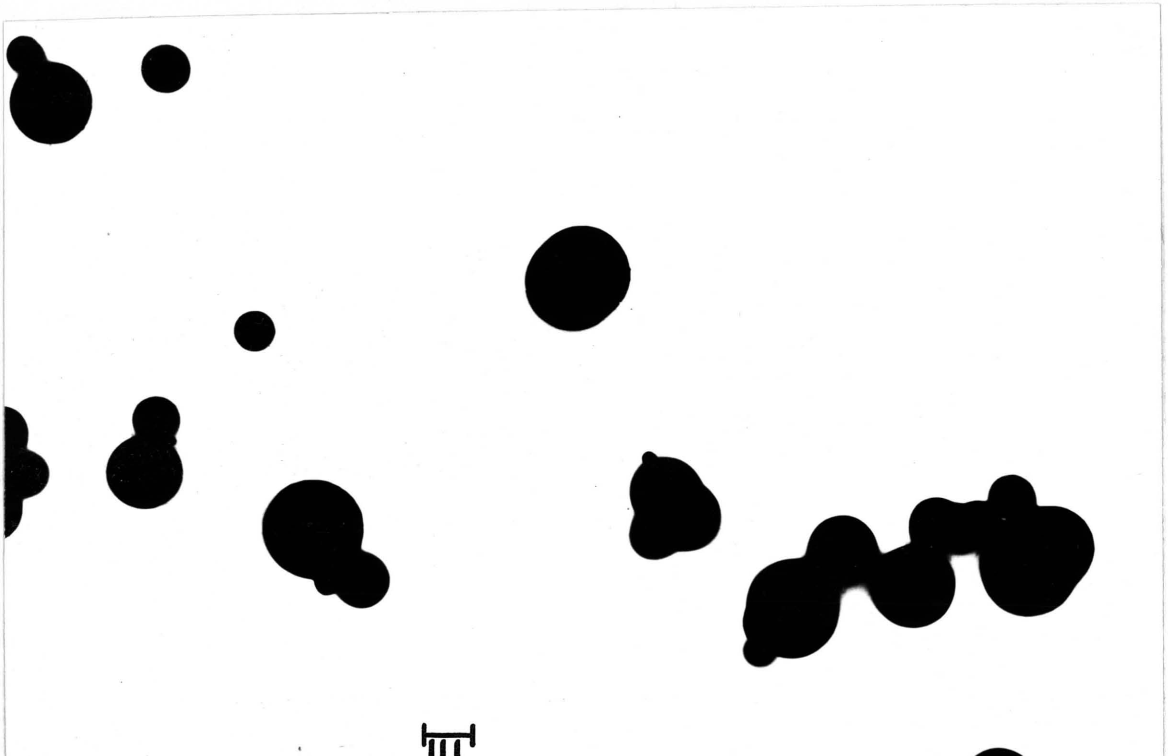
An electron micrograph of a sample of grade SF carbonyl powder illustrated in fig.(5.1) shows that it contained smooth, spherical particles. The mean diameter calculated from four electron micrographs was 0.96 microns, 84% of the particles lying in the size range 0.2-1.6 microns. Krypton adsorption on grade SF powder gave a specific surface area of $0.861m^2/g$, which is equivalent to an average particle diameter of 0.90 microns. The agreement of values for the average diameter confirmed that the surface of the particles was smooth and that there was negligible roughness, surface porosity, and internal area.

Long-chain hydrocarbon solvents were checked for freedom from surface-active contamination by the methods outlined in sections 2.2 and 4.3. AR benzene and xylene were shaken with chromatographic alumina before use in order to remove surface-active impurities and moisture. (It was found that all visible traces of water could be removed from an emulsion of 2% $^v/v$ distilled water in benzene by shaking with a moderate amount of alumina. After the treatment, the alumina still settled freely, without visible agglomeration). Fatty acids, supplied by Koch-Light Ltd., were Puriss grade. Settling characteristics were studied in soda-glass measuring cylinders of 5ml or 25ml capacity, fitted with glass or polypropylene stoppers.

5.3 Experimental procedure and results.

5.3(1) Settling of grade SF iron in hexadecane as a function of volume concentration of powder.

Fig.(5.1). Electron micrograph of grade SF iron.

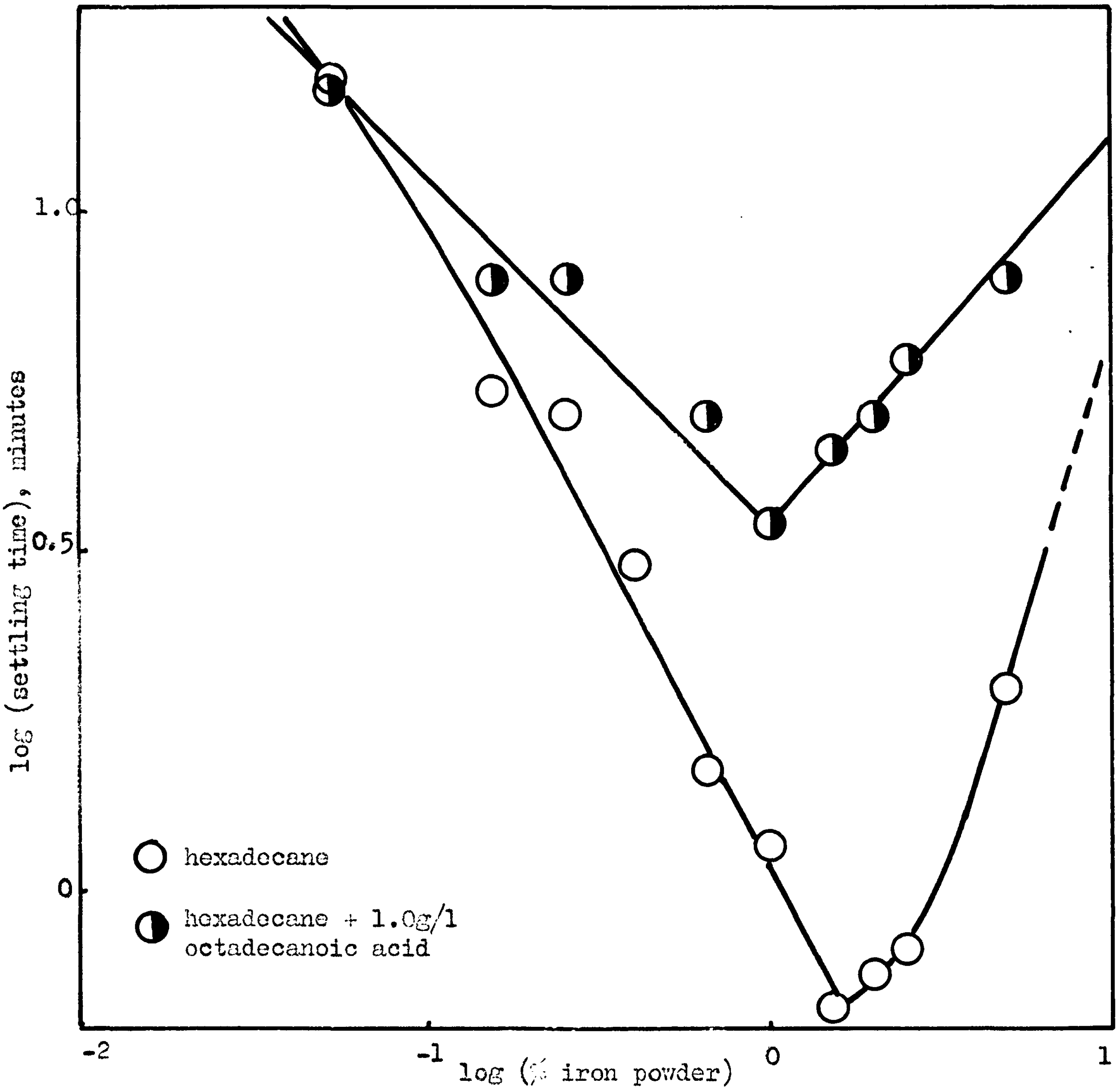


Electron Micrograph by Mr.P.Marlow(Dept.of Chem. Eng.).

Weighed increments of iron powder were added to 5ml of hexadecane contained in a stoppered 5ml measuring cylinder. After addition of each increment, the cylinder was shaken by hand for one minute, placed in a thermostat bath maintained at $25.00 \pm 0.05^{\circ}C$, and the time for "complete settling" recorded. For dilute suspensions this was taken as the time when the entire liquid column first became easily transparent. Since a fairly wide range of particle sizes were present, a well-defined boundary, the descent of which could be easily timed, was not formed except in concentrated suspensions. In the latter case the <u>initial</u> rate of descent was observed, and the settling time if this rate had been maintained to the bottom of the cylinder was evaluated.

Settling times are plotted against the volume percentage of iron powder on a logarithmic basis in fig. (5.2). As the settling time predicted by Stokes's law is about 11 hours for particles 1 micron in diameter, it is evident that some aggregation occurred even at low concentrations. Settling time decreased with increasing powder concentration until this had reached about $1\%^{v}/v$. Above this concentration, settling time <u>increased</u> with concentration, and instead of a gradual lightening of the suspension during settling, a clear boundary between settling material and supernatant liquid appeared. Although settling times could be determined accurately over this range of concentration they were evidently not closely related to the state of aggregation, as the size of the aggregates was visibly increasing, or at least being maintained, in spite of

Fig. (5.2) Settling rate of grade SF iron powder in hexadecane versus concentration.



the increase in settling time.

The settling times of a second series of suspensions, which were made up in a solution of 1.0g/l. of octadecanoic acid in hexadecane, are also shown graphically in fig. (5.2). The reduction in settling time with increasing powder concentration was greatly reduced in the presence of octadecanoic acid, and it was apparent from direct observation that the growth of aggregates was limited. The change in the slope of the curve under conditions of "hindered settling" at high concentrations of powder still occurred, however. Fig. (5.2) shows that the largest difference in the settling times of suspensions in the pure solvent and those stabilised by octadecanoic acid occurred in the 1-2% concentration range. Unfortunately, correlation of settling times with extent of aggregation was becoming unreliable at this level of concentration. Investigations of the settling characteristics of much more concentrated suspensions, which are reported in 5.3(2), showed that the settling times of unstabilised suspensions eventually exceeded those of stabilised ones for a given percentage of powder.

The increase in aggregation with concentration of the dispersed particles was found to be reversible. When a 1.5%^{v}/v suspension of grade SF iron powder in AR benzene was diluted by a factor of 25, the settling time in a 5ml sample increased from 10 seconds to 2 minutes. Qualitatively similar behaviour was observed whenever a coagulated sediment was washed out with a hydrocarbon solvent; a visible reduction in the size of the aggregates was apparent.

5.3(2) Settling characteristics of 20% $^{v}/v$ dispersions of grade HP iron powder in hexadecane, stabilised by various concentrations of octadecanoic acid.

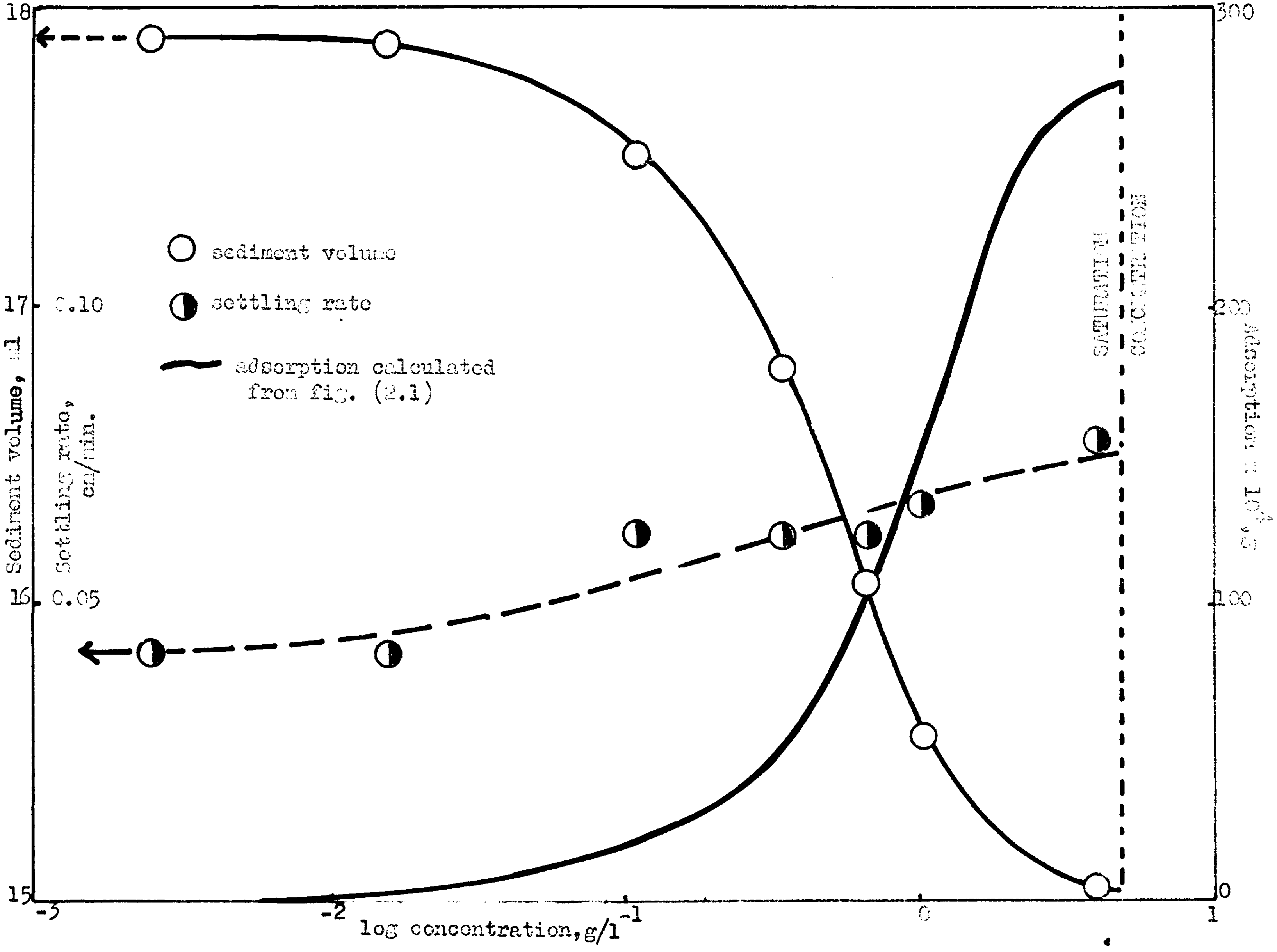
In view of the limited correlation which had been observed (section 5.3(1)) between settling rate and degree of aggregation, the equilibrium volume of the completely settled particles has been used as an alternative parameter for a comparative study of the stabilisation of suspensions by increasing concentrations of octadecanoic acid.

40g of grade HP carbonyl iron powder were added to 20ml of hexadecane contained in a 25ml measuring cylinder, and were dispersed by shaking the cylinder by hand for 2 minutes. On standing at room temperature (22.0-23.2°C), a well-defined boundary appeared between settling material and the supernatant liquid, which fell very slowly (at about 0.05cm/min). Both the initial rate of fall of the boundary and the equilibrium volume of the sediment were recorded. The latter became constant within 2 hours. Similar determinations were made after the addition of each of a series of increments of dissolved octadecanoic acid. Each increment of acid was weighed out and dissolved by warming in a few ml of the supernate which had been extracted with a syringe. This solution was added to the suspension, which was re-dispersed by a further 2 minutes' manual shaking. Settling rate and sediment volume were determined as before; repetition of this procedure after a series of additions of octadecanoic acid enabled the data in table(5.1) and fig.(5.3) to be obtained.

Table(5.1) Dependence of sediment volume, settling rate, and adsorption on octadecanoic acid concentration; dispersions of grade HP iron powder in hexadecane.

Concn.,g/l.(C)	log C	Sediment volume, ml	Settling rate, cm/min.	Adsorption x 10^4,g
0.000	-	17.90	0.42	0
0.016	-1.80	17.88	0.42	3
0.110	-0.96	17.51	0.62	19
0.345	-0.46	16.79	0.62	51
0.660	-0.18	16.07	0.62	102
1.02	0.01	15.55	0.67	149
4.00	0.60	15.05	0.78	273

Fig. (5.3) Sediment volume, settling rate, and adsorption, as a function of octadecanoic acid concentration; dispersions of grade HP iron powder in hexadecane.



