PHYSICO-CHEMICAL STUDIES

ON

SOLUTIONS OF SYNTHETIC NON-IONIC DETERGENTS

by

A. T. Florence

April 1965

University of Strathcl

Glasgow.

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The theory of the techniques used in the investigation (surface tension light-scattering, viscosity and vapour pressure techniques) is dealt with briefly, and concludes part I.

The effect of branching the hydrocarbon chain of non-ionic detergents was studied by synthesising a new series of branched-hydrocarbon chain compounds of general formula, $R_2.CH.CH_2(OCH_2CH_2)_nOH$ with n = 6 or 9 and $R = CH_3$, C_2H_5, $\underline{n}$-C_3H_7, $\underline{n}$-C_4H_9 . Three straight chain compounds were also prepared for comparative studies, these being $CH_3(CH_2)_x(OCH_2CH_2)_nOH$ with $x = 1, 3,$ and 5 and $n = 6$.

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concentration yielded the enthalpies and entropies of micellisation by the use of an equation of the Clausius-Clapeyron type.

High critical micelle concentrations were evident in some of the system and this afforded an opportunity of studying pre-micellar behaviour. Viscosity and vapour pressure measurements gave an indication of the hydrati of the detergent monomers and of three polyoxyethylene glycols. Viscosity measurements on micellar solutions yielded hydration values for the micelles and an increase in hydration of the glycol portion of the monomers was indicated on micelle formation. The positive entropy values may be explain by the loss of water structure around the alkyl chains as they enter the micelles.

Micellar sizes and aggregation numbers were obtained by light-scatterin but the smallness of the micelles precluded any inference as to their shape being drawn from the data. It was concluded, however, that the micelles were, in general, symmetrical but for those formed by the detergent, $(C_4H_9)_2CH.CH_2(OCH_2CH_2)_6OH$ which, on interpretation of viscosity measurement and Huggins' constants, were assumed to become asymmetric as the temperature of the system was raised.

Vapour pressure studies on aqueous solutions of three glycols (with 6, 9 and 12 ethylene oxide units) showed a negative deviation from Raoult's Law, interpretable in the case of the first two glycols on the basis of hydration. Other explanations of the deviation of solute activity from ideal behaviour were tested and the results discussed. Similar measurement were also made on three detergent systems. It was shown that the activity o the detergent increased above the critical micelle concentration, in agreement with the behaviour predicted by the Law of Mass Action approach to micelle formation, although at variance with the predictions of the pseudo-phase approach.

PHYSICO-CHEMICAL STUDIES
ON
SOLUTIONS OF SYNTHETIC NON-IONIC DETERGENTS

A Thesis presented by

ALEXANDER TAYLOR FLORENCE

in fulfilment of the requirements for the degree
of Doctor of Philosophy of Glasgow University

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A.T.F.

SOME ABBREVIATIONS USED IN THE TEXT

a_2 = activity of solute

a_1 = activity of solvent

γ = activity coefficient

γ = surface tension (dynes/cm)

π = surface pressure (dynes/cm)

A = area/molecule ($Å^2$)

m = molality

CMC = critical micelle concentration

PEG = polyoxyethylene glycol

$[\eta]$ = intrinsic viscosity (concentration in gm/ml)

$[\eta']$ = intrinsic viscosity (concentration in gm/100ml)

C = concentration

N = mole fraction

Abbreviations used for detergents are as follows: Commercial products, for example an octyl phenol adduct with x ethylene oxide units has been written OPn_x . Nonyl phenol adducts have been denoted by NPn_x. Pure straight chain detergents, such as hexadecane monohexaoxyethylene glyco ether, have been written as $C_{16}n_6$. The branched chain detergents used in this thesis are denoted by R_2n_6 where R is the alkyl chain in the structure $R_2.CH.CH_2(OCH_2CH_2)_6OH$

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PART I

INTRODUCTION

Only a limited number of studies have been made on synthetic non-ionic detergents, in spite of the interest that has been shown in commercial products which are chemically inhomogeneous. There is a basic interest in the surface chemical and micellar properties of these materials which are used extensively in pharmacy as suspending, solubilising and emulsifying agents. The problem of the heterogeneity of the commercial detergents is overcome by the use of pure, synthetic materials in physical studies.

Synthetic non-ionic detergents with branched hydrocarbon chains have not been prepared previously. The non-ionic detergents available form micelles, in general, at very low concentrations precluding investigation of the monomer species in solution. The synthesis of a series of compound with short branched-hydrocarbon chains was thought to be a valuable step towards elucidating the effects of chain branching and, at the same time, providing detergents micellising at concentrations large enough to permit accurate measurements to be made on monomeric solutions. As the properties of the micelles may be obtained readily, a knowledge of the state of the monomer provides data for the overall changes in properties which occur as the monomers aggregate, and these can be correlated with the various thermodynamic parameters of the detergent system.

Synthesis of Pure Non-ionic Surface-active Agentants

Until recently much of the published work on non-ionic detergents was carried out on compounds prepared by condensation of ethylene oxide with fatty alcohols or alkyl phenols in the presence of catalysts.[1-3] Such condensates have a distribution of polyoxyethylene chain lengths and, although Becher[4] has been at pains to point out that these compounds are "reproducibly heterogeneous," they are not ideal for work in which exact interpretations of physical properties are desired.

Although the problems involved are formidable, attention has now been turned towards the synthesis of homogeneous non-ionic detergents. This summary deals with some of the work carried out in the preparation of polyoxyethylene alkyl ethers, as these are relevant to this thesis.

Crook and co-workers[5] have recently compared single-species non-ionic detergents with those containing a distribution of PEG chain lengths. Their results show the difficulties involved in working with heterogeneous substances, for although these compounds showed the same qualitative properties (such as critical micelle concentration increasing with increasing glycol chain length) rigid interpretations were made difficult because of the range of polyoxyethylene chain lengths present and the consequent differences in surface activity, solubility and other properties within one sample. Areas per molecule and critical micelle concentrations are thus only mean values whose validity depends on the distribution of chain sizes. Attempts to fractionate these products[3] succeeded only in reducing the spread of properties.

The Williamson ether synthesis has been widely used to prepare pure detergents. Early examples were the synthesis of various glycol ethers by Turner and Saunders[6] and by Cooper and Partridge[7] who prepared ethylene glycol mono-n-dodecyl ether and the C5, C6, C7 and C8 straight carbon-chain homologues.

Two methods have been employed in synthesising compounds with long polyoxyethylene chains. In the first method (I) the appropriate alkyl bromide is condensed with the mono sodium derivative of the glycol of desired chain length. A ratio of glycol to sodium of 4 to 1 is used to minimise the formation of the generally water-insoluble dialkyl ethers:

$$R.Br + NaO(CH_2CH_2O)nH \longrightarrow R.O(CH_2CH_2O)nH$$

R = alkyl group and n = 1 to 9.

Method I

The second method entails the building up of the glycol ether in steps by means of various intermediates following Elworthy and Macfarlane[8]:

$$a)\quad R(OCH_2CH_2)_nOH \xrightarrow[\text{Pyridine}]{SOCl_2} R(OCH_2CH_2)_nCl$$

$$b)\quad R(OCH_2CH_2)_nCl + Na(OCH_2CH_2)_xOH \longrightarrow R(OCH_2CH_2)_{n+x}OH$$

Method II

In this manner Elworthy and Macfarlane prepared a series of pure non-ionic detergents based on n-hexadecane with glycol chains of 6, 7, 9, 15 and 21 units. Higher polyoxyethylene glycols (over 100 units) can be prepared by the method of Fordyce, Lovell and Hibbert[9] which is similar.

Using the first method Corkill, Goodman and Ottewill[10] have synthesised a series of pure detergents based on hexaoxyethylene glycol with hydrocarbon chains lengths of 4 to 16 carbon atoms, but the yields were low; yields improved for C_4, C_8 and C_{12} compounds when the second method, with trioxyethylene intermediates, was employed. Trioxyethylene glycol is available commercially and enables large quantities of such intermediates to be synthesised. Malley[11] also describes the preparation of C_6n_4, C_6n_5 and C_6n_6 from diethylene glycol and triethylene glycol ethers.

Weller[12] has detailed the preparation of pure glycol ethers, $C_{10}n_{1-8}$ from glycols obtained by fractionation of a commercial product, Shell "PEG 200". Macfarlane[13] attempted this but found the method unsatisfactory and abandoned it in favour of stepwise synthetic methods. Weller has calle such procedures tedious, but it seems that his own method of repeated fractionation and monitoring of the cuts by gas-liquid chromatography is equally tiresome, and it is doubtful even in the face of the chromatographic evidence whether there are no contaminating traces of lower or higher homologues.

The work of Gingras and Bayley[14], who described the synthesis of p,t-octyl phenol with seven ethylene oxide units, by reaction of hexaoxyethyle glycol with p,t-octyl phenyl chloro-ethyl ether, has recently been extended[15] using three synthetic routes to obtain a series with 1 to 10 ethylene oxides units. The first of the series (n_{1-3}) were obtained by redistillation of fractions isolated by distillation of oxyethylated octylphenol. The tetra- and hexa-oxyethylene derivatives were synthesised by condensation of recrystalised octyl phenol with the appropriate glycol mono chloride, purified by repeated distillation. OP_{n7-10} were prepared by method II from hexaoxyethylene glycol and the appropriate chlorides.

The final products were all chromatographed on silica.

In 1956 Chakhovskoy et al.[16] reviewed the main synthetic routes for mono-alkyl glycol ethers and pointed out that an alternative to the Williamson ether synthesis was the reaction of the mono-sodium salt of a pure glycol with the p-toluene sulphonyl ester of an aliphatic alcohol. The Williamson synthesis involves fairly drastic heating conditions with the result that considerable quantities of unsaturated by products are formed[17]. Reactions between p-toluene sulphonyl esters, however, proceed smoothly with good yields at lower temperatures[12] – which may be responsible for the absence of carbonyl impurities in non-ionics freshly prepared by this route. The high yields of 40 to 55 % reported for this method[12] have not always been achieved by other workers. Chakhovskoy et al. obtained only 20 % yield in the preparation of C_6n_4 from the tosylate of C_6n_2, although Wrigley has obtained a 50 % yield for $C_{12}n_3$[18].

The monomethyl ether of $C_{10}n_{10}$ was prepared for light scattering studies by condensing molecularly distilled commercial $CH_3O(CH_2CH_2O)_{10}H$ with decyl chloride (Williamson ether synthesis.)[20] The mono-methyl ethers of $C_{10}n_8$ and $C_{10}n_{11}$ have been similarly prepared.[21] However, while this type of "semi synthesis" is valuable, because of the difficulties inherent in the purification, it is better, wherever possible, to start a synthesis with pure monodisperse compounds.

Purification and Assessment of Purity The detergents are normally extracted from the reaction mixture by a suitable detergent-selective solvent such as warm petroleum ether (BPt 60-80°) and the crude extract distilled. Some impurities remain, however carefully the extract is distilled. But distillation can only be carried out on compounds with glycol chains of up to six ethylene oxide units, for with higher chain lengths rapid breakdown occurs.

Where the compound is solid, it can be recrystallised. Elworthy and Macfarlane[8] recrystallised $C_{16}n_9$ from ether and acetone and Carless *et al.*[25] repeatedly recrystallised the same compound from petroleum ether at room temperature and from ethanol at 0°C. Even when such procedures are possible the detergent is still not pure enough for physical measurements. This is shown to be true, apart from any chromatographic evidence, from the discrepancies in the critical micelle concentrations between the unchromatographed but recrystallised product of Carless *et al.* and the recrystallised and chromatographed former product. The CMC's were 9.9×10^{-5} Moles/l and 2.09×10^{-6} Moles/l. respectively.

Chromatography on alumina or silicic acid has been utilised by a number of investigators.[8,10,15,22,26] It is a wasteful process in terms of yield, but is essential. A disadvantage of alumina is its catalytic action on acetone, a common solvent, causing the formation of insoluble diacetone alcohol[27] which is very difficult to remove from the product. Unsaturated products and carbonyl containing compounds were the main impurities found but these were successfully removed by chromatography. Minor fractions containing the impurities were generally found to precede the main cuts. Chloroform-acetone mixtures have been used[10] but Macfarlane used alumina, adsorbing the detergents from benzene and eluting with acetone-benzene mixtures. Methanol-benzene-acetone mixtures were employed to elute compounds with longer glycol chains (n_{15} and above).

A recent paper has described a general column chromatographic method of separating non-ionic surfactants from each other and from related non-ionic materials.[28] Silica gel was used as an adsorbent and results were obtained with a number of three and four component detergent mixtures.

The removal of ionic agents from non-ionics is conveniently accomplished by ion-exchange in solution.[29,30]

Infra-red spectroscopy is a useful means of rapidly detecting impurities in the detergents before and after chromatography. Unsaturated products are readily detected[10,17] and the fractions of a chromatography run thus readily characterised.

The principles and utility of nuclear magnetic resonance in structure determination of surfactant chemicals has recently been discussed by Crutchfield and Irani.[31] Flanagan *et al.*[32] and other workers[33] have discussed its quantitative application, especially in the field of commercial ethylene oxide adducts. Properties such as average molecular weights, degree and kind of branching of alkyl chains and average lengths of ethylene oxide chains can be determined, the accuracy being in the order of ± 2% of the total hydrogen in estimations of ethylene oxide conte

Thin-layer chromatography is useful as an initial means of assessing the purity of the final product. However, Weller[12] has found the method insufficiently sensitive to reveal the impurities that caused minima in surface tension - concentration curves. Using silica plates 5μl quantiti of 1% solutions in methanol were used. Mansefield and Locke[15] were able in similar fashion to detect 5% of impurities in samples of octyl phenol ethers. In separate experiments samples were diluted with 5% of various other homologues and applied to the plates. The solvent system was 40:60 acetone:benzene and the spots were developed with aqueous potassium permanganate. In this way OPn_4, OPn_5, and OPn_6 were well separated. Obruba[34] has also employed the technique.

Gas-liquid chromatography has been used by a number of workers on lower molecular weight compounds[35-38] and recently it has been extended to compounds with six ethylene oxide units,[12] higher compounds being precluded because of their high boiling points. Pure compounds exhibit only one peak in the elution diagram.

Estimation of hydoxyl groups by conventional methods requires large samples if the results are to be of a high degree of accuracy, as the -OH group is a small part of the total molecule. Many assays have been developed to estimate the ethylene oxide content of the detergent. Some involve complex formation, for example with silico-tungstic acid[39] or with phosphomolybdic acid,[40] and the determination of the complex. Siggia *et al.*,[41] using a modification of the hydriodic acid method of Morgan,[42] have produced a specific and absolute method for the ethylene oxide content which is accurate to within ± 0.6%. The ethylene oxide content can also be rapidly determined using infra-red absorption at 2485 mμ with carbon tetrachloride as solvent.[43] Using a standard plot of extinction *vs.* % ethylene oxide, Voogt obtained a standard deviation of 0.4% for compounds with more than 30-35% glycol content. Uno and Miyajima[44] obtained an accuracy of ± 3% with a volumetric method involving sodium tetraphenyl borate on non-ionic detergents with more than ten ethylene oxide units.

Hummel[45] has recently reviewed other methods of analysis of detergents.

Foam-fractionation has been employed to separate an iso-octyl phenol condensate into fractions with differing ethylene oxide chain length,[46] and it may be used, also, to separate impurities from homogeneous compounds.[47,48] Schott[48] used a tubular cellophane membrane of average pore size of 48 Å, that is, smaller than the micellar diameter of 65 Å of the detergent used, dodecanol n_{30}. Water soluble impurities and non-associated detergent molecules were chief constituents of the ultra-filtrate and this has permitted the removal of inorganic and organic impurities, including oxidation products of the detergents. With low CMC's the loss of detergent is small.

Counter-current distribution has also been suggested as a method of analysing fatty acid ethylene oxide adducts[49] but the method is complex.

A Table of references in the literature to synthetic non-ionic detergent is given below. The dearth of compounds with ethylene oxide chain lengths o 9 units or more is a reflection of the difficulty involved in their synthesis.

Literature References to Synthetic Non-ionics

Ethylene Oxide Units : Carbon Chain Length.	1	2	3	4	5	6	7	8	9	Others
4	16		10			10				
5	7									
6	7		11	11	11	11				
7	7									
8	7					10 14			166	
9										
10	12	12	12	12	12	12 21	12	12	166	
11										
12	7 12	12 18	12 18		11 23	10 14 24	23		23	23(n_{12}
13								4		
14		18	18	18		14 24				
16		18	18	18	11	8 10 25	8	22	8 25	8($n_{12,15,2}$
18	18	18		18						

Micellisation in Solutions of Synthetic Non-ionic Detergents

Since the initial work of Gonick and McBain[50,51] on the commercial non-ionic detergent Triton X-100, micelle formation in non-ionic surfactant solutions has been studied extensively. Much of the work has dealt with commercial products but lately there has been a bias towards studies on synthetic compounds. As the earlier work has been covered in two recent reviews[52,53] the present account deals mainly with pure, homogeneous non-ionic detergents.

The standard techniques of surface tension, light-scattering and viscosity have been commonly employed. Other techniques used include osmometry[54,55] ultracentrifugation,[54,56] dye solubilisation,[23] diffusion[57] and ultrafiltration.[47]

The picture that has emerged from earlier studies is that, above a certain concentration in aqueous solution (the CMC), the monomers orient themselves with their hydrophobic chains in a liquid state in the interior of the micelle and with their PEG chains directed out into the bulk of the solution, water being trapped in the mesh of these chains. The PEG chains are not fully extended in the micelles, being coiled in some manner. Rosch[58] claimed that a contracted gauche form[59] of the chain was most likely and it was suggested[60] that this configuration was stabilised by hydrogen bonding between water molecules and adjacent ether oxygens.

Micellar Size, Shape and Hydration in Aqueous Solutions. Several authors have studied homologous series of synthetic detergents. Elworthy and Macfarlane[8,16,62] worked with a series based on hexadecane with varying polyoxyethylene chain length. Corkill and Goodman and co-workers[10,63,64] on the other hand, investigated the effect of hydrocarbon chain length on compounds based on hexaoxyethylene glycol.

The effect of hydrophobe and hydrophile on the critical micelle concentration and micelle size of these detergents is shown in Figures 1 and 2. Increase in hydrocarbon chain length results in an increase in micellar weight and decrease in CMC. Increase in the glycol chain length results in increased solubility and hence a decrease in micellar weight and an increase in CMC, the former effect being less pronounced for compounds with more than nine ethylene oxide units.

Micelles formed by detergents with short alkyl chains of up to 12 carbon atoms are relatively small and, as a result, light-scattering disymmetry studies do not indicate asymmetry of the aggregates. The work on the hexadecane series, however, provided definite information on micellar shape. $C_{16}n_9$ and $C_{16}n_{12}$ had micellar weights of 140,000 and 117,000 respectively and were spherical at 25°C.[61] $C_{16}n_6$ and $C_{16}n_7$ showed appreciable Z_{45} values at higher concentrations, indicating that some dimension of the micelle had become greater than $\lambda/20$ [8]

Light-scattering studies on the compounds $C_{16}n_6$ and $C_{16}n_7$ have indicated a fall in c/τ values with increasing concentration. This suggested that the detergents were forming larger units as the total concentration was increased. An attempt was made to analyse the results using the law of mass-action in the form,

$$K = \log c_2 - m\log c_1$$

where c_2 was the concentration of large micelles and c_1 the concentration of small micelles , m being the number of the latter aggregating to form the larger units. Using the expressions $\tau_1 = HM_1c_1$ and $\tau_2 = HM_2c_2$ for

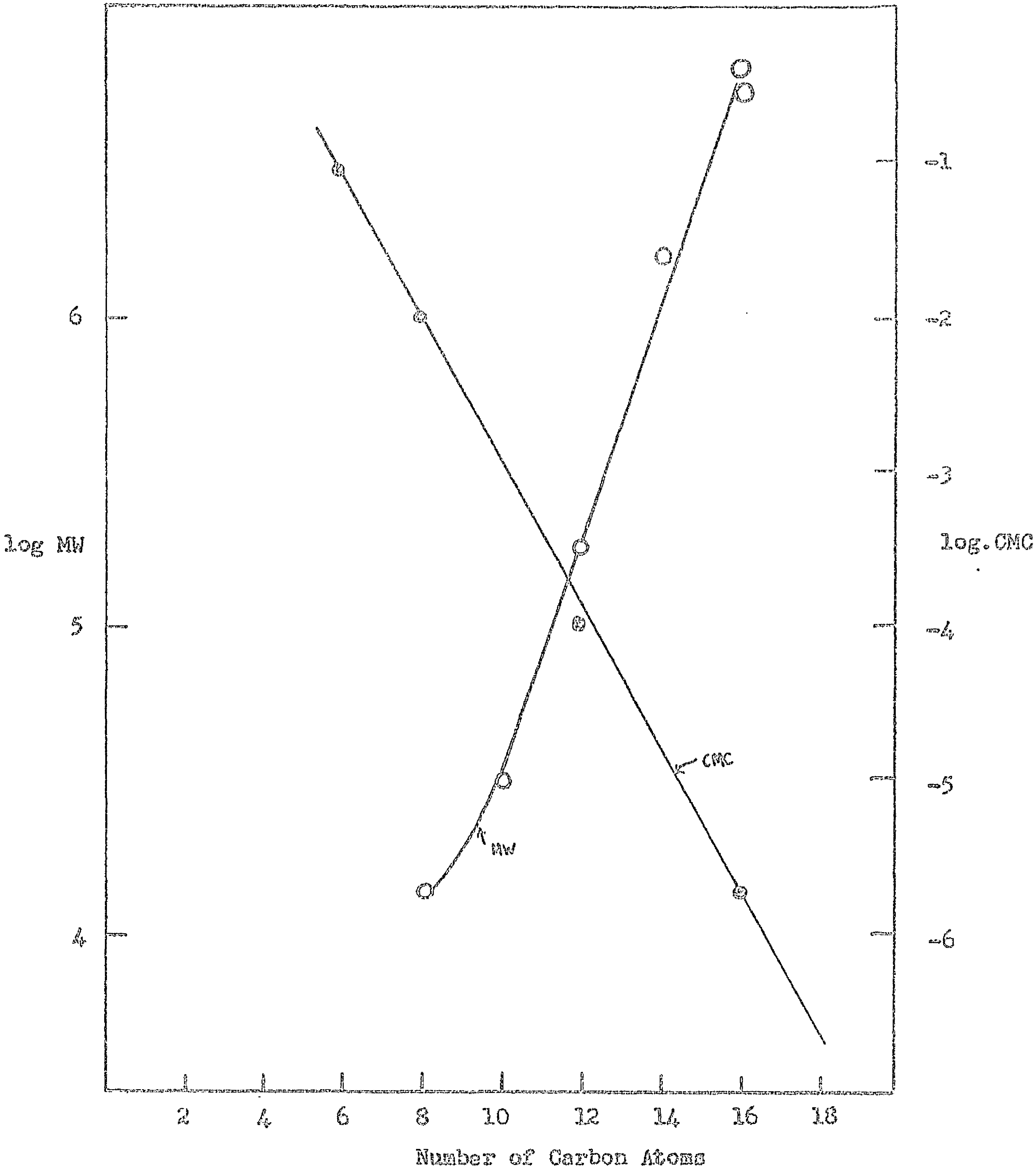


Figure 1: Effect of Hydrocarbon chain length on the micellar weights and critical micellar concentrations in the hexadecane series.

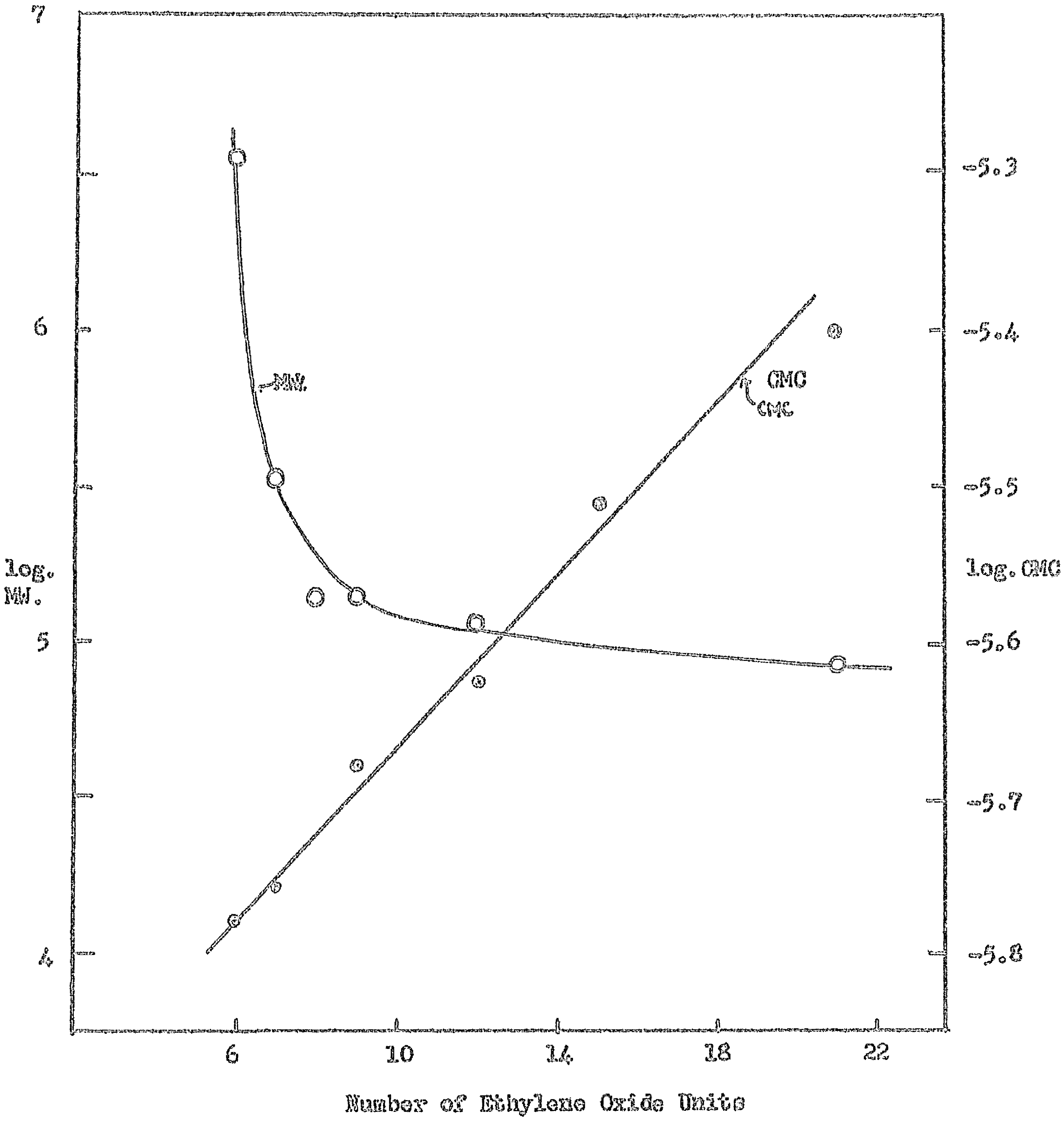


Figure 2: The effect of ethylene oxide chain length on the micellar weights and critical micellar concentrations in the hexadecane series.

the turbidities of the small and large units respectively, satisfactory agreement was obtained between observed and calculated turbidities for $C_{16}n_6$ and $C_{16}n_7$.

It is not known whether aggregation of small micelles into larger micelles is a universal phenomenon. $C_{16}n_5$ is insoluble in water[17]; $C_{16}n_6$ is soluble only over an 8° temperature range, and the heptaoxyethylen glycol derivative has a relatively low cloud point. It is thus to be expected that their solutions are, to some extent, atypical. However Debye plots for the $C_{10}n_6$ and $C_{12}n_6$ detergents were also found to have an upward curvature at lower concentrations but only when the critical micell concentration derived from surface tension measurements (Co) was used in place of the light-scattering value (C_L) inthe calculation of (C/τ) . Balmbra *et al*[63] also interpreted these results as indicating a miceller weight increase with increasing concentration. It seems unreasonable, however, to use Co, as there are always discrepancies between the two values although it would appear that they should be equal.

C_L has in most cases been found to be greater than Co. It has been suggested[13] that in the region between Co and C_L small aggregates are formed with solution turbidities almost indistinguishable from that of the solvent. This indicates a gradual formation of micelles, whereas turbidity concentration plots generally show a sharp break around the critical micell concentration, as do surface tension - concentration curves. It may be that the reason for the upswing of the Debye plots at lower concentrations in some systems - it seems genuine in compounds with very large aggregation numbers and very low CMC's - is the inaccuracy of the turbidity data at low concentrations combined with the error resulting from the choice of CMC from experimental turbidity - concentration graphs. At very low turbiditi small changes in concentration have a great effect on the value of $(C-C_L)/(\tau-\tau_L)$.

Until the problem is solved it seems logical to use C_L values for the monomer correction thus obtaining the concentration of the main colloidal species, $C-C_L$, and its turbidity $\tau-\tau_L$.

Hydration: The solubility of these non ionic detergents is due to the hydration of the PEG chain. The estimation of the degree of hydration is a complicated matter because of the difficulty in separating the effects of asymmetry and hydration in results of hydrodynamic experiments. However Boehmke and Heusch,[65] on the basis of viscosity results, suggested that 4 water molecules were associated with each ether oxygen. Kushner and Hubbar estimated that there were 43 molecules of water for each glycol chain in micelles of Triton X-100, equivalent to 4 molecules per ether oxygen, but older data of Greenwald and Brown[67] suggests that 2 water molecules are associated with each unit. Other values obtained by various means are 1, 2, 3 and 4 water molecules per ethylene oxide unit[68-70] and various arrangements of this hydrating water have been proposed with oxonium formati or hydrogen bonding as the primary cause. While suggesting that 4 molecule of water were associated with each oxygen atom Kushner and Hubbard state that of these only two could be hydrogen bonded, the rest being physically trapped.

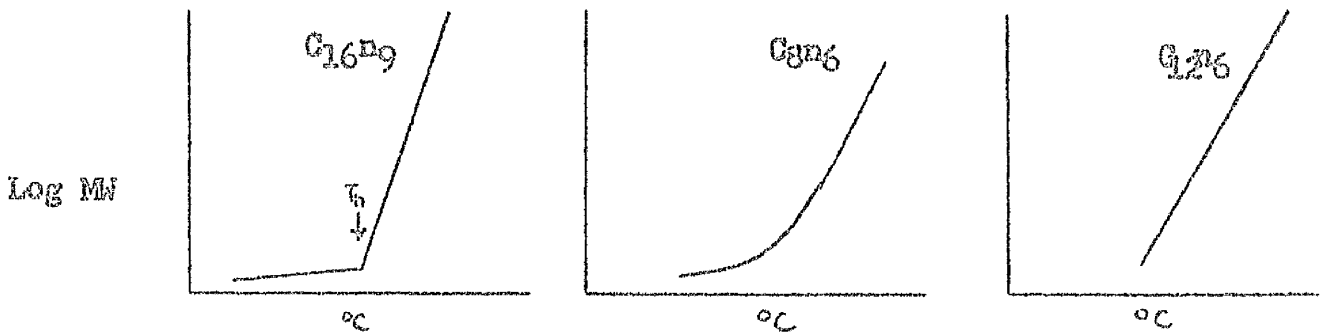
That trapping of the water molecules occurs in the mesh of PEG chains and contributes to the hydration is also suggested by the results of Elworthy and Macfarlane[8] who found that the hydration per ethylene oxide unit increased with increasing glycol chain length, but depended also on the degree of contraction and configuration of the chain and on the geometry of the micelle.

These authors developed an empirical method of estimating hydration based on vapour pressure measurements on detergent gels and solutions. In what seems to be the first direct method of measuring micellar hydration, the authors found that a specific arrangement of water molecules was not in accord with the thermodynamic results. Endothermic ΔH values and positive ΔS values indicated that the interaction between water and glycol chains represented a mixing process rather than a specific ordering in concentrated solutions.

Effect of Temperature An increase in temperature results in an increase in micellar weight[8,22,63] and decrease in CMC and in the enthalpy and entropy of micellisation.[64] At a certain temperature, termed the cloud point, phase separation occurs. The existence of cloud points has generally been explained by a decrease in the hydration of the glycol chain as the temperature is raised[64,72] and the changes in the thermodynamic parameters have been similarly explained.[64]

There appears to be two types of temperature-dependent behaviour. Some systems exhibit a slow increase in micellar weight with increasing temperature; others show a rapid increase above a threshold temperature, T_h . Recently it was found[22] that the micellar weights and intrinsic viscosities of three non-ionics, $C_{16}n_7$, $C_{16}n_8$, and $C_{16}n_9$ increased with temperature. It was concluded that the hydration, estimated independently by viscosity and vapour pressure, also increased. As the temperature was raised there was a general extension of the glycol chain and it is possible, as the authors wrote, to "visualise a state of affairs where water may come into contact with the surface of the hydrocarbon, giving rise to a sudden increase in interfacial tension...which would have a contracting effect causing the micelle to elongate." Although tentative, this picture provides a starting point in the understanding of the sudden growth of the micelles of this series at T_h. The cloud point is here visualised as being due to the growth of mammoth micelles, visible to the naked eye.

Some systems do not show this sudden exponential growth, and this is undoubtedly due to the delicate balance between hydrophobe and hydrophile. The growth in systems of $C_{16}n_8$ and $C_{16}n_9$ was less marked than in those of $C_{16}n_7$. No such increase was found in $C_{16}n_6$, $C_{10}n_6$ $C_{12}n_6$ or $C_{14}n_6$ although C_8n_6 showed the behaviour to some extent (see Figure 3.)



Behaviour of Micellar Weight with Temperature
<u>Figure 3</u>

Balmbra *et al.*[63] explained micellar growth to be due to the decreased overall hydration of the monomer resulting in increased hydrophobicity; this seems likely to be the case.

Kuriyama,[72] investigating the effects of temperature in solutions of $C_{10}H_{21}(OCH_2CH_2)_{12}OCH_3$ in the presence of *n*-decane and *n*-decanol found the micellar weight to increase with temperature and the apparent second virial coefficient to decrease. Comparison with other systems is made difficult, however, as the number of oil molecules solubilised per micelle also increased. Elworthy and McDonald[22] also noted this decrease in second virial coefficient and they obtained negative values above T_h.

Effect of Additives The effect of electrolyte on micellar solutions was studied in order to elucidate some aspects of the hydration of the detergents. While there are, at present, only isolated results on pure non-ionics,[10] results have been reported by Schick,[73,74] Becher[60] and Kuriyama[75] on commercial compounds which show that an increase in sodium chloride concentration lowered the CMC, the effect being more pronounced the more hydrophilic the compound. The nonyl phenol ether, NPn_{10}, has an aggregation number of 100 in water, 113 in 0.3N NaCl and 126 in 0.5N NaCl. NPn_{15}, however, has aggregation numbers of 52, 58 and 53 in the same solvents. Corkill *et al.*[10] found the aggregation number of $C_{12}n_6$ in 0.1M NaCl to be 133 compared with 160 in pure water. The picture is far from clear though it would appear, from lowered cloud points and CMC's[52], that the effect of electrolyte is greater on the monomer than on the micelle, reducing its hydration and resulting in a greater tendency to micellise.

The zero slope of the Debye plots in electrolyte solutions suggested that there was little charge on the micelles.[76]

0.5M urea was found to lower the critical micelle concentration of a nonyl phenol adduct but to have little effect on the aggregate size.[73] The same author recently showed[77] that the CMC of *n*-dodecanol n_{30} was increased in 3M urea. This was attributed to an increase in the hydration of the ethylene oxide chains. Urea, however, has a generally accepted action of disrupting the structure of water[78,79] and it is difficult to see how this could result in an increase in hydration.

Further experiments are obviously essential to unravel the effects of both electrolyte and urea.

Phase Equilibria. Phase diagrams have been obtained for only a few synthetic non-ionics in aqueous media. Mulley and Metcalf[80] studied the system $C_{10}n_6$ + water, and Balmbra and co-workers[81] the system $C_{12}n_6$ + water. (see Figures 4 and 5) Binary systems of monohexyl polyethers have also been investigated by Chekhovskoy.[82]

The similarity between Figures 4 and 5 is evident. It is apparently unusual to find readily characterised middle and neat mesomorphic phases separated by a narrow viscous nigre region all existing at the same room temperature[81,83,84] as was found for $C_{12}n_6$.

The cloud point marking the boundary between regions A and B is shown to be concentration dependent. It is generally agreed that the existence of a cloud point (lower consulate temperature) in aqueous media is a consequence of hydrogen bonding between solute and water. Copp and Everett[85] have suggested that the perturbation of the hydrogen bonded solvent system by the "inactive" portions of the solute molecules such as the hydrocarbon chains is also an important factor. However in the $C_{12}n_6$ + water system most of the detergent is in micellar form at the cloud point and the influence of hydrophobe is thus limited.

It has been stated before that the cloud point has been regarded as bei due to the dehydration of the glycol chains with increasing temperature with the eventual separation of the detergent. The results of Elworthy and McDonald[22] appear to indicate that this is not the case. Garret[86] has also pointed out that it is not necessary to refer to hydration of the molecule nor to dehydration as an explanation of the separation of the detergent on heating. Non-ionic detergents form micelles at low concentrations (in general) and share with the inert gases, hydrocarbons

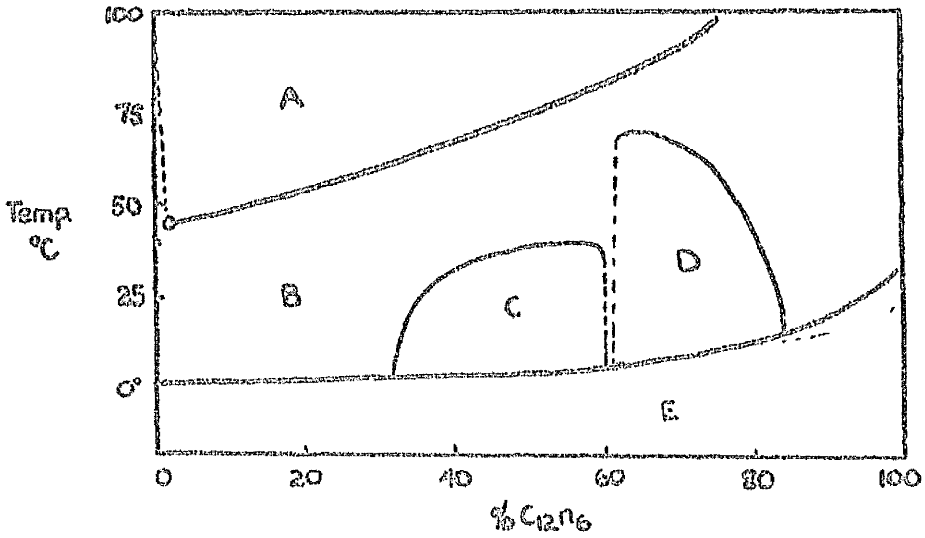


Figure 4: Phase Diagram of $C_{12}n_6$ in water, after Balmbra *et al.*

Notes: A = 2 isotropic liquids; B = one isotropic liquid; C = middle phase; D = neat phase; E = solid + ice; S = solid LC = liquid crystal.

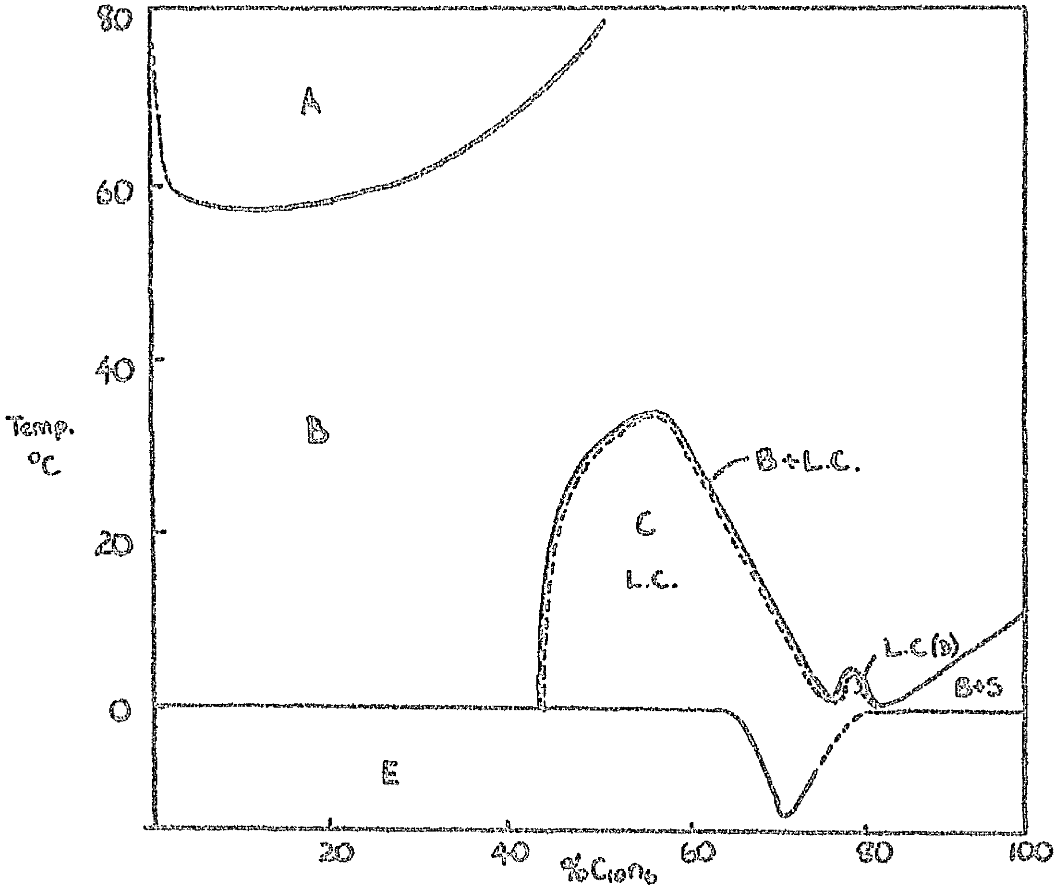


Figure 5: Phase Diagram of $C_{10}n_6$ in water, after Mulley and Metcalf.

and many calcium salts, the fact that they are more soluble at lower temperatures than higher ones.

Garret goes on to say that since compounds are known with cloud points ranging from nearly 0°C to 100°C it would be "odd indeed if a dehydration mechanism had to be invoked which required a different temperature for each of a series of compounds homologous in either hydrocarbon or polyether parts of the molecule."

The hydrophobic character of isomeric alkyl phenol has been found to depend to a large extent on the number of methyl groups in the molecule, the cloud point decreasing in a regular way with increasing number of these groups. 2,4,6 tri-sec butyl phenol required double the number of ethylene oxide groups to give the same cloud point as the straight chain analogue; this seems to give substance to the arguments of Garret and Elworthy and McDonald.

Solubilisation of Orange OT (1-o-tolyl-azo-2-naphthol) has been investigated in a non-ionic system.[81.] Other authors have studied the solubility of benzene, n-octanol, and 4-chloro-3,5-xylenol in aqueous systems[80,87] Changes in the CMC in these ternary systems were small in the presence of additive, supporting the suggestion of Ekwall that only when ionic effects are important do large changes occur in the CMC.[87] Mulley and Metcalf[80,87] suggested that the liquid crystalline phase consisted of laminar micelles in an ordered arrangement; Hartley regarded this phase as the only region in which laminar micelles existed. In ternary systems the liquid crystalline phase is found at extremely low concentrations of detergent. Short chain detergents (e.g. C_6) do not exhibit the phase at all.

It was thought that there was some connection between the decrease in turbidity with concentration above certain concentrations and the phase behaviour of two non-ionic systems, dodecylamine-oxide + water and $C_{12}n_6$ + water. The first mesomorphic phase formed by the former system has the microscopic appearance of a typical middle phase,[90] shown to be due to irregular hexagonal arrangements of cylinders.[84] However it first appears at 34% w/v; the turbidity maximum is at 9%. Similarly, for the $C_{12}n_6$ system the mesomorphic phase begins at 30% whereas the turbidity begins to fall at 5%.

There is apparently no evidence from phase diagrams for the existence of simple complexes between glycols and various solutes,[80] although such complexes have been suggested.[91]. Evans[92] found that the evidence weighed against specific interaction between benzoic acid esters and polyoxyethylene ethers. Higuchi and Lack,[91] however, suggested complexation of polyglycols and benzoic, salicylic and p-hydroxy benzoic acids. Complexation between phenols and non-ionics has been put forward as an explanation of the inactivation of preservatives by the detergents, the interaction arising from protonation of an ether oxygen.[93] A more probable explanation is the solubilisation of the preservative in the detergent micelles, although recent work has presented evidence against the micellar solubilisation of iodine in an iodine-cetomacrogol system.[94]

An interesting study has been made of benzene solubilised in aqueous surfactant systems[95] which showed that the benzene molecules were constantly exchanged between micellar and aqueous phases. A rather surprising result, however, was that the lifetime of the solubilised molecule in the micelle was in the order of 10^{-4} seconds. This was found to be reasonable on account of Brownian movement and diffusion coefficients, and the result is useful in clarifying ideas on solubilised systems.

Mixed Micelle Formation Kuriyama et al.[97] have determined the aggregate molecular weights of a non-ionic (methoxy dodecyloxyethylene dodecyl ether) and an ionic detergent (sodium dodecyl sulphate) mixture at various temperatures. With increase in temperature the aggregate molecular weight increased, but the non-ionic character was progressively suppressed by further addition of the ionic detergent until, when the concentration of the latter reached 20%, the micelles behaved as ionic micelles. Corkill, Goodman and Ottewill[10] studied $C_{12}n_6$ at a constant concentration of sodium dodecyl sulphate (SDS). The molar ratio, $C_{12}n_6$ / SDS, varied from 33 to 2 over the concentration range. The consequent large alteration in micellar charge which occurred was used to explain the marked increase in the values of the Debye plots at lower concentrations. Qualitatively it appeared that the results could be explained using a modified Prins-Hermans equation[98] if the charge on the micelle was assumed to be directly proportional to the amount of dodecyl sulphate absorbed by the micellar phase, and if the remaining SDS was assumed to function as an ordinary electrolyte in the system.

It has also been found[64] that the progressive reduction in charge density which occurs as the ratio of ionic to non-ionic decreases results in an increase in the degree of dissociation of the ionic component in the mixed micelle.

Non-Aqueous Systems There have been few studies on non-ionic detergents in non-aqueous solvents. Siriani and Gingras[24] found $C_{12}n_6$ and $C_{14}n_6$

in monomeric and dimeric states in benzene at 30° by a vapour pressure technique, but Becher[99] found an aggregation number of 99 for the very similar compound, $C_{13}n_6$ by light-scattering. A similar result with an highly branched C_{13} homologue indicated that the sizes of the micelles were largely dictated by the properties of the "solvophobic" part of the detergent molecule making up the micelle interiors.

Micellar weights of 48,000 and 89,000 at 25° and 45° respectively were found for sorbitan mono-stearate in benzene.[54] However, no systematic work has been carried out in non-aqueous solvents and it is difficult to draw conclusions as to the nature of the forces affecting aggregation in these systems.

The Structuring of Water

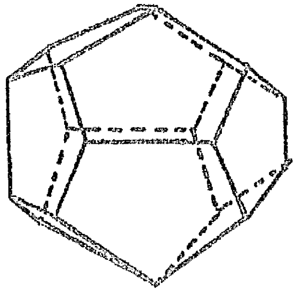
The structural aspects of water and the structuring effects of hydrocarbons and other solutes in aqueous solution are of fundamental importance in the discussion of micellisation in water, especially in elucidating the energetics of micelle formation of both ionic and non-ionic detergents.

Water is the extreme case of a hydrogen bonded liquid. Its structure is largely determined by a tetrahedral co-ordination imposed by the hydrogen bonds, and this gives rise to its anomalous properties. The water molecules can participate in four hydrogen bonds, two of them involving the hydrogen atoms, and two the lone pair of electrons of the oxygen and the hydrogens of two neighbouring molecules. This tetrahedrally arranged bonding also obtains in ice structure.

There has been much discussion in recent years on the structure of water and of dilute solutions of electrolytes and non-electrolytes.[100-106] Frank and Wen[101] first suggested that the distinctive structural features of water were "roughly" explained by the statement that it (water) retains a certain similarity or analogy to ice. This amount of "ice-likeness", indeed, has been the basis of many of the discussions. It can be altered by changes in temperature and pressure and by the presence of solute molecules.[102]

Wada[107] presented a simple model for the structure of water, and suggested that water is an equilibrium mixture of ice-like structures and close-packed structures, the relative amounts changing continuously with temperature. The mole fraction of ice structure, X, he determined using

using expansivity data. X was found to be 0.2 at 100°C and 0.4246 at 0°C. In the packed state of liquid water the first neighbour distance is 3.46 Å ; in ice-like structures it is 2.76 Å . The observed value of 3.1 Å suggested the existence of both states in water. Frank and Quist[108] prepared a statistical thermodynamic treatment of the model for liquid water proposed by Pauling[109] in terms of a variable distribution of water molecules between two states, "framework" and "interstitial" water. The model[108,109] has frameworks of ordered water so arranged as to contain voids in which non-hydrophilic molecules can be trapped. The frameworks are pentagonal dodecahedra of twenty water molecules (see figure 6), the void being 5 Å in diameter. Frank and Quist considered the interstitial molecules - the unbonded water between the frameworks - to be rotationally unrestricted. They also proposed a third state, partly unbonded but otherwise without specifications, to furnish an explanation for the deviation of the observed results from simple model behaviour. Other authors[110] have written of the "quasi-crystallinity" of water.



A pentagonal dodecahedron of 20 water molecules.

Figure 6.

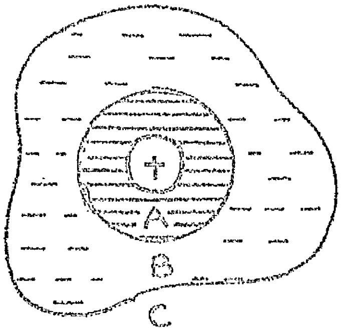
One of the difficulties in producing a well-founded theory of liquid water[103] is reflected by the fact that no reliable values exist for the energy of breaking the OH...O hydrogen bond in water, although a value of 4.5 K cals/mole has been quoted[109] and Forslind[111] gives a value of 4.44 K cals/mole for the association energy of the hydrogen bond in water.

In their model Nemethy and Scheraga[103] built on the one suggested by Frank and Wen[101,102] whose concepts of a charge separation arising in the resonance scheme of the hydrogen bond and the consequent co-operative character of hydrogen bonding were employed. These forces, in turn, lead to the formation and dissolution of clusters of hydrogen bonded molecules which are short-lived and do not extend beyond a few molecular diameters. Ice-like clusters - extensively hydrogen bonded - were considered to form. The term "ice-like", as Nemethy and Scheraga pointed out, refers only to the extent of hydrogen bonding and does not imply that clusters have the tridymite arrangement of ordinary ice. Calculation by the proponents of this model have shown that about 2/3rds. of the molecules can participate, at any given instant, in the formation of clusters. The unbonded molecules thus occupy, in this model, about one to two surface layers around the cluster.

However, the exact nature of these clusters is still uncertain, as Mysels has pointed out after consideration of the light-scattering behaviour of pure water.[113] Despite the difficulties in the determination of turbidity it seemed to Mysels that the excess turbidity due to structural heterogeneity above that due to pressure fluctuations was very small, and did not seem compatible with a model which involved compact "icebergs" separated by a "liquid" nor with a large volume fraction of molecularly sized random vacancies. A network arrangement with cavities which was predominantly filled would be acceptable, he stated, thus coming down in favour of a modified form of Pauling's and Frank and Quist's model.

Water Structure in the presence of Solute Ions or Molecules

The structural effects of ions has been discussed by Frank and Wen.[101] It is well known that most ions are surrounded by a hydration shell in which the water molecules are oriented and largely immobilised (Figure 7). The net effect of most ions is, however, a loosening of structure as in region B of the figure. This is indicated by the entropy of hydration which is more positive than might be expected if the hydrated ion was surrounded by normal water. The random nature of region B is caused by the balance between the normal structural orienting influence of neighbouring water molecules and the orienting influence of the dipole of the spherically symmetrical ionic field. In this region the formation of clusters may be prevented.



Region A : region of immobilisation. Region B : water more random than normal water. Region C : normal water polarised in normal way by the ionic field.

Figure 7: The effect of an Ion on the structure of water.

Some ions, however, have a different effect. Frank and Evans[112] postulated that an ion which was small or multiply-charged or both (for example Li^+ or Mg^{++}) might induce additional structuring beyond the first layer (A) and this could be envisaged as wiping out the second, random layer, resulting in an overall structure increase. There are thus structure breakers and structure makers. In an attempt to make these terms conceptually more precise Herts[114] found that certain properties of solution indicated a structure increase and others a decrease in the number of hydrogen bonds in solution, and concluded that the structure increase must be such that it is accompanied by rupture or deformation of hydrogen bridges.

More relevant to the study of micellisation is the effect of hydrocarbons and other non-polar solutes on water.

Aqueous solutions of non-polar substances show an apparently anomalous thermodynamic behaviour. The partial molal heat capacity, for example, is much higher in solution than in the pure liquid state.[101,104] It was Frank and Evans[112] who introduced the concept of "iceberg" formation around non-polar solutes, according to which the water molecules were more ordered around the solute, with an increasing preponderance of hydrogen bonding in this region. The "melting" of these icebergs with increasing temperature would account for the high partial molal heat capacities.

Frank and Wen postulated that the formation of hydrogen bonds in water was a co-operative phenomenon such that when one bond formed, several formed, and when one broke, whole clusters "dissolved". From this follows the picture of flickering clusters of half life 10^{-10} seconds.

Support for the ordered arrangement of water came from the existence of crystalline hydrates of several non-polar gases and liquids at various temperatures and pressures, above 0°C. Even non-polar side chains of large ions such as the tetra-n-butyl ammonium salts can participate in the formation of crystalline hydrates,[115,116] and in an analogous way non polar solutes can be expected to stabilise a near region of water molecules.

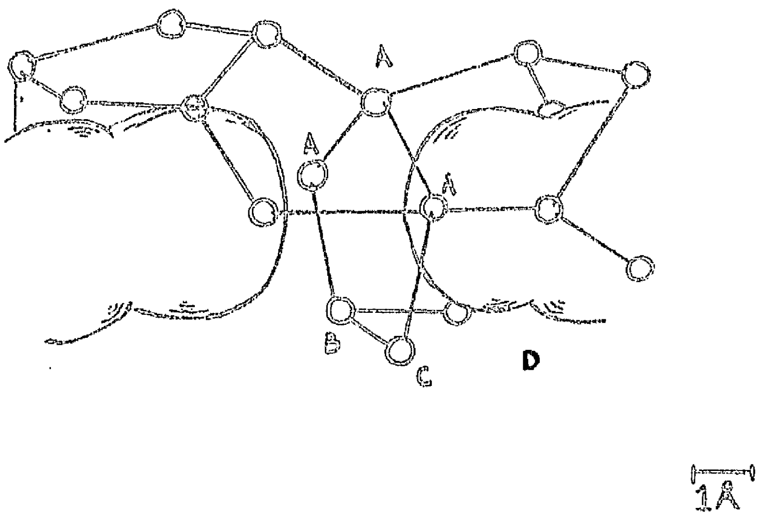


Figure 8: Schematic drawing of two hydrophobic, non-polar molecules with a single layer of water molecules between their ends. The single layer constitutes AAABC. Region D has unbonded water molecules. A, B and C are tetra-, tri-, and di-hydrogen bonded water molecules respectively. Drawing after Nemethy and Scheraga.

Clusters come into existence as in pure water, but the disruptive influences, such as the motion of thermally disordered water molecule neighbours, are not transmitted to the cluster by the non-polar molecule. Thus, as the cluster is protected, an ice-like patch exists for a longer time; a region of increased ice-likeness arises in the vicinity of the solute (see figure 6.). Herrington,[117] after studying the solubility of aromatic hydrocarbons, formed the opinion that aromatic systems do not form icebergs in water.

Frank[102] used the data of Haggis, Hasted and Buchanan[118] on dielectric relaxation times of various electrolytes and non-electrolytes in water as support for the above picture. If extra ice-likeness is characterised by lengthened half-life of the clusters, non-polar solutes should lengthen the relaxation times of the solution. This has been found in the case of $(CH_3)_4NBr$, which has a dielectric relaxation time of +5, $(C_2H_4)_4NCl$ with a time of +30, *n*-propanol with +35, iso-propanol +30 and LiCl with -10.[118] The negative value for lithium chloride indicates the structure breaking action of the ions.

Glew[106] has written a detailed account of the solubility of methane in water and a survey of the solubilities of other gases which form hydrates. He showed that the standard enthalpy changes for the transition from liquid solution to liquid water and gaseous solute were very close to those for the transition from solid hydrates to ice and gaseous solute, for a large range of solutes. This was interpreted as meaning that the solute molecules in the liquid solution were surrounded by hydration shells containing no broken hydrogen bonds. (previous interpretations had necessitated broken bonds.) The shells were considered similar to the polyhedra of solid gas hydrates.

The pictures presented by Nemethy and Scheraga[103-105] and Glew[106] are very different. Glew's view seems consistent with that of Pople[100] in which there is bending rather than breaking of hydrogen bonds i.e. in the presence of solute the hydrogen bonds are not broken but form a cage around the solute. The loss of freedom of libration or hydrogen - bond bending must account for the entropy change which is large and negative. Barker[119] has found the accounts of Frank and Wen and Nemethy and Scheraga of the origin of the stabilisation of clusters "unconvincing" for he writes, "... it is not clear why an unbonded water molecule could not play exactly the same role as a solute molecule in stabilising a cluster". However this criticism appears ill-founded as the solute molecules which are non-polar cannot participate in the same interactions as the water molecules and hence the stabilisation arises through a form of protection.

Butler[120] has viewed the process of bringing a solute molecule into a solvent as involving i) the production of a cavity in the solvent large enough for the solute and ii) the introduction of the solute into the cavity. In the case of water, the energy required to bring the solute from vapour into solution was expressed as:

$$\Delta E = \sum \gamma(W-W) - \sum \gamma(A-W)$$

where the first term represented the energy to separate the water molecules and the second represented the interaction energy of the solute (A) and water.(W) Where there are $\underline{m}$ water molecules involved, with $\underline{a}$ molecules of water adjacent to the group(solute)

$$\Delta E = m/2\,\gamma(W-W) - \sum a\,\gamma(A-W)$$

Butler calculated values for the heat of hydration using these simple equations and found excellent agreement with experimental values. He admits , however, that this theory (based on the breaking of hydrogen bonds) should not be taken too literally as it was quite possible that small cavities could be made without such an extensive breakage of bonds as visualised. It has been suggested[121] that the energy required to make small cavities in water at low temperatures was indeed zero, or very small, since cavities either existed already or could be made by small expansions of existing holes. The heat of solution would, according to this view, be mainly the London interaction energy of the solute with the surrounding water molecules.

Hydrophobic Bonding

Whatever the finer points of water structure might be, the evidence is overwhelming that structuring exists and that hydrophobic bonding is an important phenomenon in biological and macromolecular systems.

Nemethy and Scheraga based their treatment of hydrophobic bonding in protein solutions on the behaviour of aqueous hydrocarbon solutions. An hydrophobic bond[103-105] was considered to be formed when two or more non-polar groups came into contact, thereby decreasing the extent of the interaction with the surrounding water. The bonds owe their existence mainly to the entropy change connected with changes in water structure around the side chains (figure 8); the endothermic nature of this process makes the bonds stronger with increasing temperature up to 50° or 60°C. It is perhaps relevant at this point to indicate that non-ionic micelles increase in size with increasing temperature (see earlier sections), and to suggest that increase in temperature would encourage dimerisation below the CMC.

The free energy of formation of the hydrophobic bond may be attributed

Table I

Transfer of non-polar side chains from water to a non-polar region at 25°C[a]

Side Chain	Structure	N[b]	ΔH_{trans} (Kcal.mole^{-1})	ΔS_{trans}[c]
Ala	$-CH_3$	8	1.5	9.4
Val	$-CH(CH_3)_2$	12	2.2	13.7
Leu	$-CH_2CH(CH_3)_2$	13	2.4	14.3
Ileu	$-CH(CH_3)CH_2CH_3$	13	2.4	14.5
Met	$-CH_2CH_2SCH_3$	15	2.7	16.0
CySH	$-CH_2SH$	10	1.8	11.4
Pro		12	2.2	14.0
Phe	$-CH_2C_6H_5$	15	2.7	16.1

---

a. from reference 105.
b. N is the number of water molecules associated with the structure.
c. cals.mole^{-1}degree^{-1}

Table II

Transfer of Hydrocarbons from Water to Non-Polar Region

Structure	ΔS cal.mole^{-1}degree^{-1}	Ref.
$CH_3CH_2CH_3$	23	122
$CH_3CH_2CH_2CH_3$	23	122
C_6H_6	14	78
$CH_3C_6H_5$	16	78
$CH_3CH_2C_6H_5$	19	78
$CH_3C_6H_4CH_3$	20	78

Table III

Transfer of Hydrocarbons from Water to Hydrocarbon Region*

Structure	ΔH Kcal.mole^{-1}	ΔS cal.mole^{-1}deg^{-1}
CH_4	1.97	15.3
CH_3CH_3	1.85	18.8
$CH_3CH_2CH_3$	1.41	21.2
$CH_3CH_2CH_2CH_3$	1.18	23.0

*25°C.

almost entirely to the reduction in the number of contacts the non-polar alkyl chain has with water molecules. The thermodynamic values of hydrophobic bonding are small as the bond does not involve the complete removal of the hydrocarbon from the solvent.

In micelle formation the non-polar group is removed completely from any contact with water. Various thermodynamic values have been computed by Nemethy and Scheraga,[105] by Kauzmann[78] and by Wishnia[122] for the transfer of non-polar compounds from water to a non-aqueous environment and these values are extremely useful in the elucidation of the hydrophobic contribution to micelle formation by surface active agents. These values are given in Tables I, II, and III.

The values of N in Table I are much greater than those suggested by Butler.[120] However, in a later paper Scheraga et al[123] use N/2 in a discussion of dimerisation.

It will be seen from table I that ΔH_{trans} becomes more positive with increasing chain length, while, from Table III, the opposite trend is observed. Table I has values mainly for branched chains and the extent of the contact between hydrophobes increases with size more slowly than for straight chains; also the effect of the protein backbone, which a does not participate in the bond but has a restraining effect, has been taken into account and these values would be more applicable to micellisation if one drew an analogy between the protein backbone and the polyoxyethylene chain. (see figure 9)

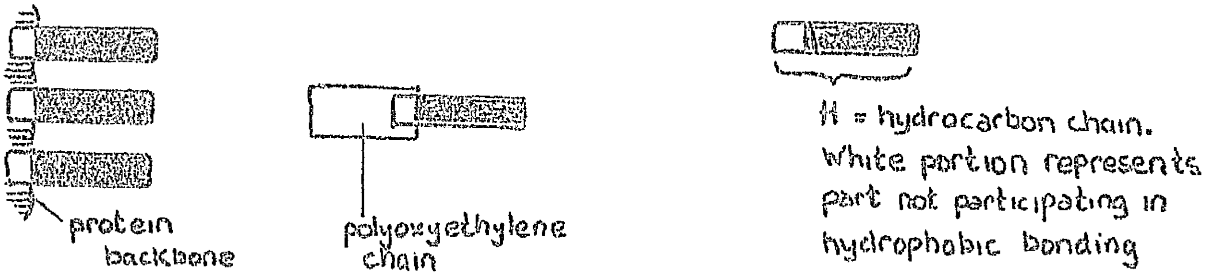


Figure 9: Analogy between protein backbone and PEG chain

Although Scheraga *et al*[124] carried out a reappraisal of their earlier calculations on hydrophobic bond formation this did not affect the values of table I nor the present arguments. Indeed further thermodynamic evidence for the process was obtained by consideration of the transfer of normal alcohols from aqueous solution into hexane and benzene at 20°C (Table IV); consideration of these values reveals that the main part of the entropy of the process arises from the contribution of the hydrocarbon chain.

While one must beware of attempting to explain every thermodynamic value on the basis of hydrogen bonding and hydrophobic bonding and the effect of water molecules, these concepts are useful in our understanding of the factors involved in micellisation. The theories of Nemethy and Scheraga have, at least, succeeded in giving values for comparisons with other data and processes.

The Importance of Water Structure in Aggregation

Dimerisation involves the approach of two hydrocarbon chains and the removal of a number of water molecules from their vicinity. Micellisation involves the complete removal of a number of hydrocarbon chains from the solvent and their placement in an environment of alkyl chains, thereby resulting in the removal of all the water molecules associated with the chain.

Mukerjee and Ray[125] investigated the effect of urea on micelle formation and hydrophobic bonding. Urea undergoes hydrogen bonding in water but has little effect on the polarity of the water. At high concentrations it reduces the co-operative structure of water, which is responsible for the solvent structure effects, without unduly affecting interfacial energies. It seems that urea affects mainly the entropy change on micellisation,

Table IV

Thermodynamic Values for the transfer of 1 Mole of Alcohol from Aqueous Solution into Non-polar Solutions

20°C

	Hexane			Benzene		
	ΔG	ΔH[1]	ΔS[2]	ΔG	ΔH[1]	ΔS[2]
Methanol	-	8.2	-	-	5.8	-
Ethanol	1.8	8.5	22.6	1.2	6.5	18.1
Propanol	0.9	9.0	27.8	0.3	7.2	23.7
Butanol	-0.15	9.6	33.2	-0.3	8.0	26.0

Taken from reference 124. [1] ΔH Kcals.mole^{-1}. [2] ΔS cals.mole^{-1}deg^{-1}

although its effect is small, raising the critical micelle concentration. A decrease in the chain length of alkyl pyridinium chlorides of only two CH_2 groups raised the CMC by a factor of 4; this suggested[125] that water effects might not be the whole cause of micelle formation and it was proposed that interfacial effects and entropic effects associated with the hydrocarbon chains were also important. They cited evidence that the addition of short chain organic compounds such as methanol and ethanol (6-8 Molar) had a greater effect on the CMC than urea, the effect no doubt being the lowering of the interfacial energy between hydrocarbon and solvent.

Solvent structure plays an important part in the association of dyes.[126] Although the detailed thermodynamics of association have not been satisfactorily worked out for any dye system, Rabinowitch and Epstein[127] derived heat and entropy values for the dimerisation of thionine, the entropy being approximately 1 cal.mole^{-1} degree^{-1}. Considering that the association of two similarly charged species should result in a loss of entropy, due to charge compaction over and above the loss of translational energy of one ion, the net positive result would suggest a large entropy contribution from a source which is most likely the water structure effect.

Uedaira and Uedaira[128] found that sucrose had a considerable effect on the association of two dyes even in low concentrations (up to 3% sucrose). As sucrose is hydrated with about 4-5 water molecules per molecule, its effect on the water structure around the hydrocarbon chains was again put forward as an explanation of its effect, especially as the more hydrophobic dye was affected.

The dissociation of insulin dimers provides further evidence of solvent effects. The large entropy loss on dissociation[129] must only arise from the immobilisation of water molecules. Using a value of 4.8 cals.degree^{-1}

for the entropy loss per mole of bound water, the dissociation was assumed to be represented by,

$$In_2 + 24\ H_2O \rightleftharpoons 2\ In + 12\ H_2O$$

On dissociation, the areas previously protected each became associated with twelve molecules of water.

Entropy of Hydration

The partial molar entropy of a substance in a solution includes not only the entropy of the solute but also any changes of entropy which the solute brings about in its action on the solvent.[120] Thus the partial molar entropy of a solute in water may be very low if, by either forming a cavity or restricting the water molecules' ability to rotate, it lowers the entropy of the water.

The presence of groups which form hydrogen bonds with water still further reduces the entropy of vaporisation and results in a decrease in the entropy of the solute. These entropy differences have a predominant effect on the solubility of any series of compounds. Frank and Evans have pointed out that ΔS_{hyd} for methanol is about the same as for ethane. The entropy drop in the case of the methanol is due to the iceberg formation around the CH_3 group and hydrogen bonding around the hydroxyl group, but the entropy effect is equivalent. Hydrogen bonding, however, produces a considerably larger value of $-\Delta H$.[120] The relative importance of hydrogen bonding and iceberg formation shifts in favour of the latter as the length of the hydrophobe increases. Benjamin also concluded that, although entropy changes provide the driving force for micelle formation with short chain compounds, with longer chain derivatives the enthalpy term predominates (see figure 10)

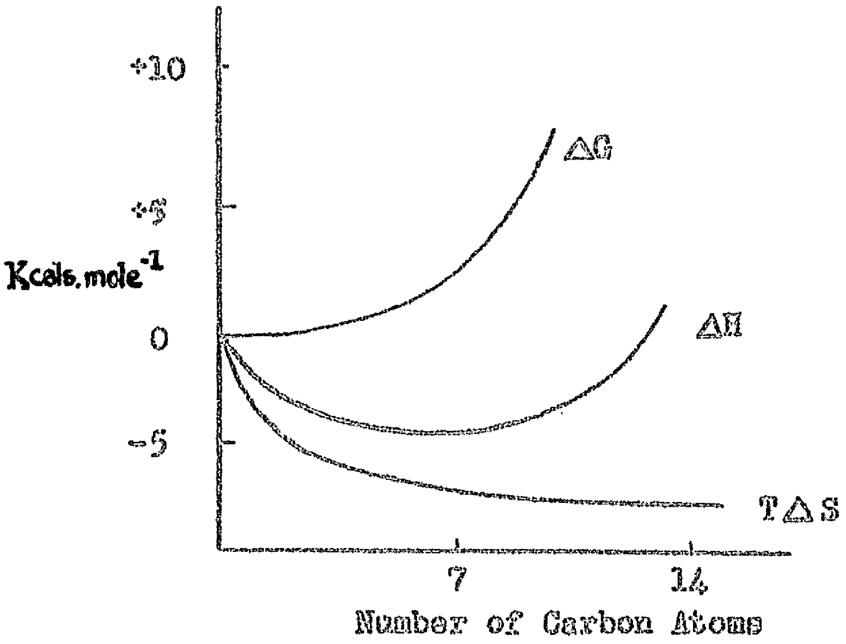


Figure 10: Standard free energy changes for solution of n-aliphatic alcohols in water at 25°C. From Benjamin, J.Phys.Chem.,1964,68,3575.

The Theoretical Basis of Micelle Formation

Micellisation is a complex phenomenon brought about by the interplay of a multiplicity of forces. It was realised early that, to distinguish between micelle formation and a complete separation of the detergent from solution, the cohesive forces leading to aggregation must be balanced by other forces. Debye[130] argued that the decrease in free energy arising from hydrocarbon-hydrocarbon interactions was eventually overcome by electrostatic repulsion. His theory has, however, been criticised,[131-133] the fundamental criticism being the fact that the calculations were based on minimising the free energy of the micelle, whereas the stable micelle must be that which results in the minimum free energy of the total system.

Reich[132] attempted to explain the stability of non-ionic micelles where there were no electrostatic effects. For ordinary solutes the energy of the system decreases indefinitely as the degree of aggregation increases. With detergents, the energy of the system reaches a minimum and no longer decreases after the micelles reach a certain size. Consequently, Reich explained, further micellar growth will not occur, as this would result in an entropy change. The picture of the non-ionic micelle drawn by Reich is that the hydrocarbon tails, curled up in the interior, are packed together until the hydrocarbon surface is completely covered and protected from the water by the polyoxyethylene chains. For the formation of this - the "complete" micelle - the aggregation number is given by N when

$$\left(\frac{A}{A-S}\right)\left(1 - \frac{1}{N^{1/3}}\right) = 1.$$

where A is the total surface of the hydrocarbon molecule, S is the area covered by the polar group in the monomer and, therefore, A-S is the exposed hydrocarbon surface. A "complete" micelle may not always be attained. If the polar group screens off a small enough portion of the molecule the aggregate may grow to its fullest extent before the surface is completely filled, and further growth would then involve flattening the aggregate. Such a change would not decrease the fraction of hydrocarbon eliminated from the solvent and hence would not be favoured. Reich was also able to postulate, correctly, that the CMC would decrease with increasing hydrocarbon chain length and increase with increasing glycol chain length.

Hoeve and Benson[134] later proposed a statistical mechanical theory of micelle formation in which the repulsive forces preventing micellisation appeared as a "crowding" term, depending on the volume to surface ratio. The interior of the micelle was again treated as a liquid and the rest of the cohesive forces were placed in the partition function of the monomer, which contained a so-called "hydrophobic interaction" between the water and alkyl chains.

Water structuring in micelle formation has been said to have a largely entropic rôle. Wishnia[135] has shown this to be emphasised by the relatively low heats of micellisation estimated calorimetrically,[136-138] by temperature dependence of the CMC,[139,140] or from vapour pressure measurements.[141] The heats of transfer of hydrocarbons from aqueous to a non-polar phase discussed in the previous section are, however, not inconsiderable. The low measured heats of micellisation are very likely to be due to the cancelling, and not the non-existence, of enthalpy effects by opposing forces such as those due to the polyoxyethylene chain in the case of the non-ionics.

The main contribution to positive entropy changes must come from the hydrocarbon chain or from its interactions with the solvent. Wishnia[135] obtained values for the transfer of short alkanes from water to micelles of sodium dodecyl sulphate (Table V). It appears that the interaction between solvent and solute is the main contributor to the entropy change, for it is difficult to imagine any significant configurational entropy change, as restriction of translational, rotational and vibrational motions for these alkanes will be limited in water. The decrease in ΔS with chain length (Table V) seems difficult to understand. It is possible, however, that the entropy of mixing effect of the short alkanes with the dodecyl chains of the detergent is significant.

Thermodynamics of Micelle Formation

There have been two main approaches to the theoretical description of micelle formation. On the one hand there is the mass-action approach in which the micelle is considered as a product of the reaction between single molecules, these being in equilibrium with the micelle. On the other hand there is the two-phase theory in which the micelles are considered to be a different phase, and the thermodynamics of a phase equilibrium are employed.

The Two-phase theory. In recent years many of the theories have been based on this approach. The model treats the micelle as a separate, but soluble, phase which begins to form at the CMC, which is regarded as the saturation concentration for the single solute species.[142-144] Shinoda and Hutchinson[145] have discussed micellar "pseudo-phase" formation. (The term "pseudo-phase" was used because of the proviso, mentioned earlier, of a limited aggregation and not a complete phase separation.

Table V

Thermodynamic Parameters for Transfer of n-alkanes from water to SDS micelles-25°

Alkane	ΔG^1	ΔH^1	ΔS^2
Pentane	-5.72	-1.08	15.6
Butane	-5.13	0.00	17.2
Propane	-4.23	1.00	17.5
Ethane	-3.45	2.00	18.3

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[1] Kcals. mole^{-1} ; [2] cals mole^{-1}degree^{-1}

Dimerisation, which is known to occur in some detergent systems below the CMC,[146] is not compatible with the theory. However, it has been pointed out[145] that acetic acid vapour separates into liquid acetic acid at a saturation vapour pressure although dimerisation occurs in the vapour beforehand, the liquid phase being in equilibrium with both monomer and dimer molecules. This analogy has been drawn in defence of the two-phase approach.