In table (5.1) and fig. (5.3) values of sediment volume and settling rate are tabulated and plotted graphically as a function of the initial concentration of octadecanoic acid. Corresponding values of adsorption of octadecanoic acid on the iron are listed in table (5.1), being interpolated from the adsorption curve shown in fig. (5.3), which was plotted using data from the "non-equilibrium" adsorption isotherm presented in fig. (2.1). Fig.(5.3) shows that the decrease in sediment volume with concentration of octadecanoic acid was closely correlated with increasing adsorption of the acid on the iron surface. A slight <u>increase</u> in settling rate was apparent at high concentrations. Stabilisation by adsorption of a fatty acid would normally be expected to cause a fall in both settling rate and sediment volume. In view of the good correlation between sediment volume and adsorption and the occurrence of "hindered settling" in concentrated suspensions, little significance can be attached to differences in settling rate under these conditions. Sediment volume, however, gives an unambiguous measure of the voids present in settled material and therefore of the extent of aggregation, provided that such a loose array does not collapse under its own weight. The implication of the results of this study will be discussed in section 5.4 in the light of the phenomena reported by Koelmans and Overbeek.[13]

If octadecanoic acid was present, a considerable amount of iron powder remained floating in the meniscus after settling was complete. It was also noticed that when the initial concentration of octadecanoic acid exceeded 0.50g/l., the walls of the soda-glass measuring cylinder were no longer wetted by the solution. These observations are consistent with the formation of an oleophobic adsorbed monolayer of octadecanoic acid on the surfaces of both the iron particles and the walls of the cylinder.

The results of exploratory experiments with sespensions of Sintrex 300 electrolytic iron powder in AR benzene in the same proportions (40g in 20ml) are included here since they do not fit in elsewhere:

The dependence of the dispersing power of an aliphatic carboxylic acid on the number of carbon atoms in its molecule was studied. Suspensions stabilised by 0.0071M solutions of acids containing from 6 to 16 carbon atoms all settled to the same sediment volume (13.2ml). A further series dispersed in 0.078M solutions of acids containing from 10 to 16 carbon atoms all gave a sediment volume of 11.1ml. It seemed unlikely, therefore, that studies of sediment volume would yield much information about the effect of the chain length of fatty acid solutes on the properties of boundary layers.

The reversibility of stabilisation, and therefore of adsorption of the stabiliser on the surface of the particles, was investigated by replacing part of the supernatant solution with pure benzene after the dispersed powder had settled. Redispersion and repetition of this procedure enabled high dilutions to be effected. Dilution of a suspension in 0.014M hexadecanoic acid by a factor of

20 did not cause any change in sediment volume. Comparable dilutions of suspensions in solutions of decanol and dodecylamine, however, resulted in increases of from 0.4 to 0.7ml in sediment volume, showing that adsorption of the amine and alcohol was reversible, whereas that of the fatty acid was not.

5.3(3) Sediment volumes and settling rates of a series of 7.8% $^{v}/v$ dispersions of grade HP powder in hexadecane, stabilised by octadecanoic acid.

A powder concentration of 7.8% $^{v}/v$ was selected in order to give values of both sediment volume and settling rate which could be conveniently and accurately measured. A series of suspensions in various concentrations of octadecanoic acid in hexadecane were made up in 5ml measuring cylinders. The suspensions were mounted in a frame which was rotated at 44 r.p.m. for 35 minutes in order to facilitate rapid attainment of adsorption equilibrium, and in an attempt to subject the suspended particles to conditions of controlled shear during the processes of dispersion and aggregation. The latter object was not achieved, however. The undispersed material was not removed from the bottom of the cylinder if the speed of rotation was too low, and centrifugation occurred if the speed was too high. It was therefore found necessary to shake the suspensions by hand both before and after the mechanical mixing in order to disperse consolidated lumps. Settling characteristics were studied after the measuring cylinders containing the suspensions had been allowed to stand in a thermostat bath at $25.00 \pm 0.05^{\circ}C$ for 15 minutes.

The times at which the boundary between settling material and supernatant liquid passed selected graduation marks on the cylinders were noted, and the initial rate of settling evaluated.

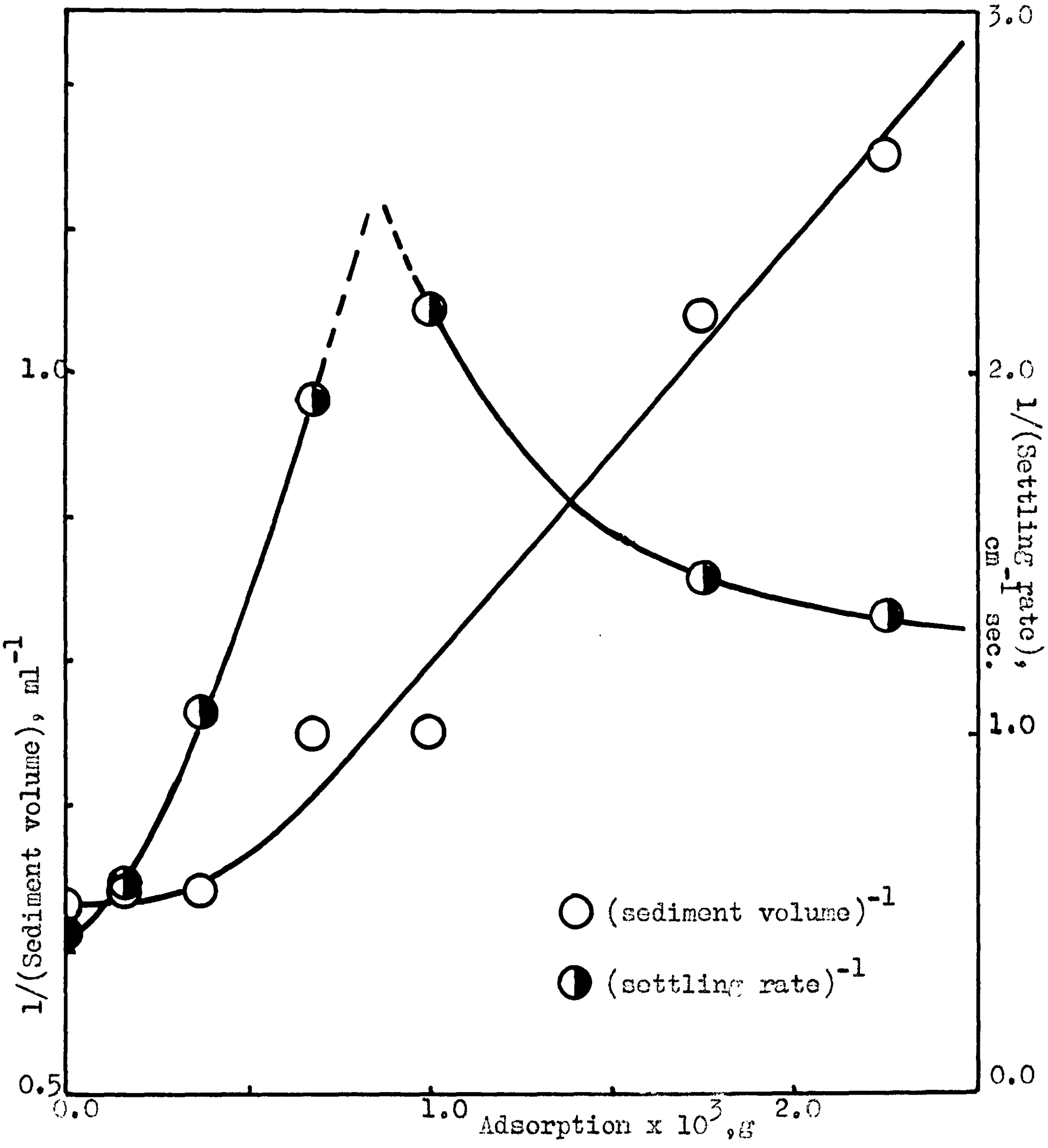
Sediment volumes and settling rates of suspensions in the presence of an increasing concentration of octadecanoic acid are given in table (5.2), together with corresponding values for adsorption of the acid calculated from the "equilibrium" isotherm shown in fig. (2.1). Reciprocals of sediment volume and settling rate values, both of which might be expected to provide a direct measure of aggregation, are plotted as a function of adsorption in fig. (5.4).

The close correlation of (sediment volume)$^{-1}$ with adsorption, except at surface coverage of less than 20%, confirms the trend which was reported in section 5.3(2). The graph of (settling rate)$^{-1}$, however, reaches a maximum after a steep initial rise, apparently suggesting that further adsorption of octadecanoic acid caused a fall in stability of the dispersion. The shape of this graph is similar to those of curves reported by Koelmans and Overbeek[13] for settling of suspensions of iron oxide particles in xylene, but the divergence of sediment volumes and settling rates at high surface coverages throws doubt on the significance of settling rate data. It was shown in section 5.3(1) that the connection between aggregation and settling rate is vitiated at powder concentrations above about 1.0% $^{v}/v$. Deviation from settling rates predicted by Stokes's law will depend on the number, size, and shape

Table (5.2) Dependence of sediment volume and settling rate of suspensions of grade HP iron powder in hexadecane on initial concentration and adsorption of octadecanoic acid.

Initial concn. x10^3,M	Adsorption x10^3,g	Sediment vol., ml	Settling rate, cm/min.	(Sediment vol.)$^{-1}$	(Settling rate)$^{-1}$
0.00	0.00	1.60	2.27	0.63	0.44
0.11	0.16	1.56	1.79	0.64	0.56
0.25	0.37	1.56	0.95	0.64	1.05
0.56	0.68	1.34	0.52	0.75	1.92
0.80	1.00	1.34	0.46	0.75	2.17
2.25	1.75	0.96	0.70	1.04	1.43
5.62	2.25	0.87	0.75	1.15	1.33

Fig.(5.4) Sediment volume and settling rate of suspensions of grade HP iron powder in hexadecane as a function of adsorption of octadecanoic acid.



of the particles at a given volume concentration. The presence of a maximum in the (settling rate)$^{-1}$ curve cannot therefore be interpreted unequivocally as corresponding to a maximum in stability.

Sediment volume and settling rate values of the suspension in 0.56×10^{-3}M octadecanoic acid solution were unchanged after the supernatant liquid had been diluted by a factor of 11.4, confirming that adsorption of the acid was irreversible.

5.3(4) Variation of settling behaviour of 2.6% $^{v}/v$ suspensions of grade SF iron powder in tetradecane with concentration and molecular chain length of fatty acid stabiliser.

In spite of reservations which have been expressed about interpretation of settling rate data, settling rates reached their maximum sensitivity to the presence of adsorbed stabiliser at powder concentrations around 2% $^{v}/v$ (section 5.3(1)). Settling rates of the most stable suspensions prepared in the presence of fatty acids were lower than that of an unstabilised suspension by a factor of more than 10. Values of sediment volume, however, seldom differed by a factor greater than 2. Settling did not deviate qualitatively from Stokes's law at this solids concentration, and settling rates of suspensions in tetradecane stabilised by various concentrations of fatty acids containing 10, 12, 14, 16, and 18 carbon atoms were compared. Tetradecane was chosen so that any optimum occurring when the molecules of the solvent and solute contained the same number of carbon atoms would be easily detected.

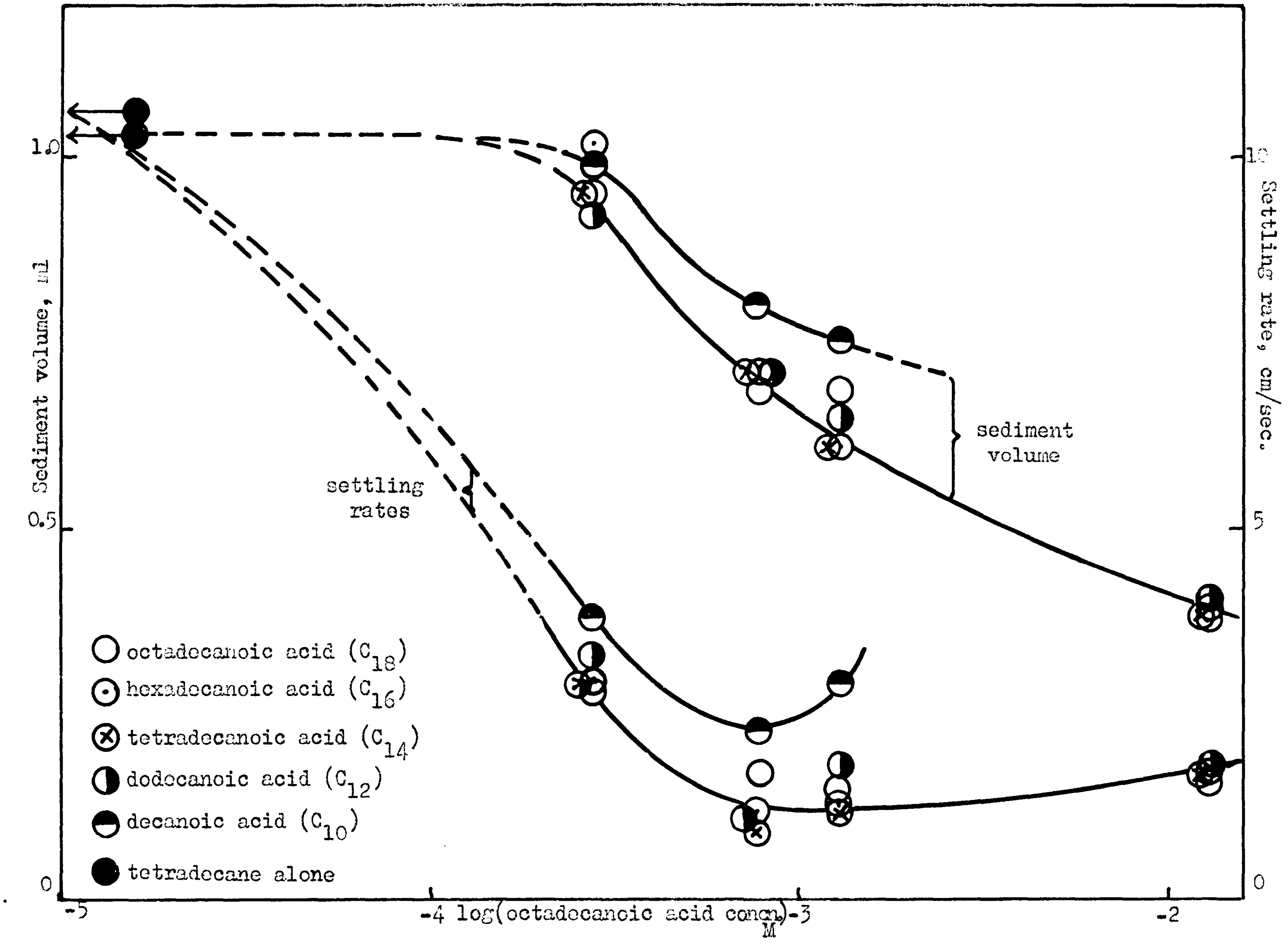
1.0g of grade SF iron powder was shaken by hand for

1 minute with 5ml of each solution in a 5ml measuring cylinder before settling behaviour was observed at $25.00 \pm 0.05^{\circ}C$. Suspensions containing increasing concentrations of a given acid were prepared individually, rather than by addition of further increments of acid to the most dilute one. Values of both initial rate of settling and sediment volume are shown graphically as a function of log (initial acid concentration) in fig. (5.5).

From fig. (5.5) it is again evident that settling rates are much more sensitive than sediment volume to the presence of low concentrations of fatty acids, but show little further change at concentrations above 10^{-3}M, where a steady decrease in sediment persists, suggesting that further stabilisation occurs. The effect of decanoic acid is considerably weaker than that of the other acids studied, and there is a hint also in the settling rate curves that dodecanoic acid is less effective than higher acids. There is a slight suggestion of a "chain-matching" optimum, points for tetradecanoic acid tending to lie below those for both higher and lower acids, although the displacement lies within the scatter due to experimental error. Values of settling rate and sediment volume for suspensions stabilised by high concentrations of the different acids lie remarkably close to each other, although sediment volumes below 0.5ml could not be determined accurately and differences in settling rate may have been masked by "hindered settling" effects.

It appears that measurements of settling rates are not sufficiently sensitive to small differences in the hydrocarbon

Fig. (5.5) Settling characteristics of 2.6% $^{v}/v$ suspensions of grade SF iron powder in tetradecane as a function of the concentration of a series of fatty acids.



chain length of fatty acid stabilisers containing more than 12 carbon atoms to demonstrate convincingly the presence or absence of a "chain-matching" optimum. The reduced efficiency of acids containing 10, and perhaps 12, carbon atoms parallels changes reported by Zisman[15,16] in the wettability and frictional properties of surfaces coated with adsorbed carboxylic acid monolayers.

5.3(5) Settling characteristics of 2.6% $^v/v$ suspensions of grade SF iron powder in xylene in the presence of various stabilisers, in methyl alcohol, and in water.

An attempt has been made to reproduce as far as possible the conditions used in the study by Koelmans and Overbeek[13] of the stability of dispersions of ferric oxide particles in xylene and the effect of fatty acids and other stabilisers. These authors did not mention the volume concentration of solids used in their measurements, but the similarity of their settling time versus adsorption curves and fig. (5.4) suggests that it may have been of the order of a few per cent. In the present investigation, suspensions containing 2.6% by volume of iron powder were studied, since this concentration has been shown to give settling rates which were a sensitive, albeit qualitative, measure of stability.

Suspensions were prepared by addition of 1.0g of grade SF iron powder to 5ml solution contained in 5ml measuring cylinders; these were shaken vigorously by hand for 2 minutes before the settling behaviour was observed. Settling rates and sediment volumes were only slightly different if 15 minutes agitation on a mechanical shaker was substituted for the brief period of manual shaking, or if the powder had been stored over saturated $Mg Cl_2$ solution at 30% r.h. for 4 weeks instead of being taken directly from the tin. Sediment volumes of below 0.5ml could not be determined accurately because the measuring cylinders were only graduated from 0.5 to 5.0ml, and are therefore approximate. Values of settling rate and sediment volume for suspensions in the presence of various stabilisers are listed in table (5.3).

The settling rate in pure xylene was about 20cm/min, while suspensions stabilised by 15mM/l. octadecanoic acid settled at 4.1cm/min. A similar concentration of GPR grade oleic acid gave a settling rate of 3.8cm/min, but impurities may have been responsible for the apparent improvement in stability. Oleic acid is notoriously difficult to obtain in a state of high purity, and Koelmans and Overbeek also observed higher stability with this acid than with octadecanoic acid.[13] The amount of powder floating in the meniscus was markedly lower in the suspension stabilised with oleic acid than in those prepared in the presence of octadecanoic acid, showing that the adsorbed layer was less close-packed. Addition of 2% or 4% by volume of AR methyl alcohol only reduced the settling rate in pure xylene to 8-9cm/min, but the stability of a suspension containing 15mM/l. of octadecanoic acid was improved so greatly by the presence of 4% methyl alcohol that settling was not complete within an hour. A similar suspension, but containing

Table (5.3) Settling characteristics of grade SF iron powder in xylene + stabilisers, methyl alcohol, and water.

Dispersion medium	Settling rate, cm/min.	Sediment volume, ml
Xylene alone	20	0.7
Xylene + 15mM octadecanoic acid	4.1	0.38
Xylene + 15mM oleic acid	3.8	0.34
Xylene + 2% methyl alcohol	9.0	0.46
Xylene + 4% methyl alcohol	8.0	0.42
Xylene + 2% methyl alcohol + 15mM octadecanoic acid	4.10	0.33
Xylene + 4% methyl alcohol + 15mM octadecanoic acid	0.013	--
Xylene + 16mM "Aerosol OT"	4.4	0.33
Pure methyl alcohol	0.5	0.40
Distilled water	0.013	--

only 2% methyl alcohol settled at 4.1cm/min. The settling rate in pure methyl alcohol was about 0.5cm/min, and in distilled water settling was still continuing after one hour. An attempt was made to measure the settling rate of a suspension stabilised by 5mM ferric octadecanoate (which was supplied by the B.P. Research Centre, Sunbury-on-Thames), but this was only slightly soluble in xylene at room temperature. The settling rate at 60°C, when the iron soap appeared to be completely dissolved, was of the same order as that of suspensions stabilised by octadecanoic acid. A 16mM/l. solution of a more soluble metal soap, "Aerosol OT" (ex B.D.H.)[*], did not give high stability at room temperature; the settling rate was 4.4cm/min, slightly higher than the figure obtained with octadecanoic acid.

The results of the work reported in this section qualitatively support the findings[13] of Koelmans and Overbeek on the settling of suspensions in pure xylene, solutions of octadecanoic acid in xylene, and solutions containing both methyl alcohol and octadecanoic acid in xylene. Settling times of suspensions in water, or in xylene solutions of octadecanoic acid containing 4% methyl alcohol, support their contention that stabilisation by fatty acids alone is partial, and slight compared with that afforded by electrical double layer repulsion. The stability of suspensions in solutions of metal soaps in xylene, however, was much lower than that of similar suspensions studied by Koelmans and Overbeek. Although this might be attributed to the presence of impurities in Aerosol OT,

[*] "Aerosol OT" = sodium dioctylsulphosuccinate

which was a commercial product, investigation suggested that the "ferric octadecanoate" was what it purported to be. It was stated by the suppliers to contain 6.6% Fe, which compares quite well with the figure of 6.15% consistent with the formula $Fe(OOCC_{17}H_{35})_3$. Its comparatively high solubility in xylene at a moderate temperature suggests that it was unlikely to have contained significant amounts of ferric hydroxide.

5.4 Discussion.

The settling rate of suspensions in xylene containing a proportion of iron powder which lay within a certain range showed a dependence on octadecanoic acid adsorption density similar to that reported by Koelmans and Overbeek.[13] The difficulty of explaining the apparent decrease in stability with increasing adsorption density above a certain fractional coverage of the surface, and the divergence of settling rate and sediment volume values at higher coverages, suggested that the apparent maxima in stability/adsorption density curves might be spurious. It will be argued in the following paragraphs that the stabilising action of fatty acids is a straightforward consequence of steric hindrance by the adsorbed molecules. If this is provisionally assumed to be the case, the forces of mutual attraction between particles, or at least between clusters of particles, would be reduced by an adsorbed monolayer of a fatty acid by some direct function of its effective thickness. It was shown in chapter 2 that adsorption of octadecanoic acid on carbonyl iron powder does not significantly exceed the equivalent of coverage by a close-packed, vertically oriented monolayer. It may be argued that the equivalence with monolayer coverage is coincidental and that localised adsorption several molecules deep occurred in some places, with sparse coverage in others. This is quite possible in view of the heterogeneous nature of all surfaces, and receives some support from the occurrence of a discontinuity in the adsorption isotherm. Limiting adsorption equivalent to monolayer coverage has been reported by many authors, however (section 2.1), and the oleophobic properties of adsorbed films of fatty acids suggest that they are uniformly monomolecular. In any case further adsorbed layers of fatty acid molecules would be extremely weakly held and unlikely to form a stable "bridge" between adjacent particles.

Koelmans and Overbeek considered that aggregation of 1-micron iron oxide particles in pure xylene was the result of London - van der Waals attractive forces. Howe, Benton, and Puddington,[17] however, concluded from studies of the aggregation in toluene of glass beads about 40 microns in diameter that the attractive forces between insulating particles shaken in a dielectric medium were due to formation of a mosaic of localised electrical charges on the surface of the particles. A reduction in the tendency to form aggregates in the presence of ionising liquids was attributed to the presence of surface conductance. Deryagin[18] has suggested that "mosaics" of positive and negative charges are formed on surfaces in air by friction or merely by contact. The literature on electrification of surfaces by rubbing or contact has been surveyed by Prosser,[19] who also demonstrated that the attraction between a pair of macroscopic glass plates was greatly increased if they were allowed to touch and were then separated. The increased attraction disappeared if electrostatic charges on the glass surfaces were neutralised by an electrical discharge near the plates. In the light of this it seems possible that mosaics of charge could be formed on the surface of insulating particles shaken in a liquid of low dielectric constant. Howe, Benton, and Puddington[17] seem to have largely ignored the alternative explanation of their observations, that aggregation occurred as a result of van der Waals attractive forces, and that reduction in aggregation in conducting liquids was due to electrical double layer repulsions.

Subsidiary experiments in the present investigation have shown that the settling rates of suspensions containing -200, +400 mesh (37-75 micron) quartz particles in hexadecane are sensitive to the presence of dissolved octadecanoic acid, and that even suspensions of -100, +200 mesh (75-150 micron) particles are slightly affected. This has confirmed the existence of attractive forces between particles up to 100 microns in size, which are sufficiently large not to be smothered by gravitation and hydrodynamic disturbance during settling. Iron particles have been found to have negligible surface conductance in a hydrocarbon environment and can therefore be regarded as insulators under these conditions. Charge mosaics could well be the main origin of attractive forces for comparatively large iron particles, but it will be assumed that the attraction between the 1-micron particles used in this investigation arose principally from van der Waals interactions. This is probably justified since adsorption of undissociated fatty acid molecules would not have been expected to influence the long-range attraction due to surface electrification.

The reversibility of the increase in aggregation with particle concentration (section 5.3(1)) suggests that aggregate formation is a reversible process, the average cluster size being governed by the balance between adhesion of further particles to existing clusters and removal of previously bound particles. During the shaking process very high rates of shear would be developed in turbulent regions, promoting both collisions between primary particles and break-up of clusters. It is evident that when the size of an aggregate reaches macroscopic proportions, it will be subjected to very large shearing forces although the bonds by which individual particles, or groups of particles, are attached are only a few multiples of the attraction between a pair of particles. The limiting aggregate size will be reached when the rate of disintegration becomes equal to the rate of attachment of new particles.

Since fatty acid molecules have the character of a hydrocarbon apart from the polar head-group, the effect of an adsorbed monolayer is to limit the closeness of approach of adjacent particles without significant alteration of the Hamaker interaction constant, A. A vertically-oriented, close-packed film of octadecanoic acid is assumed to prevent the approach of two colliding particles to within 2x20 = 40Å. In the absence of an adsorbed film particles are assumed to be able to approach until their surfaces are separated by only 2Å before Born repulsion forces predominate. It is easily shown with the equation derived by Schenkel and Kitchener[20] for partially retarded van der Waals interactions between spherical particles that the presence of an adsorbed monolayer 20Å thick would reduce the attractive energy between a pair of particles by a factor of 28 regardless of the size of the particles.

The attractive energy between 2 particles 1 micron in diameter a distance 2Å apart lies in the range $2x10^{-11}$- $2x10^{-10}$ ergs (500 - 5000kT) if the value of A is assumed to be between 10^{-13} and 10^{-12} ergs. This is reduced to 18-180kT by the presence of an octadecanoic acid monolayer, which is still a formidable attractive energy. The nearly 30-fold reduction, however, will lower the limiting size reached by aggregates very considerably. This hypothesis is consistent with the partial stabilisation by fatty acids observed by Koelmans and Overbeek and reported in this thesis, and is supported by the light-scattering measurements of Dawson and Haydon,[9] who found that dispersions of rutile particles 50Å in size in dry benzene stabilised by fatty acids contained "particles" having an average radius of 800Å.

Before an attempt can be made to relate stabilisation of dispersions by fatty acids to their effect on the lubricating or rheological properties of boundary films, some estimate must be made of the pressure exerted on the liquid separating particles about to collide. The model chosen to facilitate calculations visualizes a pair of metal discs 1 micron in diameter separated by a film of liquid and approaching each other coaxially at a constant velocity of 1000cm/sec. The pressure will probably be over-estimated, since the relative velocity of colliding particles is unlikely to be as high as this, the pressure between discs will be much higher than that between spherical particles of the same radius, and the assumption that the velocity remains constant during thinning of the film separating the particles is unrealistic. The model, however, enables an upper estimate to be made of the pressure at various separations of the particles by use of the Stefan-Reynolds equation:

$$\frac{dh}{dt} = - \frac{2F}{3\pi r^4}\eta h^3$$

where h = separation of discs, t = time, F = normal force,

η = viscosity of liquid, and r = radius of discs.

Pressure values of 6.3×10^{-4}, 0.63, and 630kg/mm^2 are obtained for separations of 10,000, 1,000, and 100Å respectively, for a liquid having a viscosity of 2cP (assumed independent of pressure). Boundary lubricants and liquids used in the squeeze film experiments of Needs,[21] Fuks,[22] and Cameron[23] are subject to pressures of the same order of the yield strength of metal surfaces i.e. up to 100kg/mm^2. In view of the tendency of the model on which the calculations were based to give unrealistically high values of pressure, it is concluded that films of liquid which separate colliding particles in dilute suspensions are not subjected to pressures as high as those encountered in sliding or static contact between macroscopic bodies. If a plastic residual layer about 1000Å thick were present between colliding particles, as is suggested by the findings of Fuks and Cameron, it would be subject to lower pressures than was the case in squeeze films.

The results of this investigation suggest that aggregation of primary particles is unaffected by the presence of fatty acids, although these additives limit the growth of clusters at a later stage. Calculations of the London attractive energy between a pair of metal spheres 0.5 microns in radius in a hydrocarbon medium show that this falls to a few multiples of kT at separations exceeding about 200Å. Thus, there is no evidence for the existence of multimolecular protective films around the particles having a thickness greater than this. The partial stabilisation afforded by fatty acids can be accounted for without assuming multimolecular adsorbed films to be present. The pressure in solution separating particles about to collide is likely to be much lower than that in the "squeeze films" studied by Fuks and Cameron, but Fuks has reported that a reduction in pressure appeared to <u>increase</u> the depth of the residual film. An anomalous zone, if it exists, might therefore be expected to have an extended depth in the present experiments, although other possible deviations from Newtonian behaviour due to the effect of pressure on viscosity, melting-points, and solubility would be minimised.

It will be seen in section 6.2(1) that the stabilising action of fatty acids on small metallic particles, in conjunction with the Rehbinder effect, enhances polishing of mild steel specimens with suspensions of alumina.

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6. THE INFLUENCE OF TEMPERATURE ON THE WETTABILITY OF LUBRICATED SURFACES

6.1 Introduction: previous literature.

It was mentioned in chapter 1 that Frewing, and Grew and Cameron, have studied the variation of lubrication transition temperatures with fatty acid concentration. The transition was assumed to occur when the unimolecular adsorbed film of acid on the sliding surfaces became depleted to below a critical fraction of the saturation coverage. It will be seen in chapter 8 that there is theoretical justification for the assumption that adsorbed films only one molecule deep can provide effective protection against friction and wear. The wettability of such coated surfaces would also be expected to undergo similar transitions, although not necessarily at the same critical coverage. Empirical observations by Zisman[1(i)] of the "oleophobic" character of the outer surface of close-packed adsorbed monolayers of amines and fatty acids have been shown by Fowkes[1(ii)] to be due to minimisation of dispersion force interactions between the adsorbed film and adjacent liquid. The wettability of such surfaces is lower than that of paraffin wax or less closely-packed monolayers, in which surfaces consisting largely of $-CH_2-$ groups are exposed. This is due to the low concentration of the comparatively large carbon atoms in a surface composed of $-CH_3$ groups (1 per 19-25$Å^2$), compared with that in one containing $-CH_2-$ groups (1 per 5.0-5.7$Å^2$).

Zisman[1(i)] determined the wettability of platinum foil immersed in solutions of polar compounds in hydrocarbons, as a function of temperature. He found that above a certain temperature, T_w, the foil no longer emerged dry on withdrawal, but was completely wetted by solution. Solutions of normal fatty acids, amines, and alcohols in hexadecane and dicyclohexyl were examined, and the relationship between T_w and the concentration (C) of each surfactant was determined. Heats of adsorption (ΔH) were calculated from the slopes of graphs of $^1/T_w$ versus log C on the assumption that the oleophobic nature of the film-covered surface was lost when the monolayer had been depleted by thermal desorption to below a critical fractional coverage. Zisman showed that for <u>reversible</u> adsorption,

$$2.303 \log_{10} C = \frac{-\Delta H}{RT_w}$$

where R = gas constant.

This equation was obtained by application of the van't Hoff isochore to the adsorption equilibrium.

More recently, Bartell and Ruch[2,3] demonstrated that the contact angle of hexadecane on a surface bearing a monolayer of octadecylamine was almost unaltered by depletion of the monolayer down to 60% coverage. Further depletion, however, caused a rapid decrease in contact angle, until complete wetting (with zero contact angle) occurred at 40% coverage. Zisman's assumption was therefore probably justifiable, although it seems unlikely that the critical coverage for wetting is exactly the same for adsorbates of different chain length, or for liquids containing molecules of different sizes and shapes. The precision of results obtained from solutions in dicyclohexyl was higher than those from solutions in hexadecane, but in both cases heats of adsorption were around 10kcal/mole for acids and alcohols, and just under 15kcal/mole for octadecylamine. The heat of adsorption from dicyclohexyl was 11.5kcal/mole for decylamine, and 6.4kcal/mole for hexylamine. Transition temperatures for solutions of a given solute in dicyclohexyl were usually higher than for the same concentration in hexadecane. This is not surprising in view of both the greater possibility of the presence of weakly-held solvent molecules in the monolayer in the presence of hexadecane, and the greater depletion required before the more bulky dicyclohexyl molecules could penetrate to the surface.

No satisfactory explanation was put forward by Zisman to account for the form of the $^1/T_w$ versus log C curves which he obtained. These showed the expected negative slope at low concentrations but became parallel with the $^1/T_w$ axis at high concentrations. The maximum value of T_w reached ($T_{w(max)}$) was tentatively identified by Zisman with the Krafft temperature for onset of micelle formation, but there is, however, no evidence for the existence of micelles in solutions of simple fatty acids, amines, or alcohols in hydrocarbons at elevated temperatures.[4] An alternative explanation put forward by Zisman, that above $T_{w(max)}$ the increasing probability of adsorption at higher concentrations is counterbalanced by the increasing solubility of the adsorbate, also does not explain the sharp change of behaviour at $T_{w(max)}$.