The model also necessitates that the activity of the detergent above the CMC is constant. Gibbs' Adsorption Equation may be written,[145]

$$-RT\Gamma_2 = \left(\frac{\partial \gamma}{\partial \ln a_2}\right)_T = \left(\frac{\partial \gamma}{\partial \ln N_2}\right)_T \left(\frac{\partial \ln N_2}{\partial \ln a_2}\right)_T$$

where γ is the surface tension and N_2 and a_2 the mole fraction and activity of the solute, respectively. Experiments involving radiotracers have shown that Γ_2 has nearly constant values over a wide range of concentrations in excess of the CMC.[147] If $\partial\gamma / \partial \ln N_2$ is zero, it follows that $\partial \ln a_2 / \partial \ln N_2$ is also zero. This has been said to be "impressive evidence of the phase separation model," as it is equivalent to the statement that the activity of the solute is independent of concentration above the CMC. The basic assumption here is that the surface tension, γ, is independent of N_2 above the CMC, and although this has been found to be true for one or two systems, it is by no means a positive fact. Indeed, dialysis experiments have shown that monomer activity increases with concentration above the CMC;[148,149] Elworthy and Mysels[150] found that the surface tension of ultrapure sodium dodecyl sulphate changed with concentration above the CMC. Recent work on non-ionic surfactants of the glucosyl alkyl benzene and glucosyl alkane class[151] and on polyoxyethylene alkyl ethers[152] indicate, directly by measurement of activity by freezing point depression in the former case and indirectly by ultrafiltration studies in the latter, that the activity of the non-ionic increases above the CMC.

The application of the phase rule to micellar systems has also been discussed by Pethica[153,154] who considered the inclusion of water in the equilibrium thus

$$mROH + hH_2O \rightleftharpoons \text{Micelle}$$

(where h represents the difference in hydration between monomeric and micellar states). The number of degrees of freedom becomes 2, he says, irrespective of whether the micelle is considered a separate phase or not. From this Pethica concluded that, when applying the phase rule, it is permissible to consider the micelle as a separate phase only if the water of hydration (not iceberg water) is taken into account. As the equilibrium of a solute between two liquid phases is determined by the chemical potential of the solute, the micelle formation equilibrium is determined by the chemical potential of the water.[153] Daniellson pointed out[155] that this does not imply that the vapour pressure of water above the two phases remains constant as concentration increases, but only that the water activity varies in a similar manner in both micelle and inter-micellar liquid.

Both Pethica[153] and Shinoda and Hutchinson[145] have assumed that the osmotic pressure is nearly constant above the CMC but vapour pressure measurements have shown a decrease in water activity above the critical micelle concentration, although this is often not pronounced.[156] According to the classical phase rule, the vapour pressure of solute should change suddenly at the critical micelle concentration and then be independent of the amount of the micellar phase. Vapour pressure changes above the CMC are, therefore, not in agreement with the phase rule approach.

On the assumption that micelles may be considered as forming a separate phase, Hutchinson, and later Matijevic and Pethica,[154] derived an equation of the Clausius-Clapeyron type, for the determination of the heat of micelle formation from the temperature dependency of the CMC:

$$\frac{\Delta H_m}{RT^2} = -k\left(\frac{d\ln \mathrm{CMC}}{dT}\right)$$

ΔH_m is the heat of transfer of detergent from the standard state in solution to the micelle. k is unity for non-ionic detergents. The equation ignores deviations from ideality, but it has been used in a number of investigations.

Mass-Action Approach. The law of mass-action was first applied to micelle formation by Bury[157,158] and by Hartley.[159] The law shows the existence of a sharp CMC when the aggregation number is sufficiently large. Murray and Hartley[160] have explained the Krafft phenomenon on the basis of the law, although the Krafft point, which has been interpreted as the point at which solid hydrated detergent and micelles are in equilibrium with monomers, has also been reconciled with the phase rule.[145]

The law of mass-action approach differs from the pseudo-phase model in that it implies an increase in monomer activity above the CMC. Where C is the total concentration of detergent, m is the concentration of micelles and n the aggregation number, for the simple equilibrium

$$n(\text{monomers}) \rightleftharpoons (\text{micelle})$$

$K = \frac{m}{x^n}$ if $C = x + nm$ where x is the concentration of monomers.

There is an additional complication of charge effects with ionic micelles. Mysels,[161] taking into account double layer interactions and micellar charge in the term,"p," gives for the equilibrium

n(monomeric ions) + (n - p) counter ions $\rightleftharpoons$ micelles

$$K = \frac{m}{x^n (x+pm)^{n-p}}$$

with m and X molar concentrations. Activity coefficients were neglected on the assumption that the values chosen for p took non-ideality into account. Lange[162] has shown that the application of the law of mass action to micelle formation indicates that the activity coefficient of the micelles has almost no effect on the CMC.

A problem in analysing theoretical mass-action curves is the determination of the CMC, especially with systems with low aggregation numbers. Corrin[163] defined the CMC as the "total concentration of long chain electrolyte at which, for compounds containing the same polar group, a small and constant number of ions are in aggregated form." Phillips[164] defined it as the concentration at which $d_3\emptyset / de^3 = 0$ where $\emptyset$ is some measureable property.

There are other difficulties. In many systems the magnitudes involved in the equation are considerable, and K thus varies by large factors, depending on small changes in activity or concentration. Indeed, Hutchinson *et al.*[144] were of the opinion that the values involved were such that the mass-action model simply did not apply in some systems. Pethica regarded this judgement as "over strong."

For large aggregation numbers the mass-action and phase rule approaches give almost identical pictures. It should be remembered, however, in the endeavour to find the correct treatment that perhaps neither is completely applicable and, at best, both may be approximations.

Because of the uncertainty in determining the equilibrium constant (K), the use of the equation,

$$\Delta G_0 = -RT. \ln K$$

to give the standard free energy of micelle formation is dangerous, although it can yield useful information on the effects of various variables on ΔG_0, variables such as aggregation number or hydration.

While the effect of charge must be taken into account when formulating the equilibrium between ionic detergents and their micelles, this complication does not arise in non-ionic systems. However, a problem common to both ionic and non-ionic systems which is still unsolved is the incorporation of the water of hydration in the equilibrium. Recent work has shown that the degree of hydration of both types of micelles is high[165] and it is to be expected that water will play an important part in the equilibrium.

<u>Thermodynamics of Micelle Formation of Non-ionic Detergents.</u>

A number of papers have appeared since 1962 dealing with the enthalpy and entropy of micelle formation of non-ionic detergents. This section contains a brief review of this work and the conclusions based on it.

Most workers have used the temperature dependence of the CMC and the equations,

$$\Delta H_m = -RT^2\left(\frac{\delta \ln CMC}{\delta T}\right)$$

$$\Delta S_m = \Delta H_m / T.$$

for the determination of the "conventional" heats and entropies of micelle formation. ΔH_m is the partial molal heat of transfer of the detergent monomer from its standard state in solution to the micelle. The heat of micellisation obtained by calorimetry, denoted here ΔH^o, is the whole

formation. ΔH_m is the partial molal heat of transfer of the detergent

heat of formation. Calorimetry has been used in only one laboratory so far, and this work is discussed first.

Corkill, Goodman and Tate,[64] using a calorimeter capable of detecting heat changes of about 0.01 calories, measured the heat of micelle formation (ΔH°) of C_6n_6, C_8n_6 and $C_{10}n_6$ at 25° and 40°C. (Table VI) They assumed that the heat of dilution was negligibly small and that the heat of micellisation was independent of concentration. The volume of the final solution was assumed to be the sum of the initial solution and diluent, variations in partial molal volume being ignored.

Table VI[1]

Thermodynamics of Micelle Formation : Calorimetric Results

	Compound	ΔG°	ΔH°	$T\Delta S^\circ$	ΔS°	
25°	C_6n_6	− 3.7	5.5	9.2	30.9	(20.7)
	C_8n_6	− 5.1	4.8	9.9	33.2	(31.5)
	$C_{10}n_6$	− 6.5	3.6	10.1	33.9	(35.9)
40°	C_6n_6	− 4.1	4.3	8.4	26.9	
	C_8n_6	− 5.6	3.5	9.1	29.1	
	$C_{10}n_6$	− 7.1	2.4	9.5	30.4	

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[1] from reference 64. ΔG° and ΔH° in Kcals.mole^{-1} and ΔS° in cals.mole^{-1} degree^{-1}

The heat of dilution is not negligible in systems with high CMC's. In the case of C_4n_6 and $C_6.n_6$, for example, it would appear that this factor was significant, contributing to the enthalpy value. In these systems the neglect of volume effects would also be important, as working concentrations are necessarly high. In an ideal system $\Delta H_m = \Delta H^\circ$, and a measure of non-ideality would be the discrepancies between these values. The entropy change in Table VI is obtained from $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / T$.

The results indicate a decrease in enthalpy and increase in entropy with increasing alkyl chain and a reduction of these values with temperature. Benjamin,[165] in a recent study of alkyl amine oxide surfactants, found calorimetric data too imprecise to show whether ΔS° actually increases or decreases with chain length or not. The values of ΔS° at 25°C in the brackets in Table VI have been computed for comparison using the enthalpy value from the variation of surface tension with temperature.

There are numerous difficulties in working with compounds of low aggregation number. The relation $\Delta G_0 = RT \ln CMC$, with CMC in mole fraction units, is strictly true only for solutions with high aggregation numbers. A more accurate relation has been obtained by Benjamin[165] where

$$\Delta G^\circ = RT\left[\left(\frac{n-1}{n}\right) \ln CMC + \left(\frac{c}{2.303}\right)\right]$$

where c is a function of n and varies from 0.455 at n = 5 to 0.041 for

where c is a function of n and varies from 0.455 at n = 5 to 0.041 for

n = 100. With values of n over 50 this expression is equivalent to the simpler one mentioned earlier.

Temperature Variation of the CMC: One of the earliest papers was that of Ginn, Kinney and Harris[295] who, using a dye - solubilisation method for the determination of the CMC, investigated a series of non-ionic ethylene oxide adducts (5 - 30 units) with tridecanol, nonylphenol, dodecylphenol and decanol hydrophobes, at three temperatures. They found that the critical micellar concentration fell with increasing temperature the sensitivity of the CMC to temperature falling with increase in ethylene oxide chain length and with increase in temperature. Although the enthalpies and entropies of micellisation were not calculated the results implied a fall in ΔH and ΔS with increasing ethylene oxide chain length and a fall in ΔH with increasing temperature. Since then numerous investigations have been carried out on the temperature variation of synthetic non-ionic detergents. The results are collected in Table VII.

In every case, ΔH_m and ΔS_m will be seen to be positive and generally of a low magnitude. As the aggregation of the monomers into micelles results in a decrease in the randomness of the system, the positive entropy change must be explained by the entropic effects of the loss of water structure around the hydrocarbon chains of the monomers. Schick[168] and Hudson and Pethica[167] have both termed this loss a "desolvation," but this is confusing as the hydrophobe is not solvated in the normal sense of the word.

Schick[52,168] has explained his results on the basis of the disruption of the "iceberg" formations around the alkyl chains and a concomitant partial dehydration of the ether oxygens of the glycol chains. Hudson and Pethica have similarly stated that "desolvation" of both hydrocarbon and ethylene oxide chain occurs in micelle formation but they present no concrete evidence to support the statement. Results for $C_{12}n_7$ and $C_{12}n_{30}$ show that ΔH_m is 5.0 and 3.7 Kcals mole^{-1} respectively.[168] Assuming that monomers of both have the same number of water molecules associated with the alkyl chains it is difficult to see how $C_{12}n_7$ would be more dehydrated than the longer adduct as the explanation suggests. The results of Elworthy and Macfarlane[8] clearly show that the longer the glycol chain, the greater its hydration in the micelle. Evans[172] has estimated that there are 41 molecules of water

Table VII

Heats and Entropies of Micelle Formation of Non-ionics

Compound	Temp. °C.	ΔH_m Kcals.mole^{-1}	ΔS_m cals.mole^{-1}deg.$^{-1}$	Reference
C_6n_3	25	3.3		166
C_8n_3	25	3.7		166
C_8n_6	25	4.3		166
C_8n_9	25	3.7		166
$C_{10}n_3$	25	2.3		166
$C_{10}n_4$	5	6.8	28.6	167
	10	6.4	24.4	167
	20	3.3	11.1	167
$C_{10}n_5$	5	6.9		167
	10	5.5		167
	15	3.1		167
	20	1.8		167
$C_{10}n_6$	25	4.2		166
$C_{10}n_8$	5	9.9	35.8	167
	10	8.8	31.2	167
	20	5.6	18.9	167
	30	3.6	11.9	167
$C_{10}n_9$	25	1.6		166
$C_{12}n_6$	25	3.5	11.7	10
	25	3.9		166
$C_{12}n_7$ +	27.5	5.0	16.6	168
$C_{12}n_{30}$+	27.5	3.7	12.3	168
$C_{16}n_{30}$+	27.5	6.6	21.9	168

+ commercial products.

continued over page.

Table VII
continued

Compound	Temp. °C	ΔH_m Kcals.mole^{-1}	ΔS_m cals.mole^{-1} degree^{-1}	Reference
$C_7H_{15}COOn_{7.5}CH_3$	27	2.4		169
$C_{10}H_{21}COOn_{12}CH_3$	27	3.3		170
$C_{12}H_{25}N(CH_3)_2O$	25	1.9	6.3	171
$C_{12}n_{30}$$^{+}$	27.5			
in 0.43M NaCl		6.0	19.9	168
in 0.86M NaCl		6.5	21.6	168
in 0.86M NaCNS		4.1	13.6	168
in 0.86M$\frac{1}{2}Na_2SO_4$		9.1	30.2	168

+ commercial product

per monomer in micelles of $OPn_{8.5}$. Kushner and Hubbard[66] have calculated that there are 43 molecules of water per monomer of OPn_{10}. These values most certainly do not represent dehydrated states.

The enthalpy of micellisation increases in the presence of electrolyte. Schick suggested that this was evidence that the ethylene oxide desolvation was a major contributing factor to the entropy change. This premise, at first sight, seems reasonable as the non-ionic $C_{12}H_{25}N(CH_3)_2{-}O$, which is hydrated with ten molecules of water per monomer in the micelle[173] has a much lower entropy and enthalpy of micellisation at 25°C than any of the C_{12} polyoxyethylene ethers. On the other hand, White and Benson[138,174] have found a decrease in ΔH_m with increasing salt concentration for ionic detergents and have attributed this to the "solvent depolymerising effect of the added salt."

It may be relevant to examine the effects of electrolyte on non-ionic detergent behaviour. Unfortunately, there are no results on the micellar weights of $C_{12}n_{30}$ in electrolyte solutions, but in Table VIII the effect of electrolytes on NPn_{50} in terms of aggregation number and CMC are compared with the effect of the same electrolytes on the enthalpy values of the former compound.

Table VIII

The Effect of Electrolytes on Non-Ionics

Compound	Solvent	$\Delta H_m{}'$	Compound	Solvent	Agg.No.	CMC''
$C_{12}n_{30}$	H_2O	3.7	NPn_{50}	H_2O	20	280
	0.43M NaCl	6.0		0.43M NaCl	19	200
	0.86M NaCl	6.5		0.86M NaCl	26	150
	0.86M NaCNS	4.1		0086M NaCNS	19	227
	0.86M$\frac{1}{2}$$Na_2SO_4$	9.1		0.86M$\frac{1}{2}$$Na_2SO_4$	32	7

' Kcals mole^{-1} '' μmoles/litre.

These electrolytes had little effect on the compound $NP n_{15}$ but the effect was pronounced on compounds with higher chain lengths.[74] ΔH_m and ΔS_m increase as the CMC decreases (Table VIII). Lowering of the CMC is brought about by an increase in hydrophobicity, which may result from either desolvation of the polyoxyethylene chain or an increase in interfacial tension between the hydrocarbon chain and water, in the monomer. Hence, the possibility of desolvation of the glycol chains as they enter the micelle is reduced, and one is thus bound to disagree with Schick's explanation of the increase in entropy.

The ethylene oxide chains in the micelle are in the form of a truncated cone,[13] their configuration in the monomeric state being unknown. The configurational entropy change on micellisation is therefore also unknown. With compounds having long hydrocarbon chains there will be an increase in configurational entropy as the contracted hydrocarbon finds itself in the freer environment of the micelle interior. The data of Corkill, Goodman and Tate[64] showed that there is a significant enthalpy contribution, presumably reflecting a change in cohesional energy of the hydrocarbon chains on micellisation. Aranow and Witten's suggestion[180] that this is entirely an entropic change is thus placed in doubt.

The decreasing entropy increment which is seen as the series is ascended (e.g. C_6n_6 to $C_{10}n_6$) has been explained as due to the decrease in the surface/volume ratio of the hydrocarbon chain in solution which decreases the proportion of the monomer in contact with the water.

Temperature Dependence of ΔHm and ΔSm

The change in the thermodynamic parameters with temperature appears to reflect an alteration in the extent of the hydrocarbob-solvent interaction. As the temperature rises, the iceberg clusters break down.

reducing the entropy increase on micellisation. Hudson and Pethica[167] assumed, contrary to the evidence of Elworthy and McDonald,[22] that the glycol chain in the micelle was dehydrated with increase in temperature, and that this led to smaller enthalpies and entropies. Decrease of ΔH_m and ΔS_m with temperature also occurs with the ionic detergents, dodecyl pyridinium chloride (DPC) [175] and sodium dodecyl sulphate.[176] It would seem that the water structure effect is again prominent. The increase in configurational entropy of the alkyl chain in the micelle which occurs with temperature must also have some influence on the thermodynamic values obtained.[176,139] As the environment of the polyoxyethylene chain in both monomer and micelle is water, this part of the detergent molecule might be expected to contribute a smaller amount to the energetics of the micellisation process.

Heat Capacity

ΔCp_m, the heat capacity of detergent in a micellar system, has recently been calculated for a series of non-ionic detergents,[167] from the changes in the enthalpy of micelle formation with temperature as

$$\Delta Cp_m = \left(\frac{d(\Delta Hm)}{dT}\right)_P$$

Heat capacities have also been obtained for DPC over a range of temperatures and these values, together with some calculated values for C_6n_6, C_8n_6 and $C_{10}n_6$ are listed in Table IX. Hudson and Pethica's results[167] indicate a large excess heat capacity which may be explained by the breakdown of the water structure around the alkyl chains as the temperature is raised, causing extra heat to be absorbed. The heat capacity of tetra-n-butyl ammonium bromide in aqueous solution is -270 cals mole^{-1}degree^{-1}, whereas without solvent structuring , as the heat capacity is approximately -10 calories per mole per CH_2 or CH_3, it should be between −120 and −150 cals degree^{-1}mole^{-1}.[101] ΔCp (ice to liquid water) is +9 cals degree^{-1} mole^{-1}, therefore increased ice-likeness results in a larger, more negative, heat capacity figure. Benjamin[177] has recently obtained for the alkyl amine oxide detergents a value of −28 cals mole degree^{-1} per CH_2, again emphasising the excess heat capacity.

The heat capacity falls with increasing temperature as is shown clearly by the results for DPC at 20° and 25°, and presumably this is the explanation for the discrepancy between the heat capacity results for the $C_{10}n_x$ detergents at 5°–20° and those calculated for $C_{10}n_6$ in the 25°–40° range, from the results of Corkill et al.[64] A plot of $-\Delta Cp_m$ vs. temperature for DPC exhibits a minimum around 50°C. A minimum has also been observed in the value of $-\Delta Cp$ for the ionisation of cyanoacetic acid, and explained by the change in the structure and properties of water at 30° to 40°, for which there is considerable evidence.[179,] Accurate measurements of heat capacity of varibus solutes in aqueous solution by Ginnings and Furakawa[181] confirm that there is a well marked minimum near 35°. Similar effects are no doubt in evidence in the results of Table IX. It is possible that micellar changes which appear with increased temperature result from the effect of the "melting" of the water structure at 35° and other factors consequent on this change.

Correlation of Thermodynamic Data

There is, as yet, insufficient calorimetric data on non-ionic detergents for a detailed comparison to be made with data obtained by other means. Pethica believed that there are fundamental difficulties in comparing such results, as ΔH^o (calorimetry) measures the whole heat of formation and ΔHm (temperature dependence of CMC) is the heat of transfer of the hydrated monomer to the micelle.[153]

Herrmann[171] constructed the following triangle relating the different standard states of the detergent with the corresponding enthalpy and entropy changes for the non-ionic dimethyl dodecylamine oxide, for the ideal case where $\Delta H_m = \Delta H^0$ or $\Delta H_d = 0$.

$$\begin{tikzcd}
\begin{array}{c}\text{SOLVATED MONOMER}\\ (N_2 = 1)\end{array} \arrow[rr, leftrightarrow, dashed, "\begin{array}{l}\Delta G^0 = -6.1 \text{ Kcals.mole}^{-1}\\ \Delta H^0 = +1.9 \text{ Kcals.mole}^{-1}\\ \Delta S^0 = +26.6 \text{ cals.mole}^{-1}\text{degree}^{-1}\end{array}"] \arrow[dr, "\begin{array}{l}\Delta G_d = -6.1\\ \Delta H_d = 0\\ \Delta S_d = +20.3\end{array}"'] & & \begin{array}{c}\text{SOLVATED MICELLE}\\ (N_m = 1)\end{array} \arrow[dl, dashed, shift right] \\
& \begin{array}{c}\text{SOLVATED MONOMER}\\ (N_2 = \text{CMC})\end{array} \arrow[ur, shift right, "\begin{array}{l}\Delta G_m = 0\\ \Delta H_m = +1.9\\ \Delta S_m = +6.3\end{array}"'] &
\end{tikzcd}$$

The solvated monomer ($N_2 = 1$) is a hypothetical state, which may be looked upon as the detergent with just sufficient water to hydrate it. When the system is not ideal there will be some heat of dilution effects as the monomer is diluted from this state at $N_2 = 1$ to $N_2 =$ CMC. It would appear that the values of ΔH_m and ΔS_m are more valuable, as they reflect changes in the monomer as it enters the micelle, whereas calorimetric data gives the thermodynamic picture over a wider range - through dilution to the critical micelle concentration and subsequent micellisation - and the results are consequently more difficult to interpret.

Summary

Where the detergent has a high aggregation number, the two-phase model and the mass-action model give similar results; thermodynamic values calculated from either calorimetry or temperature variation of the CMC in such a case should coincide. Where the CMC is low, there is ideality

Table IX

Heat Capacities of Some Detergents

Compound	Temperature Range	ΔCp_m^x	Reference
$C_{10}n_4$	5 – 20°	–230	Hudson & Pethica[167]
$C_{10}n_5$	5 – 20°	–250	*Ibid.*
$C_{10}n_8$	5 – 20°	–290	*Ibid.*
$C_{10}n_6$	25 – 40°	–80	Calculated from results of Corkill[64] *et al.*
C_8n_6	25 – 40°	–87	
C_6n_6	25 – 40°	–80	*Ibid.*
DPC	25°	–150	Adderson & Taylor[175]
DPC	20°	–190	*Ibid.*

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x in calories $mole^{-1}$ $degree^{-1}$.

up to the point of micelle formation. It is in systems with low aggregation numbers and the consequent uncertainty of the activity of the solute or the applicability of many of the relationships used, that interpretation becomes difficult.

Further calorimetric studies are essential, especially to determine the heat of dilution of non-ionics with high CMC's so that the triangle of results ΔH_m, ΔH_d, and ΔH^o may be interpreted correctly. Lack of specific information on the hydration and configuration of the detergent monomers has, in the past, hampered the development of more precise explanations of the thermodynamics of micellisation. The experimental section of this thesis outlines some work which was done in an attempt to clarify the situation.

Table X

Hydration Numbers of Non-electrolytes in Aqueous Solution

Compound	Temp. °C	Hydration No.	Method	Reference
Sucrose	0	10.5	Viscosity	189
	0	6.0	Freezing Pt.	213
	10	3.4 6.6	Vapour Pres.	212
	25	5.0	Vapour Pres.	206
	25	5.0	Vapour Pres.	208
	25	6.0	Viscosity	189
	25	4.7	Diffusion	191
	25	7.7	Viscosity	191
	25	7.0	Viscosity	188
	25	9.0 10.0	Vapour Pres. Osmotic Pr.	214
	225	5.0	Vapour Pres.	214
	25	4.0 5.0	Vapour Pres.	215
	30	5.0	Osmotic Pr.	215
	55.7	4.0	Osmotic Pr.	215
	100	4.0	Vapour Pres.	215
	100	2.4	Viscosity	189
Glycerol	0	3.0	Freezing Pt.	215
	25	3.0	Vapour Pres.	215
	25	1.0	Vapour Pres.	215
	25	1.2	Vapour Pres.	191
	25	1.0	Viscosity	191
Erythritol	0	4.0	Freezing Pt.	215

continued

continued.

Table X

Hydration Numbers of Non-electrolytes in Aqueous Solution

Compound	Temp. °C	Hydration No.	Method	Reference
Methyl-glucoside	0	3.0	Vapour Pr.	215
	0	5.0	Vapour Pr.	215
Glucose	20	4.0	Adiabatic compressibility	196
Raffinose	90	{2.1 8.4}"	Vapour Pr.	204
	90	5.0	Vapour Pr.	205
Glucose'	20	4.3	Ultrasonic interferometry	197
Maltose'	20	3.6	"	197
Dextrose'	20	4.0	"	197

' In water-ethanol mixtures. " Figures in brackets are range for h.

Non-Electrolyte Solutions

The influence of electrolytes and non-electrolytes on the properties of water has already been discussed. It is not unexpected that non-electrolytes, especially those with hydroxyl groups, are solvated in aqueous solution and many attempts have been made to explain the behaviour of such solutions on the basis of their deviation from ideal solution behaviour as exemplified by Raoult's Law.

Non-electrolyte solutions have a comprehensive literature and it is too vast to review here. Hildebrand and Scott have dealt at length with the subject[182] and other accounts include that by Moelwyn - Hughes.[183] This thesis is concerned with aqueous systems and especially with the phenomena of association and solvation. In the following section the measurement of hydration,* and its thermodynamic consequences are discussed.

Non polar substances are only slightly soluble in water. A cursory examination of solubilities, however, indicates that appreciable solubility is conferred by hydroxyl, carboxyl and similar groups which can form hydrogen bonds with water.

In a series of aliphatic alcohols, amines and acids the lowest members may be completely water soluble but the solubility decreases as the length of hydrocarbon increases, which, according to Butler,[120] is a consequence of the increasing activity in the dilute solutions.

The existence or non-existance of hydrates in solution is of considerable

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*Hydration in this section is to be understood as the binding of water molecules to the solute molecule through hydrogen bonding etc. to ether or hydroxyl groups and not cluster of "iceberg" water.

importance to an understanding of solution phenomena. However, even a simple system such as sucrose-water has not lent itself to a direct determination of the degree of hydration and numerous indirect methods have been developed. Some of the results that have been obtained from these are listed in Table X: their divergence reflects the difficulty involved in the measurement of hydration.

Phillip[184] determined the degree of hydration of sucrose molecules from his results on the solubility of hydrogen in aqueous solutions. Jones et al[185] observed the broadening of absorption bands of cobalt salts with varying concentration of solution and deduced from this the amount of solvation.

Using the ultrafiltration method of McBain and Jenkins[186], McBain and Kistler[187] claimed to have made the first direct measurements of the hydration of sucrose. They added a small quantity of reference substance, and forced the solution through a membrane of sufficient fineness to retain solute. The water not available as solvent could then be estimated.

More widely used methods are discussed below.

Viscosity The use of viscosity in determining the hydration of macromolecules will be treated in a later section of the thesis. Most interpretations of solution viscosity attempt to explain deviations from the Einstein equation for unsolvated, rigid spheres in dilute solution; many attempt to measure the so-called "hydrodynamic volume" which is the volume of solute plus the volume of the bound water. Einstein[188] concluded that there were seven water molecules attached to each molecule of sucrose, if it was assumed that the sucrose molecules were spheres, large when compared with the solvent molecules. Vand[189] assumed that the sucrose molecules behaved as a suspension of rigid particles resembling ellipsoids of axial ratio 1.84 and found that at 0°C h was 10.54 and at 100°C. h was 2.43, and the energy required to be overcome to allow the release of the hydrating water, 2.58 Kcals mole^{-1}.

An equation of the form,

$$\eta_{rel} = 1 + A\sqrt{c} + B.c$$

was employed by Jones and Talley to explain non-electrolyte solution behaviour.[19

A less exact form,

$$\log \eta_{rel} = \frac{A_3 . c}{1 - Q' . c}$$

where $A_3 = \frac{2.5\,\bar{V}}{2.303}$ and $Q' = Q\bar{V}$, $\bar{V}$ being the effective molar volume (l.mole^{-1}) and Q' an arbitrary constant, has been employed to determine $\bar{V}$ for sucrose and glycerol and hence to estimate the degree of hydration, from a knowledge of the unhydrated volume. Values of 7.7 and 1.2 moles/mole were found for sucrose and glycerol respectively. The hydration of a colloidal unit has been estimated from the hydrodynamic volume defined by $([\eta])/2.5$; for Aerosol M A this is 1.62 indicating 38% by volume of kinetically associated solvent.[192] Bell and Magdin[193] have similarly determined the molal volume of lactose and sucrose, using a viscosity concentration relationship to give hydration.

Diffusion The diffusion method is said to be weighted in favour of firmly bound water.[191] It will thus tend to reveal the lower limits of hydration. Sucrose has a limiting diffusion coefficient of 52.26 x 10^{-7} cm.sec^{-1} at 25° and a Stokes Law radius of 4.69 Å. An hydrodynamic volume of 0.301 l.mole^{-1} was obtained from this, corresponding to 4.7 moles of bound water per mole, rather lower than some viscosity estimates, though agreeing well with the thermodynamic value of 5.

Compressibility The partial compressibility of either component (i) in a binary solution may be defined as,[183]

$$\beta_i = -\frac{1}{V_i}\left(\frac{dV_i}{dp}\right)_T$$

where V is the partial molecular volume and P is the pressure. When n is the concentration in molecules per ml., then

$$\beta_{solution} = \beta_1 + (\beta_2 - \beta_1)n_2V_2$$

(1 and 2 refer to solvent and solute respectively)
In electrolyte solutions it is assumed that the molecules of hydrating water are compressed to their maximum extent by the intense electrical forces around the ion and that, on increasing the pressure, it is the remainder of the solvent that is compressed. The method is proving valuable because of advances in the technique of measuring the velocity of ultrasonic waves, this being the basis of the method as $\beta = 1/v^2d$ where v is the velocity of the waves and d the density of the solution.

It has been shown that, where h is the hydration in gm. water per gm. of solute and g is the concentration in gm. per 100gm, β and β_0 the compressibilities of solution and solvent respectively,[194,195]

$$h = \frac{(1 - \beta/\beta_0)(100 - g)}{g}$$

A similar relationship has been given by Moelwyn-Hughes.[183] Adiabatic compressibility of non-electrolyte solutions also yields values of h : glucose, sucrose, maltose and galactose have been studied in this way.[196] Monosaccharide molecules were found to be hydrated with 4 water molecules. As the polysaccharide units were, apparently, also hydrated with the same number of water molecules this suggested that some hydroxyl groups were involved in intra-molecular hydrogen bonding. The hydration of glucose, maltose and dextrose has been determined in a similar way in water-ethanol mixtures.[197]

Syrnikov and Tao[198] have discussed the problem of the compressibility of aqueous non-electrolyte solutions and have postulated that the solute affects the structure of water and that the new structure is in thermodynamic equilibrium with the free solvent.

Dielectric Methods The dielectric dispersion method[199,200] has been used in the study of solvation, although it has not yet been employed extensively. It is based, briefly, on the fact that bound water molecules are unable to rotate under the influence of the applied alternating field, and the dispersion pattern is thus altered.

Other methods Nuclear magnetic resonance studies are gaining prominence with the availability of commercial spectrometers, but the interpretation of results is difficult. The greatest volume of work has stemmed from measurements of the colligative properties of aqueous non-electrolyte solutions and calculation of theactivity of the solute to obtain a measure of the non-ideality of the solution.

Colligative Methods Scatchard[201] found evidence of a hexahydrate in sucrose solutions from osmotic pressure measurements. Hunter[202] also assumed that hydration accounted for the osmotic data of sucrose solutions. Using the equation $\pi(V - b) = RT$ and taking hydration as the excess of b over the volume of unhydrated solid (0.214 l.mole^{-1}) he obtained an hydration number of 6, at molalities of 0.6 and over.

Poynting[203] attributed deviations from Raoult's Law in aqueous solutions to be due to the formation of involatile hydrates. If each of n_2 solute molecules is regarded as being permanently solvated with h molecules of solvent, the conventional mole fraction of solvent is reduced to,

$$N_1 = \frac{n_1 - hn_2}{n_1 - hn_2 + n_2} \qquad \ldots 1$$

Porman and Price[204] and Callendar[205] were thus able to interpret vapour pressure data on the basis of hydration as the water activity, a_1, may be written, $a_1 = p/p_0 = (n_1 - hn_2)/(n_1 - hn_2 + n_2)$. Much later, Stokes and Robinson[206] employed an equation which is directly derived from this:

$$a_1 = \frac{n_1 - hn_2}{n_1 - hn_2 + n_2} = \frac{1 - h.n_2/n_1}{1 - h\,n_2/n_1 + n_2/n_1} = \frac{1 - 0.018.hm}{1 - 0.018(h-1).m} \quad \ldots 2$$

as $\frac{1000\,n_2}{18.01\,n_1}$ = molality, m.

In the same manner,

$$\Pi = -\frac{RT}{V_1}.\ln(p/p_0) \quad \ldots 3$$

$$\Pi = \frac{RT}{V_1}.\ln\left[1 + \frac{n_2}{n_1 - hn_2}\right] \quad \ldots 4$$

Using equation 4 Callander obtained an hydration number of 5 for sucrose. However, the difficulty in reconciling experimental results with such simple equations or explanations of non-ideality is emphasised by the divergence of some of the results in Table X.

The less direct thermodynamic method of determining hydration involves the calculation of the activity coefficient of the solute, γ_2, and fitting the results with values obtained from relationships ascribing the source of non-ideality to hydration (see below).

There are three main equations used in the treatment of non-electrolyte solutions of small molecules which relate the activity coefficient of the solute to h, the hydration number, b, the heat of mixing and r, the ratio of the molar volumes of the components, respectively. These equations are:

$$\ln\gamma_2 = -h.\ln\left[1 - 0.018hm\right] + (h-1).\ln\left[1 - 0.018(h-1)m\right] \ldots$$

$$\ln\gamma_2 = \frac{0.018r(r-1)m}{1 + 0.018rm} - \ln\left[1 + 0.018rm\right], \quad \ldots 6$$

and $$\ln\gamma_2 = \frac{b}{RT}\left[\frac{1}{(1 + 0.018m)^2} - 1\right] - \ln\left[1 + 0.018m\right]. \quad \ldots 7$$

Equation 5 was derived initially for concentrated electrolyte solutions by Stokes and Robinson[207] by making allowance for the hydration of the ions in solution, an approach neglected by others but similar to the ideas of Poynting and of Callander for non-electrolytes. Robinson and Stokes[191] derivation has been followed for the present case of non-electrolytes.

Consider S moles of solvent, 1, h moles of which are associated with one mole of anhydrous solute, 2. The total free energy of the unhydrated state will be,

$$G = S\bar{G}_1 + \bar{G}_2 \qquad \ldots 8$$

and for the hydrated state

$$G = (S-h)\bar{G}_1 + \bar{G}'_2 \qquad (\bar{G}_1 = \bar{G}_1') \ldots 9$$

These must be equal. Rearranging we obtain from those equations,

$$h\bar{G}_1 + \bar{G}_2 = \bar{G}'_2 \qquad \ldots 10$$

Substituting $(\bar{G}_1^o + RT.\ln a_1)$ for $\bar{G}_1$ we obtain,

$$h\bar{G}_1^o + hRT.\ln a_1 + \bar{G}_2^o + RT.\ln a_2 = \bar{G}_2'^o + RT.\ln a'_2 \qquad \ldots 11$$

i.e. $h\bar{G}_1^o + hRT.\ln a_1 + \bar{G}_2^o + RT.\ln N_2 + RT.\ln f_2$

$$= \bar{G}_2'^o + RT.\ln N'_2 + RT.\ln f'_2 \quad \ldots 12$$

Dividing by RT and rearranging we arrive at,

$$\frac{h\bar{G}_1^o}{RT} + h\ln a_1 + \frac{\bar{G}_2^o - \bar{G}_2'^o}{RT} + \ln\frac{N_2}{N'_2} + \ln f_2 = \ln f'_2 \qquad \ldots 13$$

Since $N_2 = 1/(S+1)$ and $N'_2 = 1/(S-h+1)$ we have,

$$\frac{h\bar{G}_1^o}{RT} + \frac{\bar{G}_2^o - \bar{G}_2'^o}{RT} + h\ln a_1 + \ln\left(\frac{S-h+1}{S+1}\right) + \ln f_2 = \ln f'_2 \qquad \ldots 14$$

As infinite dilution is approached, that is as $S \longrightarrow \infty$, the system approaches ideality and thus the logarithmic terms disappear. In extremely dilute solutions $\bar{G}_2^o = \bar{G}_2'^o$ and $\bar{G}_1^o = 0$. Therefore

$$\ln f'_2 = \ln f_2 + h\ln a_1 + \ln\left(\frac{S-h+1}{S+1}\right) \qquad \ldots 15$$

It can be seen from equation 2 that:

$$\ln a_1 = \ln\left[1 - 0.018hm\right] - \ln\left[1 - 0.018(h-1)m\right]. \qquad \ldots 16$$

By definition $\quad f_2 = \gamma_2 \, x(1 + 0.018m) \qquad \ldots 17$

and $\quad S = 1000/W_1m = 1/0.018m.$

Therefore, combining equations (15) and (17) and neglecting squared terms, assuming that the activity of the hydrated species is ideal ($\ln f' = 0$) the final equation is obtained :

$$\ln \gamma_2 = -h.\ln\left[1 - 0.018hm\right] + (h-1).\ln\left[1 - 0.018(h-1)m\right]$$

This equation explains the behaviour of sucrose and glycerol in aqueous solution even up to concentrations of 3 molal, with h = 5 and 1.2, respectively. Expansion of $\ln a_1$ (equation (2)) in a series, and converting to osmotic coefficient, one obtains when higher terms of m are neglected the expression:

$$\phi = 1 + 0.018(h-\tfrac{1}{2})m + (0.018)^2(h^2-h+\tfrac{1}{3})m^2 \qquad \ldots 18$$

which shows that there is a contribution of $0.0045m^2$ to the osmotic coefficient which cannot be accounted for by hydration. Nevertheless, the hydration hypothesis can be used to obtain $\phi = 1.17$ at 2M sucrose against $\phi = 1.188$ calculated by equation (18). Therefore the major cause of non-ideality, at least up to 2 or 3 M, can be ascribed to hydration.

The second of the main equations is derived using the concepts of athermal solutions in which the molecular volumes of solute and solvent are taken into account in a term "r" , the ratio of the free volumes of solute and solvent, V_2/V_1. The entropy of mixing of athermal solutions composed of molecules of different size is described by

$$\Delta S_{mix} = -R\left[n_1 \ln\frac{n_1}{n_1 + rn_2} + n_2 \ln\frac{rn_2}{n_1 + rn_2}\right] \qquad \ldots 19$$

As $\Delta H_{mix} = 0 \qquad \Delta G_{mix} = -T\Delta S_{mix} \qquad \ldots 20$

$$\therefore \quad \Delta G_{m} = RT\left[n_1 \ln \frac{n_1}{n_1 + rn_2} + n_2 \ln \frac{rn_2}{n_1 + rn_2}\right] \qquad \ldots 21$$

and

$$\left(\frac{\partial \Delta G}{\partial n_2}\right)_{n_1} = RT\left[\frac{n_1.(1 - r)}{n_1 + n_2 r} + \ln \frac{n_2 r}{n_1 + n_2 r}\right] \qquad \ldots 22$$

Since

$$\left(\frac{\partial \Delta G}{\partial n_2}\right)_{n_1} = \mu_2 - \mu_2^{0} = RT \ln a_2 = RT \ln f_2 + RT \ln N_2$$

$$\ln f_2 = \frac{n_1(1 - r)}{n_1 + n_2 r} - \ln \frac{r(n_1 + n_2)}{n_1 + n_2 r} \qquad \ldots 23$$

At infinite dilution $n_2 \rightarrow \infty$ and the activity coefficient of the solute, $f_2 \rightarrow 1$. Converting to molality and the corresponding activity coefficient, where $\ln f_2 = \ln \gamma_2 + \ln (1 + 0.018m)$, one obtains the expression:

$$\ln \gamma_2 = \frac{0.018r(r-1)m}{1 + 0.018rm} - \ln (1 + 0.018rm). \qquad \ldots 6$$

This equation can also be obtained from the relationship obtained by Glueckauf for electrolyte solutions[209] placing $h = 0$ and $\nu = 1$ in his equation.

The system water-sucrose required a volume ratio of 5 to account for the observed activity coefficients, whereas the true mole volume ratio is approximately 12. It has been said[210] that it is an oversimplification to treat aqueous systems in terms solely of r. It is possible that the structure-breaking effect of the solute molecules is yet another factor to be considered. Volume fraction statistics have, however, been successful in treating non-aqueous systems such as benzene-diphenyl and high-polymer systems. r is equivalent to the σ of the Flory-Huggins treatment.

The third equation, on the other hand, is based on the concepts of regular solutions in which an energy parameter, instead of a volume ratio or hydration number, is employed. The excess free energy of mixing of non-electrolyte solutions arising from heat of mixing effects may be represented by

$$\Delta H_{mix} = n_1 N_2 b = \frac{n_1 . n_2}{n_1 + n_2} b. \qquad \ldots 24$$

b is given variously in other texts as $\Delta\epsilon$ (Tanford[211]), $\Delta\mu^\circ$ (Van Laar[183]) and is the heat of mixing of one mole of component with a large amount of the other. It is a constant depending only on the nature of the solute-solvent interaction and is independent of the size of the solute molecules.

In regular solutions the entropy of mixing is defined by the ideal case:

$$\Delta S_{mix} = -R\left[n_1 \ln \frac{n_1}{n_1 + n_2} + n_2 \ln \frac{n_2}{n_1 + n_2}\right] \qquad \ldots 25$$

And, as $\Delta G = \Delta H - T\Delta S$

$$\Delta G = \left[\frac{n_1 n_2}{n_1 + n_2}\right] b + RT\left[n_1 \ln . n_1 + n_2 \ln . n_2 - (n_1 + n_2)\ln(n_1 + n_2)\right] \ldots 26$$

$$\left(\frac{d\Delta G}{dn_2}\right)_{n_1} = b\left[\frac{n_1^2}{(n_1 + n_2)^2}\right] + RT \ln \frac{n_2}{n_1 + n_2} \qquad \ldots 27$$

$$\text{i.e.} \quad \ln a_2 = \frac{b}{RT}\left[\frac{n_1^2}{(n_1 + n_2)^2}\right] + \ln \frac{n_2}{n_1 + n_2} \qquad \ldots 28$$

$$\text{or} \quad \ln f_2 = \frac{b}{RT}\left[\frac{n_1^2}{(n_1 + n_2)^2}\right] \qquad \ldots 29$$

Converting to molality and considering at infinite dilution $f_2 = 1$ then

$$\ln \gamma_2 = \frac{b}{R.T}\left[\frac{1}{(1 + 0.018m)^2} - 1\right] - \ln(1 + 0.018m). \qquad \gamma$$

b is negative for a good solvent and positive for a poor one. Moelwyn-Hughes, using the equation obtained by Van Laar for hydrated non-electrolytes,

$$a_1 = N_1 e^{(1-N_1)^2 \Delta\mu^\circ / RT} \qquad \ldots 30$$

found that $\Delta\mu^\circ$ was -7.06 RT for aqueous sucrose solutions. This compares with the value of b obtained by Robinson and Stokes[191] for the same system which was -5.4 RT. However, there still appears to be some dubeity as to the significance of b or $\Delta\mu^0$ and as to whether they represent the heat of mixing or not. A regular solution with $b = hRT$ will affect the activity coefficient of solute to the same extent as would the hydration of each solute molecule with h water molecules.

The parameters h, b and r are obviously related. Hydration results in negative values of b which, in turn, result in an increase in activity with increasing concentration. However, no constant value of b or r explains the experimental results for aqueous solutions of small non-electrolytes, although all treatments give close approximations in the case of glycerol where the deviations are not great in any case. Even in this case the "best" value of r is much lower than the real value of 4. In polymer solutions the picture is somewhat altered, but a discussion of this is beyond the scope of this thesis.

It is thus apparent that one can obtain a number of mathematical relationships to describe the behaviour of solutions of non-electrolytes. Where the solute molecules are not too large, hydration appears to offer the best explanation of activity coefficients. The hydration numbers obtained from equation (5) agree well with the hydrodynamic values from viscosity and diffusion methods, even up to 5 Molar concentration[191], which lends substance to the belief that hydration is an adequate explanation for non-ideal behaviour. In polymer solutions it is possible that volume ratio effects far outweigh the effects of hydration and that equations involving r would fit the experimental data.

Polyethylene Glycol Solutions

No attempts to measure the hydration of glycols in solution are reported in the literature. Most of the work on polyethylene glycol solutions has been concerned with the elucidation of the configuration of the glycol molecules in solution.

Davison[216] concluded from infra-red studies on polyethylene glycol in molten and crystalline form that the configuration of the chains was essentially "gauche," this being consistent with the highly crumpled helical structure suggested by X-ray measurements.[217,218.] Other workers[219] have found evidence of both trans and gauche forms of the $-O-CH_2-CH_2-O$ groups. The helical structure of higher members changes to a less regular structure in the lower members of the series.

From viscosity and dipole measurements in benzene[220] it was found that the glycols (from diethylene glycol upwards) consisted of a helical chain with possibilities of oscillation about the gauche position, making the molecule flexible and capable of winding up on itself. Dipole measurements of shorter glycols ($n_2 - n_7$) in dioxane were inconsistent with the helical state.[221.]

In aqueous solution, Rosch[222] claimed that the more condensed gauche or "meander" form of the chains was more likely, the compact arrangement being stabilised by carbon-oxygen dipoles, with each oxygen attracted to a carbon atom three carbons and one oxygen away. Becher[60] found this form "somewhat crowded" and suggested that the configuration required stabilisation with a chain of hydrogen-bonded water molecules between adjacent chain oxygens. A constant of 0.72 - 0.76 in the Mark-Houwink equation indicated that none of the glycols with molecular weights over 1000 were spherical entities in water.[233] Carbowax 400, however, can be regarded as being spherical in aqueous solution.[224] In a poor solvent such as toluene even Carbowax 1000 had an axial ratio close to unity (using the relations of

Huggins, Kuhn or Simha). The axial ratio of Carbowax 4000 was 12.9, revealing its highly contracted form in aqueous solution, as its extended ratio is of the order of 180.[224]

A study has been made recently of the factors affecting the association of polyethylene glycol and polyacrylic acid in water.[225] The hydrogen bonding affinity of the ether oxygens was used to explain the complexation between the polyethers and polymeric acids. Neither the addition of urea, nor the application of heat was effective in disrupting the complex, although sodium chloride at pH conditions above 7 essentially eliminated the association. The effect of increase in temperature on the viscosity of long chain glycols in carbon tetrachloride and in dioxane has been regarded as being a desolvation, although the effect in dioxane was small.[226.] Higher molecular weight glycols have an inverse solubility-temperature relationship in water. By studying intrinsic viscosity temperature characteristics of a sample of high molecular weight glycol, Bailey and Callard[227] were able to deduce some thermodynamic values for the system: negative entropy of dilution and heats of solution were found which implied a high degree of solvent-solute interaction. The vapour pressures, heats of mixing and thermodynamic dilution functions of low molecular weight polyoxyethylene and polypropylene glycols have been determined.[228] Heats of dilution were negative and exhibited a small positive temperature coefficient.

The heats of mixing at infinite dilution of polypropylene glycol and dipropylene glycol have been found to be -2.3 Kcals mole^{-1} and -4.1 Kcals mole^{-1}, respectively.[229] Cunningham and Malcolm[230] obtained a value of -15.8 Kcals mole^{-1} for polypropylene 400 - the theoretical value, calculated on the assumption that the compound had an average of 6.5 ether links per molecule, is - 14.0 Kcals mole^{-1}. Polypropylene glycol 400 and polyethylene glycol

300 have the same number of chain units per molecule and it might be expected that the heat of mixing with water would be more negative for the polyethylene glycol, but this is not borne out. It has been suggested to explain the value of -12 Kcals mole^{-1} that the terminal hydroxyls are involved in intramolecular hydrogen bonding with other groups. This is not feasible in the polypropylene compounds.

Alexandrowicz[231] has determined the osmotic activity of glycol solutions (of Carbowax 6000) by light-scattering measurements, and has found the osmotic coefficients to be unusually high. The second virial coefficients of polyethylene glycol (in benzene and ethylene dichloride) have been obtained as a function of molecular weight.[232] In both solvents negative values of virial coefficient were obtained for compounds of molecular weight from 210 to 560, and the values increased with increasing molecular weights, but neither the lattice model theory not the excluded volume theory of solutions could explain this behaviour.

Theory of Experimental Methods

Surface Tension : Drop Volume Method

A common method of measuring surface tension involves the determination of the volume or weight of drops of solution which are allowed to fall slowly from the tip of a vertical tube. An early, crude formula relates the weight of the drop (W) to the surface tension γ,

$$W = 2\pi r\gamma$$

where r is the radius of the dropping tip, but is erroneous because i) the edge of the drop at the tip is rarely vertical and ii) only a part of the drop falls. In practice it is found that approximately 40% of the drop does fall.[232]

Although no satisfactory simple corrections can be made, the work of Harkins and Brown[233] has made it a practical method of some accuracy. These authors found, by carefully measuring the weight of falling drops from tubes of different diameters, that the weight of a drop is a function of r/a if r is the radius of the tube and a the square root of the capillary constant. Thus,

$$W = 2\pi r.\gamma.f(r/a)$$

f(r/a) is determined uniquely by the value of r/a. a is unknown but is a function of $r/V^{\frac{1}{3}}$, V being the volume of the drop. Hence

$$W = 2\pi r.\gamma.\psi(r/V^{\frac{1}{3}})$$

The surface tension is readily calculated from the weight or volume of a falling drop as V, d (the density) and r are known. The correction factor, F, has been determined by Harkins and Brown[233] where $F = f(V/r^3)$ such that $F = 1/2\pi\left[\psi(r/V^{\frac{1}{3}})\right]$ and

$$\gamma = \frac{m.g}{r} \times F.$$

Experimental values of V/r^3 are obtained and F taken from a standard curve.[235] Experimental error is within 0.1% when V/r^3 lies between 2.637 and 1.209. When V/r^3 is between 10.29 and 0.865 the error is increased to 0.2%. A tip radius is therefore chosen to give values of V/r^3 within the first group.

Areas per Molecule

Areas per molecule of adsorbed detergent were obtained using the simple form of the Gibbs' Adsorption equation,

$$\Gamma_2 = -\frac{1}{RT}\,\frac{d\gamma}{d\ln.c_2}$$

where Γ_2 is the surface excess in gm.moles/cm.^{2} and R is in ergs mole^{-1} degree.$^{-1}$ If A is in square Angstroms and is the area per molecule at the interface,

$$\Gamma_2 A.N \times 10^{-16} = 1.$$

The area per molecule is thus readily obtained from these equations, $d\gamma / d\ln.c_2$ being calculated from plots of surface tension vs. log c.

Viscosity

Viscosity measurements were employed to assess the degree of hydration and asymmetry of the detergents and glycols in solution. Einstein's original relationship for suspensions of rigid, completely wetted non-interacting spheres,[236]

$$\eta_{rel} = 1 + 2.5\ \phi$$

$$\text{or} \quad \eta_{sp} = 2.5\ \phi$$

(η_{rel} is the viscosity of the solution relative to water and ϕ is the volume fraction of the particles) applies only to dilute solutions. For practical use results must be extrapolated to infinite dilution where

$$\mathcal{L}\,\frac{\eta_{sp}}{\phi} = 2.5$$

The validity of this relationship has been confirmed by Eirich et al.[237] Shape and hydration factors result in an increase in the viscosity intercept above 2.5, and the equations explaining the increase are the basis of its use in macromolecular and micellar systems. Oncley[238] obtained for spherical particles, where w was the number of gms. of hydrating water per gm. of compound the relation,

$$\left(\frac{\eta_{sp}}{\phi}\right)_{\phi=0} = 2.5\left(1 + \frac{w\bar{V}_1}{\bar{V}_2}\right)$$

$\bar{V}_1$ and $\bar{V}_2$ are the specific volumes of solvent and solute respectively. In terms of concentration, c, in gm. per ml.,

$$\left(\frac{\eta_{sp}}{c}\right)_{c=0} = [\eta] = 2.5\left[\bar{V}_2 + w\bar{V}_1\right]$$

or, more generally

$$\left(\frac{\eta_{sp}}{c}\right)_{c=0} = [\eta] = \nu\left[\bar{V}_2 + w\bar{V}_1\right]$$

where ν is Simha's shape factor, a function of axial ratio for ellipsoidal molecules and equal to 2.5 for spheres. The factor has been obtained for both prolate and oblate ellipsoids.[239,240]

Jeffery,[241] Kuhn,[242] Guth[243] and Kirkwood and Riseman[244] have, among others, developed equations which extend the application of these methods to the treatment of flexible polymers.

The Huggins Constant, K_H.

The coefficient K_H was introduced by Huggins[245,246] and independently by Kuhn[242] as a hydrodynamic correction factor. It was shown that

$$\frac{\eta_{sp}}{c} = [\eta] + [\eta]^2 K_H \cdot c$$

where c is the concentration in gm. per 100mls. K_H appears as a numerical coefficient of the square term, and is a constant depending on the solvent and shape or configuration of the macromolecule. For solid uncharged spheres in solution K_H is approximately 2.0, in theory and in practice. For flexible polymers in good solvents K_H is often near 0.35, higher values being found in poor solvents. The interdependency of shape and solution effects on K_H has been discussed at length by Eirich and Riseman.[247] Guth and Simha[248] obtained an expression for spheres in the form,

$$\eta_{sp}/\phi = 2.5 + 14.1\,\phi.$$

If the term $K_H[\eta]^2$ in the Huggins equation can be considered to be analogous to the equivalent term in this equation, then it may be interpreted in terms of solute-solvent interactions. As $[\eta]$ is roughly a measure of molecular size in polymers, the presence of $[\eta]$ in the interaction term is explicable. Other similar empirical equations expressing viscosity concentration relationships have been derived and many reduce to the Huggins equation.[248]

Light Scattering Theory

The theory of light-scattering has been reviewed by Tanford[249] and by Stacey[250] in recent years. The treatment here is therefore brief and deals only with small-particle theory.

Scattering by Particles smaller than $\lambda/20$ The simplest case to consider is that of a molecule in a dilute gas. When placed in the path of a wave whose equation is:

$$\mathcal{E} = \mathcal{E}_0 . \cos 2\pi\,(vt - x/\lambda) \qquad \ldots 31$$

(with $\mathcal{E}_0$ the maximum amplitude, λ the wavelength, v the frequency, x the distance along the line of propagation and t the time)

the molecule is subjected to a periodic electric field. It has induced in it an oscillating dipole of moment p which acts as a secondary light source or scatterer, and is proportional to $\mathcal{E}$. Thus

$$p = \alpha\mathcal{E} \qquad \ldots 32$$

if α is the polarisability of the particle.

Therefore,

$$p = \alpha \mathcal{E}_0 \cos 2\pi (vt - x/\lambda) \qquad \ldots 33$$

The field strength of the scattered light can be shown to be proportional to the sine of the angle between the axis of the dipole and the line of observation of the scattered light (θ_1), to 1/r (the reciprocal of the distance from the dipole to the observer) and to $\partial^2 p/\partial t^2$. Noting this, one obtains for the field strength of the scattered light,

$$\mathcal{E}_s = \frac{4\pi^2 v^2 \alpha \mathcal{E}_0 \sin\theta_1 . \cos 2\pi (vt - x/\lambda)}{c^2 \quad r} \qquad \ldots 34$$

(c^2 is in the devisor to correct the dimensions of the equation.)

The frequency of the scattered light is identical to that of the incident light and its intensity is proportional to the square of the amplitude:

$$i_s = \mathcal{E}_s^{\,2} = \frac{16\pi^4 v^4 \alpha^2 \mathcal{E}_0^2 \sin^2\theta_1 . \cos^2 2\pi (vt - x/\lambda)}{c^4 . r^2} \qquad \ldots 35$$

Rayleigh's equation[251] gives the relationship, derived from equation (35), between the intensity of the scattered light and the incident light (i_s) for one particle:

$$\frac{i_s}{i_0} = \frac{16\pi^4 \alpha^2 \sin^2\theta_1}{\lambda^4 r^2} \qquad \ldots 36$$

as $c/v = \lambda$. The polarisability, α, cannot be directly evaluated so a substitution is made with measureable terms. α is related to the dielectric constant of the medium and may be expressed in terms of the specific refractive index increment, dn/dc.

$$\alpha^2 = c^2 \left(\frac{dn}{dc}\right)^2 / 4\pi^2 N^2 \qquad \ldots 37$$

N is the number of molecules per cc., c is the concentration in gm./ml.

Introducing the molecular weight, M, and Avogadro's number, $\mathcal{N}$, for plane polarised light,

$$\frac{i_s}{i_o} = \frac{4\pi^2 c\ (dn/dc)^2\ M.\sin^2\theta}{\lambda^4 \mathcal{N} r^2} \qquad \ldots 38$$

as $N = \mathcal{N}c/M$. For unpolarised light, a super-imposition of two plane-polarised beams of equal intensity,

$$\frac{i_s}{i_o} = \frac{2\pi^2 c.\ (dn/dc)^2\ M.(1 + \cos^2\theta)}{\lambda^4 \mathcal{N} r^2} \qquad \ldots 39$$

where θ is the angle between the line of observation and the direction of the incident light.

Scattering by Solutions

In liquids there is more order than in dilute gases where there is a random motion of the molecules. Where complete ordering exists, as in crystals, no scattering occurs because of destructive interference between the fixed volume elements. If we consider a solution as a series of fixed volume elements we find that there are fluctuations in density, refractive index etc., within these mythical elements which results in the light arriving at the observer passing from unit to unit and not being destroyed. Fluctuations in solvent are accounted for by subtracting the solvent scatter.

In a medium of refractive index n_o, we obtain for an ideal solution, using equation (39)

$$\frac{i_\theta}{I_o} = \frac{2\pi^2 n_o^2\ (dn/dc)^2\ M\ c\ (1 + \cos^2\theta)}{\lambda^4 \mathcal{N} r^2} \qquad \ldots 40$$

The fluctuations in concentration (δc) and polarisability ($\delta\alpha$) that occur in non-ideal solutions (concentrated solutions) can be regarded as being responsible for the scattering. If one considers a volume element of solution ψ such that $N = 1/\psi$, then

$$\frac{i_\theta}{I_o} = \frac{2\pi^2 \psi n_o^2\ (dn/dc)^2\ (1 + \cos^2\theta)\ (\overline{\delta c})^2}{\lambda^4 r^2} \quad \ldots 41$$

c being the average value of the fluctuations over a large number of elements, related to the change in free energy with concentration, $\delta G/\delta c$. This, in turn, is related to the chemical potential (μ) and the partial molal volume ($\bar{V}_1$) of the solvent. That is,

$$\overline{\delta c^2} = kT\ (\delta^2 G/\delta c^2)_{T,P}$$

$$\left(\frac{\delta^2 G}{\delta c^2}\right)_{T,P} = -\frac{\psi}{c\bar{V}_1}\left(\frac{\delta \mu_1}{\delta c}\right)_{T,P}$$

Therefore

$$\frac{i_\theta}{I_o} = \frac{2\pi^2 n_o^2 \cdot (dn/dc)^2 . (1 + \cos^2\theta) . c}{\lambda^4 r^2 \left[-(1/\bar{V}kT)\ (d\mu_1/dc)_{T,P} \right]} \qquad \ldots 42$$

The relationship between solvent chemical potential and solute concentration is $\mu_1 = \mu_1^o - RT\ Vc\ (1/M + Bc + Cc^2 + \ldots\ldots)$, B and C being the second and third virial coefficients respectively.

Substitution in equation (42) yields the relation,

$$\frac{i_\theta}{Io} = \frac{2\pi^2 n_o^2\ (dn/dc)^2\ (1 + \cos^2\theta) . c}{\lambda^4 \mathcal{N} r^2\ (1/M + 2Bc + 3Cc^2 + \ldots)} \qquad \ldots 43$$

In dilute solutions the difference between n_o and n is negligible.

Rayleigh's ratio is defined as

$$R_\theta = \frac{r^2 i_\theta}{I_o(1 + \cos^2\theta)} \qquad \ldots 44$$

The turbidity of the solution is defined as

$$\tau = \frac{16\pi R_\theta}{3} \qquad \ldots 45$$

Equation (43) therefore simplifies to

$$\frac{H.c}{\tau} = \frac{1}{M} + 2Bc + 3Cc^2 + \ldots\ldots \qquad \ldots 46$$

where H is the optical constant,

$$\frac{32\pi^3 n_o^2\ (dn/dc)^2}{3\lambda^4 \mathcal{N}} \qquad \ldots 47$$

τ is measured by the light-scattering photometer, H calculated at finite concentration and M obtained by extrapolation to $c = 0$. in plots of $H.c/\tau$ vs. concentration. B may be obtained from the slope of these plots, C being neglected in most cases.

Depolarisation

It has been assumed that the scattering particle is optically isotropic. However, when this is not true there is an additional scatter due to fluctuations in the orientation of the particles, so that the true value of R_θ is less than the observed value. Cabannes[252] has shown that the excess scattering which is due to anisotropy may be related to the depolarisation ratio ρ, and the correction factor for R_θ is $\frac{6 - 7\rho}{6 + 6\rho}$. Tanford[249] has pointed out that in most cases where non-zero values of ρ have been observed, it is not certain whether the values of ρ reflect anisotropy at all.

Scattering from Larger Particles

The treatment of particles smaller than $\lambda/20$ depends on the fact that they can be considered as point scatterers. A larger particle must be thought of as a continuous series of scattering elements with a destructive interference between light scattered from separate points, due to phase differences in the separate light waves. A function, $P(\theta)$ is used to describe the effect, and is defined by

$$P(\theta) = \frac{\text{scattered intensity for a large particle}}{\text{scattered intensity without interference}}.$$

θ is the angle of observation of the scattered light. At angles greater than zero, light scattered by a larger particle is diminished by a factor $P(\theta)$. Values of the dissymmetry Z_{45} where $Z_{45} = \frac{P(45^\circ)}{P(135^\circ)} = i_{45^\circ}/i_{135^\circ}$ have been tabulated as a function of $P(90^\circ)$ From measurements of Z_{45} and the choice of a suitable model, i_{90} may be corrected for internal interference and M may be calculated and the principle particle dimension evaluated. For values of Z_{45} less than 1.2 little error is introduced into the calculation of M.

Vapour Pressure Measurements and the Calculation of Activity

Measurements of the vapour pressures of binary solutions show that there are two main types of deviation from ideal behaviour, as exemplified by Raoults Law, namely positive and negative deviations. In both cases ideality is approached in dilute solution. As mentioned in the section on non-electrolytes, the activity and activity coefficients can be employed to assess hydration. The water activity, a_1, is readily measured. It is essential to be able to obtain, from water activity values, the activity of the second component, a_2.

The Gibbs-Duhem equation enables the activity curve for the second component of a binary solution to be obtained from the activity-composition curve of the first. It can be shown that

$$S\ dT - V\ dP + \quad n_i d\bar{G}_i = 0$$

where n_i indicates the number of moles of the ith species present in solution Where the system is at constant temperature and pressure

$$n_1 d\bar{G}_1 + n_2 d\bar{G}_2 + n_3 d\bar{G}_3 + \ldots\ldots = 0$$

In a solution with one solute,

$$n_1 d\bar{G}_1 = - n_2 d\bar{G}_2$$

If both sides of the equation are multiplied by $1000/W_1 n_1$ we get for an aqueous system where $W = 18.01$,

$$\frac{1000}{18.01}\ d\bar{G}_1 = - m\ d\bar{G}_2 \quad \text{where m is the molality.}$$

$$\text{or} \qquad N_1 d\bar{G}_1 + N_2 d\bar{G}_2 = 0 \qquad (\underline{\text{Gibbs-Duhem}}).$$

The osmotic coefficient, ϕ, has been defined previously as

$$\phi = \frac{-1000 \ln a_1}{W_1 m} = \frac{-55.51 \ln a_1}{m}$$

Also, as $d\overline{G}_1 = RT \, d\ln a_1$, the Gibbs-Duhem equation may be written,

$$d\ln a_1 = -\frac{N_2}{N_1} d\ln a_2$$

or $$-55.51 \, d\ln a_1 = -m \, d\ln a_2$$

i.e $$+55.51 \, d\ln a_1 = -m \, d\ln (\gamma_2 m)$$

However, $$55.51 \, d\ln a_1 = -d(\phi m) \qquad \text{by definition.}$$

Thus $$m \, d\ln \gamma_2 + m \, d\ln m = d(\phi m)$$

or $$d\ln \gamma_2 + d\ln m = \phi m^{-1}.dm + d\phi$$

On integration this gives the equation relating solute activity coefficient to osmotic coefficient:

$$\ln \gamma_2 = (\phi - 1) + \int_0^m (\phi - 1) \, d\ln m.$$

Scatchard, Hamer and Wood[214] used this equation with isopiestic data on sucrose solutions. The integral is given by the area under the curve from $m = 0$ to $m = m$ of a plot of $(\phi - 1)$ vs. ln(molality) Activity coefficients may then be readily calculated.

PART II

EXPERIMENTAL

Materials and Methods of Synthesis

The Williamson ether reaction, employed in earlier studies in this laboratory, was chosen for the reaction of the appropriate alkyl bromides with mono-sodium glycol salts.

As no commercial source was available for the higher branched alkyl bromides, these were prepared by the following route using diethyl malonate as a starting point:

$$2R.Br + CH_2(COOEt)_2 \xrightarrow{2Na} R_2.C(COOEt)_2 \longrightarrow R_2.C(COOH)_2$$

$$\xrightarrow{-CO_2} R_2.CH.\ COOH \xrightarrow[3\%H_2SO_4]{MeOH} R_2.CH.COOCH_3 \xrightarrow{LiAlH_4}$$

$$R_2.CH.CH_2OH \xrightarrow[H_2SO_4]{HBr} R_2.CH.CH_2Br + Na(OCH_2CH_2)_nOH$$

$$\longrightarrow R_2CH.CH_2(OCH_2CH_2)_nOH$$

where R = Pr, Bu, Pt and Ht. and n = 6 or 9

Route for preparation of branched alkyl bromides and detergents

Fig. 11.

The glycols, hexaoxyethylene glycol and nonaoxyethylene glycol, were prepared from diethylene and triethylene glycols as before[13]:

a) $2HO(CH_2CH_2O)_2Na + ClCH_2CH_2OCH_2CH_2Cl \longrightarrow HO(CH_2CH_2O)_6H + 2NaCl$

monosodium digol — dichlorodiethyl ether — hexagol .

b) $2HO(CH_2CH_2O)_3Na + ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl \longrightarrow HO(CH_2CH_2O)_9H + 2NaCl$

monosodium trigol — dichlorotriethylene glycol — nonagol

Preparation of Glycols

It was originally intended to prepare and study a series of compounds of varying alkyl chain length, based on hexa- and nona-oxyethylene glycols. However, the first two compounds prepared, $[CH_3(CH_2)_6]_2$ CH $CH_2(OCH_2CH_2)_nOH$, n = 6 and 9, proved to be insoluble in water. This was the first indication of the effect of branching the hydrocarbon chain, as the equivalent straight-chain detergents were soluble in water at normal temperatures. Attempts to prepare the dipentyl compound (R = Pt, n = 9) and the dibutyl compound (R = Bu, n = 12) were abandoned due to low yields and difficulty in purification and the first useful compounds prepared were the branched ten carbon detergents with six and nine ethylene oxide units.

Unlike the longer straight chain compounds, all the branched detergents were liquid and this proved to be a difficulty, as recrystallisation had been a useful preliminary feature in the purification of the hexadecane series by Macfarlane.[13] Because of this difficulty and because of the low yields of branched alkyl bromides obtained, attention was directed to a series based on hexagol, with the detergent $[CH_3(CH_2)_3]_2$ $CH.CH_2(OCH_2CH_2)_6OH$ as its highest member. The lower homologues could be prepared more readily and distilled prior to chromatography.

The following non-ionic detergents were synthesised.

Hydrocarbon Chain	No. of Carbon Atoms	No. of Ethylene Oxide Units	Representative Symbols
CH_3CH_2-	2	6	C_2n_6
$CH_3CH_2CH_2CH_2$	4	3,6	C_4n_6
$CH_3CH_2CH_2CH_2CH_2CH_2$	6	6	C_6n_6
$(Me)_2CH.CH_2-$	4	3,6	Me_2n_6
$(Et)_2CH.CH_2-$	6	6	Et_2n_6
$(Pr)_2CH.CH_2-$	8	6	Pr_2n_6
$(Bu)_2CH.CH_2-$	10	6,9	Bu_2n_6

Hydrocarbon Chain	No. of Carbon Atoms	No. of Ethylene Oxide Units	Representative Symbols
$(\text{Pt})_2\text{CH.CH}_2$-	12	3	Pt_2n_3
$(\text{Ht})_2\text{CH.CH}_2$-	16	6, 9	Ht_2n_9

Yields. As the critical micelle concentrations of the short alkyl chain detergents were high, large quantities were required in a pure state for physical measurements. In the direct reaction between alkyl bromide and hexaoxyethylene glycol monosodium salt one is limited by the quantities of glycol available as the glycol is present in four molar excess. Therefore when large quantities of product were required the reaction involving the trioxyethylene glycol intermediate was employed, which, although yields per gm. of bromide were not significatly higher, was useful because of the availability of commercial "trigol" which was easily purified.

Yields in most cases were low in the Williamson ether reaction, being of the order of 20 - 30%. Alkyl bromide are readily dehydro-halogenated and unsaturated products are also formed; final products are curiously susceptible to oxidation and breakdown. Some dialkyl ether derivatives will be formed from traces of disodium glycol salts. These factors contribute to the even smaller overall yield of pure detergent.

Extraction of Crude Detergent. Water was added to the reaction mixtures, which were then treated with successive portions of hot petroleum ether (B.P. 60°/80°C) until no more detergent was extracted. For detergents with short chains diethyl ether-petroleum ether mixtures were employed.

Purification. The solvent was distilled off, leaving crude detergent, which, for compounds with ethylene oxide chains of six units or less, was then distilled under vacuum. In longer-chain compounds distillation induces oxidation and breakdown, and even with detergents with lower boiling points the product is still not in a sufficiently pure state for physico-chemical studies, probably because many of the by products are structurally similar.

Alumina proved less successful as a chromatographic adsorbent than a 27:7 silicic acid- celite mixture. The solvent systems employed were similar to those used before,[13] in each case the detergent (~2g) being adsorbed from benzene onto columns (2cm diameter) containing adsorbent mixture (30g). Acetone-benzene mixtures were run down the column under a slight positive pressure. The acetone content was increased by degrees (2%, 5%, 7.5% etc.) until the impurities had been removed. Careful elution with a 24:25:1 acetone:benzene:methanol mixture gave pure detergent (c. 1g), free from unsaturated impurities.

Infra-red spectra of chromatography preruns indicated that carbonyl-containing products and mono-chloro-derivatives of trioxyethylene glycol ethers (method II) were eluted before the main detergent fraction. Unreacted glycol was held firmly on the column.

<u>Assay.</u> The detergents were all hygroscopic. Before assay or analysis the compounds were dried in a vacuum oven at 30° - 40°C over phosphorous pentoxide for 48 hours. C and H analyses were carried out by Drs. Weiller and Strauss, Oxford, and the Microanalytical Laboratory of the University. For determination of ethylene oxide content the method of Siggia *et al*[41] was employed.

<u>Assay for ethylene oxide content.</u> The principle of the assay is the breakdown of ethylene oxide chains by excess hydriodic acid and titration of the iodine released. The suggested mechanism[41] of the process is

$$-(CH_2CH_2O)_n- + 2n\,HI \longrightarrow nICH_2CH_2I + nH_2O$$

$$2ICH_2CH_2I \xrightarrow[\text{HI}]{\text{Excess}} 2CH_3CH_2I + I_2$$

$$\text{or } 2ICH_2CH_2I \xrightarrow[\text{HI}]{\text{Excess}} 2CH_2 = CH_2 + 2I_2$$

A sample of detergent (c. 0.3g) is refluxed with excess hydriodic acid (25 mls.) (B.D.H. Analar Grade) for 2 hours at 135° - 140° in an inert atmosphere of CO_2. After completion of the reaction the amount of iodine released, compared with a blank containing no detergent, is obtained on addition of potass. iodide solution and titration with sodium thiosulphate.

Materials

Silicic Acid: Mallincrodkt Brand.

Celite: Evans Medical Ltd., washed with acetone and benzene and dried for 24hrs. in vacuum oven over $CaCl_2$.

Acetone and Benzene were redistilled and dried before use.

Synthesis of Alkyl Bromides.

1. 1-bromo-2-methyl propane (dimethyl bromo-ethane) was redistilled BDH material having BP. 91-92°, n_D^{20} 1.4347. (literature values: 91°, n_D^{20} 1.43475)

2. 1-bromo-2-ethyl butane (diethyl bromo-ethane). Redistilled parent alcohol, BP 147-149° (383mls) was treated with 48% Hydrobromic acid and sulphuric acid by the method of Vogel,[253] and the product was twice distilled to give 1-bromo-2-ethyl butane (260g), BP 95°/18mm, n_D^{20} 1.4512, n_D^{25} 1.4482. Literature values, n_D^{20} 1.4512, n_D^{25} 1.4495. $C_6H_{13}Br$ requires C, 43.6%; H, 7.9%; Br, 48.4%. Found C, 44.1%; H, 8.1%; Br, 48.0%.

3. 1-bromo-2-propyl pentane (dipropyl bromo-ethane)* was prepared by the route described in Figure 11, starting from diethyl malonate as follows:

dipropyl diethyl malonate: Sodium (29g) was dissolved in dry ethanol (300 mls.) and diethyl malonate (200g.) added and stirred. n-propyl bromide (155g.) was added slowly. A second portion of sodium (29g.) was dissolved in dry ethanol (300mls.) and added to the mixture. n-propyl bromide (155g.) was then added slowly. The mixture was refluxed (1 hour) and the residue, after filtration and removal of ethanol gave, on distillation, dipropyl malonate (160g.) BP 136°/13mm, n_D^{14} 1.4300. Literature value: BP 248°/760m; 125-6°/12mm.

Dipropyl acetic acid. The above product (150g.) was treated with ethanolic solution of sodium hydroxide (200g. NaOH) and boiled for several hours. After cooling, the mixture was neutralised with concentrated sulphuric acid (130-150mls.). An upper semi-solid layer separated and was removed, dissolved in chloroform and washed with water. Removal of chloroform and distillation of the residue (the dicarboxylic acid) on a Wood's metal bath at atmospheric pressure (280°-300°C) gave dipropyl acetic acid (52g.) BP 220°C/760mm, n_D^{20} 1.4234 Lit. value: BP 219-222°C. Found C, 66.98%; H, 11.3%; $C_8H_{16}O_2$ requires C, 66.6%; H, 11.2%.

Dipropyl acetic acid, methyl ester. Dipropyl acetic acid (52g.) was treated with an excess of methyl alcohol (400mls.) and concentrated H_2SO_4 (8mls.) and refluxed on a water bath (8 hours). Half of the methanol was removed and aqueous sodium carbonate added to neutralise the mixture. Water (300mls.) was added and the ester extracted with ether (3x200mls.), the extract being washed with water, dried over sodium sulphate and distilled to give dipropyl acetic acid, methyl ester (38g.) BP 170°/760mm, n_D^{20} 1.4125.

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*This preparation is given in detail. Subsequent analogous preparations are outlined only.

Literature values BP 172°/760m, 118-122°/14mm. Infra red spectra showed no broad band at 3.3μ, indicating absence of acid.