Although the form of Zisman's $^1/T_w$: log C curves does not seem to have been explained satisfactorily, Sakurai and Baba[5] have reported a very similar relationship in studies of the critical temperature for rupture of the film between a ball on a metal plate in a pool of fatty acid/hexadecane solution. The adsorbed films were assumed to have broken down when no further rectifying effect was detectable on a high-frequency a.c. applied across the gap. Graphs of $^1/T_w$ versus log C consisted of two straight lines, one of which was vertical, the other having a negative slope. The form of the graph was the same for platinum surfaces and pure fatty acid solution, for similar surfaces and fatty acid solution which had been in contact with iron powder at 100°C, and for steel surfaces in pure fatty acid solution. Although the existence of micelles was demonstrated by "solubilisation" of Rhodamine B in solutions which had been in contact with iron powder or steel at elevated temperatures, this does not explain the breaks in the curves, firstly because these also occurred with solutions of pure fatty acid on platinum, and secondly because the existence of micelles was demonstrated at temperatures far below $T_{w(max)}$. $T_{w(max)}$ can therefore hardly be argued to mark the temperature below which micelles cannot exist. Experiments with solutions of fatty acids containing 12,14,16, or 18 carbon atoms gave graphs with very similar slopes but with the longer-chain acids displaced progressively to higher concentrations. There was no sign of a maximum slope when the chain length of the fatty acid matched that of the solvent. Heats of adsorption were calculated to lie in the range 10-11 kcal/mole. (Difficulties in translation of the Japanese rendered a more detailed understanding of this paper impossible.)

It is desirable to relate more closely the dependence of wettability, "lubricity", and boundary film cohesive strength on temperature and to explain divergences in the form of the dependence. Wettability data are lacking on more reactive metal substrates, such as iron, steel, and copper. Zisman[6] has stated, however, that wettability transitions on these metals could not be used for quantitative comparisons because of the difficulty of obtaining clean surfaces.

6.2 Experimental procedure and results.

6.2(1) Preparation of oleophobic surfaces.

Soda-glass surfaces which had been cleaned in chromic acid, washed with distilled water and oven-dried could be rendered oleophobic within about a minute simply by immersion in a solution of 1g/1 octadecanoic acid in hexadecane. It was much more difficult, however, to form an oleophobic surface on steel. Stainless steel specimens (18% Cr, 8% Ni), which had been degreased by Soxhlet extraction with iso-octane or benzene, did not emerge dry after prolonged immersion in octadecanoic acid-hexadecane solution, and were not even hydrophilic. Polishing under water with grade 3/50 alumina (50% of which consisted of particles below 1 micron in size) on a Hyprocel parchment disc gave a smooth hydrophilic surface. After the steel had been vacuum-dried and immersed in octadecanoic acid-hexadecane solution, however, reproducible retraction could not be obtained. It was noticed that exposure of an initially clean, hydrophilic steel surface to the atmosphere even for a few minutes rendered it hydrophobic.

Retraction was obtained consistently, however, on specimens which had been polished with alumina under a fatty acid-hydrocarbon solution and rinsed vigorously with distilled water in order to remove adhering alumina particles. The hydrophobic nature of the surface ensured spontaneous removal of this water. Surfaces of stainless steel specimens treated in this way were bright, although carrying light but visible scratches. However, microscopic examination under a magnification of 400x and illumination at grazing incidence showed that the scratches, which appeared as deep scores, were on average separated by at least 30 microns. The remainder of the surface contained few irregularities large enough to act as light-scattering centres, and had a uniform black appearance. Darkening of the parchment was much more pronounced during polishing under fatty acid-hydrocarbon solutions than when distilled water was used as a polishing medium, when only a slight rust-brown colouration developed, although a high surface finish was obtained. This showed that grinding, with considerable removal of metallic particles from the steel surface, occurred during polishing with fatty acid-hydrocarbon solutions. In very dilute fatty acid solutions, solutions of low-molecular-weight acids, or pure hydrocarbons, the rate of darkening was very slow, the specimen would not slide easily over the parchment and its surface did not become oleophobic or even hydrophobic.

It has been reported in chapter 5 that aggregation of fine metal particles in hydrocarbons is reduced by fatty acids and a subsidiary experiment has shown that aggregation of the polishing alumina is similarly curtailed. It appears that improved dispersion of both alumina and wear particles may contribute to the superiority of fatty acid-hydrocarbon solutions over pure hydrocarbons as polishing (or grinding) media. With an aqueous polishing medium it is presumed that electrical double layer repulsion completely prevents aggregation of alumina or wear fragments, and is at least partly responsible for the reduction in "grinding" and surface damage. The phenomenon discovered by Rehbinder[7] may also be an important factor: growth of cracks and faults in the surface of a solid subjected to continual stress is accelerated by the presence of a surface-active agent. Adsorption of the surfactant on new surfaces created by increases in the depth of cracks due to the applied stress reduces the solid/liquid interfacial energy and facilitates further extension of cracks, thus weakening the material.

Oleophobic surfaces were obtained only when the polishing solution contained at least 0.05g/l octadecanoic acid in hexadecane, although specimens which had been polished in 1.0g/l acid and subsequently immersed in solutions of at least 0.005g/l retained their oleophobic nature. When specimens which had been rendered oleophobic were immersed in more dilute solutions or in pure hexadecane, however, their oleophobic character was lost completely within 4-5 hours. This was also the case with oleophobic films adsorbed on mild steel surfaces, showing that adsorption on both types of steel was at least partially reversible. Oleophobic surfaces could be prepared under solutions of fatty acids containing at least 14 carbon atoms in dodecane. Bewig and Zisman[8] stated that retraction could not be obtained with dodecane, and were apparently under the impression that the surface tension of this solvent is below the critical surface tension of wetting for a surface of close-packed methyl groups, which is 24 dynes/cm. Haydon[9] and Gillap[10] have shown, however, that the surface tension of dodecane is close to 25 dynes/cm at 25°C. Samples polished under solutions of fatty acids containing as few as 10 carbon atoms in hexadecane and tetradecane were oleophobic, although retraction was slow and incomplete with the C_{10} acid.

The following procedure was adopted as standard treatment for preparation of the 5x7x1mm stainless steel test pieces used in wettability studies. The specimens were ground for five minutes with 600 grit carborundum paper under distilled water, washed thoroughly in a jet of distilled water, and dried under vacuum for 15 minutes. Each specimen was then polished for 8 minutes under the appropriate fatty acid-hydrocarbon solution. Adhering alumina particles were removed by vigorous washing in a stream of distilled water, residual traces of which were removed by a further 15 minutes drying under vacuum. Microscopic examination of the surfaces under

400 x magnification verified that specimens were free from particulate matter. Each specimen was immediately immersed in the solution under investigation for a period of 24 hours, so that equilibrium might be established between the adsorbed film and the solution before changes in the wettability of the specimen were studied.

The temperature, T_w, at which a captive bubble in contact with the surface of a specimen no longer formed a finite contact angle was found not to be sensitive to the concentration of octadecanoic acid in hexadecane solutions when this exceeded about 0.1g/l. Since oleophobic films could not be deposited directly from very dilute solutions, polishing was always carried out under the same concentration of fatty acid (1.0g/l), and specimens subsequently immersed overnight in the solutions under investigation, the concentration of which might be either higher or lower than 1.0g/l. The fact that steel surfaces bearing an adsorbed film of octadecanoic acid lost their oleophobic character after being immersed in pure hexadecane for only five hours suggested that this procedure allowed the adsorbed monolayer to come to equilibrium with the test solution. In later investigation with a simple dip-cell solutions of various acids were studied at a single molar concentration, the value of which was selected to allow polishing and testing of the specimens in solution of the same concentration.

6.2(2) Determination of oleophobic-oleophilic transition temperatures.

Attempts were made to measure both changes in the magnitude of the angle formed at the solution/metal/air boundary with temperature, and the temperature at which a zero contact angle was reached and the metal surface became completely wetted. The specimen was placed in 0.5ml of the fatty acid-hydrocarbon solution under investigation, contained in a 10mm square spectrophotometer cell. A Pyrex capillary 6.4mm in diameter was mounted vertically above the specimen and about 1mm from its surface. The capillary was connected to the barrel of an "Agla" micrometer syringe, which enabled air to be expelled, forming bubbles of a reproducible, and, if necessary, variable size, bounded by the rim of the capillary and the surface of the specimen. The cell was illuminated from the side and a magnified image of the profile of the bubble was focussed on a ground-glass screen. Contact angles were measured by drawing on the screen tangents to the surface of the bubble at points of contact with the specimen. Angles measured on each side of the bubble and in duplicated determinations did not differ by more than $\pm 2^\circ$. The cell was mounted in an oil-filled thermostat bath so that changes in contact angle with temperature could be determined. Contact angles below 20° could not be measured with accuracy, but a sharp distinction could be made between small, but finite angles and zero angles. Withdrawal of an air bubble from the surface of a specimen which was not wetted by the solution (i.e. formed a finite contact angle) resulted in pronounced "cling" of the bubble to the surface, with accompanying distortion of the bubble. No "cling" or distortion was evident when the contact angle was zero and the solution wetted the specimen completely.

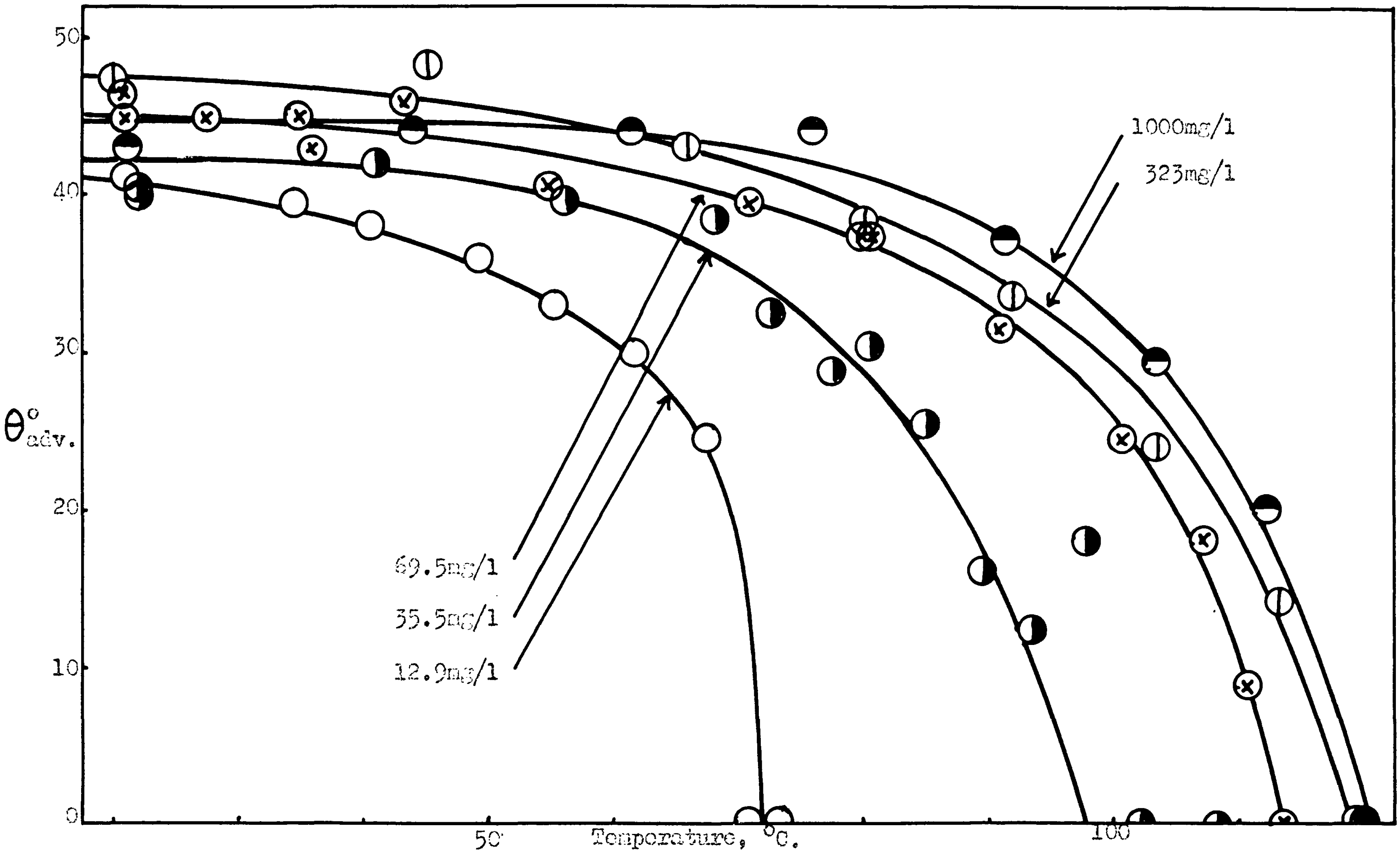
Although it was realised that contact angles and adsorption were only smoothly correlated over a limited range of surface coverage,[2,3] values of both "advancing" and "receding" angles were recorded at 10°C intervals as the temperature was raised. After each increase in temperature, a period of 30 minutes was allowed for re-establishment of adsorption equilibrium. Then the micrometer plunger was lowered until the air bubble which was exuded from the tip of the capillary just touched the surface of the specimen. The receding contact angle, (the solution had receded although the bubble had advanced), was measured after 1 minute. The plunger was racked down a further 0.1mm, and raised to its previous position after a 1-minute interval. The advancing contact angle was measured after a further 1-minute interval. It was found in practice that hysteresis was always small: the difference between advancing and receding angles was never more than 5°. Measurements were taken at more frequent temperature intervals when values of contact angle began to drop appreciably. A stream of "oxygen-free" nitrogen was passed through the cell continuously in order to minimise atmospheric oxidation of hydrocarbon solvents at elevated temperatures.

In a later series of experiments the captive-bubble apparatus was replaced by a simple dip-cell similar to that described by Zisman.[1(i)] Specimens were prepared by the method described in section 6.2(1) and immersed in a series of equimolar solutions of a series of fatty acids and amines in hexadecane, contained in 1x5cm glass specimen tubes. Each specimen was attached to a length of fine, nickel-based wire so that it could be withdrawn from the solution for observation of its wettability. Before the contents of each tube were tested, a cork bearing a 0-110°C thermometer and a short glass capillary through which the wire attached to the specimen passed, was inserted. The dip-cell was mounted in a beaker of mineral oil on a sand-bath heated by a small Bunsen burner. The temperature of the cell was raised steadily, the specimen being pulled up periodically until it was only partly immersed. At low temperatures specimens were oleophobic and the solution retracted, leaving an apparently dry surface. Retraction became slow and incomplete, however, at temperatures approaching T_w, and the specimen became completely wetted at T_w, with smooth drainage of the solution from its surface. Initially the temperature was raised at about 3°C/min, but this had dropped to 1°C/min at 70°C. In most cases T_w was greater than 70°C; a reduced rate of heating was used for solutions which gave lower values of T_w. Minor variations in the rate of heating did not appear to influence values of T_w, however.

6.2(3) Results.

Values of advancing contact angles (which were more reproducible than receding angles) of a series of solutions of octadecanoic acid on stainless steel are plotted as a function of temperature in fig. (6.1). Contact angles given by solutions of all 5 concentrations were fairly close at near-ambient temperatures, but the temperature at which values of contact angle began to fall

Fig. (6.1) Contact angle of octadecanoic acid/hexadecane solutions on stainless steel as a function of temperature.



significantly varied considerably with concentration. Fairly large differences in behaviour were observed between solutions containing 12.9, 35.5, and 69.5 mg/l of octadecanoic acid, but further increases in concentration had only a slight effect on contact angle.

Following Frewing,[11] Zisman,[1] Sakurai,[5] and Cameron[12], transition temperature data are plotted as log C versus $^1/T$ in fig. (6.2) for a series of concentration of octadecanoic acid and hexadecanoic acid in hexadecane. Although the data for octadecanoic acid appear to show a trend similar to that reported by Zisman and Sakurai (section 6.1), there is excessive scatter in points for solutions of hexadecanoic acid. If it is assumed that the slope of the line in fig. (6.2) is related to the heat of adsorption of the acid by the van't Hoff isochore (section 1.2(5)), a value of 12.9 kcal/mole is obtained. The scatter shown by points from solutions of hexadecanoic acid rendered comparisons of the behaviour of the two acids impracticable. In view of this, and of the inconvenience of working at high temperatures which was necessitated by the high T_W values of even dilute solutions, further studies of changes in wettability with temperature were made with the simplified apparatus described in section 6.2(2).

Fig. (6.3) shows values of T_W obtained by this direct but subjective method. T_W is plotted as a function of the number of carbon atoms contained in the molecules of a series of fatty acid and amine solutes dissolved in hexadecane. All solutions were 3.52mM; the amines were of 95% purity and were manufactured by

Fig.(6.2) Graphs of log C versus 1/T for solutions of hexadecanoic acid and octadecanoic acids in hexadecane.