Dipropyl diethyl alcohol. Lithium aluminium hydride (42g.) in dry ether (200mls.) was reacted with the above ester (158g.) in ether (200mls.) the latter mixture being added slowly to the first, and the whole refluxed after the initial reaction ceased (2 hours). Water was added (50mls.) and sufficient conc. HCl to dissolve the gel. The material was extracted with ether, and on distillation gave dipropyl diethyl alcohol (26.1g.) BP 180°/760mm, n_D^{21} 1.4291. Literature value BP 180°/760mm. Found C, 72.8%; H, 13.95%; $C_8H_{18}O$ requires C, 73.7%; H, 13.9%.

Dipropyl bromo-ethane. Concentrated H_2SO_4 (7mls.) was added to 48% HBr (33.8g.) in portions, and dipropyl diethyl alcohol added (26g.). A further quantity of H_2SO_4 was added (6ml.) and the mixture refluxed (20 hours) The product was extracted with ether, washed with water and sodium carbonate solution and dried over sodium sulphate. On distillation dipropyl bromo-ethane (20g.) was obtained BP 182-190°/760mm, n_D^{20} 1.4518. No literature figures could be traced.

4. 1 bromo-2 butyl hexane (dibutyl bromo ethane)

dibutyl diethyl malonate: Sodium (32g.) in dry ethanol was reacted with diethyl malonate (222g.) and n-butyl bromide (190g.) added as described for the dipropyl derivative. Sodium (32g.) in dry ethanol (160mls.) was added to the mixture and n-butyl bromide (190g.) added. Distillation of crude product gave dibutyl diethyl malonate (200g.), BP 144°/12mm, n_D^{20} 1.4340. Literature value[254] BP 153-154°/14mm.

dibutyl acetic acid: The above product (190g.) was hydrolysed with NaOH (167g in 400mls. of a 1:1 water: ethanol mixture) by refluxing for 2 hours.

Distillation at atmospheric pressure gave dibutyl acetic acid (95g), BP 238-240°/760mm, n_D^{17} 1.4341. Literature values,[254,255] BP 255°/corrected, $n_D^{17.4}$ 1.4345. Found C, 70.40%; H, 11.7%. $C_{10}H_{20}O_2$ requires C, 69.72%; H, 11.74%.

Dibutyl acetic acid, methyl ester: Dibutyl acetic acid (93g) was esterified with methyl alcohol (230mls.) and sulphuric acid (13mls.), as before. Distillation of the product gave the ester (57g), BP 205°/760mm, n_D^{18} 1.4212. Literature figure,[256] BP 158-9/18mm. Infra-red spectrum showed no broad band at 3μ, distinguishing it from the parent acid.

Dibutyl ethyl alcohol: The methyl ester (57g) was reduced with lithium aluminium hydride (13g) in ether as before. On distillation the alcohol, dibutyl ethyl alcohol (40g) was obtained with BP 208°/760mm and n_D^{20} 1.4353. Literature value:[254] BP 218°/corrected, atmospheric.

Dibutyl bromo-ethane: The above alcohol (45g) was brominated using 48% Hydrobromic acid (48g) and concentrated sulphuric acid (15mls) following the usual procedure.[253] Distillation of the product gave pure dibutyl bromo-ethane (41g) with BP 194°/760mm and n_D^{20} 1.4542. No literature figures were found.

5. *1-bromo-2-pentyl heptane* (dipentyl bromo-ethane)

Monopentyl malonic acid, diethyl ester: was prepared from diethyl malonate (400g), sodium (46g) and *n*-pentyl bromide (378g) and ethanol (800mls) as before. The product gave, on distillation, monopentyl diethyl malonic acid (350g), BP 240-242°/760mm, n_D^{20} 1.4240. Literature values BP 134-136°/14mm, n_D^{20} 1.4253.

Dipentyl diethyl malonate was prepared from the above compound (350g), *n*-pentyl bromide (275g) and sodium (42g) in dry ethanol (650mls). Distillation gave dipentyl diethyl malonate (274g), having BP 163-168°/13mm, n_D^{20} 1.4362, n_D^{25} 1.4348. Literature values[258]: BP 158-161/11mm, n_D^{25} 1.4343.

Dipentyl acetic acid: Dipentyl diethyl malonate (240g) was hydrolysed with a solution of sodium hydroxide (192g in a 1:1 ethanol:water mixture) by refluxing for 7 hours. The crude dicarboxylic acid (200g) was distilled on a Woods metal bath at atmospheric pressure to give dipentyl acetic acid (132g), BP 258-260°/760mm, n_D^{21} 1.4372. Literature figures,[258] BP 141-143°/14mm n_D^{20} 1.4381.

Dipentyl acetic acid, methyl ester: Dipentyl acetic acid (132g) was esterified with methyl alcohol (277g) and concentrated sulphuric acid (8.5g). Treatment as before gave dipentyl acetic acid, methyl ester, (90g), BP 237-240° at 760mm.

Dipentyl ethyl alcohol: The methyl ester (136g), in ether, was reduced with lithium aluminium hydride (27g) in ether, as before. Distillation gave the alcohol (44g), BP 196/760mm, n_D^{20} 1.4418. Assay by the Pharmacopoeial method[259] gave molecular weight 187.4 (theoretic value, 186.4).

Dipentyl bromo-ethane: Dipentyl ethyl alcohol (42g) was treated with 48% HBr (43g) and concentrated H_2SO_4 (25g). On distillation the compound 1-bromo-2-pentyl heptane was obtained (32g), BP 146°/ 20mm, n_D^{21} 1.4571.

6. 1-bromo-2-heptyl nonane (diheptyl bromo-ethane).

Diheptyl diethyl malonate was prepared by reaction of 1-bromo heptane, n_D^{20} 1.4506 (360g) with diethyl malonate (160g) and sodium (46g) in dry ethanol. The product, diheptyl diethyl malonate (180g) had BP 152°/0.005mm, n_D^{20} 1.4432. Literature[260] figure: BP 178-180°/3mm.

Diheptyl acetic acid: The above compound (350g) was hydrolysed with a sodium hydroxide solution (240g NaOH in a 1:1 ethanol:water mixture) and refluxing for 6 hours. Neutralisation with concentrated HCl caused the dicarboxylic acid (160g) to separate. This, when heated at 300° on a Wood's metal bath formed diheptyl acetic acid (70g) BP 213°/15mm, n_D^{23} 1.4446. Literature values: BP 187-189°/4mm, 200°/13mm, n_D^{16} 1.4497.

Diheptyl acetic acid, ethyl ester: Diheptyl acetic acid (50g) was esterified with ethyl alcohol (100g) and concentrated H_2SO_4 (3g) and refluxing. On distillation the ester (45g) had BP 180°/13mm, n_D^{22} 1.4378. Literature figure:[261] 181-182°/15mm.

Diheptyl ethyl alcohol: The ester (45g) was treated with lithium aluminium hydride (6.3g) in ether as before. On distillation the product (33g) had BP. 180°/12mm, n_D^{20} 1.4485. Cox and Reid[261] give BP. 181°/15mm, n_D^{25} 1.4470. Found C, 79.3%; H, 14.1%. $C_{16}H_{30}O$ requires C, 80.1%; H, 13.9%.

Diheptyl bromo-ethane was prepared, as before, from diheptyl ethyl alcohol (10g), concentrated H_2SO_4 (4.7g) and 48% HBr (8.6g). On distillation, the crude product gave 1-bromo-2-heptyl nonane (8g), BP 275-280°/760mm, n_D^{20} 1.4612. No literature figures were found. Gas chromatography showed the presence of only one compound.

Preparation of the Glycols.

1. 3, Oxapentane-1,5-diol (diethylene glycol) was redistilled British Drug Houses' "Digol," BP. 129°/10mm, n_D^{20} 1.4469. Curme and Johnstone[59] give BP. 128°/10mm, n_D^{20} 1.4472.

2. 3,6 Dioxaoctane-1,8-diol (triethylene glycol) was redistilled British Drug Houses' "Trigol," BP. 154°/11mm, n_D^{20} 1.4550. Curme and Johnstone[59] give BP. 162°/10mm, n_D^{20} 1.4559. Found CH_2CH_2O, 87.97%. Calculated for $C_6H_{14}O_4$, CH_2CH_2O, 88.00%.

3. 3,6,9,12,15 Pentaoxaheptadecane-1,17-diol (hexaoxyethylene glycol) was

prepared by the method of Fordyce *et al.*[9] from redistilled diethylene glycol (846g), sodium (46g) and α,ω dichloro-diethyl ether (143g). Excess diethylene glycol was removed, and the hexaoxethylene glycol distilled (144g) BP. 184°/0.03 Found C, 49.4%; H, 9.3%; CH_2CH_2O, 93.65%. Calculated for $C_{12}H_{26}O_7$ C, 51.1%; H, 9.3%; CH_2CH_2O, 93.6%.

4. *3,6,9,12,15,18,21,24 Octaoxahexacosane-1,26-diol* (nonaoxyethylene glycol) was prepared by the method of Fordyce *et al.*[9] and of Macfarlane.[13] Sodium (46g) was dissolved slowly in triethylene glycol (1200g) and α,ω dichloro-triethylene glycol (see below) (187g) added. The mixture was heated and stirred at 115° until neutral, then filtered and the excess triethylene glycol distilled off. The crude product was distilled in a short path still, giving nonaoxyethylene glycol (180g), BP. 256°/0.02mm, n_D^{20} 1.4672, n_D^{38} 1.4614. Macfarlane gives n_D^{38} 1.4612. Found C, 52.4%; H, 9.9%; CH_2CH_2O, 95.6%. $C_{18}H_{38}O_{10}$ requires C, 52.2%; H, 9.2%; CH_2CH_2O, 95.6%.

5. *1,8 Dichloro-3,6-dioxaoctane* (α,ω dichloro-triethylene glycol.) was prepared by the method of Macfarlane.[13] Thionyl chloride (520g) was reacted with triethylene glycol (300g) in pyridine (350g). Excess thionyl chloride was removed by distillation and the residue extracted with ether (2.5litres). The ether layer was washed with dilute HCl (2 X 100mls.), water, sodium carbonate solution and water and dried over sodium sulphate. Distillation of the residue gave α,ω dichloro-triethylene glycol (300g), BP. 114°/12mm. n_D^{38} 1.4530, n_D^{20} 1.4615. Macfarlane gives n_D^{38} 1.4526, BP. 124°/18mm

Synthesis of Detergents

In the preparation of 3,6,9,12,15,18 hexaoxaeicosane-1-ol, the direct reaction of 1-bromo-ethane with the mono-sodium derivative of triethylene glycol would have met with difficulties in extraction and purification because of the similarity between the glycol and the product. The following method was therefore employed, using the commercial product ethyl troxitol as a starting point.

1. 3,6,9 trioxaundecane-1-ol (C_2n_3) Ethyl trioxitol (Shell Chemicals) was twice distilled and had BP. 110°/11mm, n_D^{20} 1.4385. Shell Chemicals quote for "pure" product, BP. 255°/760mm, n_D^{20} 1.4390. Found CH_2CH_2O, 74.10%. $C_8H_{18}O_4$ requires CH_2CH_2O, 74.16%.

2. 1-chloro-3,6,9 trioxaundecane: 3,6,9 trioxaundecane-1-ol (100g) in pyridine (44g) was treated with thionyl chloride (136g) and the product obtained as for α,ω-dichlorotriethylene glycol. Distillation gave the product 1-chloro-3,6,9-trioxaundecane (70g), BP. 130°/11mm, n_D^{20} 1.4340. Found, Cl, 18.6%. $C_8H_{17}O_3Cl$ requires Cl, 18.1%. Infra-red spectroscopy showed the absence of hydroxyl groups.

3. 3,6,9,12,15,18 hexaoxaeicosane-1-ol (C_2n_6) Sodium (7g) was reacted with triethylene glycol (183g) as before, and 1 chloro-3,6,9-trioxaundecane (60g) added. The mixture was stirred and heated until neutral (12hours), and the product extracted with a 90% ether- 10% petroleum ether (BP 60-80°) mixture. Distillation of the residue gave 3,6,9,12,15,18 hexaoxaeicosane-1-ol (30g), BP. 160°/0.05mm, n_D^{20} 1.4541. Found C, 53.99%; H, 9.60%; CH_2CH_2O, 84.92%. $C_{14}H_{30}O_7$ requires C, 54.17%; H, 9.7%; CH_2CH_2O, 85.16%.

4. 3,6,9,12,15,18 hexaoxadocosane-1-ol (C_4n_6) Sodium (11.4g) was dissolved in hexaoxyethylene glycol (490g) as before, and n-butyl bromide (80g) added.

The mixture was stirred at 110° for 16 hours, and the detergent was extracted into an ether-petroleum ether mixture, distilled (giving 17g) and chromatographed. On a small scale, the material (2.2g) was adsorbed from benzene onto silica-celite (30g) as described before, and the pure material (1.3g) obtained had BP. 170°/0.03mm, n_D^{20} 1.4499, n_D^{40} 1.4432. Found C, 57.0%: H, 10.0%; CH_2CH_2O, 77.9%. Calculated for $C_{16}H_{34}O_7$, C, 56.8%; H, 10.1%, CH_2CH_2O, 78.1%. Corkill *et al.* quote n_D^{40} 1.4440.

5. *3,6,9,12,15,18 hexaoxatetracosane-1-ol* (C_6n_6): Sodium (1.64g) was dissolved in hexaoxyethylene glycol as before, n-hexyl bromide (11.8g) added and the mixture heated and stirred until neutral. The detergent was extracted and distilled in the usual way giving 19.7g before chromatography. This distilled material (2.7g) was chromatographed on silica-celite and pure 3,6,9,12,15,18 hexaoxatetracosane-1-ol (1.8g) obtained, BP. 180°/0.05mm, n_D^{20} 1.4519, n_D^{40} 1.4442. Found C, 58.64%; H, 10.22%; CH_2CH_2O, 72.2%. Calculated for $C_{18}H_{38}O_7$, C, 58.99%; H, 10.45; CH_2CH_2O 72.12%.

6. *3,6,9,12,15,18 hexaoxahexacosane-1-ol* (C_8n_6): was a sample prepared by Mrs. M. McCubbin. Found C, 60.56%; H, 10.87%; Calculated for $C_{20}H_{42}O_7$, C, 60.86%; H, 10.73%.

7. *3,6,9 trioxa-11 methyl-dodecane-1-ol* (Me_2n_3): Sodium (7.7g) was dissolved in trioxyethylene glycol (200g), and 2-methyl 1-bromo propane (46.3g) added. On completion of the reaction (12hours) the detergent was extracted with ether and distilled to give 3,6,9 trioxa-11 methyl-dodecane-1-ol (14g), BP. 100°/0.05mm n_D^{20} 1.4378. Found C, 58.7%; H, 10.81%. Calculated for $C_{10}H_{22}O_4$: C, 58.2%; H, 10.75%.

8. *1-chloro-3,6,9 trioxa-11-methyl-dodecane* : 3,6,9 trioxa-11 methyl-dodecane-1-ol (30g) in pyridine (12g) was treated with thionyl chloride (36g)

as previously described. On distillation, the compound 1-chloro-3,6,9-trioxa-11 methyl-dodecane (27g) was obtained with BP 100°/0.07mm, n_D^{20} 1.4400, n_D^{22} 1.4386. Found C, 53.9%; H, 9.7% . Calculated for $C_{10}H_{21}O_3Cl$, C, 53.4%, H, 9.4%. Infra-red spectroscopy showed no trace of hydroxyl groups.

9. 3,6,9,12,15,18 hexaoxa-20 methyl-heneicosane-1-ol (Me_2n_6)

Method i. Sodium (2.84g) was dissolved in trioxyethylene glycol (74g), and the compound 1-chloro-3,6,9, trioxa-11 methyl-dodecane (28g) added. The mixture was heated for 8 hours at 140°. The detergent, after extraction with petroleum ether and ether, and distillation gave 9.6g. Chromatography on silica-celite gave pure detergent having BP 188°/0.05mm, n_D^{20} 1.4516. Found C, 57.44%; H, 10.27%; CH_2CH_2O, 77.92%. Calculated for $C_{16}H_{34}O_7$, C, 56.8%; H, 10.13%; CH_2CH_2O, 78.1%.

Method ii. Sodium (2.3g) was dissolved in hexaoxyethylene (113g), 1-bromo-2 methyl propane (20g) added, and the mixture treated as before. Distillation gave 4.3g. of 3,6,9,12,15,18 hexaoxa-20 methyl-heneicosane-1-ol before chromatography.

10. 3,6,9,12,15,18 hexaoxa-20 ethyl-docosane-1-ol (Et_2n_6): Sodium (2.3g) was dissolved in hexaoxyethylene glycol (113g) and 1-bromo-2 ethyl butane (16.5g) added. The mixture was heated overnight at 100°C , and the detergent extracted as before. The crude compound (8g) was distilled giving 7g. Chromat ography (2g) gave pure Et_2n_6 (1g), BP 177°/0.008mm, n_D^{20} 1.4532. Found C, 59.4%; H, 10.49%; CH_2CH_2O, 72.3%. Calculated for $C_{18}H_{38}O_7$, C, 58.99%; H, 10.45%; CH_2CH_2O 72.12%.

11. 3,6,9,12,15,18 hexaoxa-20 propyl-tricosane-1-ol (Pr_2n_6): Sodium (2.6g) was dissolved in hexaoxyethylene glycol (125g) and 1-bromo-2 propyl pentane (22g) added. The mixture was heated and stirred for 6 hours at 110°

to 140°C. The crude extract (15g.) was distilled and chromatographed. The pure detergent Pr_2n_6 had BP 198-202°/0.05mm, n_D^{21} 1.4529. Found C, 61.01%; H, 10.64%; CH_2CH_2O 67.2%. Calculated for $C_{20}H_{42}O_7$ C, 60.86%; H, 10.73% CH_2CH_2O 67.03%

12. 3,6,9,12,15,18 hexaoxa -20 butyl-tetracosane -1-ol (Bu_2n_6)

Sodium (2.3g.) was dissolved in hexaoxyethylene glycol (112g.) and 1-bromo-2-butyl hexane (21.7g.) added and the mixture treated as before. The crude detergent (8g.) was distilled (6.5g.). Chromatography of a portion (1g.) gave pure Bu_2n_6 (0.5g.), BP 210°/0.005mm, $n_D^{21.5}$ 1.4532. Found C, 62.59%; H, 1070%; CH_2CH_2 62.51%. Calculated for $C_{22}H_{46}O_7$, C, 62.53%; H, 10.97%; CH_2CH_2O 62.5%.

13. 3,6,9,12,15,18,21,24,27 nonaoxa-29-butyl-tritriacontane -1-ol (Bu_2n_9)

Sodium (1.7g.) was dissolved in nonaoxyethylene glycol (120g.) and 1-bromo-2-butyl hexane (16g.) added. The mixture was heated and stirred at 140° for 16 hours. Extraction as before gave crude detergent (7.7g.) but this was not distilled. Chromatography of a portion (4.4g.) gave pure product (2.3g.) n_D^{20} 1.4550. Found CH_2CH_2O 71.03%. Calculated for $C_{28}H_{58}O_{10}$, CH_2CH_2O, 71.47%.

14. 3,6,9,12,15,18 hexaoxa-20 heptyl-heptacosane-1-ol (Ht_2n_6)

Sodium (1.2g.) was dissolved in hexaoxyethylene glycol (56g.), 1-bromo-2 heptyl nonane (15g.) added and the mixture stirred at 140° overnight. The crude product (15g.) was not distilled but chromatography (11g.) gave pure detergent (c. 0.5g.) n_D^{25} 1.4520. Found CH_2CH_2O 51.6%. Calculated for $C_{28}H_{58}O_7$, CH_2CH_2O 52.16%.

15. 3,6,9,12,15,18,21,24,27 nonaoxa-29 heptyl-hexatriacontane-1-ol (Ht_2n_9)

Sodium (1.2g.) was dissolved in nonaoxyethylene glycol (82g.) as before and 1-bromo-2 heptyl nonane (15.2g.) added and the mixture heated and stirred for 12 hours at 140°C. Extraction yielded crude detergent (16.6g.).

Chromatography of 4.5g on alumina gave pure detergent (1.5g), n_D^{20} 1.4559. Found CH_2CH_2O, 61.6%. Calculated for $C_{34}H_{70}O_{10}$, CH_2CH_2O, 62.05%.

16. 3,6,9 trioxa-11 pentyl-hexadecane-1-ol (Pt_2n_3)

Sodium (4.1g) was dissolved in trioxaethylene glycol (106g), 1-bromo-2-pentyl heptane (44g) added, and the mixture heated for 6 hours at 140°. The crude detergent was extracted with ether and distilled to give Pt_2n_3 (21g), BP 210 /0.01mm., n_D^{18} 1.4489. Found C, 67.85%; H, 12.53%. Calculated for $C_{18}H_{38}O_4$ C, 67.80%,; H, 12.03%.

Some Observations on the Synthetic Work

Impurities in Non-ionic Detergents

The infra-red spectrum of a pure non-ionic detergent is given in Figure 13. Two principle impurities which are detected by such spectra are carbonyl-containing compounds, absorbing at 5.8 - 5.9 μ, and unsaturated products, which absorb at 6.1 μ.

Conventional tests on the detergent Bu_2n_9 which had been stored in a closed flask for some months after preparation showed that it contained aldehydic impurities. The infra-red spectrum of this sample is shown in Figure 14. Oxidation of the compound had occurred, the most likely structure of the oxidation product being $(C_4H_9)_2CH.CH_2(OCH_2CH_2)_8OCH_2CH{=}O$. Traces of unsaturation were also present.

The impurities were not completely removed from distilled products by chromatography on alumina. Initial work on alumina-purified materials had thus to be repeated, but this yielded some interesting data. The cloud point - concentration curves of Bu_2n_6 and Bu_2n_9 after chromatography on alumina exhibited dips in the region of the critical micelle concentration,

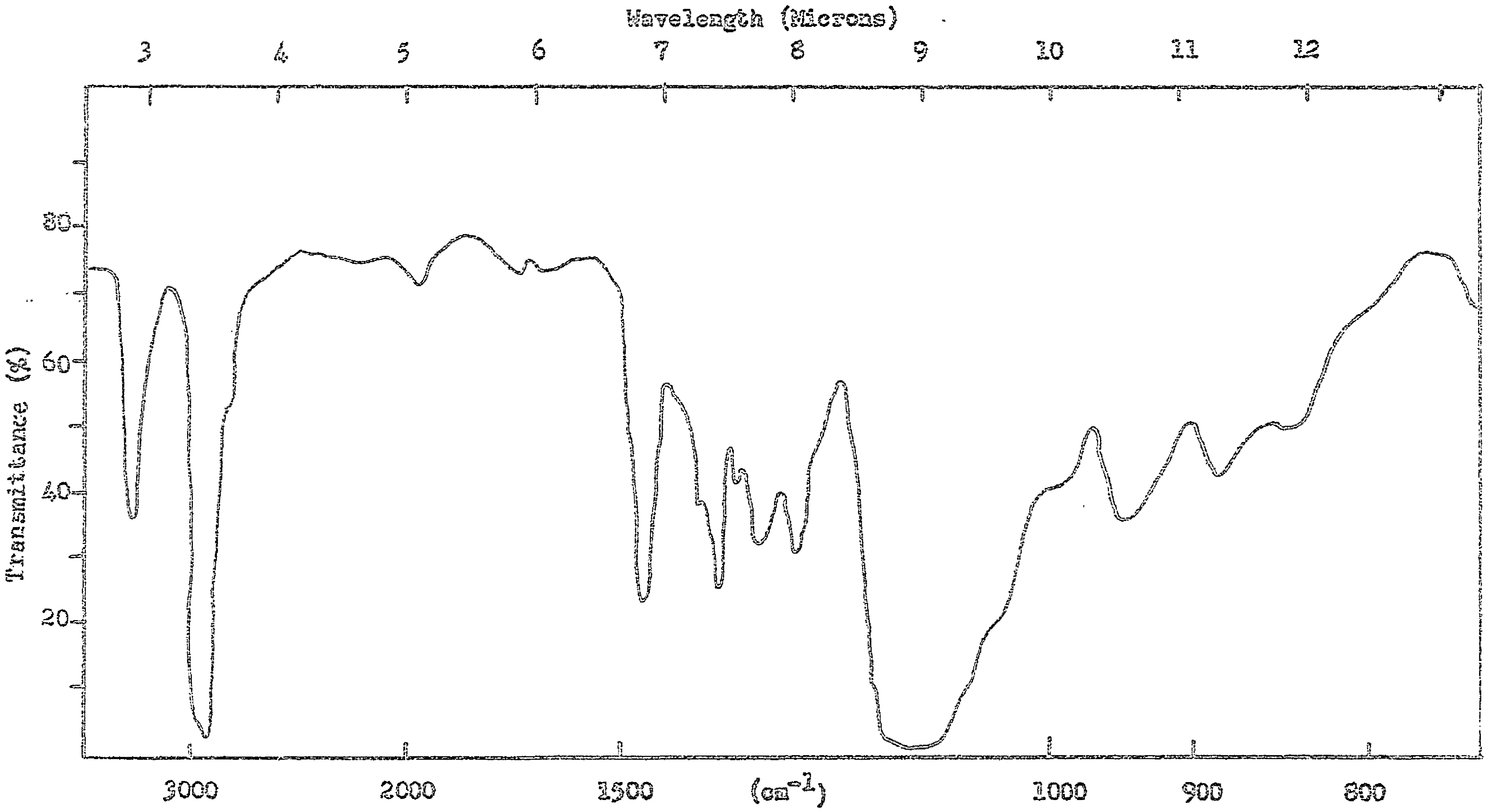

__Figure 13:__ Infra-red Spectrum of a Pure Non-ionic Detergent, the compound Pr_2n_6 after distillation and chromatography.

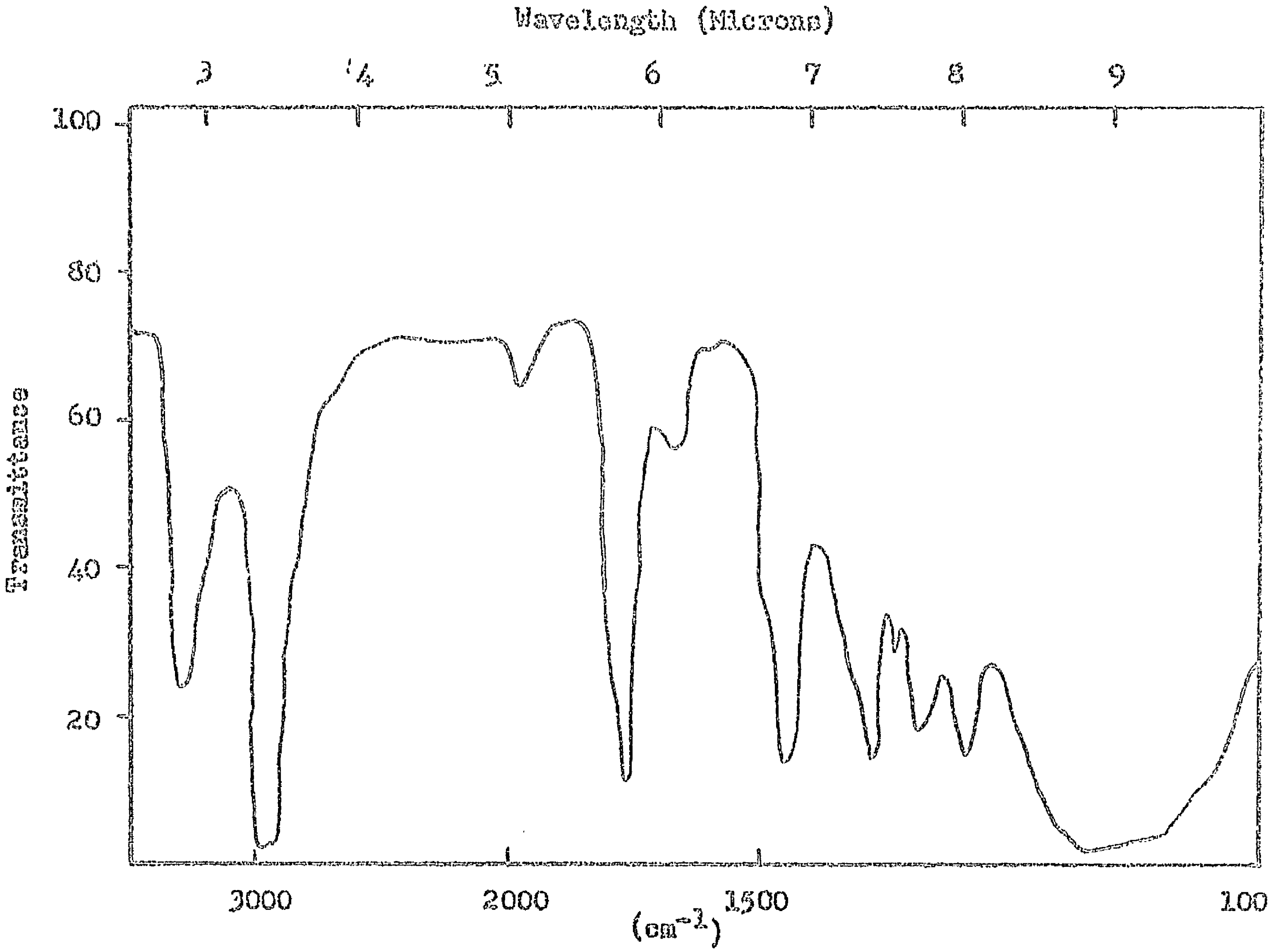

Figure 14: Infra-red Spectrum of a sample of Bu_2N_9 after storage for a number of months after preparation, showing carbonyl absorption, shown by conventional tests to be due to aldehydic impurities.

which suggested that the insoluble impurities were solubilised in the micelles are were being released on dilution below the CMC.(Figure 15). The compounds after chromatography on silica-celite did not exhibit this anomalous behaviour, and the cloud points were raised significantly over the whole concentration range.

Oxidation of the product takes place on storage even after chromatography. The difference in state of purity of two samples of Pr_2n_6 are undoubtedly reflected in the light-scattering behaviour of their solutions. The older sample had larger S_{90} values but the Debye plots of both samples were almost identical. Similar behaviour has been noted by Corkill and co-workers with different samples of straight-chain non-ionic detergents.[10]. The S_{90} - concentration plots of the two samples are given in the light-scattering section.

Surface properties are most sensitive to impurites. In impure surface-active agents minima are observed around the CMC in surface tension - log (concentration) plots. An impure sample of Pr_2n_6 gave a series of surface tension curves at different temperatures which were entirely erroneous, showing low CMC's and small areas/molecule. Purification of the samples on silica-celite led to much higher CMC values, higher limiting surface tensions and an absence of minima at the CMC. (Figure 16) Impurities, generally less soluble than the pure detergent, are adsorbed preferentially at the air/water interface and lower the surface tension.

Yields in the reactions between alkyl bromides and glycols were low, because of the competing reactions in which unsaturated compounds and di-alkyl derivatives were formed. Branched-chain bromides, especially those with short alkyl chains, undergo dehydrohalogenation much more readily than their straight chain isomers, although Mulley[17] reported the formation of unsaturates

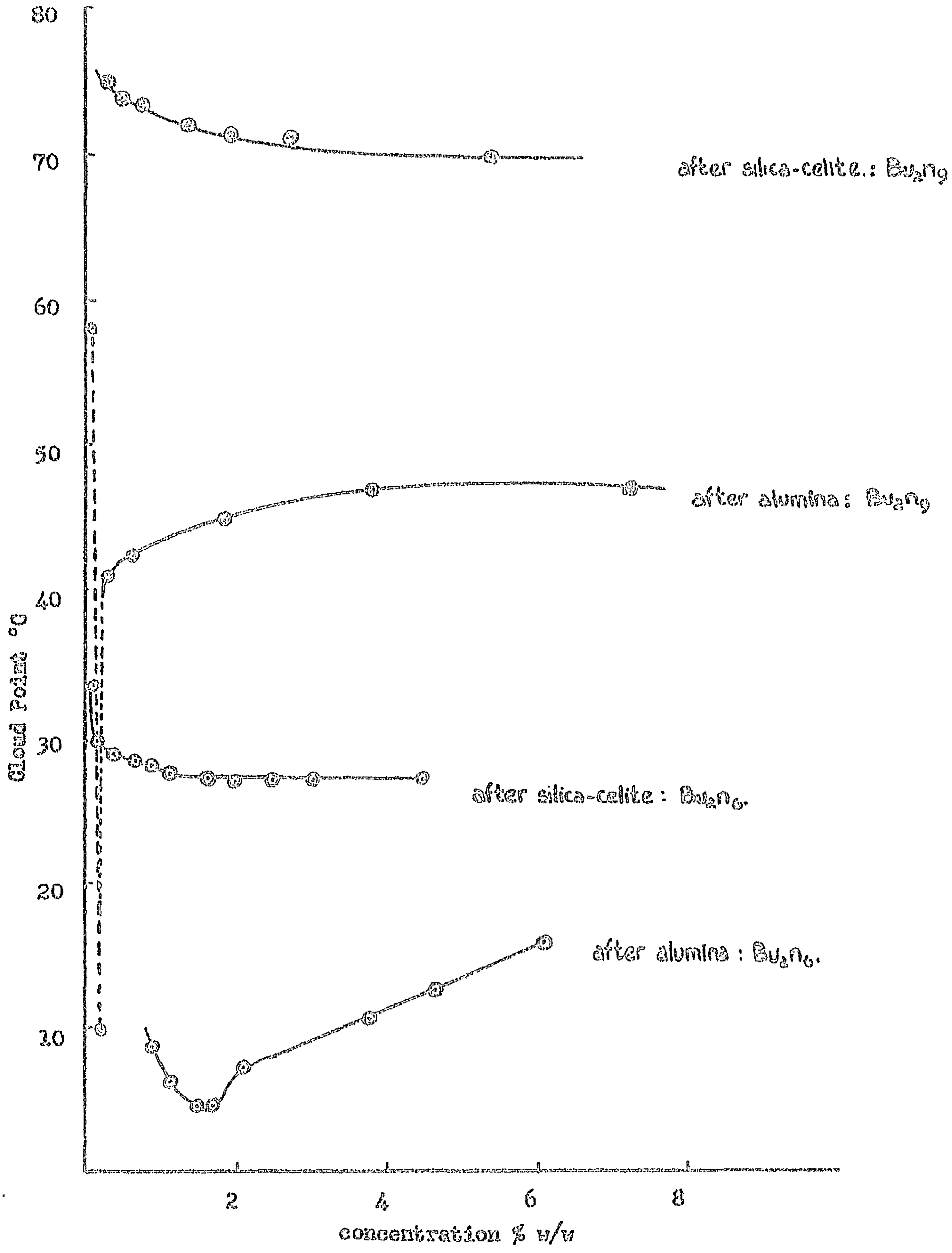

Figure 15: Cloud Point Diagrams for Bu_2n_6 and Bu_2n_9 after chromatography on alumina and after chromatography on silica-celite.

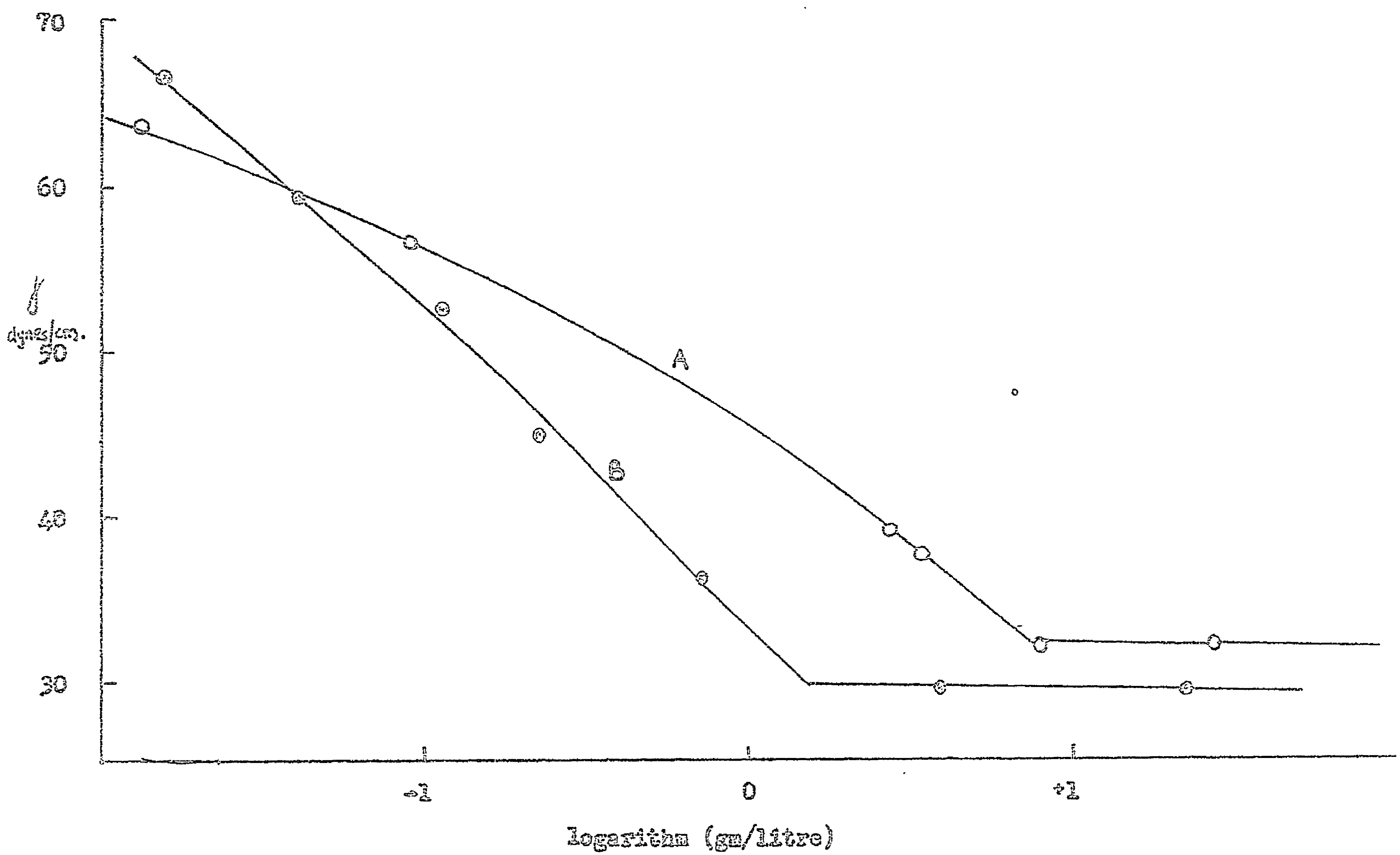

Figure 16: Surface tension - concentration plots of two samples of Pr$_2$n$_6$. Sample A has been purified on silica-celite; sample B has been purified on alumina. Sample B is impure and has a lower CMC and lower surface tension above the CMC than sample A. The limiting area per molecule for B is about 45 Å^2, which is much lower than that found for the pure sample.

in the synthesis of straight chain non-ionic detergents. In the preparation of 3,6,9 trioxa-11 methyl-tridecane-1-ol (Et_2n_3), for example, 2-ethyl-1-butene was isolated (Found BP 67°/760mm, n_D^{23} 1.3985. Literature values, BP 67.2°/760mm n_D^{20} 1.3990. Infra-red spectrum in Nujol had -C=C- peaks at 6.1 μ and 11.25 μ, with smaller vinyl absorption at 16.4 μ.) Excess bromide has thus to be used in the reaction.