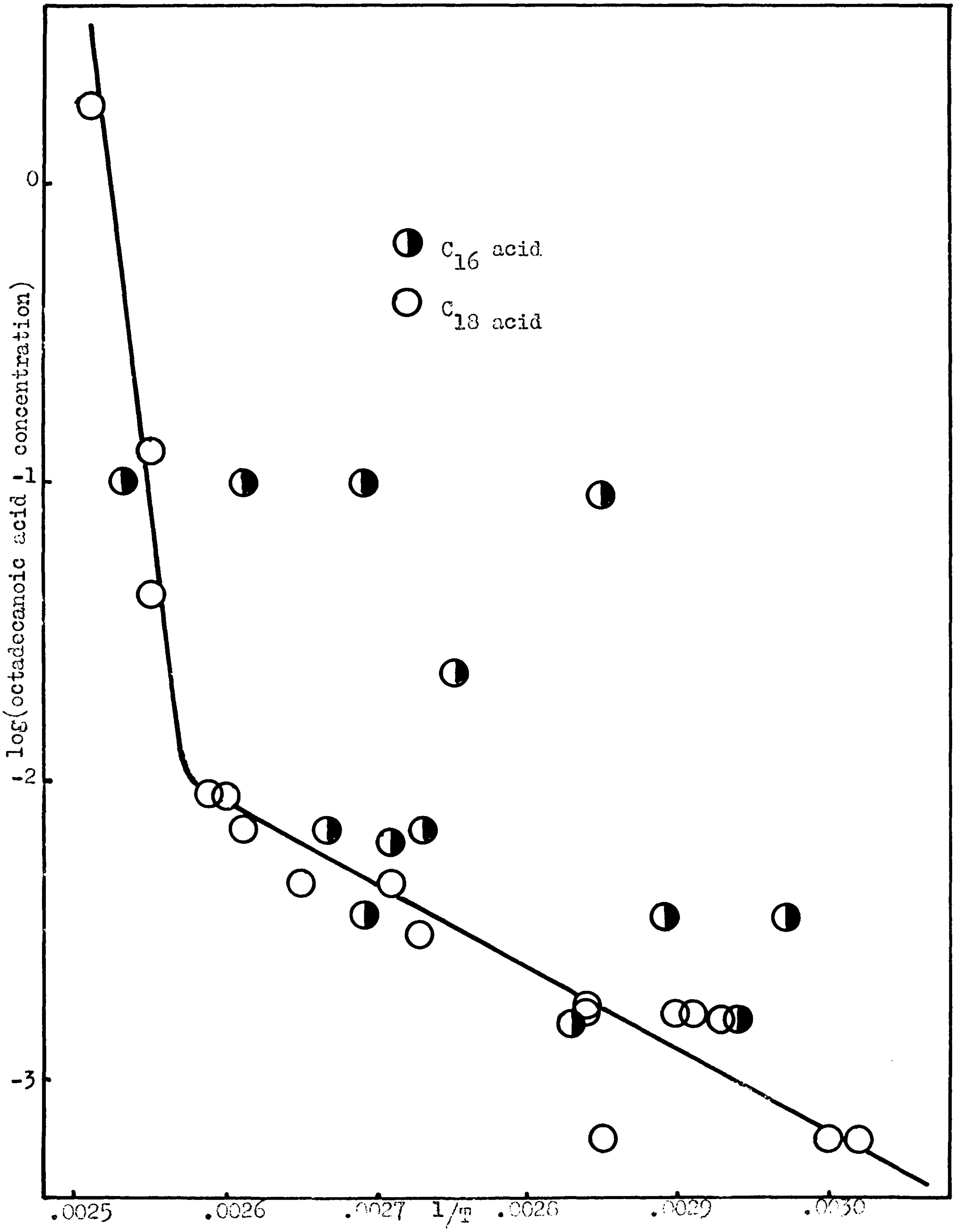
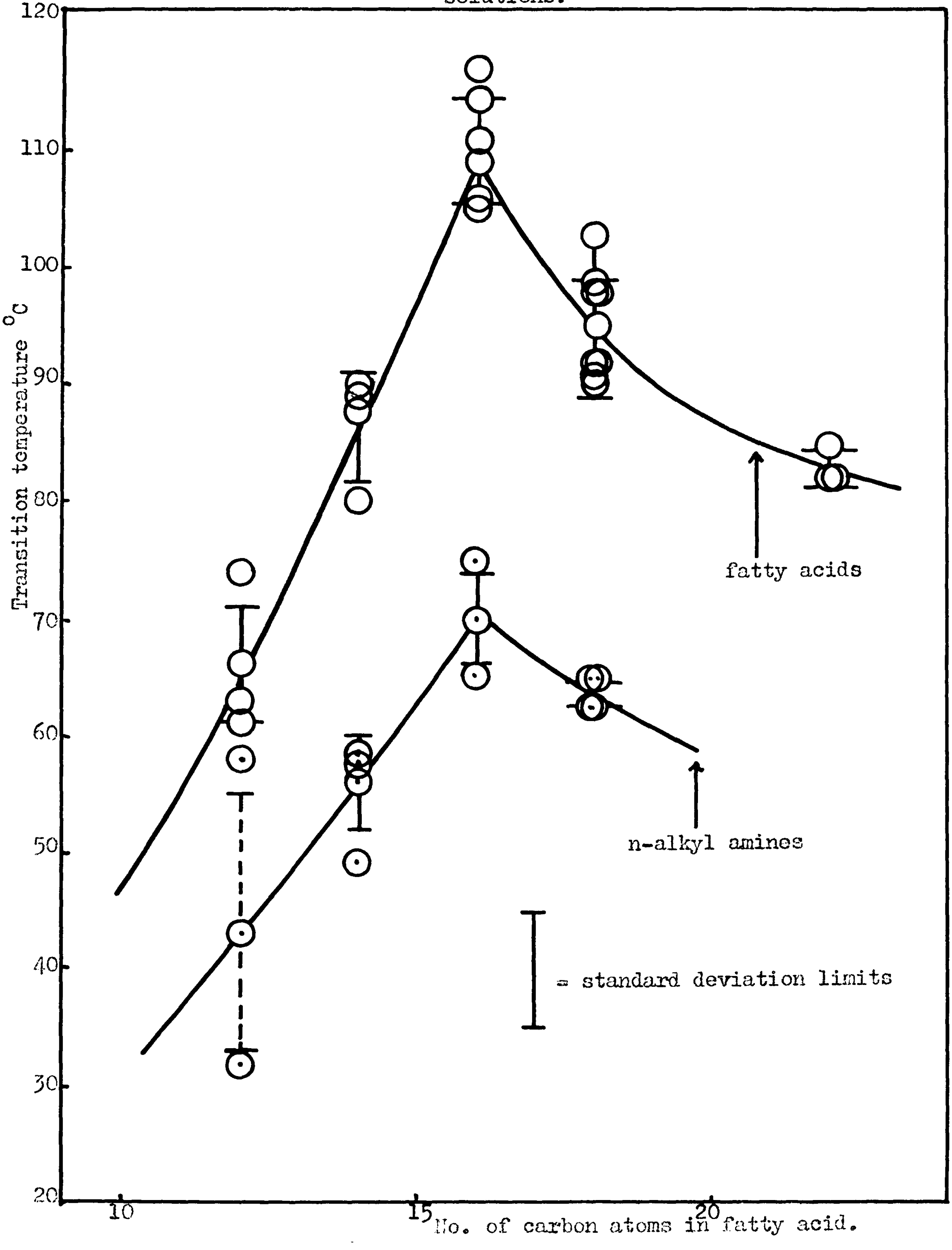


Fig.(6.3) Autophobic transition temperatures of fatty acid/hexadecane solutions.



Liljeholmens Stearinfabriks AB, of Sweden. At least 4 specimens were studied at each concentration, and frequently more; in only one or two cases a sample failed to "retract", so that only 3 points were available. Standard deviation limits (68% confidence) are plotted in fig. (6.3), as well as individual readings. The increase in T_W with solute chain length which was observed for both fatty acids and amines containing up to 16 carbon atoms appeared to be reversed for solutes of greater chain length. Data for the lowest members of both series of solutes were less reliable as the polishing process was visibly less efficient and retraction tended to be non-uniform even at room temperature.

6.3 Discussion.

Although the surfaces of stainless steel specimens which had been polished under fatty acid-hydrocarbon solutions appeared fairly smooth except for a few deep scores at relatively large intervals, irregularities several hundred Ångstroms deep were almost certainly present. Since studies of oleophobic adsorbed films and "retraction" entail differentiation between zero and small but finite contact angles, it is important that the effect of surface roughness is recognized. Wenzel[13] and Deryagin[14] have proposed that the apparent contact angle, θ^1, of a liquid on a surface having a "roughness factor" (i.e. ratio of true surface area/apparent surface area) equal to k, should be given by the equation $\cos\theta^1 = k\cos\theta$, where θ is the true contact angle. Zisman[15] has stated that, as a consequence of this, a liquid with a true contact angle of 10° on a surface with a roughness factor of 1.02 will have an apparent contact angle of 5°. Substitution of these values for k and θ in the equation, however, gives an apparent contact angle of zero! Following common practice, Timmons, Patterson, and Lockhart[16] used as substrates for contact angle measurements copper and iron specimens which had been polished with 0.3 micron alumina and had a roughness factor (determined by adsorption of radio-octadecanoic acid) of 1.33. Contact angles of methylene iodide drops on surfaces prepared in this way and partially covered with adsorbed octadecanoic acid molecules ranged from 27 to 70°. Application of the Wenzel equation would suggest that only <u>apparent</u> contact angles were observed, the true values lying in the range 48-75°. Timmons et al. found that the roughness factors of iron surfaces which had been ground under 6 micron diamond paste or 600 grit silicon carbide were 1.90 and 3.63 respectively. Surfaces ground under 400 grit silicon carbide did not give "retraction", which prevented determination of a roughness factor. It had been demonstrated earlier by Brockway and Karle[17] that retraction is inhibited on roughened surfaces. When the height of irregularities in the surface of the substrate becomes comparable with the capillary constant of the liquid or with the macroscopic curvature of its surface near the air/liquid/solid boundary, the effect of roughness on the apparent wettability of the surface is no longer confined to masking the true contact angle: the liquid remaining after drainage can no longer be treated as a continuous film[12]. If it is assumed that the stainless steel surfaces used in the present study had an average roughness factor of about 1.5, it is clear that reservations must be made in the interpretation of the contact angle values plotted in fig. (6.1) and the oleophobic-oleophilic transition temperatures in figs. (6.2) and (6.3).

Thermodynamic analysis of the curves in fig. (6.1) on the lines proposed by Whalen and Wade[18] has not been attempted, because evaluation and comparison of heats of immersion by this method requires a knowledge of θ and $\frac{d\theta}{dT}$ at a constant temperature. The curves are not suitable for comparison at a particular temperature and, in any case, contain considerable irregularities which would lead to errors in evaluation of θ and $\frac{d\theta}{dT}$.

The excessive scatter shown in fig. (6.2) by results for hexadecanoic acid/hexadecane solutions may be due at least partly to adsorption of a comparatively stable "mixed monolayer" containing a considerable proportion of solvent molecules. Earlier data for octadecanoic acid solutions, which are not plotted in fig. (6.2), had also shown a large scatter, but this had been ascribed to variations in the rate of heating and the procedure used for establishing contact of the air bubble with the surface of the specimen. There was a considerable improvement when these had been standardised, but the technique was subject to other, less easily controlled variables: sub-microscopic roughness, the effect of which was noted in a previous paragraph, may vary over the surface of a specimen. Since captive-bubble measurements of contact angle depend on the properties of only a small area of the solid, contact angle values could vary considerably over the surface and the single series of readings obtained for each specimen were not necessarily typical of the whole. It is doubtful, moreover, whether the pause of 30 minutes after each 10°C rise in temperature was sufficient to allow complete equilibrium to be re-established, as Fowkes,[19] Haydon,[20] and others[21,22] have shown that adsorption of long-chain compounds on ferrous surfaces from hydrocarbons may not reach equilibrium for a week, particularly when chemisorption occurs.

Zisman's analysis of transition temperatures for obtaining values of heats of adsorption, which ignored the effect of surface roughness, has also been used by Frewing,[11] Sakurai and Baba,[5] and Grew and Cameron[12] to relate changes in other surface properties to the heat of adsorption. It is doubtful, however, whether systems involving fatty acids and steel surfaces can legitimately be analysed in this way, although this has been attempted by the latter authors. It has been established that fatty acids react on the surfaces of ferrous metals to form iron soaps, and the values of frictional transition temperatures suggest that it is the <u>soap</u> which is desorbed when the surface is heated. The dependence of transition temperature on concentration for specimens immersed in solutions of fatty acids, and its reversibility, suggests that when a specimen is cooled after desorption, a large proportion of the "new" adsorbed layer consists of fatty acid molecules. The adsorption/desorption process cannot therefore be described by true equilibrium equations such as

$$\text{Acid}_{\text{(dissolved)}} \rightleftharpoons \text{Acid}_{\text{(adsorbed)}}$$

or,

$$\text{Soap}_{\text{(dissolved)}} \rightleftharpoons \text{Soap}_{\text{(adsorbed)}}.$$

The real situation would be more accurately described by the non-equilibrium "equation":

$$\left[\begin{tikzcd} \text{Acid}_{\text{(dissolved)}} \arrow[r] & \text{Soap}_{\text{(adsorbed)}} \arrow[d] \\ & \text{Soap}_{\text{(dissolved)}} \end{tikzcd}\right]_{\text{repeated}}$$

If this is so, adsorption cannot be described by a single equation with an equilibrium constant, and analysis of transition temperatures in terms of the van't Hoff isochore does not appear to give ΔH values having a definite significance.

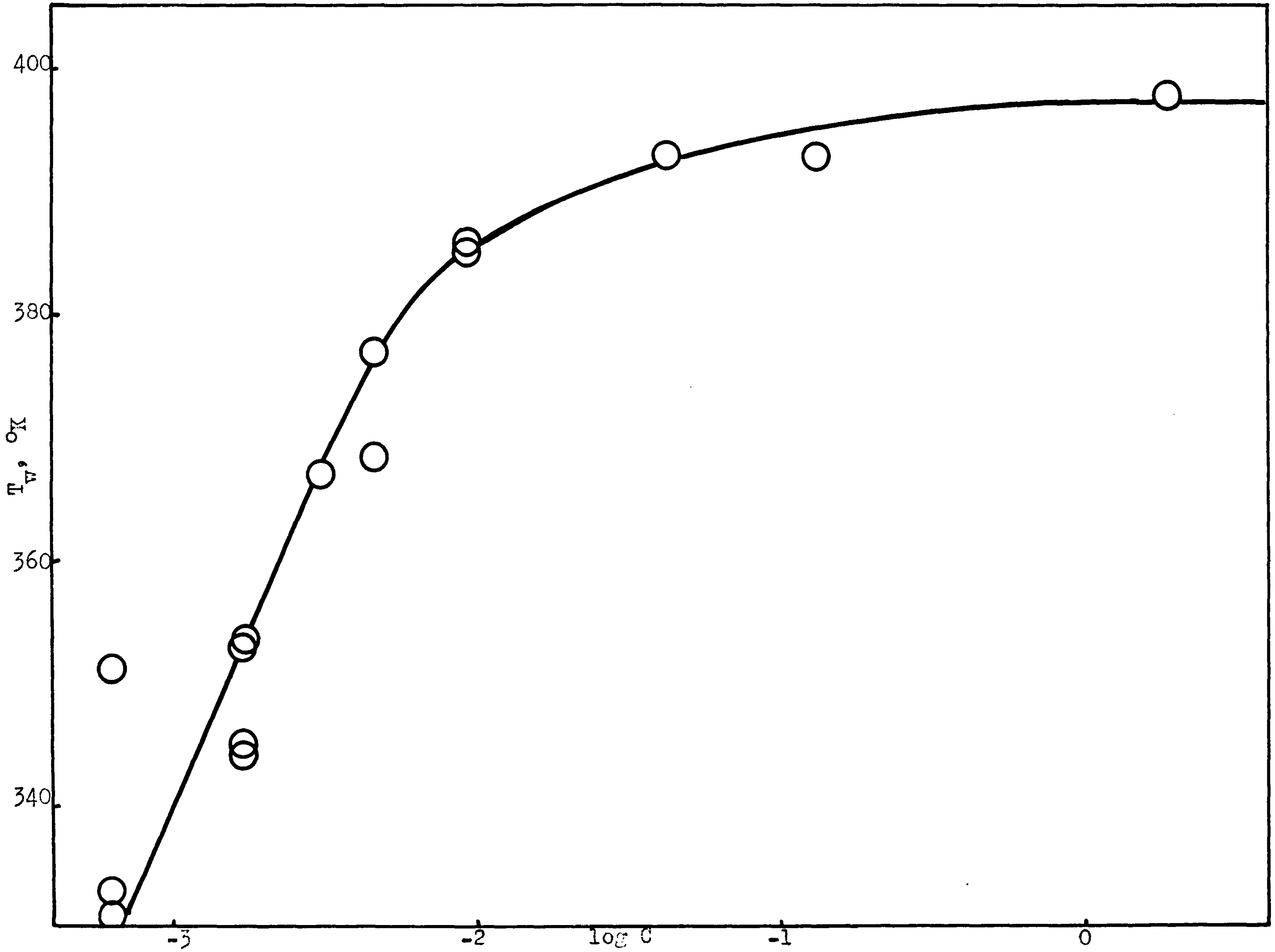
With this reservation, the so-called "heat of adsorption" calculated from the lower part of the line in fig.(6.2) (12.9 kcal/mole), is in fair agreement with those obtained by other authors under a variety of conditions. Observations by Zisman[1(i)] of changes in the wettability of a platinum foil by solutions of fatty acids in hexadecane gave a considerable scatter, especially with octadecanoic acid, for which no value of ΔH was calculated. ΔH values for other fatty acids, however, lay around 10 kcal/mole. Measurements by Sakurai and Baba[5] of the temperature at which a film of octadecanoic acid/hexadecane solution separating a steel ball and a steel plate in loaded contact broke down gave a value for ΔH of 11.4 kcal/mole. Similar solutions between platinum contacts gave 10.6 kcal/mole. Graphs obtained by Grew and Cameron[12] of frictional transition temperatures on stainless steel as a function of concentration for solutions of dodecanoic acid in decane, dodecane, tetradecane, and hexadecane give ΔH values of 10, 43, 28, and 17 kcal/mole respectively. The particular combination of octadecanoic acid and hexadecane was not, however, studied. Frewing[11] found that the heats of adsorption on mild steel of decanoic, tetradecanoic, and octadecanoic acid from a highly-refined, non-polar mineral oil, calculated from frictional transitions, were all close to 13 kcal/mole.

With the exception of some of the data from Grew and Cameron, "heats of adsorption" of fatty acids on surfaces of varying reactivity deduced from changes in properties, not all of which are obviously a function only of adsorption density, show a remarkable similarity. Heats of adsorption calculated by Sakurai and Baba for platinum were only slightly below values obtained by the same investigators for steel surfaces. This is also the case when heats of adsorption obtained on steels by Frewing and in the present work are compared with values reported for platinum by Zisman.

It was mentioned in section 6.1 that the presence of two sections of log C : $^1/T$ graphs, with a sharp transition from a moderate, negative slope to an almost vertical region, has not been satisfactorily explained. The sharp change in slope is, however, illusory, curvature at low $^{1}/T_{w}$ values being exaggerated by the procedure of taking reciprocals. If the data in fig. (6.2), or those reported by Zisman[1] or Sakurai[5], are plotted in the form C versus T_w or log C versus T_w, as in fig. (6.4), no <u>sharp</u> changes in slope are visible. A smooth increase in T_w with C or log C occurs until a limiting value is reached. It is obvious that a temperature will eventually be reached above which the thermal energy of adsorbate molecules is so high that a stable adsorbed phase cannot exist in equilibrium (if this is reached) even with concentrated solutions. (If this were not the case molten fatty acids would retain their autophobic and boundary lubricant properties until gross chemical decomposition or oxidation occurred). Although the average effective translational energy of adsorbed molecules is kT, the Boltzmann distribution law shows that, for every 100 molecules having this energy, 13 will have 2kT and 5,3kT. A complete adsorbed layer will only be retained if ΔG^{o}_{ads} is large in comparison with the thermal energy. It was shown in section 2.3 that ΔG^{o}_{ads} is about -7kcal/mole (-10kT/molecule) at 25^{o}C. Since entropy is lost on adsorption, ΔG^{o}_{ads} will become smaller (less negative) at higher temperatures, until a temperature is reached at which it is exceeded by the translational thermal energy.

A final comment on the values of contact angle plotted in fig. (6.1): values of advancing angles for the more

Fig. (6.4) Transition temperatures of solutions of octadecanoic acid in hexadecane.



concentrated solutions are 5-7° above those reported by Bartell and Ruch[2,3] for drops of pure hexadecane on films of octadecylamine retracted onto chromium from relatively concentrated solutions.

Transition temperatures for a 3.52mM (0.13wt.%) solution of hexadecanoic acid in hexadecane measured in the dip-cell were similar to values observed for the same concentration of octadecanoic acid in the captive-bubble apparatus. Solutions of both higher and lower acids gave appreciably lower transition temperatures. It is well established that the degree of orientation normal to the surface of the substrate, "oleophobicity", and lubricating power of adsorbed polar compounds increase with their chain length up to a certain point. The form of the curves in fig.(6.3) is not unexpected, therefore, except for the fall-off in transition temperature with chain length when the solute contains more carbon atoms in its molecule than the solvent. The purity of the docosanoic (C_{22}) acid (90%) was lower than that of the other fatty acids (99%), so that points corresponding to results from this acid possibly have less significance than others. Numerous points were obtained for the C_{16} and C_{18} acids, however, establishing the existence of the maximum beyond doubt; the lower and upper standard deviation limits (±68% confidence) for the respective acids differ by 7°C, and the means are 16°C apart. The number and precision of data for the amines was insufficient to establish a statistically significant trend, but they appear to confirm the existence of a maximum T_w at the "chain-matching" condition. Grew and

Cameron[12] have reported that the frictional transition temperature for stainless steels lubricated by similar solutions also reaches a maximum when the chain length of the fatty acid is equal to that of the hydrocarbon carrier. Fig. (6.3) closely resembles graphs of "scuffing loads" in a 4-ball tribometer against solute chain length obtained by Askwith, Cameron, and Crouch.[23] Thus, the resistance of the adsorbed film to desorption by an increase in temperature or by a combination of this with mechanical shearing, appears to be greatest when the molecular structures of the solvent and solute are closely matched. This is at first surprising in view of Zisman's finding[8] that the tendency for adsorbed films to retain a percentage of weakly-held, "adlineated" solvent molecules is greatest under this condition. An attempt is made in the following paragraphs, however, to show that Zisman's observations are not incompatible with the existence of a chain-matching optimum.

Proposed hypothesis to explain dependence of T_w on chain length of solute.

It was mentioned in section 6.1 that the low wettability of close-packed adsorbed films of polar compounds, which was observed experimentally by Langmuir[24] and later by Zisman,[15] has been attributed by Fowkes[1(ii)] to reduced London-van der Waals interactions of the terminal $-CH_3$ groups with adjacent liquid. Zisman, and Adam and Elliott,[25] have shown that surfaces composed mainly of $-CH_2-$ groups are more easily wetted by liquids of a given surface tension, and Schaefer[26] demonstrated that this is also true of mixed monolayers containing fatty acids of different chain lengths (15 and 20 carbon atoms).

The wettability by n-alkanes of both close-packed and depleted monolayers of octadecylamine on chromium was found by Bartell and Ruch,[2,3] however, not to be directly related to their surface tension, as Fowkes's theory would have predicted. Contact angles of tetradecane and hexadecane (surface tensions 26.7 and 27.6 dyne cm^{-1} respectively) on a close-packed monolayer were considerably greater than that of 1, 3, 5 - trimethylbenzene (surface tension 28.5 dyne cm^{-1}), and were only slightly lowered by depletion of the monolayer with benzene or ether to 60% of its original coverage, whereas the contact angle of the trimethylbenzene fell sharply after only slight depletion. Contact angles of the alkanes fell rapidly when coverage of the surface by amine molecules was decreased further, reaching zero at coverages in the range 35-55%. Finite contact angles were shown by hexadecane at lower amine coverages than was the case with tetradecane. Depletion of a monolayer of dodecylamine by only a few per cent caused a sharp fall in the contact angle of hexadecane. Bartell and Ruch proposed[2,3] that the retention of oleophobic character by depleted films in contact with liquids of similar molecular shape was due to "plugging" of "holes" in the monolayer by solvent molecules. The resultant mixed monolayer would possess a uniform outer surface of $-CH_3$ groups if the lengths of solute and solvents molecules were exactly matched, but composite monolayers containing solute and solvent molecules of even slightly different lengths would have a "ragged" surface in which a proportion of $-CH_2-$ groups would be exposed. Monolayers of amphipathic compounds in contact with n-alkanes containing the same number of carbon atoms would therefore be expected to retain their oleophobic character at a lower coverage by adsorbate molecules than would those of slightly mis-matched compounds.

The energy of adsorption of a polar compound on a metal from solution in hexadecane would be expected to rise with an increase in its chain length owing to the increasing number of attractive, lateral interactions between $-CH_2-$ groups. If T_w corresponded to desorption of the monolayer to the same critical coverage for all the fatty acids, T_w might be expected to increase indefinitely with the chain length of the adsorbate. If, however, fatty acid or amine molecules, which begin to desorb as the temperature is increased, tend to be replaced by adlineated solvent molecules (possibly only as the specimen is withdrawn for inspection) the wettability of the surface will depend not only on the surface concentration of adsorbate molecules, but also on whether these can combine with adlineated solvent molecules to form a uniform surface of $-CH_3$ groups. Thus, as the number of carbon atoms in the solute is increased from 12 to 16, not only would desorption of a given fraction of adsorbate molecules be delayed until a higher temperature is reached, but the surface would retain its low-energy (non-wettable) nature to a lower coverage, thus reinforcing the expected increase in T_w. If the chain length of the solute exceeds 16 carbon atoms, however, the surface of the mixed solute/hydrocarbon monolayer formed after desorption has commenced will become ragged once more, so that oleophobic character is lost at lower depletions. This will oppose the increase in T_w to be expected from further increases in the energy of adsorption, or if this approaches a limiting value, will cause a fall in T_w. The maximum in fig. (6.3) might be due to such factors.

A similar mechanism may account for the optimum load-bearing properties and lubrication transition temperatures reported by Cameron and his collaborators[12,23] for solutions of polar compounds in "matching" hydrocarbons. Deryagin's theory of friction (see chapter 8) shows that adhesion forces between lubricated surfaces must be low if friction is to be minimised. This condition is fulfilled when the outer surfaces of lubricant monolayers are composed mainly of $-CH_3$ groups. It is postulated that frictional heating would result in partial desorption of, say, a fatty acid, from areas of real contact well before the film broke down completely and seizure occurred. It is assumed that the gaps could be "plugged" by solvent molecules bound to the remaining acid molecules. A mixed film containing solute and solvent molecules of the same chain length and having an outer surface composed mainly of $-CH_3$ groups would have the same low attraction for a similar surface as would a close-packed solute film. The attractive energy between surfaces bearing mixed monolayers of solvent and solute molecules having different lengths would be increased owing to interactions of $-CH_2-$ groups from opposite surfaces and interpenetration of the layers.

When this hypothesis is put forward to explain "chain-matching" optima in lubrication, its validity turns on the implicit assumption that hydrocarbon molecules held only by lateral van der Waals forces can withstand the pressures, shearing forces, and temperatures involved. Rough calculations show, however, that if the free energy of "adsorption" of adlineated hydrocarbon molecules is at least $\frac{1}{3}$rd that of the fatty acid molecules (taken as being around 6 kcal/mole - see chapter 2), the very high concentration of solvent molecules (800 x that of the solute) will ensure that solvent molecules will be "adlineated" in preference to adsorption of further fatty acid molecules. This, of course, presupposes sufficient coverage by fatty acid molecules to form a network to which solvent molecules can adhere.

Zisman has demonstrated[8] the exceptional stability of mixed monolayers containing "matched" amine and alkane molecules. Monolayers retracted on platinum specimens after 24 hours immersion in solutions of amines in alkanes which had the same number of carbon atoms still contained about 15% of solvent molecules. Mixed monolayers containing "matched" fatty acid and alkane molecules were found by Ries and Gabor[27] to provide ferrous surfaces with exceptional protection against rusting. This implies that the surfaces are covered by a coherent insulating layer, impervious to ions. The inferior protection afforded by monolayers of fatty acids deposited from alkanes of a different chain length was presumably due to increased surface energy. The ragged profile of a monolayer containing a proportion of alkane molecules of non-matching chain length would result in exposure of $-CH_2-$ groups. Under these conditions wetting and leaching of the protective molecules by water or other liquids would be facilitated, leading to break-up of the film and corrosion. The value of this work as corroborating evidence of the exceptional stability and impermeability of mixed monolayers containing components of equal chain length is limited, however, by the lack of details given in the original paper. It is not stated, for instance, whether uniform retraction occurred in all cases after treatment of the specimens: the surfaces of some specimens may have been partially covered by an "oil" layer.

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7. SOLUBILITY OF FATTY ACIDS IN HYDROCARBONS AND DENSITY OF FATTY ACID/HYDROCARBON SOLUTIONS.

7.1 Aims and methods of study.

The solubility of fatty acids in hexadecane has been determined over a range of temperatures between the melting-points of the solvent and the solute. (They were completely soluble at temperatures above the latter). Compound formation, phase changes, or micellisation should be revealed by discontinuities in the solubility curves. The temperatures at which a fixed mole fraction of a series of fatty acids dissolved completely in several hydrocarbons have been compared. This should throw light on whether the apparent optimum protective action of films adsorbed from solutions of "matched" additive and carrier is associated with differences in solubility.

The densities of solutions of fatty acids in hydrocarbons have been studied in an attempt to detect differences in the packing of solute molecules (cf. "cybotaxis"). Furthermore, the change in total volume upon dissolving a given weight of fatty acid in a fixed mass of hydrocarbon should yield a qualitative indication of the effect of pressure on the solubility of the acid, and thus on the possibility of precipitation of acid from solution dynamically trapped between solid surfaces under load.

7.2 Experimental procedure.

Solutions containing 0.0033 mole fractions of a series of fatty acids in hexadecane and tetradecane, similar concentrations of a series of alcohols in tetradecane, and 0.5wt.% solutions of fatty acids in hexadecane, were prepared by warming mixtures of the weighed components in 1-inch diameter stoppered test-tubes. After the solutions had been allowed to cool, they were agitated by a mechanical shaker while immersed in an ice-water bath; this caused complete solidification in all cases. The temperature of the water-bath was slowly increased, being controlled by a "Tempunit" stirrer-regulator, while shaking was continued. The temperature at which each solution became clear and homogeneous was recorded. Observations of the dissolution temperature made in this way were not vitiated by supersaturation, as would be the case with determinations of the temperature at which crystallisation commenced. Dissolution temperatures were also determined for a series of solutions of tetradecanoic, hexadecanoic, octadecanoic, and docosanoic acid in hexadecane over the entire concentration range 0-100% by weight.

The densities of tetradecane and solutions of dodecanoic, tetradecanoic, and hexadecanoic acids in tetradecane were determined with a pyknometer of 10ml capacity. Those of the fatty acids, in both the solid and molten states, were measured in specific gravity bottles of 50ml capacity. It was decided to examine 0.5M solutions, which were sufficiently concentrated to have densities which differed appreciably from that of the solvent. Owing to the limited solubility of long-chain fatty acids in tetradecane, it was necessary to carry out comparative determinations of the densities of the acids, hydrocarbons, and solutions at an elevated temperature. 0.5M solutions of the three acids cleared at 45°C but in early determinations carried out at 50°C, some crystallisation of hexadecanoic acid occurred in parts of the pyknometer which were not completely immersed in the thermostat bath. Later measurements were therefore made at 65°C (at which temperature, incidentally, all three acids were molten). The densities of the acids were also checked at 25°C as follows. After measurements at 65°C had been completed, the s.g. bottles were about half emptied of the molten acids, the residue was allowed to solidify, and the bottles were weighed, topped up with distilled water in the usual way, and weighed once more. Disturbance of the fatty acids by addition of the distilled water appeared to be negligible, and no difficulty was encountered in removing air bubbles.