Two routes were investigated in the synthesis of Bu_2n_9, since Corkill <u>et al.</u>[10] had reported better yields for straight chain non-ionics when an intermediate step was employed. The first method used was the straightforward reaction of dibutyl bromo-ethane with the mono-sodium salt of nonaoxyethylene glycol; the second method involved the intermediate Bu_2n_3. Bu_2n_3 is readily separated from the final product, Bu_2n_9, whereas Bu_2n_9 and nonaoxyethylene glycol, which would be the constituents of the reaction mixture if the first method was used, are more alike chemically. However, as the hydrocarbon group is relatively large in the present case the difference is sufficient for their successful separation. In practice, neither method held the advantage, as the yields calculated on the basis of starting bromide were 21% and 20% respectively. The second method probably minimises the formation of dialkyl glycol ethers, but it increases the possibility of contamination with the alkyl glycol chlorides. However, both dialkyl ethers and glycol chlorides are eluted in the pre-runs of a chromatographic separation. Figure 17 shows the spectrum of the first fraction of a chromatography run (n_D^{21} 1.4462) of a detergent prepared thus: R_2n_3-Cl + mono-sodium hexagol. It appears to consist chiefly of the chloride (n_D^{20} 1.4485). Figure 18 is the spectrum of the first fraction of C_6n_6, prepared by direct reaction of bromide with the sodium salt of hexagol. The fraction is most likely to be mainly the dialkyl ether, $C_6H_{13}(OCH_2CH_2)_6OC_6H_{13}$.

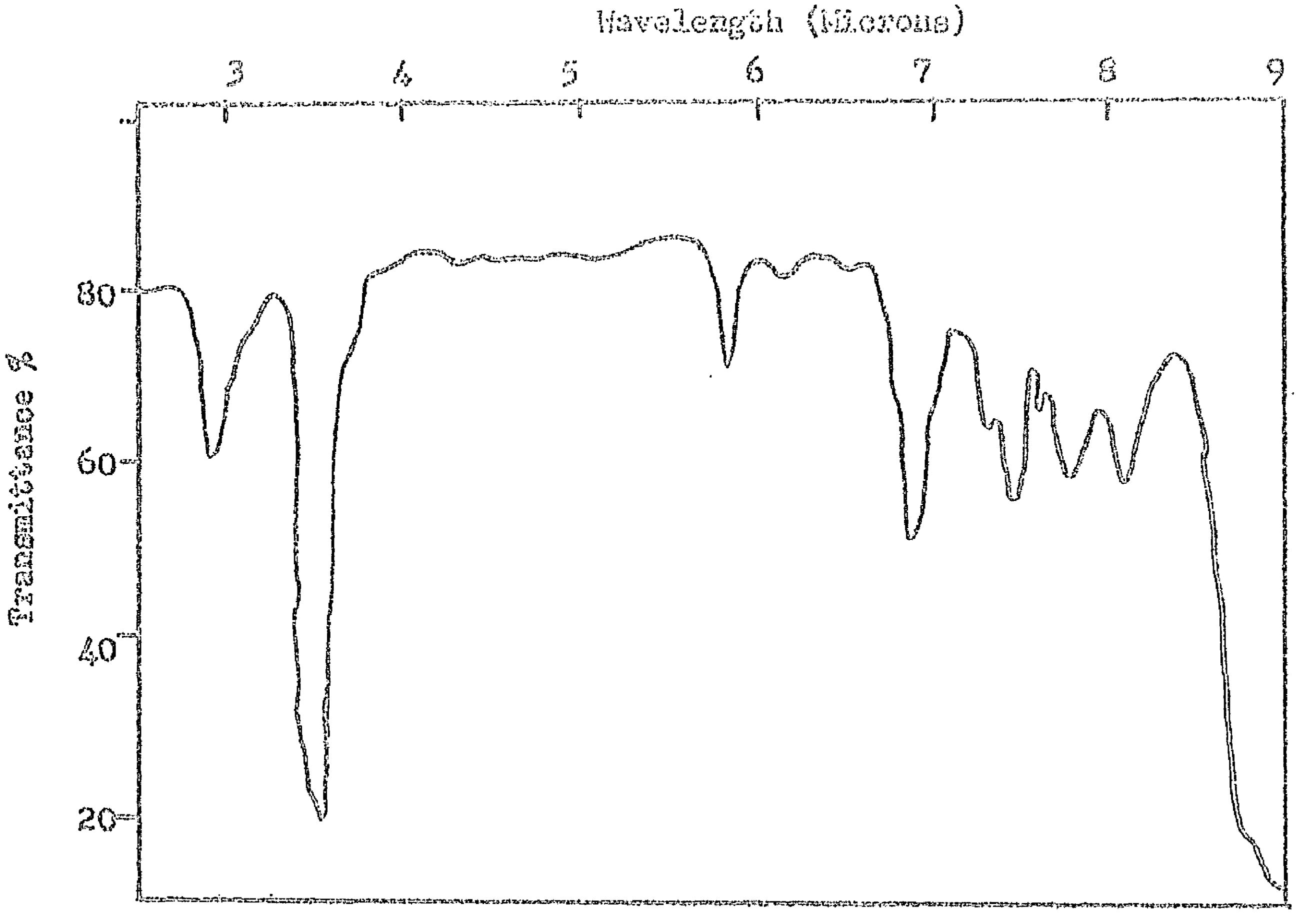

Figure 17: Infra-red spectrum of the first chromatography fraction of Et$_2$N$_6$ - prbably a mixture of Et$_2$N$_3$ and Et$_2$N$_3$Cl.

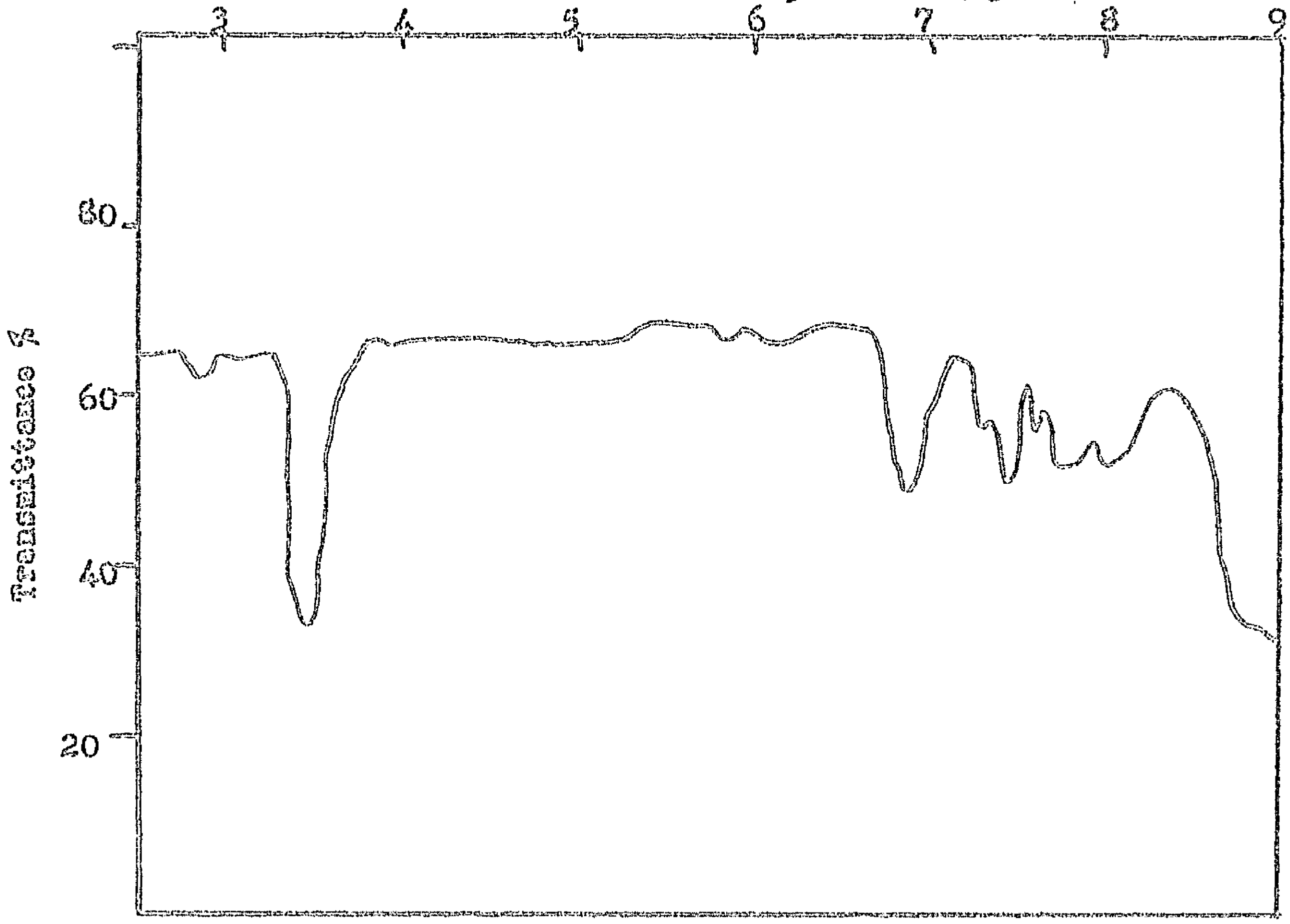

Figure 18: Infra-red spectrum of first chromatography fraction of C$_6$N$_6$

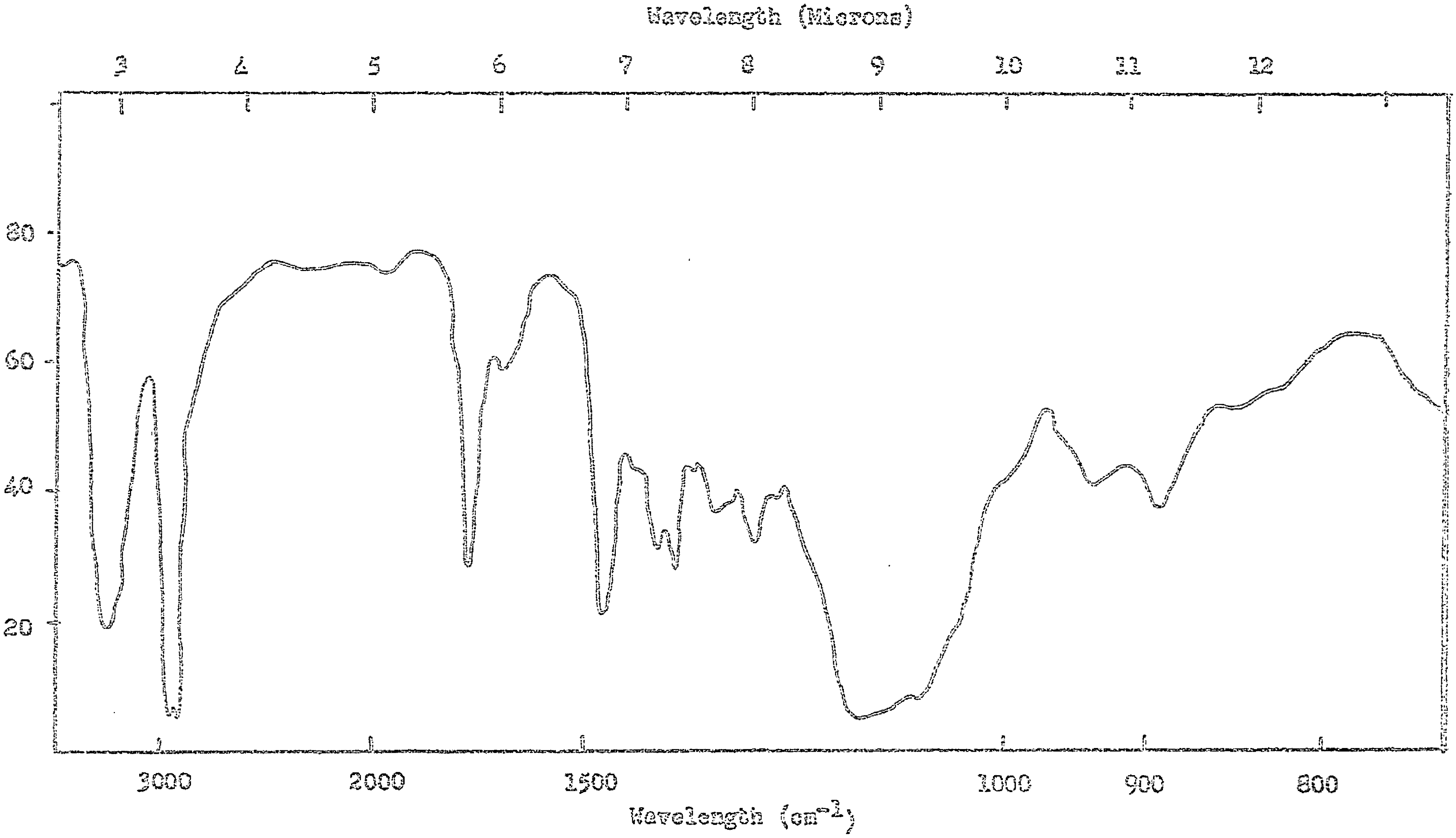

Figure 19: Distillation prerun of Pr_2B_6 showing marked absorption at 5.9 μ .

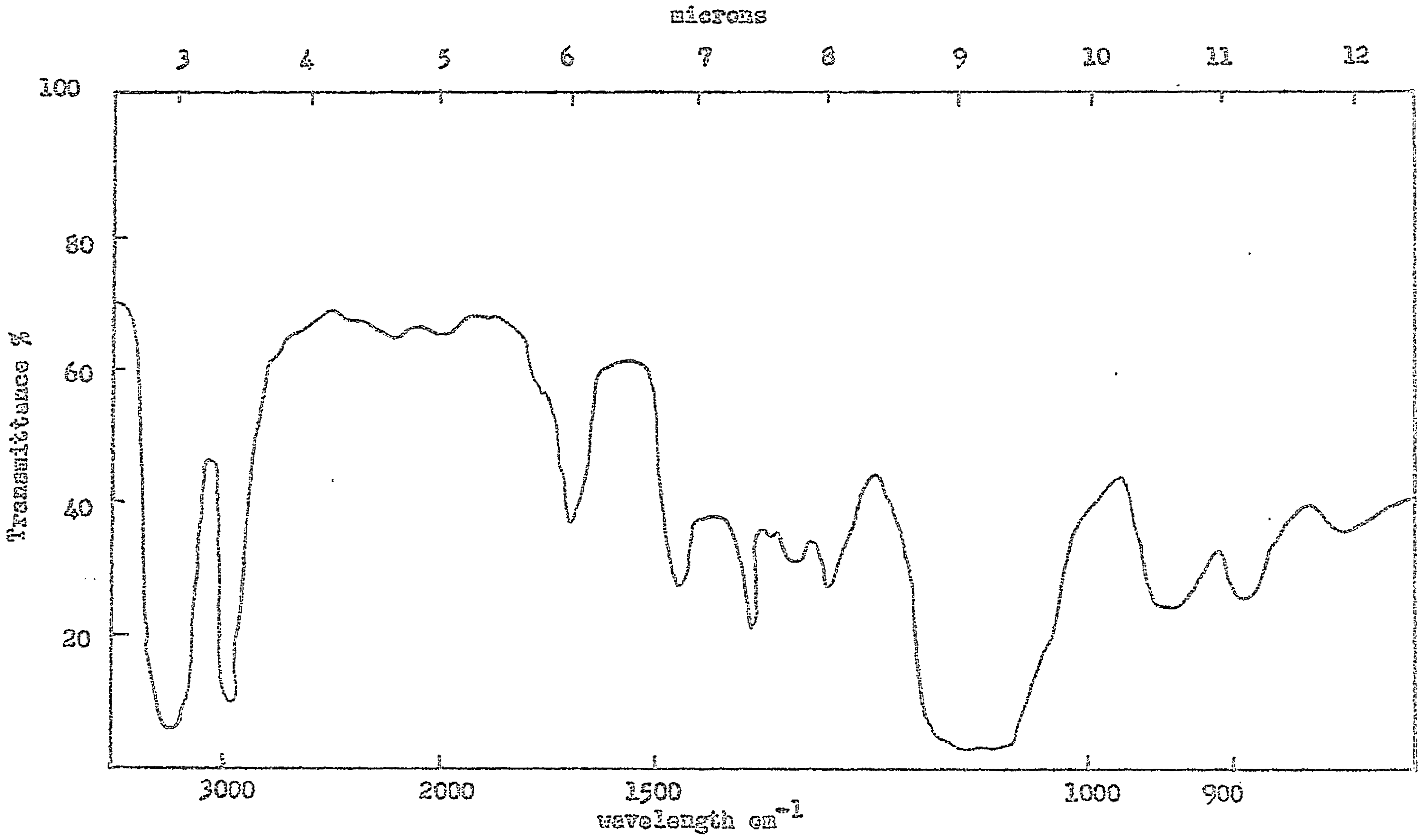

Figure 20: Distillation prerun of hexagol, showing presence of impurities absorbing at 5.8 - 6.1 μ

The occurence of carbonyl-containing impurities was detected during the distillation of the detergent Pr_2n_6. The first fraction was of low boiling point and contained some traces of carbonyl compounds, which indicated that some oxidation had occured during the synthesis, during which long periods of heating at high temperatures are essential. Although the crude extract had no prominent carbonyl peak in its infra-red spectrum, the distillation residues showed pronounced carbonyl absorption. The heating involved in the distillation induced further oxidation in the detergent. Distillation pre-runs of hexaoxyethylene glycol also absorbed at 6.1 μ, the possible structures being $HO.CH{=}CH.(OCH_2CH_2)_5OH$ and $CH\ {=}CH.(OCH_2CH_2)_5OH$. Some of these results are illustrated in Figures 19 and 20.

Section 2:

SURFACE CHEMISTRY AND THERMODYNAMICS

Surface Chemical Studies

Surface tension data on non-ionic detergents with branched hydrocarbon chains are available only for tridecanol condensates[4,73,262] and for commercial branched alkyl phenols,[263] although there are a number of surface-chemical studies on synthetic straight-chain non-ionics.[5,10,62,87] Because of this and because of the intrinsic interest in the surface chemistry and the information obtainable from surface-tension - concentration curves, an investigation of the surface-chemical properties of the present series of branched chain compounds was undertaken.

Apparatus and Method

The apparatus has been described in Weissberger.[235] It is illustrated in Figure 21. A brass dropping tip, of radius 0.3434cm., which was large enough to give a reasonably sized drop yet small enough to ensure that wetting was no problem, was soldered onto an ordinary syringe needle. The tip could therefore be removed for cleaning. To ensure complete wetting of the tip, it was occasionally rubbed with an abrasive surface. The test of complete wetting was consistent consecutive readings and visual observation of the drops.

The apparatus was immersed in a thermostat bath controlled to ± 0.01°. When tested with water distilled from potassium permanganate, the surface tension of water was found to be at 20° C, 72.67 dynes/cm. (Literature value 72.70[235]) and at 30° C, 71.11 (Literature value[235] 71.18 dynes/cm.) Reproducibility of any result was in the region of ± 0.09 dynes/cm., and at one filling of the syringe (0.5mls) four consecutive readings could be made on dilute solutions and up to 12 or more on solutions with low surface tensions.

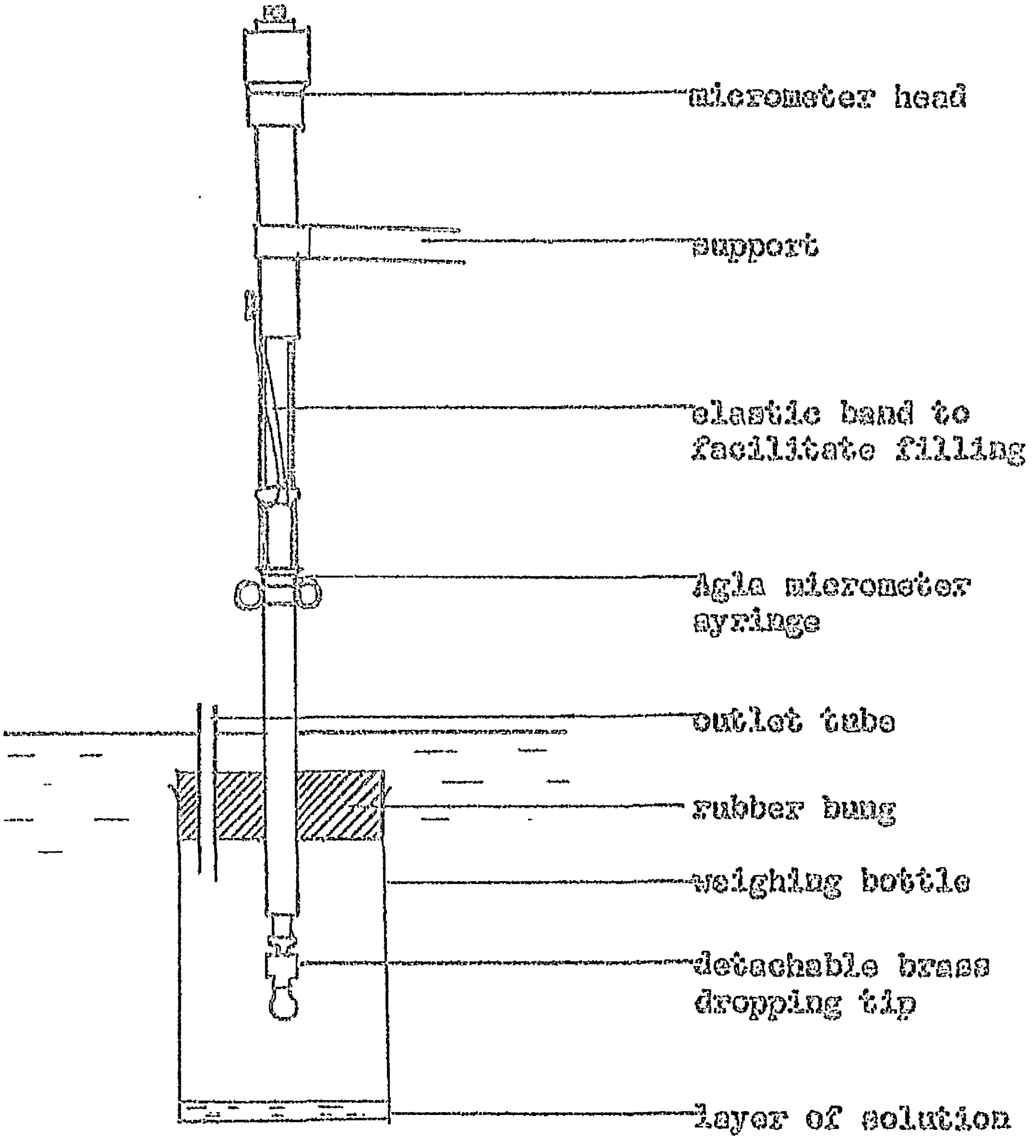

Figure 21: Diagram of Surface Tension Drop-Volume Apparatus.

The Agla micrometer syringe, on which the apparatus is based, can be read to ± 0.0002 mls.

Method: Solutions were prepared in glass-ware cleaned with chromic acid and rinsed with several changes of distilled water. Precautions were taken with dilute solutions to minimise adsorption of the detergent on the glass surfaces, by preparing solutions in glass-ware that had already contained non-ionic detergent solutions and which had been thoroughly drained.

The syringe was filled with the solution and the assembled apparatus allowed to equilibrate in the thermostat bath for up to 30 minutes. Initial measurements were made to determine the approximate size of the drops, and subsequent readings were obtained by forming a drop to approximately 90% of its final size. The drops were allowed to equilibrate with the saturated atmosphere in the weighing bottle, which was produced by a layer of solution at the foot of the bottle. After 5 to 30 minutes, the drop was slowly completed and allowed to fall, the final operation taking not more than 60 seconds. The initial and final micrometer readings gave the volume of each drop.

Ageing effects have been reported, by other workers, in solutions of of straight-chain non-ionic detergents,[10,62,73.] but tests on representative solutions of each detergent system showed no significant ageing after 20 minutes. The absence of such effects in these solutions is perhaps due to their relatively short alkyl chains, for ageing is most pronounced in the hexadecane series. Had there been any ageing, the drop-volume apparatus would not have been ideal as evaporation and condensation occurs (especially at higher temperatures) and would tend to upset the behaviour of the drop.

The surface tension, γ, was calculated using the equation:

$$\gamma = \frac{m.g}{r} \times F. \quad \text{dynes/cm.}$$

where m = mass of the drop, obtained from volume and density,

g = 981 dynes/cm.

r = 0.3434cm

F = correction factor of Harkins and Brown.[233]

Surface tension-concentration graphs were obtained for each detergent at three temperatures (where possible) and the critical micellar concentrations obtained from the sharp break in the plots of γ vs. log(concentration). The areas of the detergent molecules at the air-water interface were calculated from the simple form of the Gibbs equation. From the temperature variation of the CMC, the enthalpies and entropies of micelle formation were calculated using the equations described in the Introduction.

Results and Discussion

Plots of surface tension vs. log(concentration) are shown in Figures 22 and 23. No minima were found in these curves for any of the detergents studied, which, in the past, has been taken to be an indication of the purity of the solute. Above the critical micelle concentration, there appears to be no variation of the surface tension with increasing detergent concentration. Other workers[144] have considered this to mean that the activity of the solute is constant above the CMC, but doubt has been placed on this being so.[149] This aspect is dealt with more fully in the last section of the thesis.

The branched chain detergents have higher CMC's than straight chain detergents having the same number of carbon atoms in the alkyl chain. (Table XI). This is to be expected, as branched hydrophobes are more compact than their straight chain analogues and thus present a smaller

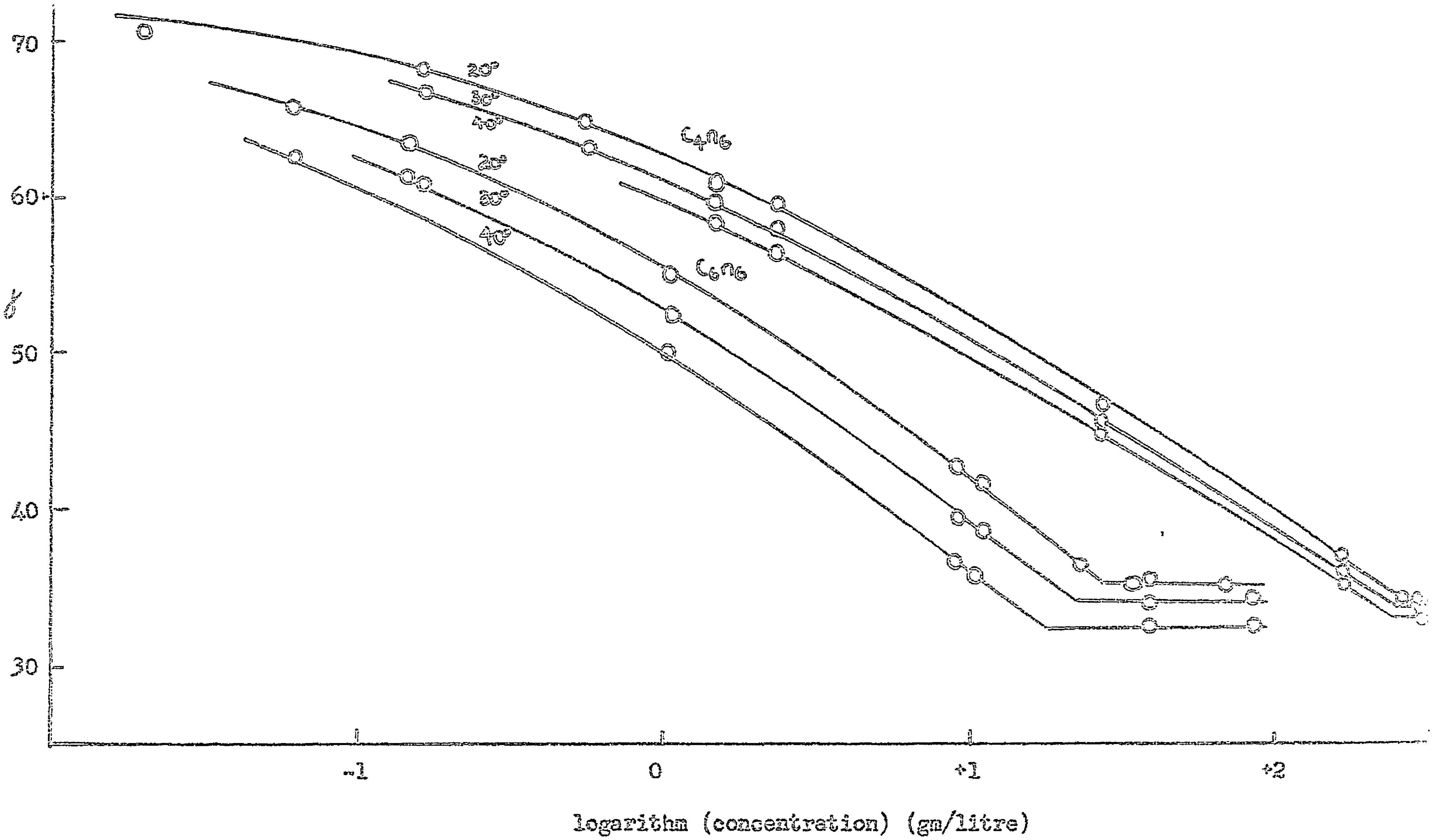

Figure 22: Surface tension plots of the straight chain detergents, C_4n_6 and C_6n_6 .

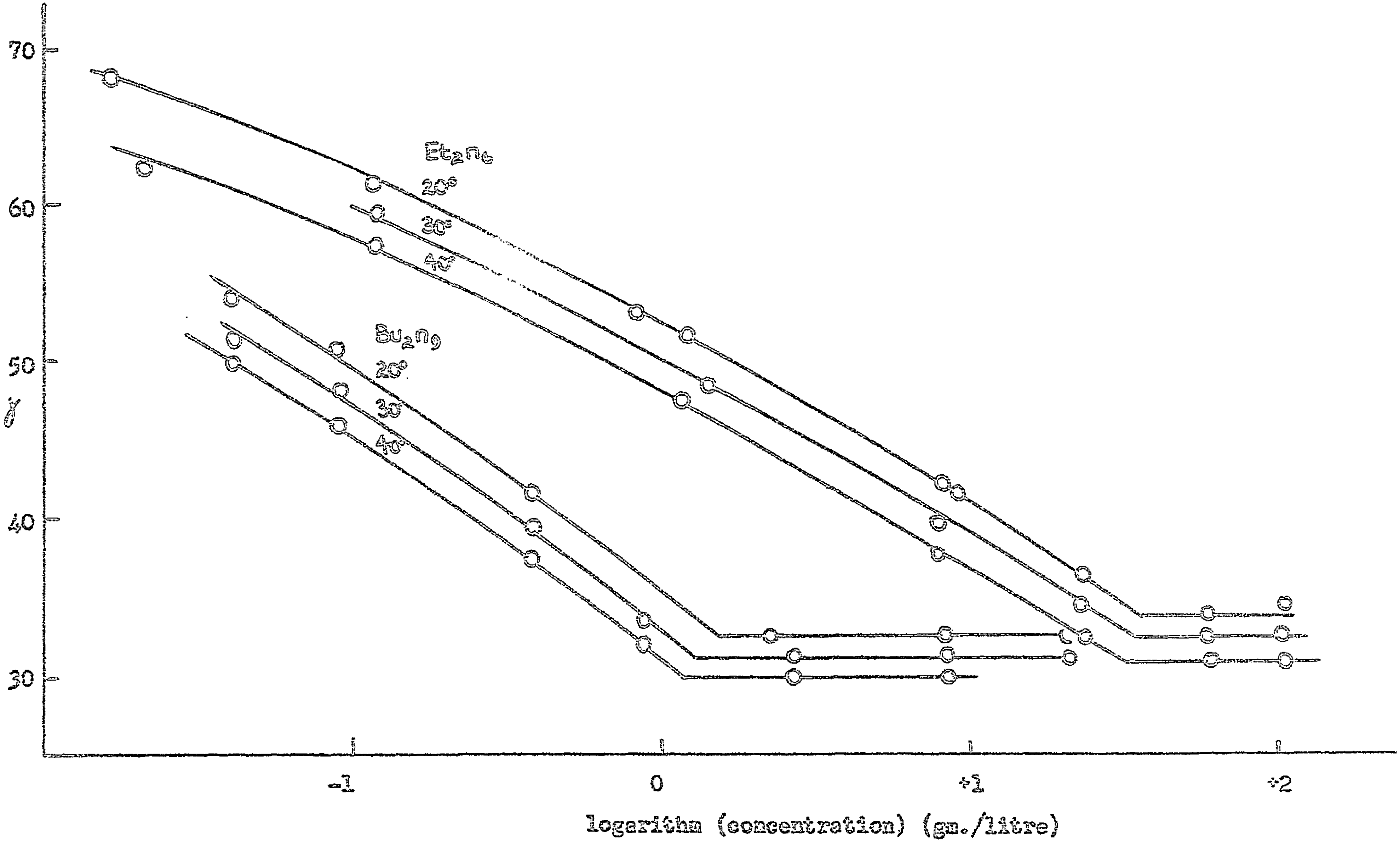

Figure 23: Surface tension plots for Et_2n_6 and Bu_2n_9 at three temperatures.

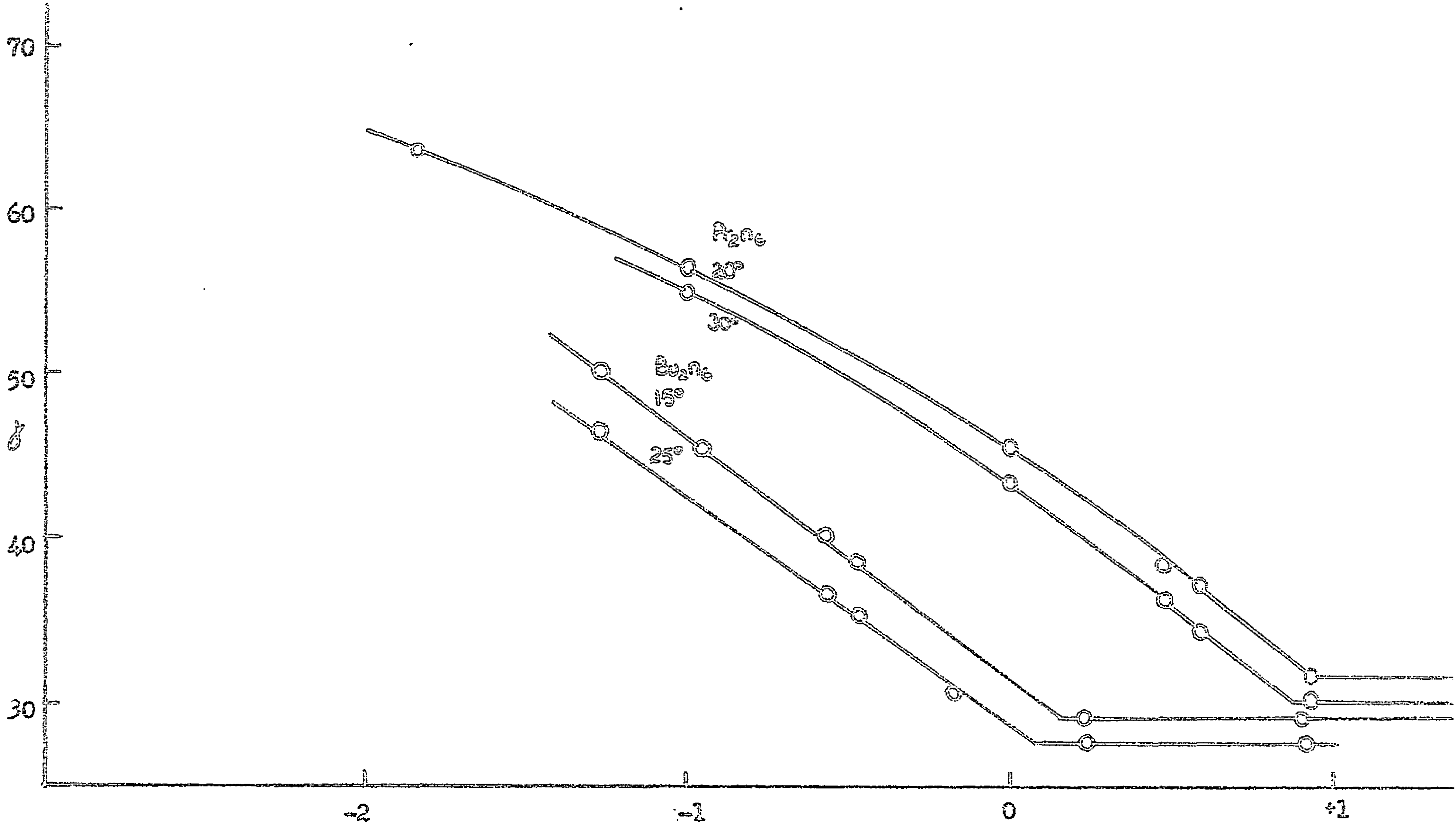

Figure 23a: Surface tension plots for Pr$_2$n$_6$ and Bu$_2$n$_6$ at two temperatures.