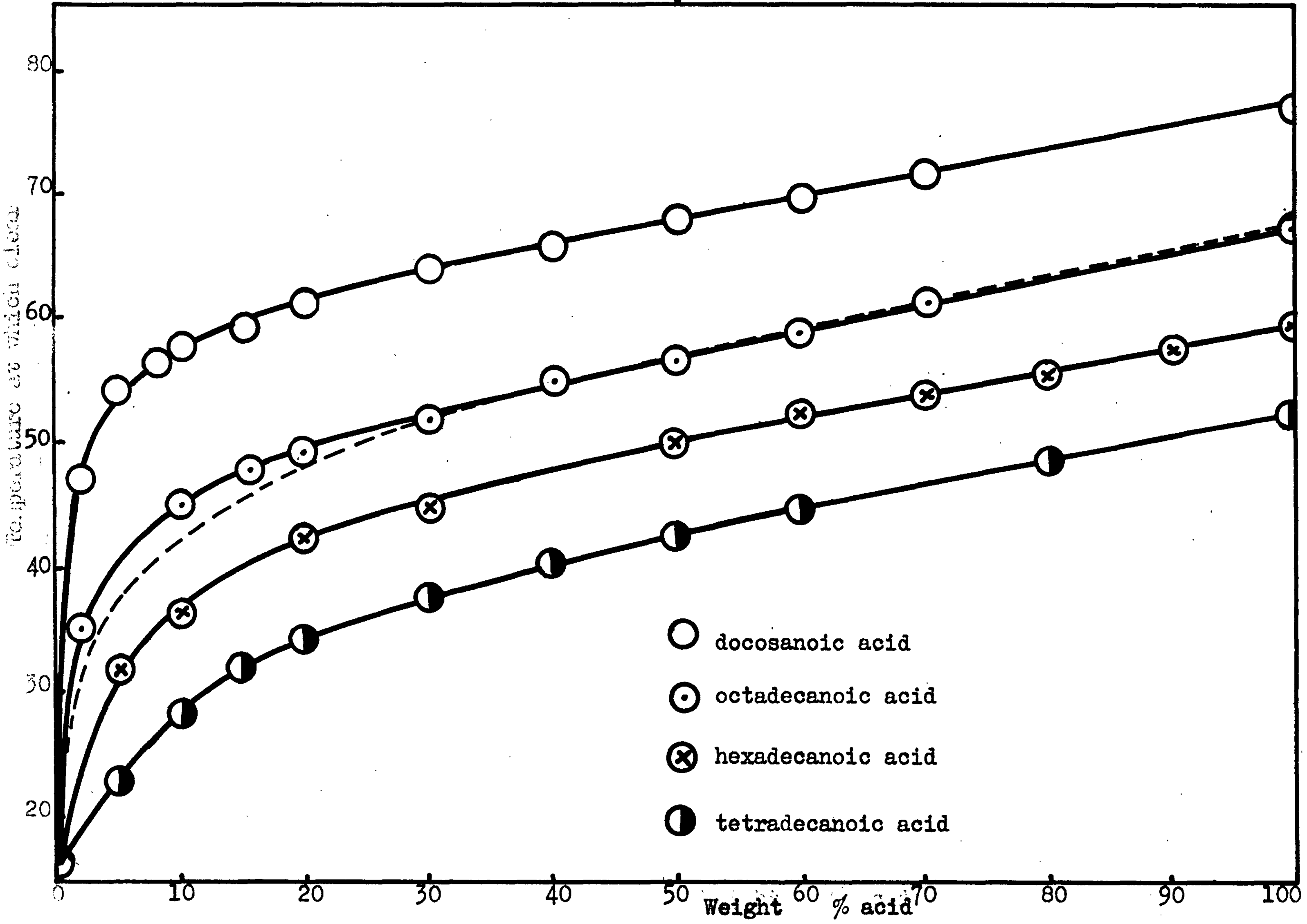
"General purpose reagent" grade fatty acids were used in the solubility studies, but those in the density determinations were "Puriss" grade (greater than 99% pure). It was not considered necessary to use expensive materials of particularly high purity for measurement of bulk properties, and hydrocarbons were not specially checked for freedom from surface-active impurities.

7.3 Results.

The dependence of the solubility of tetradecanoic, hexadecanoic, octadecanoic, and docosanoic acids in hexadecane on temperature is shown in fig. (7.1). Points for each acid lie on smooth curves which contain no discontinuities, maxima, or minima. There is thus no evidence of micellisation, complex formation, or separation of new phases. The theoretical curve for the solubility of octadecanoic acid in any solvent is shown by the dashed line in fig. (7.1). This has been calculated on the assumptions that the solution is ideal, i.e. Raoult's law is obeyed, that no solid solutions are formed, and that the acid exists as dimers both in the solid state and in solution[2] (see chapters 2 and 3). Deviation from "ideal" behaviour is slight.

Dissolution temperatures for a fixed mole fraction (0.0033) of a series of fatty acids in tetradecane and hexadecane are shown in fig. (7.2). This particular mole fraction was chosen so that results would be directly comparable with those of investigations of the lubricating properties of similar solutions carried out by Askwith, Cameron, and Crouch.[1] Dissolution temperatures for acids in which the number of carbon atoms did not exceed that contained in the solvent molecule differed only slightly from one another and were only just above the melting-points of the solvents, which were 5.5°C for tetradecane and 16.5°C for hexadecane. Acids containing more carbon atoms than the solvent, however, were not completely soluble at such low temperatures. Dissolution temperatures rose linearly with increases in the number of carbon atoms in the fatty acid molecule when this exceeded that contained by the solvent. Similar trends were found in solutions of alcohols

Fig. (7.1) Solubility of tetradecanoic, hexadecanoic, octadecanoic, and docosanoic acids in hexadecane as a function of temperature.

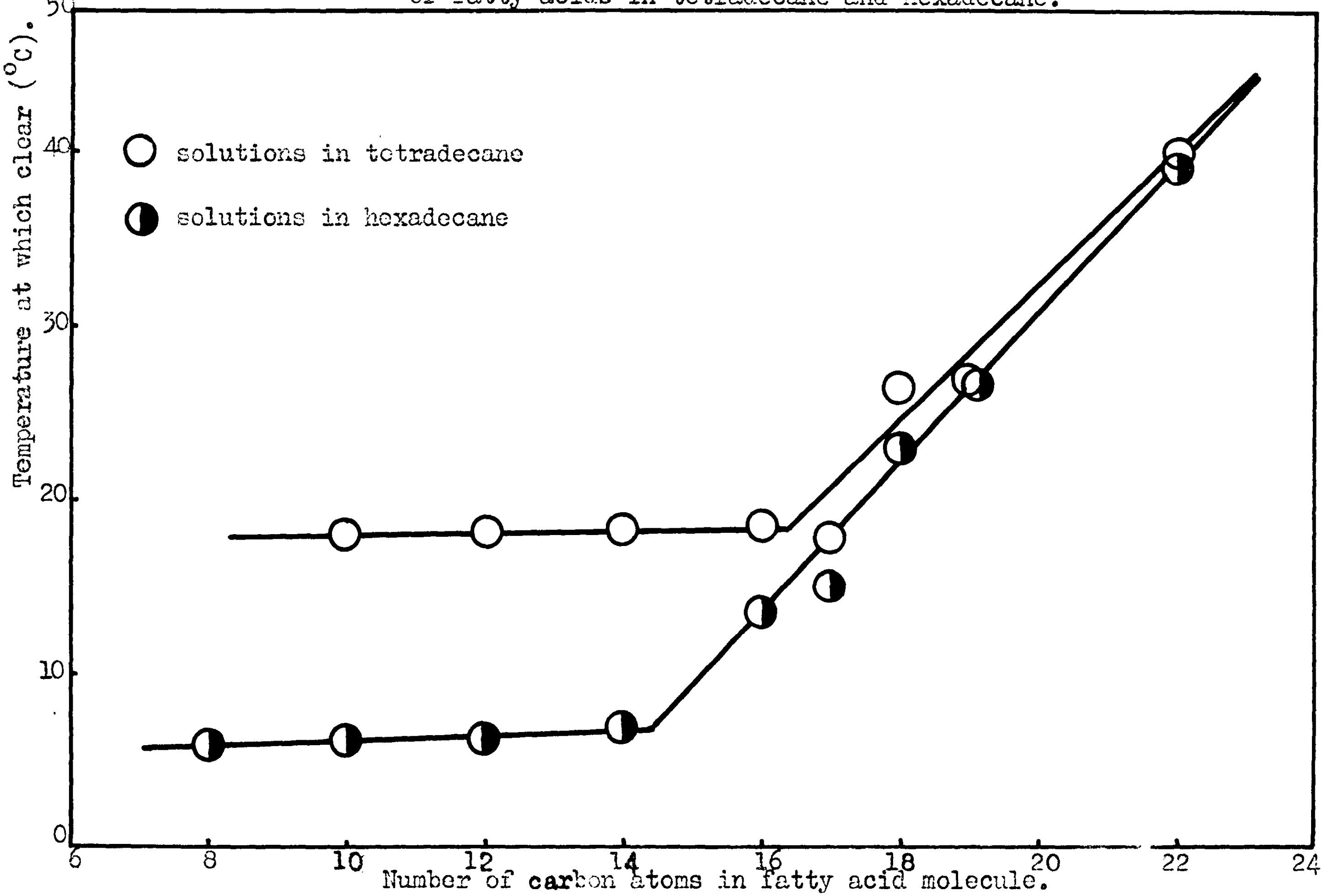


in tetradecane and those of acids in 1-hexadecene, although these have not been included in the data shown in fig. (7.2).

Densities at 65.00±0.05°C of dodecanoic, tetradecanoic, and hexadecanoic acids, tetradecane, and 0.5M solutions of the acids in tetradecane are given in table (7.1). All the acids were molten in the pure state at this temperature. Duplicate determinations gave density values which agreed to within 1 part in 10,000 for solutions and 1 part in 1,000 for the molten acids. The volume of 100g of solutions differed from the sum of the volumes of the separate components by less than 0.1ml (0.1%) for each acid. There was, therefore, no evidence of changes in volume during mixing, accompanying changes in the structure of the solvent or the solutes.

The densities of dodecanoic acid, tetradecane, and a 0.5M solution of dodecanoic acid in tetradecane were also determined at 25.00±0.05°C. This acid was completely soluble at this concentration and temperature (unlike the others), but was solid in the pure state. The density of the acid was 0.931g/ml, and those of the solvent and solution 0.7603g/ml and 0.7750g/ml respectively. The density of a solution diluted by a factor of two was 0.7678g/ml at this temperature. Duplicate readings agreed to within 1 part in 10,000. It will be shown in the next section that these figures indicate that there <u>is</u> a change in the volume of dodecanoic acid upon dissolution in tetradecane at 25°C.

Fig. (7.2) Dissolution temperatures for mixtures containing 0.0033 mole fraction of fatty acids in tetradecane and hexadecane.



7.4 Discussion.

It has already been noted in section 7.3 that solubility curves suggest that no compound formation or separation of new phases occurs in solutions of fatty acids in n-alkanes of similar chain length. It can be inferred from fig. (7.1) that apparent sharp changes in the relationship between fatty acid solubility and chain length, such as that in fig. (7.2), occur only in dilute solutions containing less than about 1% $^w/w$ of acid. The results of investigations by Askwith, Cameron, and Crouch[2] into the lubricating properties of 0.003M solutions of fatty acids in hexadecane in a 4-ball apparatus were therefore liable to be vitiated by precipitation of the acids containing more than 16 carbon atoms. The optimum protection afforded by hexadecanoic acid could therefore be the result of the sharp reduction in solubility of higher acids, superimposed on a real increase in load-carrying ability with chain length. Subsequent studies of frictional transition temperatures by Grew and Cameron[3] with solutions containing up to 6% $^w/w$ were largely unaffected by solubility limits, however, and suggested that the "chain-matching" optimum was not merely the result of differences in solubility.

Density figures are not easily analysed to give an unequivocal measure of the ordering effect of polar molecules on those of the solvent, if this exists. Such an effect would tend to increase the density of the solution, but at the same time the molar volume of a fatty acid dissolved in a hydrocarbon, would be expected to be greater than that of the solid acid, and more closely related to the molar volume of the acid in the less closely packed molten state. The ambiguity of comparisons of the volume of a chosen mass of solution with the total volume occupied by its separate components is greatly reduced if all measurements of density are carried out at a temperature above the melting-point of the solute. Differences in volume can then be attributed to structural changes in the solvent with more confidence. Table (7.1) on p.200 shows, however, that there is practically no change in total volume when molten dodecanoic, tetradecanoic, and hexadecanoic acids are dissolved in tetradecane. The density of the solutions was that which would have been expected from a direct addition of fixed volumes of one component to another. There is no sign of the contraction of the solution which might have been anticipated in view of X-ray diffraction evidence of the ordering effect of polar solutes reported by Clark, Sterrett, and Lincoln.[4]

The molar volume of dodecanoic acid when dissolved in tetradecane at 25°C was 5% greater than that of the solid acid at the same temperature. This was not unexpected as the density of the solid acid at 25°C was 8% higher than that of the molten compound at 65°C; a similar difference in density was observed between the liquid and solid forms of the other acids. It follows that the solubility (at a given temperature) would be reduced by an increase in pressure. The effect of an externally applied pressure on the solubility of a solid in a liquid is given by the equation[2]:

$$\left(\frac{\partial \ln m_s}{\partial P}\right)_T = \frac{v' - \bar{v}}{RT}$$

where m_s is the molal concentration of a saturated solution, P is pressure, R is the gas constant, T is the absolute temperature, v' is the molar volume of the solute alone, and $\bar{v}$ is the partial molar volume of the solute in a saturated solution. This equation is only approximate, since v' and $\bar{v}$ are unlikely to be independent of pressure; indeed, it is not impossible that $(v' - \bar{v})$ changes sign at some high pressure. If, however, it is provisionally assumed that $(v' - \bar{v})$ remains constant over a moderate range of pressure, it is possible to calculate the change in solubility of dodecanoic acid in tetradecane with pressure from the results of density measurements.

When the volume of "1 mole of solution" is plotted against the mole fraction of solute the partial molar volume of the solute at any concentration is given by the intercept made by the tangent to the curve on the volume axis.[5] Data calculated from the results of density determinations carried out at 25°C are given in table (7.2). When these data are plotted graphically (not shown), it is clear that the partial molar volume of dodecanoic acid present as less than a mole fraction of 0.1 is constant, and equal to about 225. The term $(v' - \bar{v})$ in the above equation can be put equal to 215-225 = -10, assuming that $\bar{v}$ at the measured concentration was approximately equal to that in a saturated solution.

This is justifiable, since the stronger of the two solutions studied was not far from saturation. The effect of pressure on the solubility of low concentrations of dodecanoic acid in tetradecane has been calculated on this basis; results are given in the table below :

Increase in pressure, kg/mm^2	Fraction of original solubility
nil	1.00
1	0.96
10	0.68
100	0.018

It appears almost certain, therefore, that the solubility of fatty acids in hydrocarbons is drastically lowered when their solutions are subjected to pressures of the same order as the yield pressures of work-hardened metals, which are, for instance, 31kg/mm^2 for copper and 65kg/mm^2 for steel. Surfaces lubricated by such solutions, therefore, may be separated, intermittently at least, by bulk fatty acid precipitated locally by the action of pressure. It has not been possible to decide whether nucleation of the acid would occur under dynamic conditions, but the discovery of this possibility throws doubt on the assumption that the lubricating role is strictly limited to monomolecular adsorbed layers. The validity of this suggestion depends, of course, on whether the sign of $(v' - \bar{v})$ is independent of pressure up to the values quoted. This is supported, however, by the structural similarity of the solvent and solute molecules (although these are mainly dimerised), and the shape of the solubility curves in fig. (7.1), both of which suggest that anomalous dependence of $(v' - \bar{v})$ on pressure is unlikely.

Table (7.1) Density of solutions of fatty acids in tetradecane, and volumes occupied by 100g of solutions and their separate components.

Material	Density @ 65°C.g/ml	Volume/100g, ml	
		Separate Components	Solution
dodecanoic acid	0.860	---	---
tetradecanoic acid	0.855	---	---
hexadecanoic acid	0.856	---	---
tetradecane	0.7323	---	---
0.5M dodecanoic acid/ tetradecane	0.7468	133.94	133.87
0.5M tetradecanoic acid/ tetradecane	0.7485	133.64	133.60
0.5M hexadecanoic acid/ tetradecane	0.7501	133.31	133.33

Table (7.2) Volumes of solutions of dodecanoic acid in tetradecane containing same total number of molecules (6.02×10^{23}).

Mole fraction of acid	Volume of solution (ml)
0.000	258.1
0.066	255.8
0.131	253.8
1.000	215.1

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5. See reference 1, p.207.

8. REVIEW AND DISCUSSION.

8.1 Summary of conclusions reached in previous chapters.

Adsorption of octadecanoic acid on iron from solution in hexadecane does not significantly exceed the equivalent of a close-packed monolayer. Molecular orientation in the interfacial region has been shown by X-ray diffraction to be restricted to a zone less than 125Å deep. Direct investigations of the depth of any viscous boundary layers which might exist at the metal-solution interface indicate that anomalous flow properties are restricted to a zone equivalent in effect to an immobilised layer not more than 200 or 300Å deep; preliminary experiments with non-rigid powder beds had suggested that stationary layers at least 1000Å in depth might be present but these must be regarded as unreliable, in the light of subsequent experiments with sintered plates. Partial stabilisation of suspensions of iron powder in hydrocarbons by fatty acids is entirely explicable by steric hindrance due to a monomolecular adsorbed layer of fatty acid, and settling data correlate well with the adsorption measurements. Since aggregation of primary iron particles is not prevented by fatty acids, the particles cannot be surrounded by immobilised polymolecular layers more than 200-300 Å deep. Observations of the effect of temperature on the wettability of stainless steel specimens bearing adsorbed layers have revealed trends similar to those reported by Zisman for platinum surfaces. Values of transition temperature for equimolar solutions of a series of fatty acids or amines in hexadecane suggest, however, that as desorption of the polar compound proceeds, the ability of solvent molecules to "plug the gaps" plays an important part in delaying break-up of the adsorbed film. Solubility curves for fatty acids in hydrocarbons contain no features indicative of micelle formation or separation of a new phase. Determinations of the density of such solutions and their separate components show that applied pressure may cause a considerable reduction in the solubility of the fatty acids at temperatures below their melting-points.

8.2. Relevance of this work to boundary lubrication.

Contrary to the contentions of Deryagin and Fuks regarding the properties of boundary layers of liquids (see chapter 4), almost all the phenomena studied could be explained by adsorption of a unimolecular film of fatty acid on metal surfaces, without assuming the existence of an anomalous interfacial layer of liquid of the order of 1000Å in depth between this film and the bulk, i.e. normal, liquid. Experiments were admittedly carried out in the absence of externally applied pressure, whereas lubricants in the contact area of sliding solids are subjected to extremely high pressures for short periods. This will probably affect the solubility of additives in an oil and will certainly increase its viscosity greatly. The pressure exponent of viscosity of long-chain fatty acids (around 30) is almost double that of hydrocarbons with similar molecular structure (16-18)[1]; the viscosity under pressure of an oil locally enriched in fatty acid by multilayer adsorption or deposition would therefore be greater than that of the pure oil. In the following paragraphs, however, it is argued that there are theoretical grounds for supposing that adsorbed films of long-chain compounds only one molecule deep can act as effective boundary lubricants.

Hardy[2] proposed that the action of boundary lubricants was due to the presence of thin, probably unimolecular adsorbed films of vertically oriented molecules which masked the "attractive fields of force" between the sliding surfaces. Bowden and Tabor,[3] however, do not explicitly take the mutual attraction of the surfaces into account in their equation describing the action of boundary lubricants.

This is $F = A(s_m + (1 - \alpha)s_l)$ ______ equ. (1)

where F is the frictional resistance to sliding, A is the area which supports load, α is the fraction of this area over which breakdown of film has occurred, s_m is the shear strength of the junctions at the metal-metal contact, and s_l is the shear strength of the lubricating film.

According to the view of Bowden and Tabor, the main function of a boundary lubricant is to reduce α , the area of contact between bare metal surfaces. It is also important that s_l is low, i.e. two adsorbed layers back-to-back should slide easily over each other. This equation gives little information about the origin of frictional forces, but Deryagin and his co-workers[4,5] have related the friction of lubricated surfaces to the attractive forces between the areas of metals in "real" contact. It seems remarkable that Bowden and Tabor did not apparently find Deryagin's theory worthy of inclusion in part II of their monograph[6]. Deryagin proposed that friction could be described by a two-term law, in which the importance of attractive interactions between the sliding metals is explicitly recognised:

$$F = \mu_o (N + Sp_o) \quad \underline{\qquad\qquad} \text{ equ. (2)}$$

where F is the static frictional resistance, μ_o is the "true" coefficient of friction, N is the load, S is the area of real contact, and p_o is the adhesion force/unit area of real contact.

Now $S = \frac{N}{p}$, where p = yield pressure of metal,

and $\mu = \frac{F}{N}$, where μ = observed coefficient of friction.

Hence equ. (2) may be written in the form

$$\mu = \mu_o \left(1 + \frac{p_o}{p}\right)$$

If $p = 70$ kg/mm^2, a typical value for steels, equ. (2) predicts the dependence of μ (in terms of μ_o) on p_o shown in fig. (8.1). Since μ begins to rise rapidly when p_o becomes greater than 10^9 dynes/cm, <u>whatever the applied load</u>, it follows that a boundary lubricant which reduces the attractive force to below this figure will cause μ to fall to a low, constant level. Values of the van der Waals attractive force between two plane parallel metal surfaces in a hydrocarbon environment are plotted as a function of the distance separating them, R, in fig. (8.2). If the van der Waals inter-

Fig. (8.1) Theoretical dependence of experimentally observed coefficient of friction on force of adhesion.

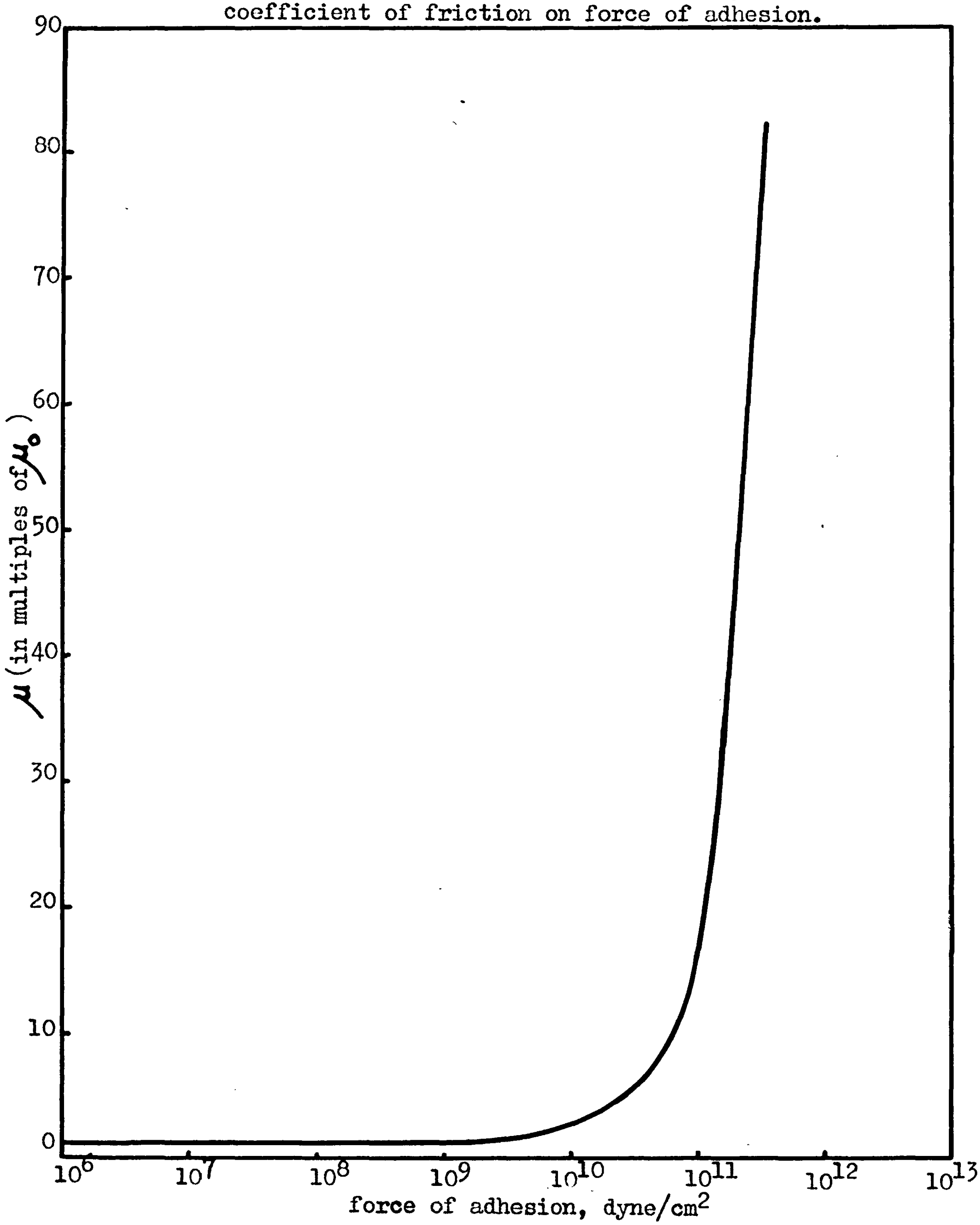
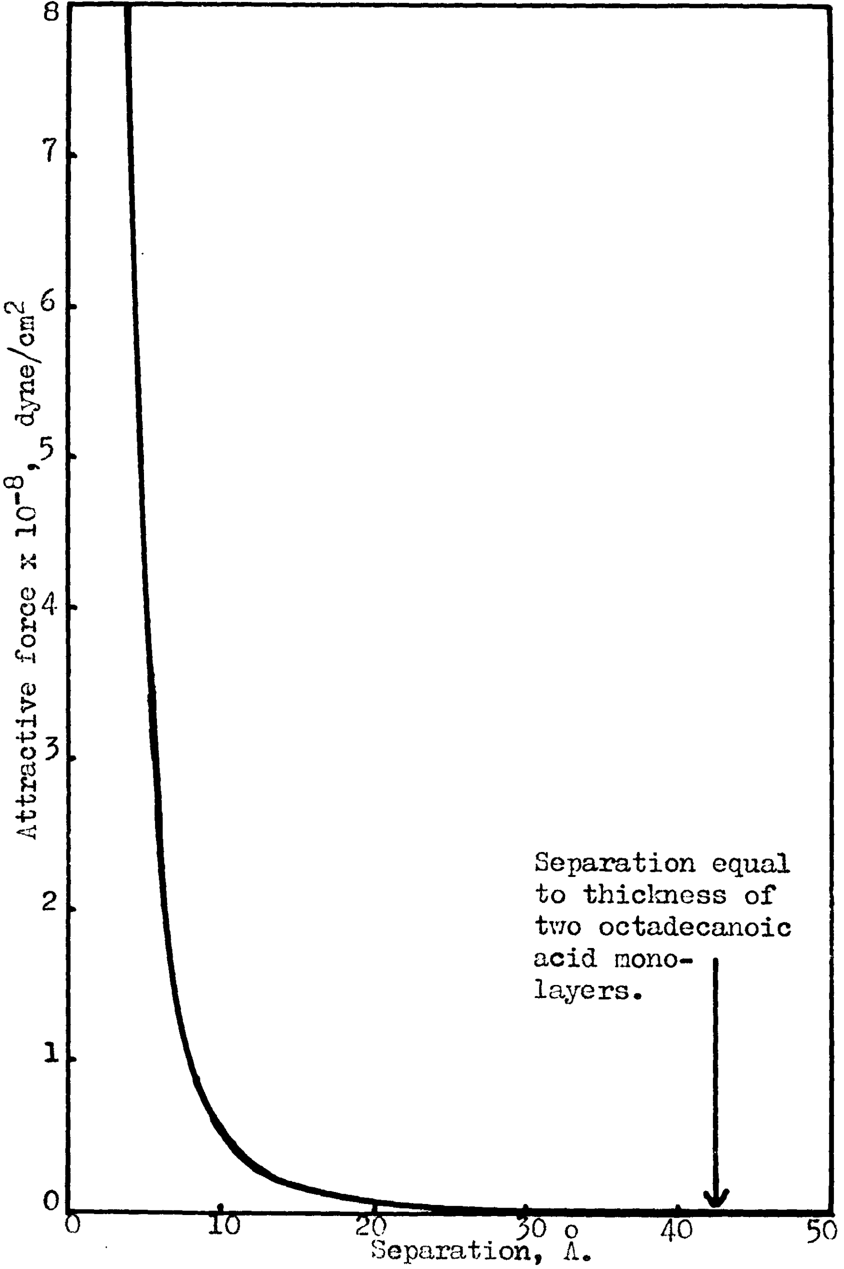


Fig.(8.2) van der Waals attractive force between plane-parallel metal surface as a function of their separation.



action constant, A, is assumed to be about 10^{-12} erg,[7,8] the force of attraction f_A decays rapidly with increasing R according to the equation $f_A = \frac{-A}{6\pi R^3}$, reaching a negligible value at separations exceeding 30Å. Values of p_o in excess of 10^9 dynes/cm are reached when R is less than about 4 Å. It is clear that the mutual attraction of surfaces bearing adsorbed monolayers of octadecanoic acid about 21Å deep would be extremely small. Deryagin's theory, in conjunction with calculations of the reduction in adhesion force due to the presence of an adsorbed monolayer, can therefore explain the action of boundary lubricants, at least in principle. This is consistent, of course, with Hardy's theory mentioned above, but Deryagin and Fuks maintain the opposite view,[4,9] that the action of lubricants cannot be explained without invoking abnormal properties in boundary layers of oils. These claims have been made the more vehemently because both of these workers are committed to the idea that liquids containing polar molecules have anomalous properties to a depth of at least several hundred Ångstroms in interfacial regions. It has been mentioned in chapter 3, however, that films of aqueous solutions of electrolytes studied by Fuks had equilibrium thicknesses under load much greater than values calculated from "disjoining pressures" arising from van der Waals attraction and electrostatic repulsion.[10] This deviation from the expected behaviour could only be explained by extravagant postulates of the existance of "remote hydration layers" surrounding individual ions. It seems probable, therefore, that this work, and similar studies of solutions in hydrocarbons, gave exaggerated values of equilibrium film thickness. It was also mentioned that investigations by Deryagin[4] into the properties of boundary layers of solutions of fatty acids in hydrocarbon oils by the so-called "blow-off" method were vitiated by their autophobic nature. Results from extremely dilute solutions were unconvincing and hardly justify the inference drawn by the author, that successive regions of molecular orientation extend 1000Å into the bulk solution. It would appear, therefore, that the somewhat dogmatic views of Deryagin and Fuks have limited experimental support, estimates of range of action of "surface effects" being rather suspect in the investigations quoted.

An attempt has also been made by Cameron[11] to explain the origin of friction between lubricated surfaces in terms of van der Waals attractions. He assumed that the gap between two monolayer-covered plane surfaces in contact under zero load was similar to that between adjacent (end-to-end) molecules in a hydrocarbon crystal. Attractive and repulsive energies and X-ray diffraction data reported by Müller for hydrocarbon crystals were used to estimate the energy barrier to be surmounted during lateral movement of one monolayer-covered surface over another. Values obtained for the coefficient of friction lay in the range 0.10-0.24, according to the applied load. The net attractive energy between a pair of hydrocarbon chains situated on opposite surfaces was computed to be 5.21×10^{-14} erg, or 26 erg/cm^2 if each chain occupies 20Å^2 of surface. Now the van der Waals attractive energy between metal surfaces separated by, for instance, 20Å, is about 0.17 erg/cm^2. It follows, then, that the major source of friction between monolayer-covered surfaces is the attraction between the outer atoms of the hydrocarbon chains of the adsorbate molecules. It is suggested that this is the origin of the "true" coefficient of friction, μ_0, in the Deryagin equation.

The maximum in oleophobic/oleophilic transition temperatures observed for a solute and solvent with matching molecular structure, and reported in chapter 6, supports the findings of Askwith, Cameron, and Crouch,[12] and Grew and Cameron,[13] that such solutions are most effective as boundary lubricants. This is in agreement with the observations of Ries and Gabor[14] on the resistance to corrosion of ferrous surfaces bearing fatty acid monolayers adsorbed from a "matching" solvent and is consistent with the results of studies by Tamai[15] of friction between steel surfaces lubricated by solutions of various compounds in tetradecane. Values of oleophobic/oleophilic transition temperature determined for platinum specimens by Zisman,[16] and of "film breakdown" temperatures observed by Sakurai and Baba[17] on both platinum and steel surfaces, however, show no sign of a chain-matching optimum, and are difficult to reconcile with the observations of Cameron and those reported here. If the latter are valid, however, the effectiveness and durability of an adsorbed monolayer in reducing the adhesion and friction between metal surfaces is greatly influenced by the molecular structure of the carrier oil.

Reduction of friction by adsorbed films may not be due solely to their action in masking attractive forces between metal surfaces. Cameron,[18] and Sakurai and Baba[19], have suggested that an important part is played by improvements in the dispersability of wear fragments, which prevent formation of large, abrasive aggregates in the contact zone. The Rehbinder[20] effect may be important in this connection. Rehbinder has claimed that adsorption of surface-active compounds in surface faults of solids under stress can reduce the solid/liquid interfacial energy to such an extent that spontaneous dispersion of the solid as colloidal particles occurs. The presence of a surfactant would therefore assist "running-in" of sliding surfaces, asperities being rapidly worn away and dispersed as colloidal particles. Thus, although the Rehbinder effect predicts a superficial weakening of the sliding solids, severe wear by the "ploughing" of asperities through the opposite surface would be greatly reduced.

8.3 Final conclusions.

The surface-chemical properties of the hydrocarbon solution/metal system appear to be consistent with retention of normal "bulk" properties by the liquid adjacent to monolayers of polar compounds adsorbed on metal surfaces. Under the particular experimental conditions used, layers of immobilised liquid greater than about 300Å in depth have definitely been proved not to exist in the interfacial zone.

The action of boundary lubricants can be explained at least qualitatively by prevention of close approach of metals in sliding contact by adsorbed layers of long-chain compounds only one molecule thick on their surfaces. There are indications that repair of depleted monolayers of fatty acids on steel surfaces by "adlineated" solvent molecules has an important effect on their wettability and frictional properties. Adlineated solvent molecules are most tightly held, and form a mixed monolayer of minimum surface energy, when the chain lengths of the adsorbate and solvent molecules are the same.

Under conditions of high local pressures such as are encountered in boundary lubrication, however, it is possible that changes in viscosity and solubility invalidate this simplified picture.

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