Table XI

Variation of CMC's with temperature and Enthalpies and Entropies of Micellisation

Detergent	Temperature	CMC (Moles/l.)	ΔH_m^1	ΔS_m^2
C_4n_6	20	7.96×10^{-1}	0.8	2.7
	30	7.60×10^{-1}		
	40	7.10×10^{-1}		
C_6n_6	20	7.4×10^{-2}	2.2	7.4
	30	6.5×10^{-2}		
	40	5.2×10^{-2}		
Me_2n_6	20	9.1×10^{-1}	0.6	2.2
	30	8.8×10^{-1}		
	40	8.5×10^{-1}		
Et_2n_6	20	10.0×10^{-2}	1.2	4.0
	30	9.3×10^{-2}		
	40	8.7×10^{-2}		
Pr_2n_6	20	2.3×10^{-2}	2.0	6.7
	30	2.0×10^{-2}		
Bu_2n_6	15	3.36×10^{-3}	2.9	9.7
	20	3.10×10^{-3}		
	25	2.84×10^{-3}		
Bu_2n_9	20	3.20×10^{-3}	2.3	7.7
	30	2.79×10^{-3}		
	40	2.43×10^{-3}		

---

1. Kcals $mole^{-1}$
2. cals.$mole^{-1}degree^{-1}$

surface area to the water, resulting in a smaller interfacial energy change on micellisation.

Phillips[164] and Overbeek[264] arrived at an equation relating ΔG_m^o, the standard free energy change per mole of monomer on micellisation, to the CMC:

$$\Delta G_m^o = \Delta H_m^o - T\Delta S_m^o \approx RT \ln CMC$$

The expression is valid so long as the monomer activity coefficient approximates to unity. ΔG_m^o may be obtained from plots of the logarithm of the CMC vs. hydrocarbon chain length (see Figure 24) as:

$$\ln CMC = x.c + \text{constant}$$

where x is the gradient of the line and c is the number of carbon atoms in the alkyl chain.

$$\frac{d\Delta G_m}{dc} = x.RT$$

For the branched-chain detergents a value of 0.97 RT (568 calories) per methylene group was obtained for the free energy change, compared with 1.11 RT (644 calories) per methylene group for the straight chain detergents. The difference in the values for the two types of compound probably reflects the differences in interfacial energy between branched and straight hydrocarbons and water. The value of ΔG_m^o depends on the hydrophobe alone, and not on the nature of the rest of the detergent molecule - as is borne out by the similar results obtained by other workers on detergents of varied molecular structure. Shinoda[143] found a value of 1.09 RT per methylene group for non-ionics; Stitger and Overbeek[265] found 1.0 RT per methylene group for sodium alkyl sulphates; Hermann[171] obtained 1.10 RT for dimethyl alkyl oxides. The critical micelle concentrations of branched chain sodium sulphosuccinates[266] were higher than those of their straight chain analogues: this was explained by the fact that the

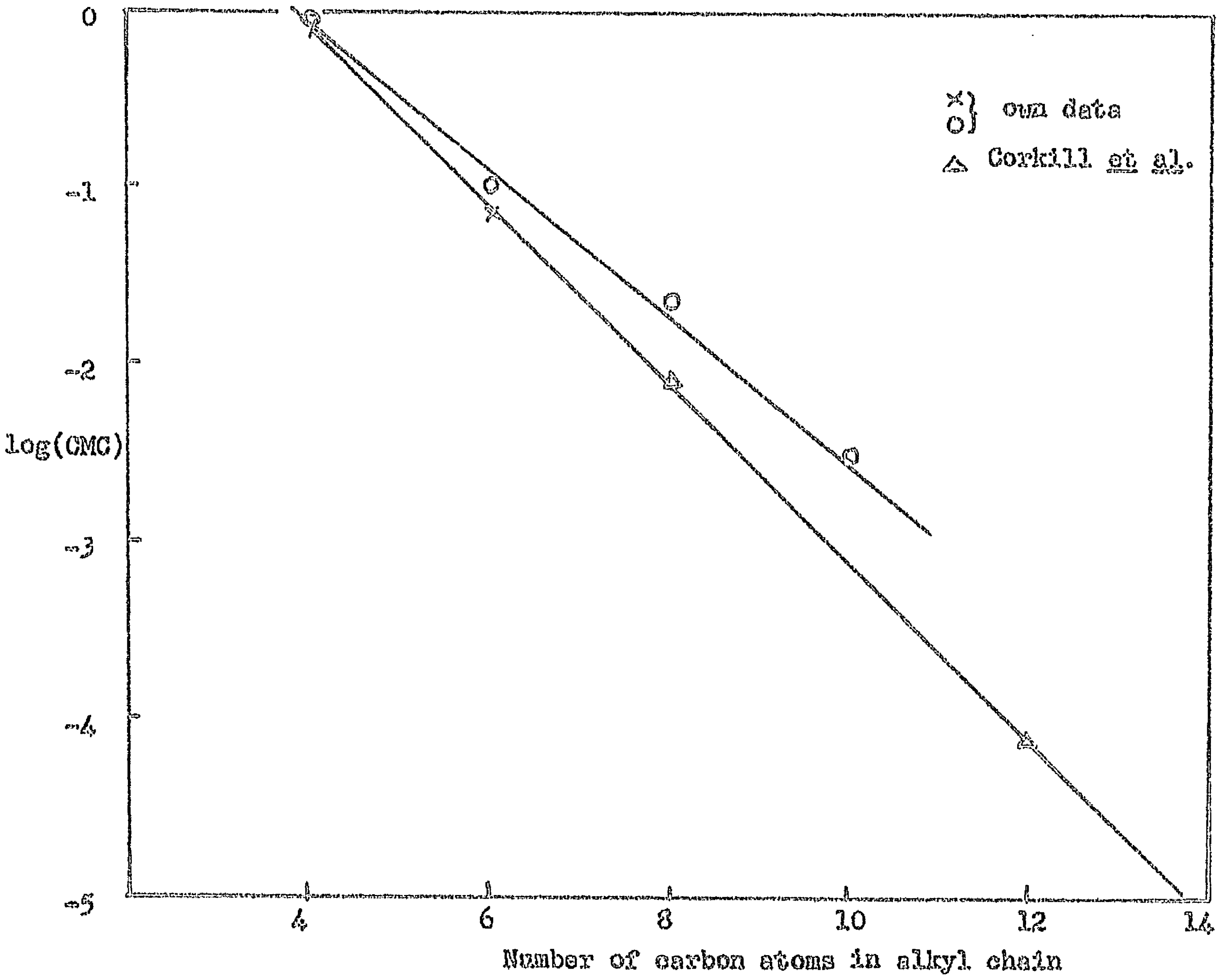

Figure 24: Plot of logarithm (CMC) vs. alkyl chain length, from which standard free energy was obtained (see text).

Table XII

Areas per molecules at air-water interface and surface tensions above CMC at 20°

Compound	Area/molecule (Å^2)	Surface T.[1]
C_4n_6	70	34.3
C_6n_6	62	35.0
Me_2n_6	61	35.0
Et_2n_6	77	33.6
Pr_2n_6	66	31.7
Bu_2n_6	61	28.3
Bu_2n_9	71	32.6

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[1] surface tension above CMC in dynes/cm.

free energy decrease due to aggregation of a branched detergent is less than that for a straight chain one.

Areas per molecule were calculated for the detergents using the simple form of the Gibbs' equation, in which activities were replaced by concentrations. The limiting areas/molecule were obtained from the gradient of the surface tension curve just prior to the CMC, and the values varied between 60 and 80 Å^2 With the exception of Me$_2$n$_6$ there is a general decrease of limiting area/molecule as the hydrocarbon chain length increases (see Table XII). The areas are greater than the cross-sectional area of one hydrocarbon chain in the case of the straight chain series, and greater than two hydrocarbon chains in the case of the branched detergent series. This indicates, as has been suggested before,[62] that the polyoxyethylene chain is the principle area-determining part of the molecule. However, it is obvious from the results that the hydrocarbon influences the area also. A survey of other work on non-ionics shows the same trend. This is emphasised particularly by the results for the dodecyl and hexadecyl series of Lange and Elworthy and Macfarlane, respectively, which are shown in Table XIII

Table XIII

Areas/Molecule of Non-ionic Detergents[23,62]

Compound	Area (Å^2)	Compound	Area (Å^2)
$C_{12}n_5$	54	$C_{16}n_6$	38
$C_{12}n_7$	59	$C_{16}n_7$	44
$C_{12}n_9$	71	$C_{16}n_9$	53
$C_{12}n_{12}$	77	$C_{16}n_{12}$	72

The results in Table XIII also show the increase in area/molecule at the air-water interface with increasing glycol chain length. This increase rules out an extended orientation of the PEG, and coiling of this part of the molecule has been suggested, with the coils presumed to increase in cross-section as the number of ethylene oxide units increased. The influence of the water of hydration is, no doubt, also felt. Crook *et al.*[5], obtained a value of 23 Å^2 for the cross-sectional area of *p*,*t*-octyl phenol-n, which, as the area of a benzene molecule is approximately 25Å^2 , suggests a perpendicular adsorption at the surface.

As the detergents studied here were based on hexaoxyethylene glycol, the influence of the hydrophile may be considered equal in all cases. As the carbon chain length is increased, the attraction between the chain increases, reducing the area/molecule. This attraction between the hydrocarbon chains may, in some way, cause the PEG to elongate. It follows that the area per molecule of the branched detergents will be higher, because of the shorter effective length of their alkyl chains at the interface. The value for Me_2n_6 might have been expected to be larger but it is possible that the low value found for the area at the interface is due to the compact structure of the head group, which allows a closer packing at the surface at high surface pressures. It is possible that, under these conditions of high surface pressure the molecules are arranged as depicted in Figure 25.

From the surface tension - concentration curves and areas per molecule, ΠA vs. Π curves were constructed (Π = surface pressure in dynes/cm and A = area per molecule in Å^2). Examples of these curves are shown in Figures 26a and 26b. Above 10 dynes/cm. surface pressure, these are reasonably linear and may be fitted by an equation of the type,

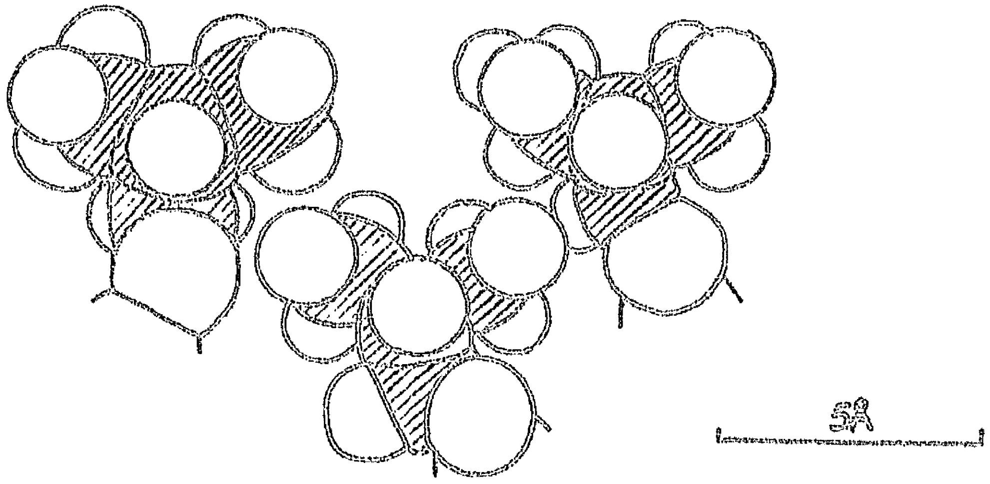

Figure 25: Possible arrangement of the hydrocarbon chains of Me$_2$n$_6$ at the air-water interface at high surface pressures, resulting in low areas per molecule.

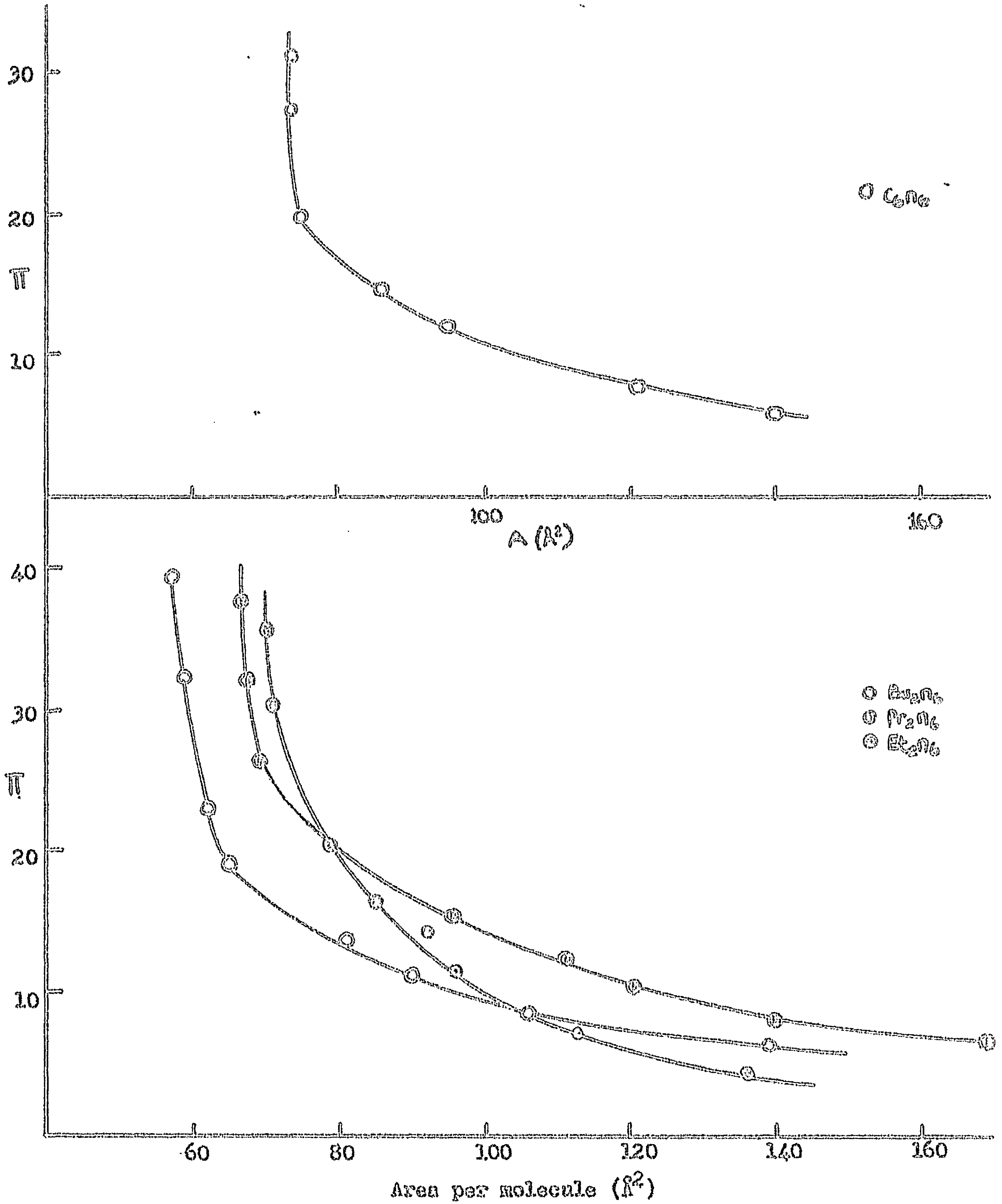

Figure 26a: π vs. A plots of some of the detergents, from which the πA vs. π diagrams were drawn. See Figure 26b.

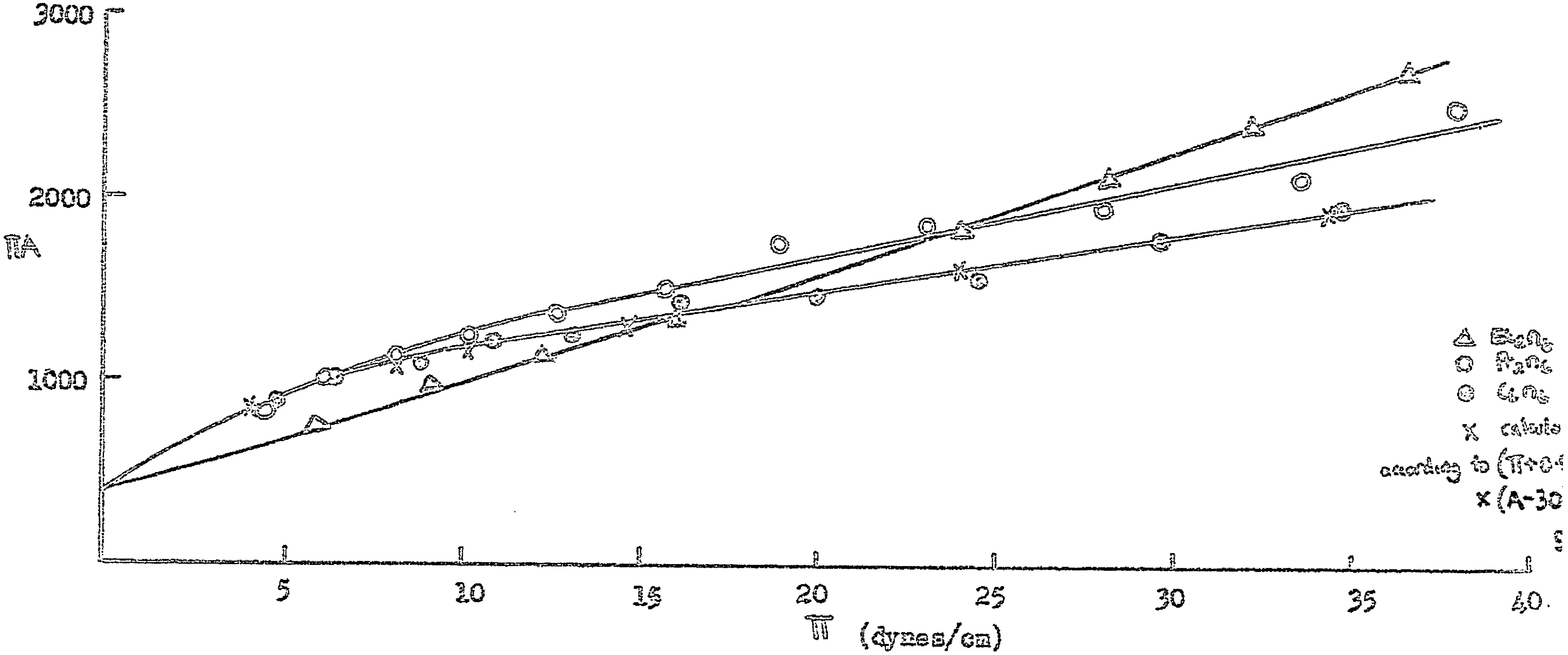

Figure 26b: ΠA vs. Π plots for Et$_2$n$_6$, Pr$_2$n$_6$ and C$_6$n$_6$ showing experimental (o) and calculated (x) points for C$_6$n$_6$.

$$\Pi(A - A_0) = \text{constant}.$$

For surface pressures above 2 dynes/cm the experimental results were represented by an equation

$$(\Pi - \Pi_0)(A - A_0) = C,$$

where C is a constant. The values of Π_0, A_0 and C are given in Table XIV.

The values in Table XIV suggest that the films are liquid expanded, although the constants for each system do not seem to follow any trend. Adamson[267] has stated that A_0 and Π_0 are essentially empirical constants and that values of A_0 found in other systems have been unexpectedly small compared to the space actually occupied by the molecules. However, A_0, which is termed the "co-area"[268] is thought to be the theoretical cross-sectional area of the adsorbed molecule. A_0 is 20.5 Å^2 for a fatty acid in a condensed state. In normal conditions, and in the present experiments the molecules are not in this state. The values of A_0 again seem to indicate that the PEG chain is the main determinant of the area per molecule. If this were not so, one would expect significant differences between the straight and branched chain detergents. The value for Me_2n_6 is again low, although it is perhaps significant that at constant surface pressure (Π = 20 dynes/cm.) the area per molecule of Me_2n_6 is greater than the area occupied by any other compound in the series. (See Table XIV)

There is evidence to suggest that A_0 is higher in adsorbed soluble films, as we have here, than in spread or in less-soluble adsorbed films. Pethica[269] has used a value of 31 Å^2 for the co-area of the lauryl sulphate ion, while Cook and Talbot[270] suggest a figure as high as 50 Å^2. Cockbain[271] suggested that the reason for the large co-area is the coiling of the hydrocarbon and its extension into the aqueous phase. This tendency will

Table XIV

Surface Pressure Data

Detergent	C	$-\pi_0$[1]	A_0 (Å^2)	A at π= 20 dynes/cm.
C_4n_6	724	0.7	45	78
C_6n_6	938	0.9	30	74
Me_2n_6	1520	5.0	20	84
Et_2n_6	992	7.0	45	82
Pr_2n_6	1192	3.2	35	83
Bu_2n_6	540	1.4	40	70

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[1] dynes/cm.

increase as the chain length increases; this might well explain the higher co-areas of the straight chain detergents C_4n_6 and C_6n_6 compared to that of Me_2n_6.

The constant π_0 is a measure of the attraction between the hydrocarbon chains at the interface; values of between 1-10 dynes/cm for a C_{10} chain and -22 dynes/cm. for a C_{22} chain have been reported.[272] The values for C_4n_6 and C_6n_6, however, are small (-0.7 and -0.9 dynes/cm respectively) and $-\pi_0$ decreases with increasing chainlength in the branched series. More exact interpretations of these results requires a more detailed investigation of the areas per molecule and their variation with surface pressure.

Exact Form of the Gibb's Equation

In the systems Me_2n_6 and C_4n_6 the activity coefficients of the solute are not unity, and it is therefore not permissible to substitute concentration for activity. The exact values of activity and activity coefficients of these detergents have been determined from vapour pressure measurements (see Section 4), and these were substituted in the exact form of the Gibbs' equation,

$$\Gamma_2 = \frac{1}{2.303\ RT} \cdot \frac{d\gamma}{d\ \log . a_2}$$

and the limiting area for C_4n_6 and Me_2n_6 using this were found to differ significantly from those determined without the activities. The limiting area/molecule for Me_2n_6 was raised from 61 $Å^2$ to 75 $Å^2$ and for C_4n_6 from 71 $Å^2$ to 92 $Å^2$. The error entailed in the neglect of activities in the Et_2n_6 is in the order of 0.4% in the calculation of d log c_2 and the resulting error in A is well within the limits of experimental error. The effect of the corrected values of area on the π - A plot of Me_2n_6 is illustrated in Figure 26c.

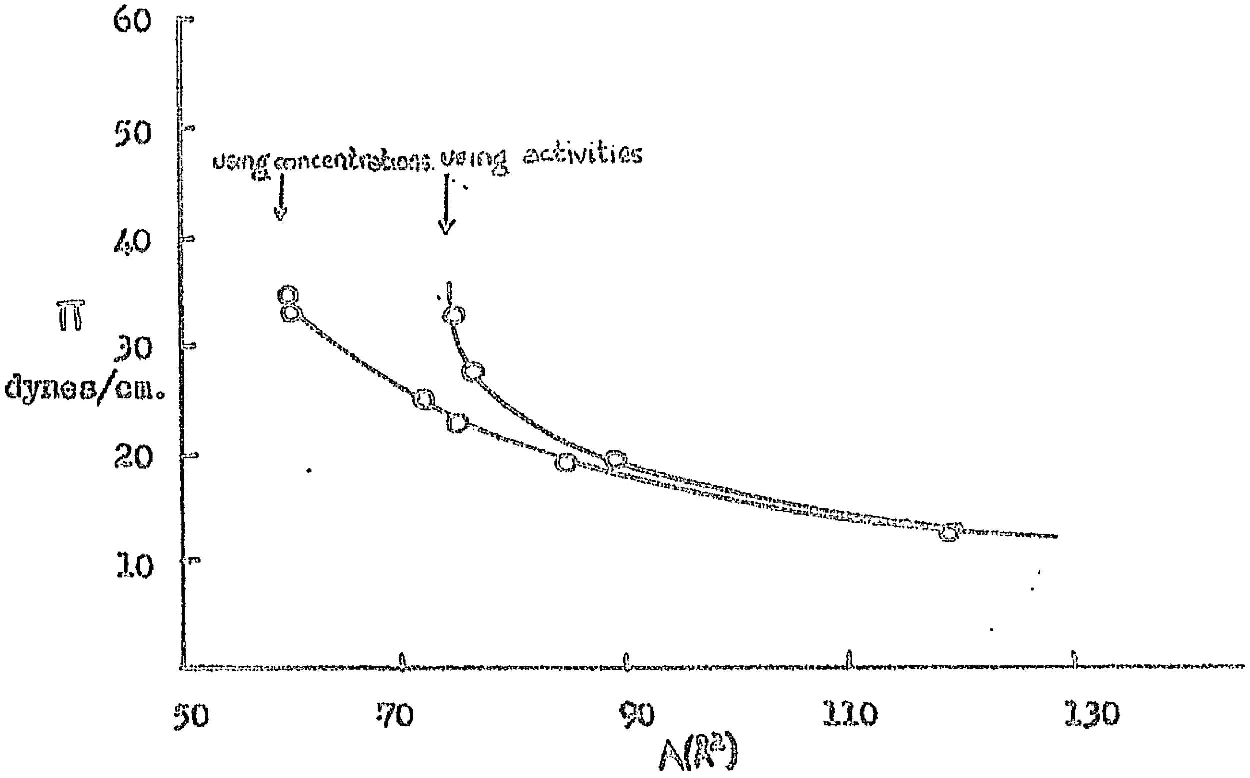

Figure 26c: Force-area diagram for Me_2N_6 solutions, comparing the results using the simple form of the Gibbs' equations and the more correct form using activities in place of concentrations.

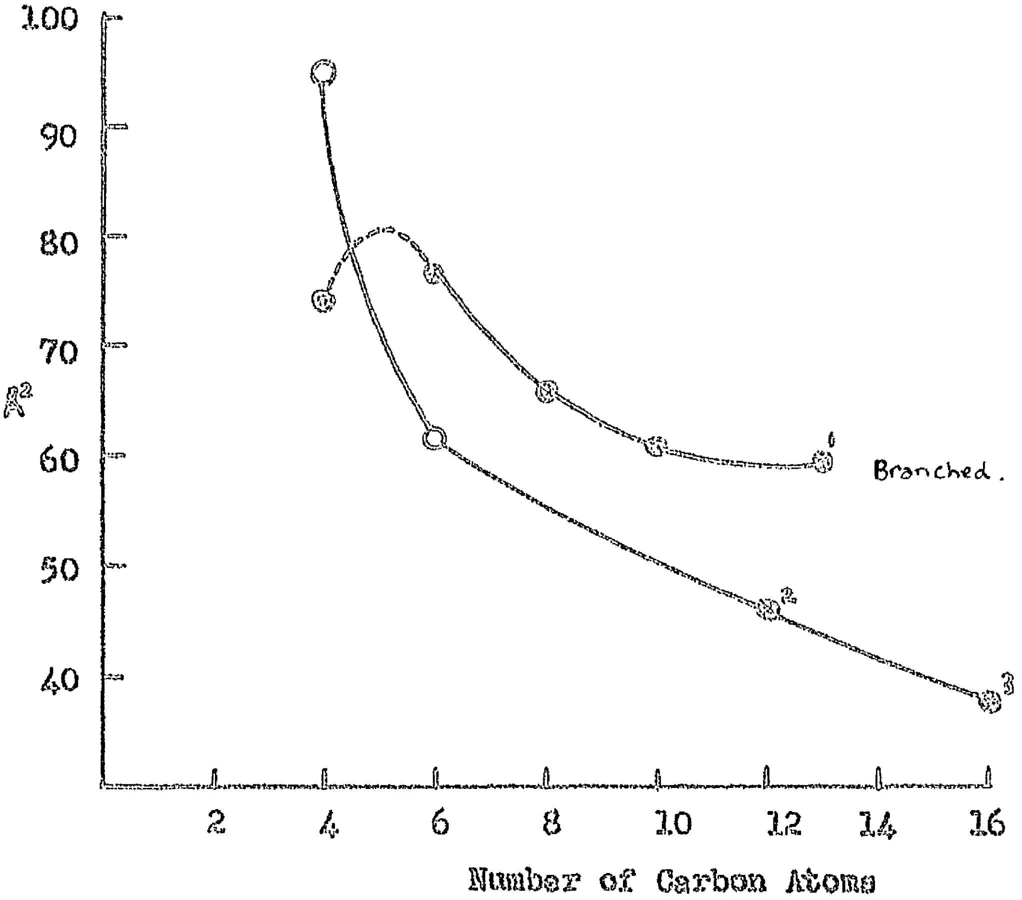

Figure 27: Areas per molecule of hexaoxyethylene glycol ethers as a function of hydrocarbon chain length. (2) Calculated from results of Corkill *et al.*[10.] (3) Elworthy and Macfarlane[62.] (1) Branched tridecanol-n_5 from Schick.[73.]

In Figure 27 the areas per molecule of the detergents are plotted as a function of hydrocarbon chain length, using the revised values of A for the C_4 detergents. The low value of Me_2n_6 still is evident, and the explanation put forward before still holds.

The Thermodynamics of Micelle Formation, Part I

In the Introduction a review of the published work on the thermodynamics of micellisation of non-ionic detergents was given. This discussion of the enthalpy and entropy results (Table XI) will be divided into two parts. This section will deal with the results obtained from the surface tension plots, and the second part will discuss the results in the light of the hydration changes on micelle formation as assessed by vapour pressure and viscosity measurements. Part II is included in the last section of the thesis.

The heats and entropies of micelle formation were calculated according to the equations of Matijevic and Pethica[154]:

$$\Delta H_m = -RT^2 \left(\frac{d \ \ln CMC}{dT} \right)_P$$

$$\Delta S_m = \Delta H_m / T.$$

The results are listed along with the CMC data in Table XI.

Increase in alkyl chain length for a constant PEG chain resulted in an increase in ΔH_m and ΔS_m., in both straight and branched-chain series. Positive values of ΔS_m have been suggested to be due to the loss of the "icebergs" or "clusters" of water around the hydrocarbon chains on micelle formation. The present results seem to bear this out. The branched chain compounds had lower entropies and enthalpies of micellisation, which may be explained by the smaller area of hydrocarbon surface which these compounds present to the water. There are, however, many factors at work.

One can list the changes resulting in positive or negative entropy changes on micellisation thus:

+ve entropy change	-ve entropy change
1. loss of water structure	1. increased solvation of PEG
2. extension of hydrocarbon chain	2. contraction of hydrocarbon chain
3. extension of PEG chain	3. contraction of PEG chain.
4. desolvation of PEG chain	

Many of these factors oppose one another. Extension of the polyoxyethylene chain (+ve ΔS) leads to increased micellar hydration (-ve ΔS). The net contribution of the PEG chain in many cases is negative: ΔS_m for Bu_2n_9 is 7.7 calories mole^{-1} degree^{-1} whereas that of Bu_2n_6 is 9.7 calories mole^{-1} degree^{-1}.

The hydrocarbon chains of detergents are highly contracted in aqueous solution,[273] and would be expected to extend when placed in the non-aqueous micelle interior. The contraction of the PEG would not be expected to alter much as in both monomeric and micellar states its enviromment is aqueous. In the branched series the configurational changes will be less than in the straight chain series, for sama total Carbon atoms and it seems reasonable to suppose that the water structuring and hydration changes account for the larger part of the heat and entropy effects. Wishnia showed that the entropy change in transferring _n_-butane from aqueous solution into a liquid alkane phase (equivalent to micellisation) is 23 calories degree^{-1} mole.$^{-1}$ As ΔS_m for C_4n_6 is 2.7 calories mole^{-1} degree,$^{-1}$ considerable order producing changes must be operating in the transition of a monomer into a micelle. Increased solvation of the polyoxyethylene chain would result in a negative entropy change. This is investigated in sections 3 and 4.

The calorimetric data of Corkill and his co-workers show large entropy values - in the order of +30 calories $mole^{-1}$ $degree^{-1}$. These represent t the entropy change ΔS^o, which results from the transition of the hydrated monomer in the hypothetical state ($N_2 = 1$) into the micelle. The difference between ΔS^o and ΔS_m is represented by ΔS_{dil}, the entropy of dilution from $N_2 = 1$ to $N_2 =$ CMC. As this is a mixing process the entropy change is positive.

Values of ΔG^o are given in Table XV. Because of the low critical micelle concentration of Pr_2n_6, Bu_2n_6 and Bu_2n_9 it is quite legitimate to place $\Delta H_m = \Delta H^o$. Using the values of ΔG^o and ΔH_m, therefore, it is possible to calculate the corresponding values of ΔS^o for these detergents.

These are for Pr_2n_6, $\Delta S^o = 22.3$ calories $mole^{-1}$ $degree^{-1}$; Bu_2n_6 29.2 calories $mole^{-1}$ $degree^{-1}$ and for Bu_2n_9, 27.2 calories $mole^{-1}$ $degree^{-1}$. The magnitude of the values of some order as those derived calormetrically by Corkill *et al.*[64] Both ΔS^o and ΔS_m follow the same trend of increasing with increasing alkyl chain length. The same trend is evident in the series $C_6n_6 - C_{10}n_6$ and the recent results of Benjamin[165] for the non-ionic dimethyl *n*-alkylamine oxides seem to confirm these results. (Dimethyl C_8AO, $\Delta S^o = 25.2$; $DC_{10}AO$ $\Delta S^o = 28.5$ calories $mole^{-1}$ $degree^{-1}$ $DC_{12}AO$ $\Delta S^o = 29.2$ calories $mole^{-1}$ $degree^{-1}$)

It must be concluded, therefore, that as both calormetric and other data indicate an increasing entropy change on micellisation as a series

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This should be considered as an array of hydrated monomers with no "free" water available.

Table XV

Free Energy Changes on Micelle Formation

Detergent	CMC (Mole fraction)	ΔG^{o}[1]
C_4n_6	1.41×10^{-2}	-1.37
C_6n_6	1.33×10^{-3}	-3.19
Me_2n_6	1.61×10^{-2}	-1.31
Et_2n_6	1.79×10^{-3}	-3.15
Pr_2n_6	4.14×10^{-4}	-4.54
Bu_2n_6	6.09×10^{-5}	-5.65
Bu_2n_9	5.76×10^{-5}	-5.68

[1] Kcals. mole^{-1}. The more exact form of equation is used for the first four detergents viz:

$$\Delta G^{o} = RT\left(\frac{n-1}{n}\ln CMC + C\right)$$

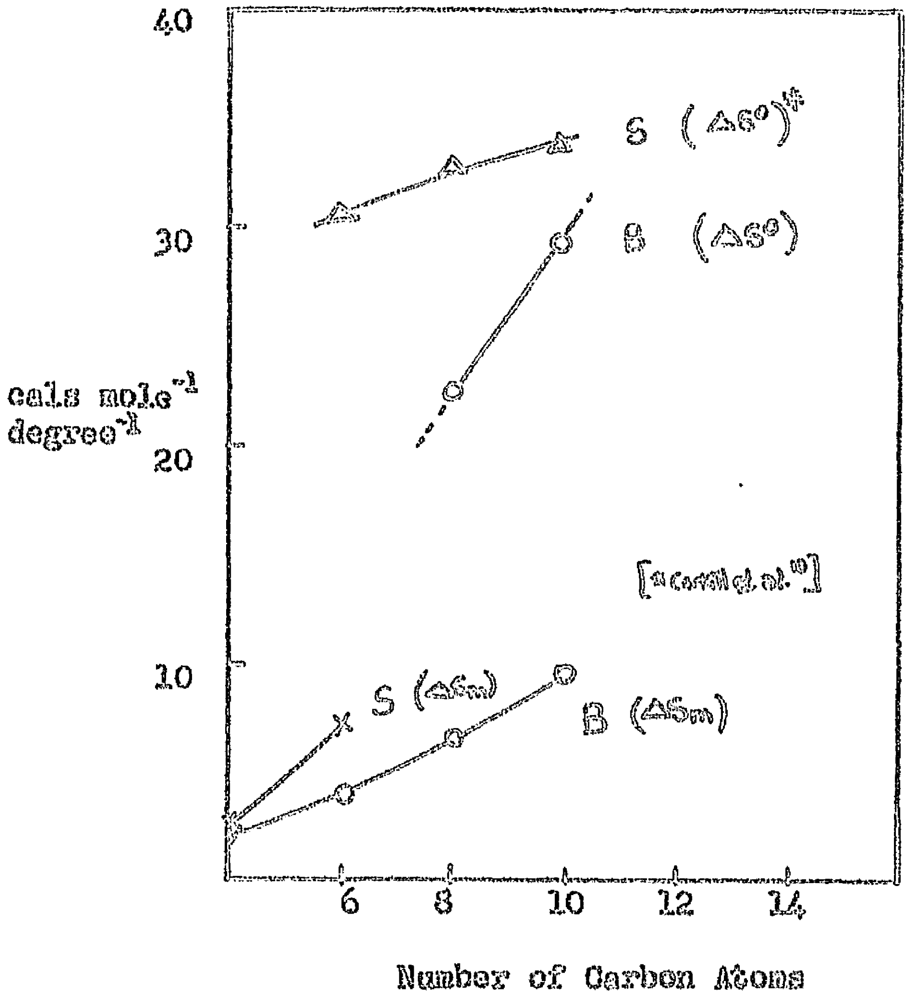


Figure 27a: Difference between ΔS^0 and ΔSm for straight (S) and branched non-ionic detergents, showing the lower values for the branched (B) detergents.

is ascended the positive entropy change is due to the loss of water structure around the alkyl chains of the monomers. This would agree with the smaller entropy change obtained when a branched-hydrocarbon chain detergent micellises compared with the change found with its straight chain analogue. The difference between branched-chain and straight-chain entropy effects is illustrated in Figure 27a.

Section 3

LIGHT-SCATTERING AND VISCOSITY

Light Scattering and Viscosity Studies

This section describes the investigation of micellar size and hydration by light scattering and viscosity techniques.

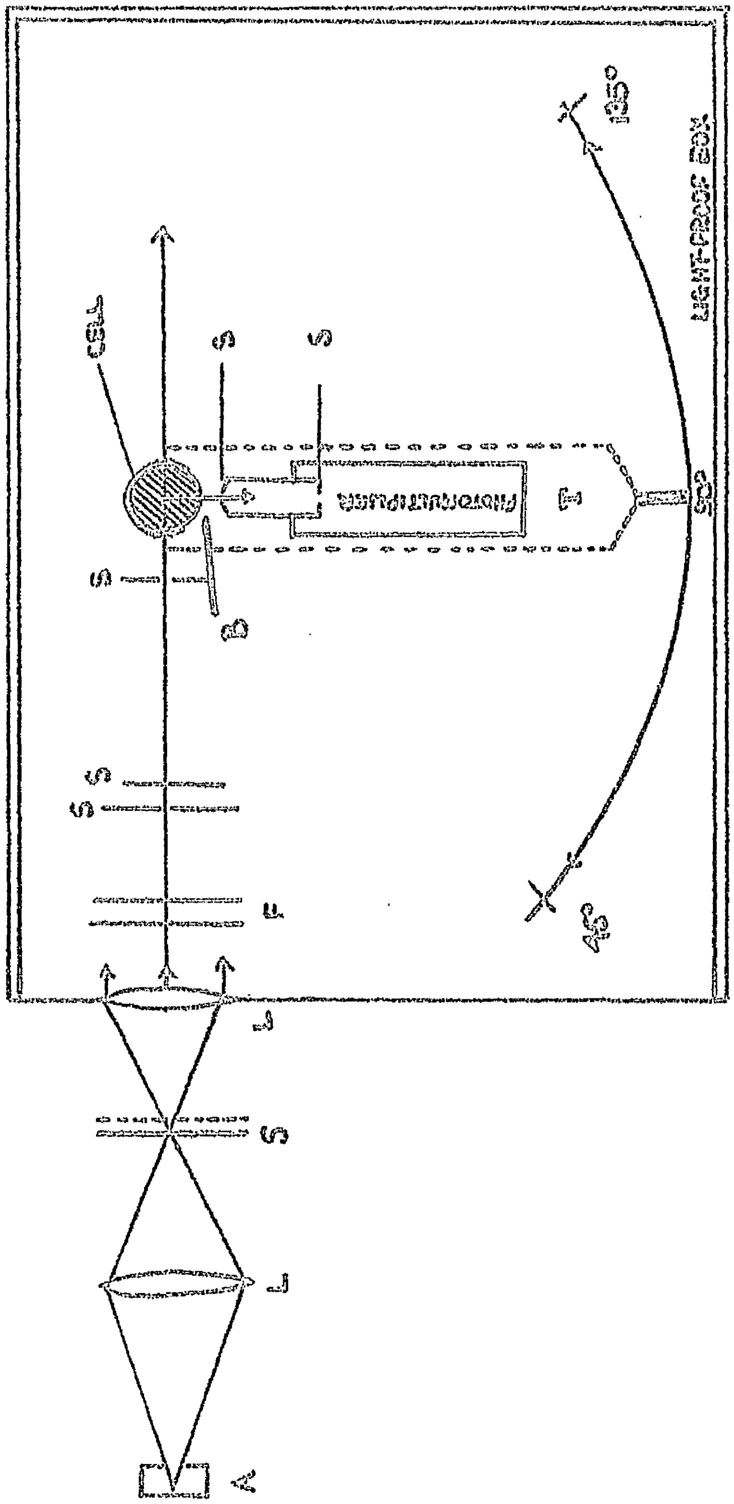
Apparatus and Methods

The Light Scattering Photometer: The light scattering photometer used in this work has been described by McIntosh.[274] Light from a 250 watt mercury vapour lamp (Osram ME/D) passed through an optical system of slits and lenses, the green line (5461Å) being isolated by means of an interference filter and a neodymium glass which removed all trace of yellow light. The beam was collimated before reaching the cell by means of two 2 x 25mm slits, 32cms apart, and the resulting beam passing through the cell measured 2 x 26mm.

To minimise lamp intensity fluctuations, the light source power was stabilised by an "Advance" Voltstat voltage control.

The light scattered was received by an eleven stage photomultiplier (EMI tube, type 6097 B) and the signal was recorded by a d'Arsonval galvanometer and a 50cm. scale. Voltage was supplied to the photomultiplier through two power units (Siemens Ediswan, type R 1184) in series, and the total output was restricted to 1500 volts. At higher voltages dark current effects from the photomultiplier made readings difficult to obtain.

The light reaching the photomultiplier passed through two 3 x 10mm slits, 8cm apart to ensure the correct viewing of the beam. The photomultiplier unit was mounted on a tufnol arm, pivoted beneath the centre of the cell, allowing a smooth movement of the unit around the cell. (Figure 28)



A. Lamp

B. Light Shield

L. Lens

S. Slit

T. Tufnol arm

F. Filters

Figure 28: Diagram of Light-Scatterer.

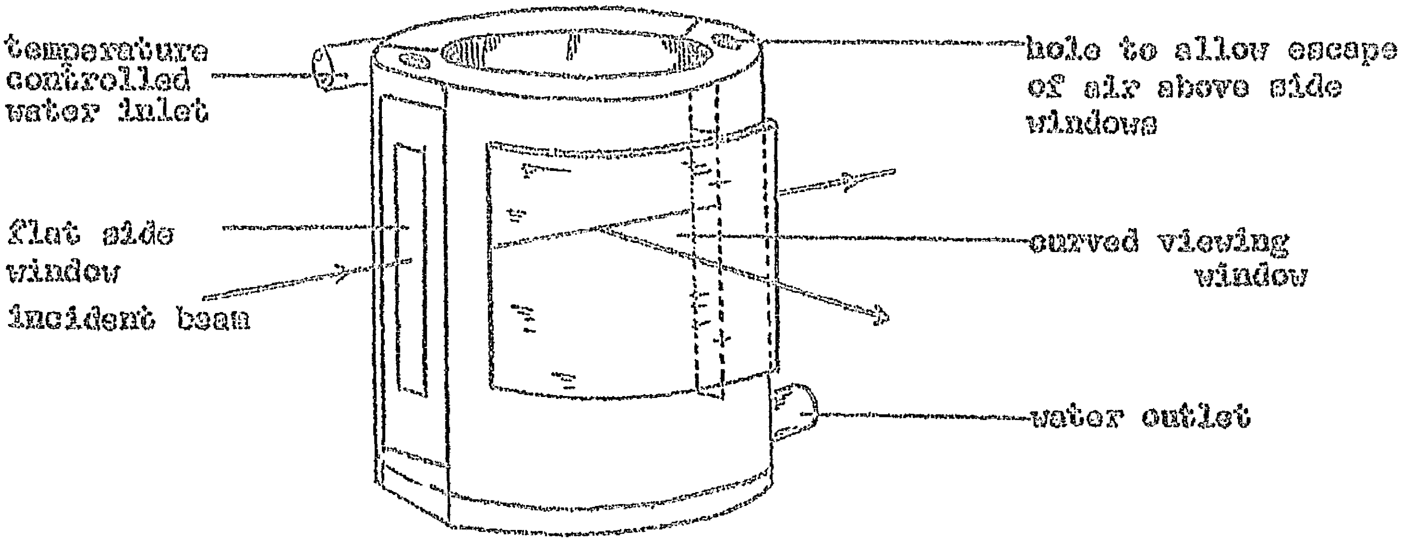


Figure 29: Light-scattering cell, drawn full size.

The cell was made from a solid cylinder of brass which had two parallel flattened faces to accomodate the windows through which the incident beam passed. These windows were made from microscope slide glass (1mm thick), and the curved viewing windows from tubing having the same curvature as the cell. The broad window allowed readings to be made at 45° and 135° to the incident beam to obtain Z_{45} values. (Figure 29)

Thermostatting of the cell was carried out by passing water from a controlled temperature bath through a series of channels drilled in the cell walls. The entire cell was blackened by the Relonol process. The windows were attached by "Araldite" resin. The cell capacity was about 45mls.

Dust was removed from solutions by three successive filtrations through a "Millipore" filter, using filter membrane of mean pore diameter 0.45 μ. Glassware and cells were washed and dried in a stream of acetone vapour, care being taken to exclude dust. The solution was first filtered into a clean flask, then refiltered, and filtered a third time into the cell, the the first few mls. being used to rinse the cell and then discarded. A blackened lid prevented access of dust to the cell during measurements.

Determination of Molecular Weight

The three principal factors to be measured in the determination of molecular weight by light scattering are 1) the specific refractive index increment , 2) the depolarisation of the scattered light and 3) the Rayleigh ratio or turbidity.

Specific Refractive Index Increment, dn/dc : This must be determined precisely as it appears as a squared term in the optical constant, H. Measurements were thus carried out in a Rayleigh interference Refractometer with 1cm. cells (Hilger and Watt, type M 154) the cells being thermostatted to the desired temperature ± 0.01°. The light source was a "Pointolite" lamp, the light passing through filters similar to those in the light scatterer.

Solutions were compared with solvent or another solution of known concentration, as the concentration difference had to be less than 2%. This enabled the zero-order band to be located with ease, and facilitated the counting of bands. The method used follows the procedure of Bauer et al.[275]

With solvent in both half-cells the zero reading was obtained by matching the zero order band of the upper and lower patterns, using white light and inserting filters before final adjustment. One of the compartments of the cell was filled with solution and the bands were approximately matched with white light, and accurately with filters, to give r. The micrometer was returned through F complete bands until the region of r_0 was approached, and the bandpatterns matched exactly at r'.

The scale reading equivalent to 1 band = $\frac{r'-r}{F}$ = r_f

The fraction of a band between r' and r_0 = $\frac{r'-r_0}{r_f}$ = f

The total number of bands resulting from the refractive index difference, dn, is F + f = ΔF

Since the refractive index difference is given by

$$n_2 - n_1 = \left(\frac{\lambda}{d}\right) \Delta F$$

λ = the wavelength of light in cms., and d is the optical path of the cell in cms.

$$\frac{dn}{dc} = 5461 \times 10^{-8} \frac{\Delta F}{\Delta c}$$

where Δc is the solute concentration difference between the half-cells in g./ml.

Depolarisations were obtained by isolating and measuring the horizontally and vertically polarised components of the scattered light by inserting a polaroid disc, cut with one edge parallel to one axis of transmission, in the path of the scattered light. The solvent contribution to both horizontal and vertical components was subtracted from these values.

The horizontal (Hs) and vertical (Vs) components of the light scattered by a solution of concentration c were measured with reference to the vertical component of light scattered by the standard perspex block (Vb). Similar measurements were made on solutions of concentration c_1, and the depolarisation ratio, ρ was obtained from

$$\rho = \frac{H}{V}$$

$$H = \frac{Hs}{Vb} - \frac{Hs_{c_1}}{Vb} \qquad\qquad V = \frac{Vs}{Vb} - \frac{Vs_{c_1}}{Vb}$$

In the present study no corrections for depolarisation were applied because of the small values of ρ and the inaccuracy of the values.

Measurement of Molecular Weights

The light scattered at 90°, S_{90}, was measured with reference to a standard perspex block, and the turbidity, Υ, calculated by means of the calibration factor, C.

$$\Upsilon = 16\pi R_{90}/3 = C.S_{90} = 2.303\ D/L$$

where D = optical density, L = path length. A value of $C = 2.71 \times 10^{-4}$ was obtained for the apparatus.[274] The procedure has been described by McIntosh[274] and by Macfarlane.[13] Twenty Ludox solutions were used in the calibration of the instrument to obtain C at zero turbidity, according to Maron and Lou's procedure.[276] $\Upsilon = S_{90} \times 2.71 \times 10^{-4} \text{cm}^{-1}$

The degree of accuracy in molecular weight determination by light-scattering has been stated variously to be ± 5% (Stacey[250]), ± 7% (Robinson and Saunders[277]) and ± 10% for solutions of non-ionic detergents (Elworthy and Macfarlane[8]). The error in measuring detergent solutions is doubtless accentuated by the difficulty in removing the last traces of dust from these solutions.

The concentration of a solution after filtration was checked using standard graphs of concentration against refractive index, and an Abbé refractometer for concentrated solutions and a Hilger-Rayleigh interferometer for dilute solutions. Cone angle corrections were applied to S_{90} measurements, as these were significant in the more concentrated solutions:

$$S_{90}^{corr} = S_{90}^{expt.} \times \left(\frac{n}{n_o}\right)^2$$

n = refractive index of the solution and n_o = refractive index of solvent. Micellar weights were calculated using Debye's equation:

$$\frac{H\,(c - c_L)}{\tau - \tau_L} = \frac{1}{M_W} + 2B(c - c_L)$$

in which τ is the turbidity at concentration c and τ_L the turbidity at c_L, which is the concentration corresponding to the CMC. The observed disymmetries were all in the region of 1 - 1.04 indicating that no dimension of the micelles exceeded $\lambda/20$. The micellar weights were obtained from plots of $H(c - c_L) \,/\, (\tau - \tau_L)$ vs. $(c - c_L)$ at $(c - c_L) = 0$. The reciprocal of the intercept, $\left[\frac{H(c - c_L)}{(\tau - \tau_L)}\right]_{(c-c_L)\to 0}$ gives M_W, the slope of the plot giving the second virial coefficient B.

Viscosity Measurements were made in a suspended level dilution viscometer at temperatures controlled to ± 0.01°C. For non-micellar solutions $\eta_{rel.}$ was the viscosity relative to water. With detergent solutions $\eta_{rel.}$ was the time of flow relative to the time of flow at the CMC. The viscosity of the micellar species was thus obtained, and the intercept $[\eta]$ obtained from plots of $\eta_{sp}/(c - c_o)$.

Results. The light scattering results for C_4n_6 are given as a plot of S_{90} vs. concentration in Figure 30. The break in the plot correspond to the CMC.

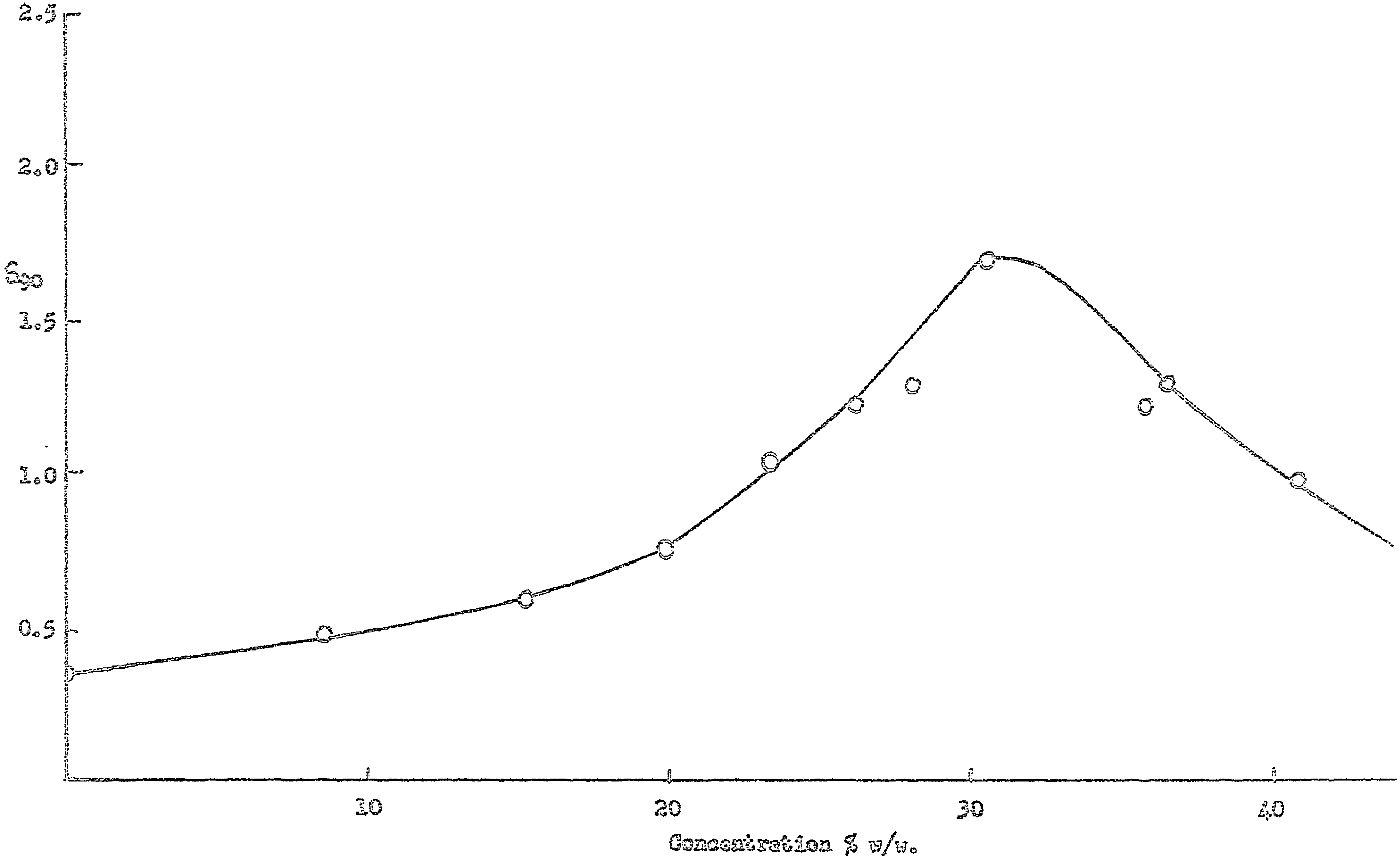


Figure 30: Plot of S_{90} vs. concentration for C_4n_6 , showing turbidity maximum. Behaviour of Me_2n_6 is similar, although the whole curve is displaced to the right, with the maximum around 44%.

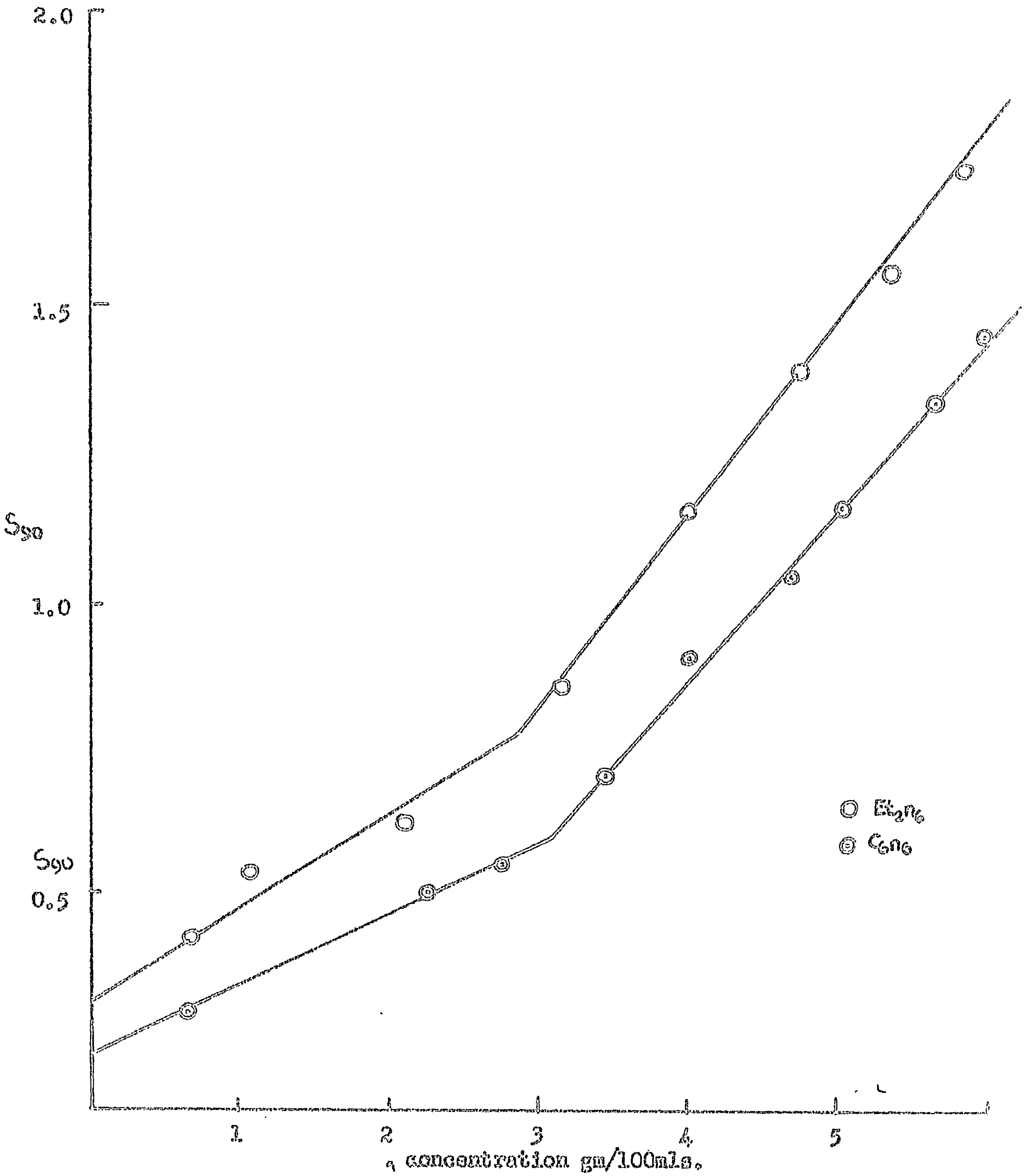


Figure 31: S_{90} plot for Et_2n_6 and C_6n_6 at 20°.

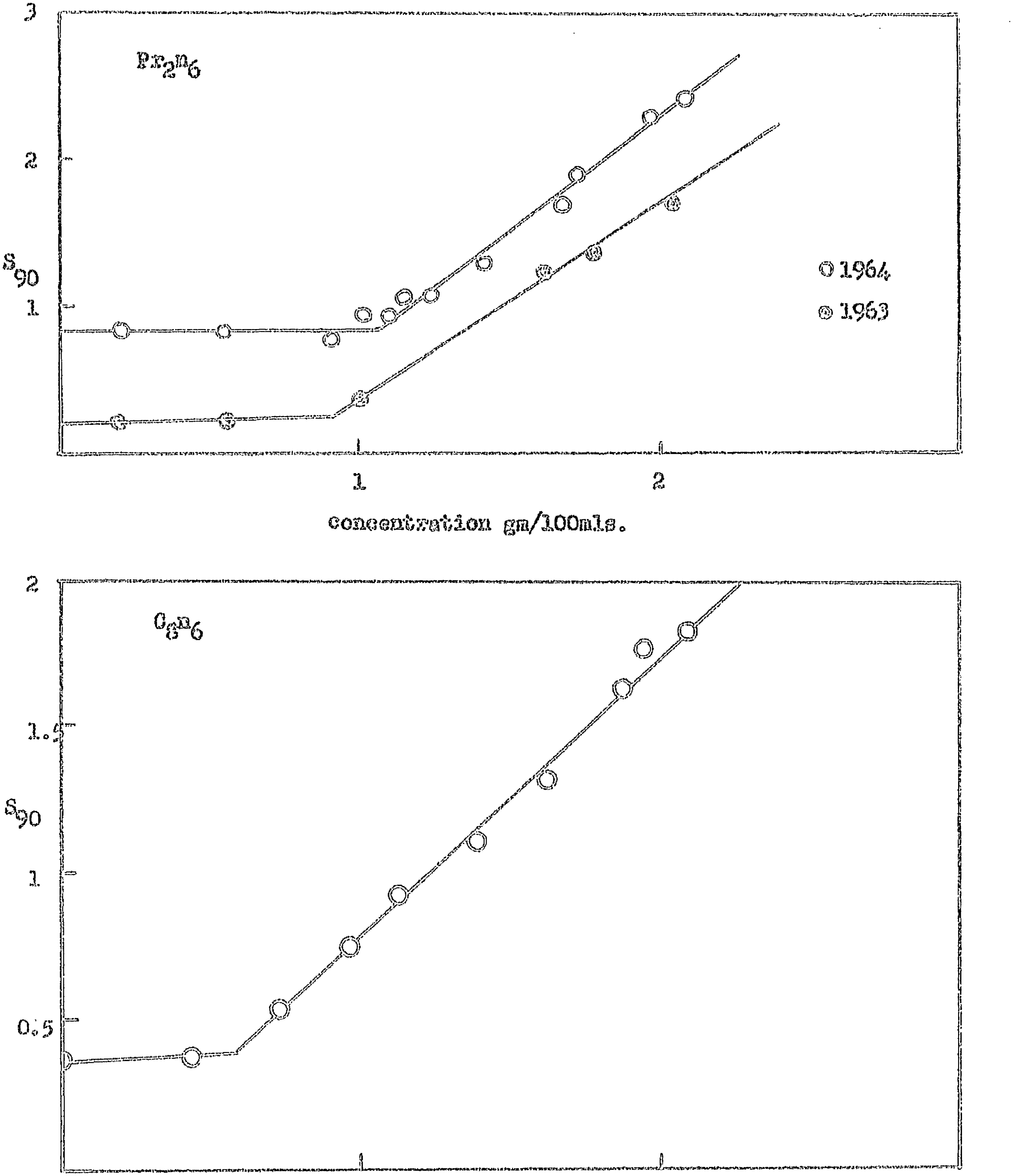


Figure 32: S_{90} vs. concentration plots for Pr_2n_6 , showing variation between old (1964) and new samples (1963). These gave identical micellar weights. Lower diagram is S_{90} vs. conc. plot for C_8n_6.

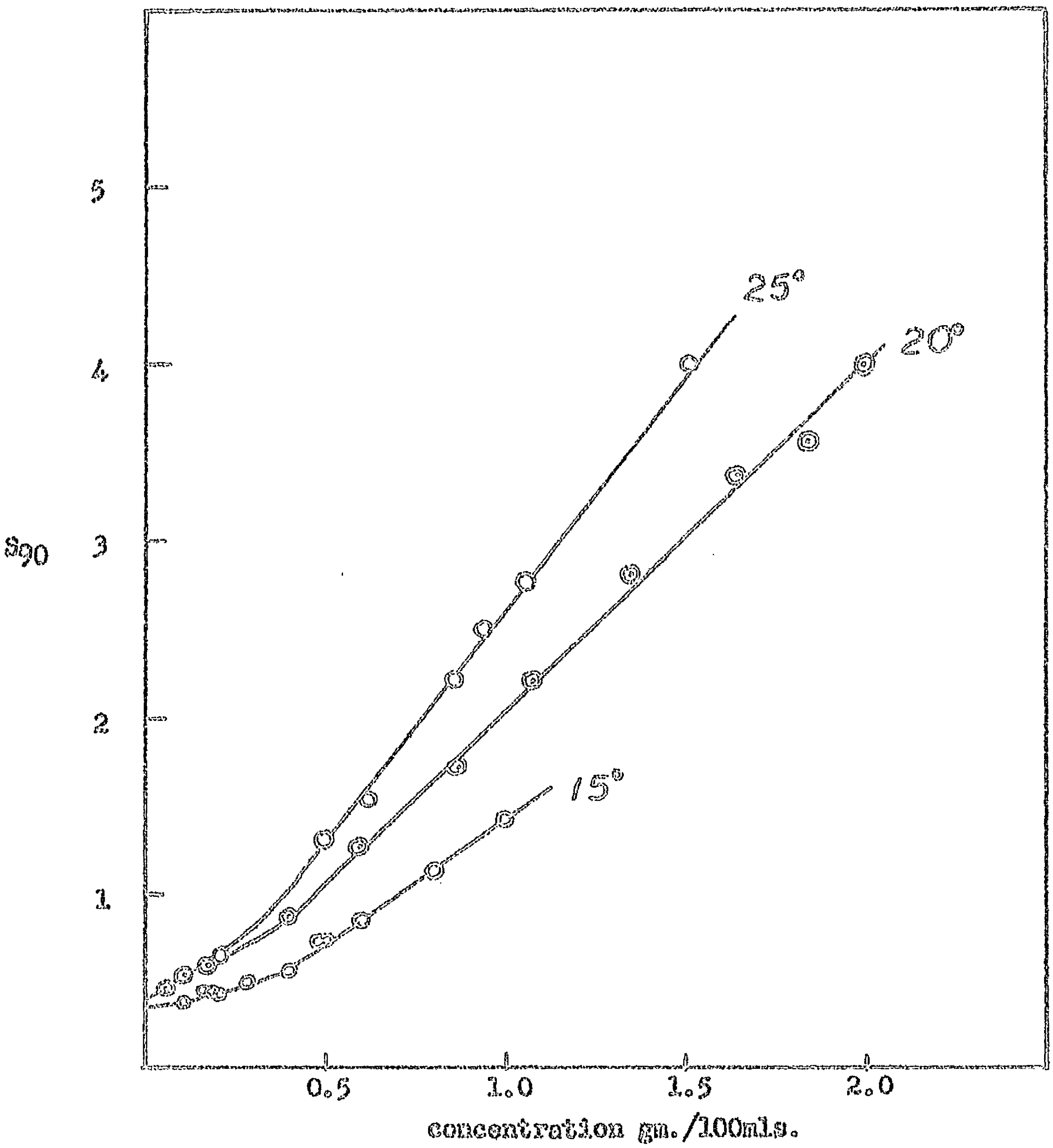


Figure 32a: S_{90} vs. concentration plot for Bu_2N_6 at three temperatures.

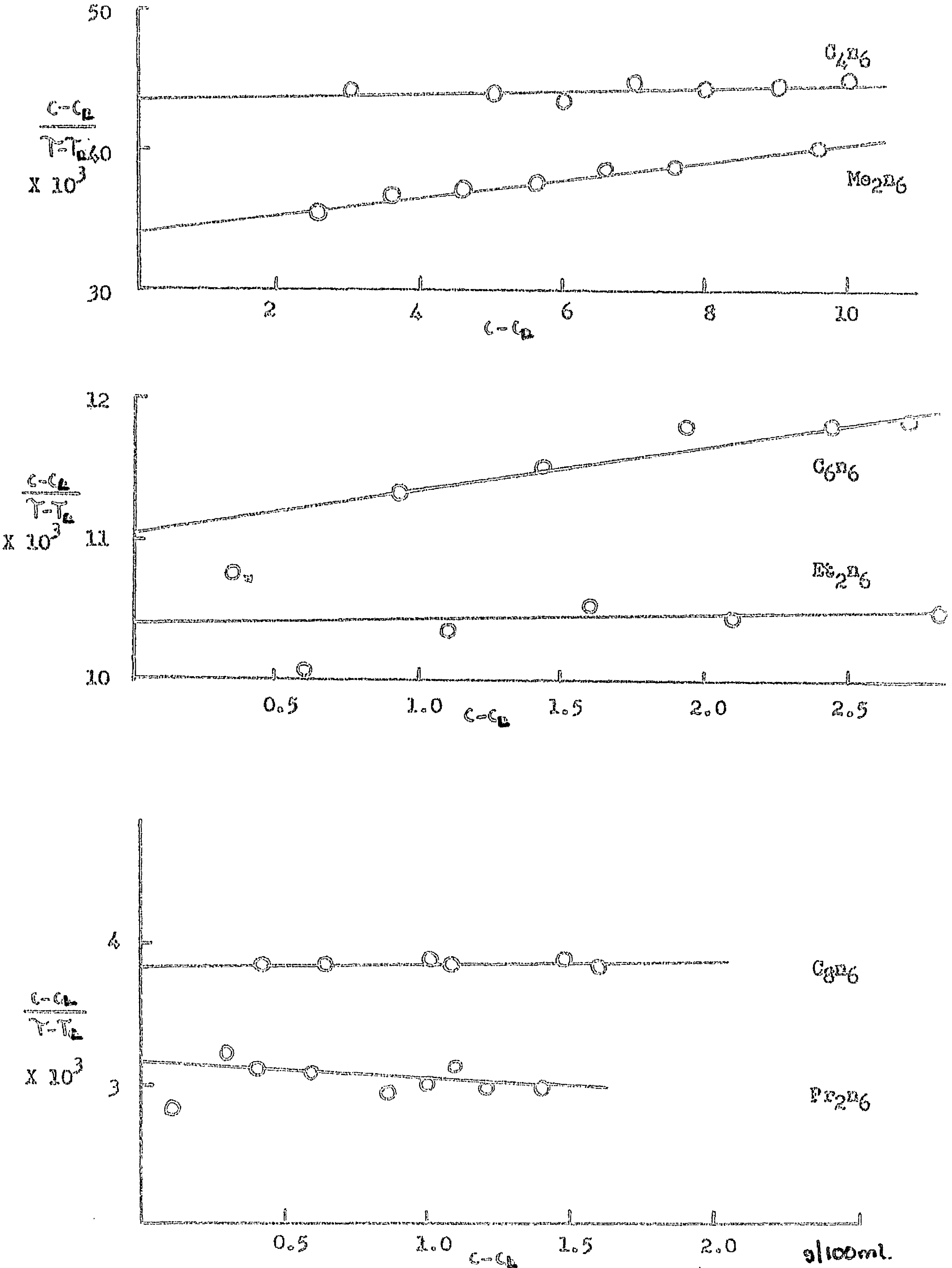


Figure 33: Plots of $(c - c_b)/(\gamma - \gamma_b)$ vs. $c - c_b$ for the detergents marked.

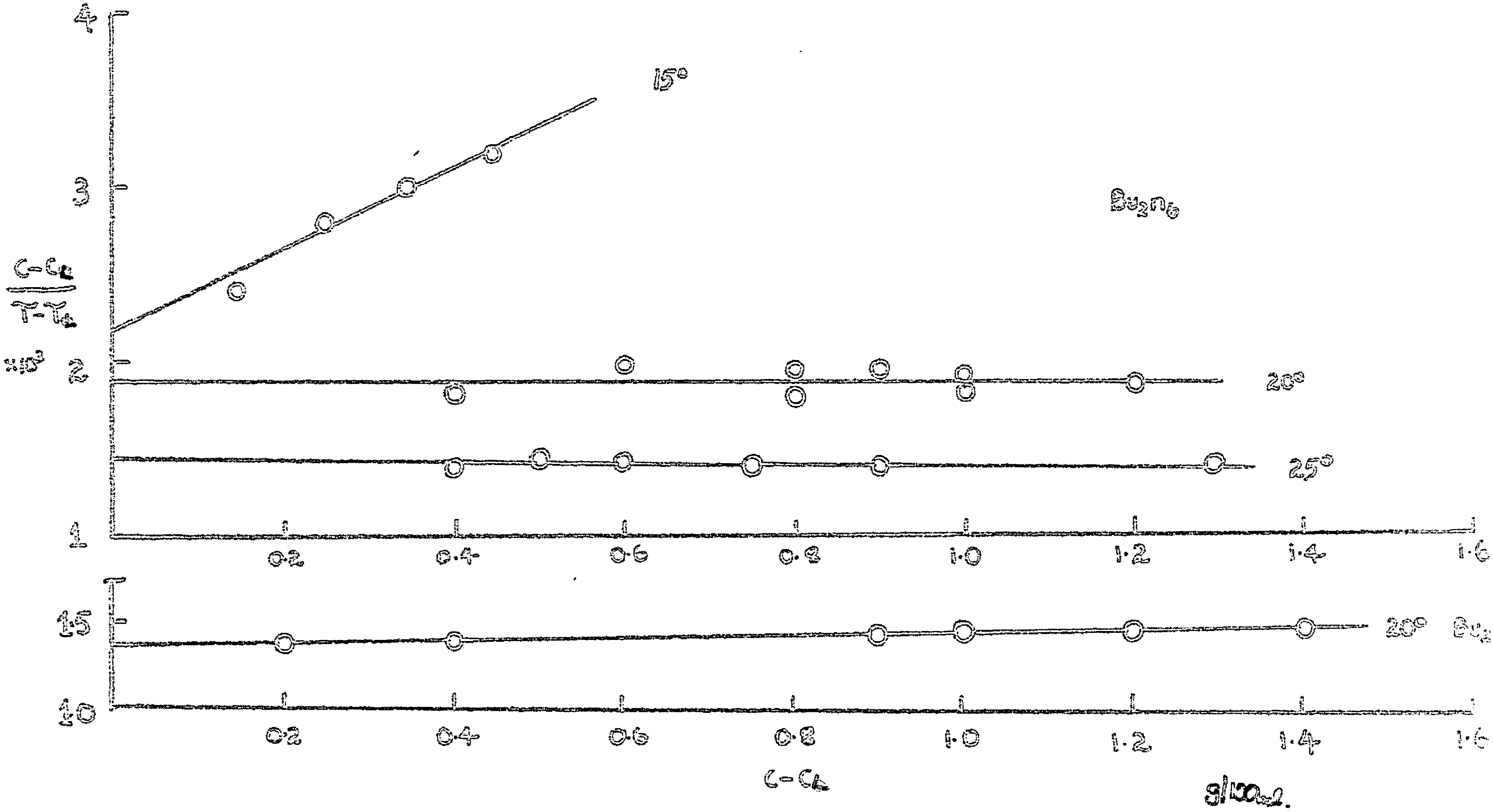


Figure 34: Plots of $(c - c_{\Delta})/(T - T_{\Delta})$ vs. $(c - c_{\Delta})$ for Bu_2n_6 at 15°, 20°, and 25° and for Bu_2n_9 at

It is seen that a maximum occurs in the curves, the turbidity decreasing with increasing concentration above this point. Similar effects have been found by Corkill and Herrmann[90] in solutions of the non-ionic dimethyl dodecylamine oxide, which they explain, on the basis of X-ray data, to be due to steric interference between the micelles. In a 40% w/w solution which is approximately the concentration at which the turbidity maximum of the Me_2n_6 system occurs, the hydrated micelles occupy approximately 70% of the total volume of solution. Close-packed spheres occupy 74% of the volume of a container. Presumably this interference results in the decrease in scattered light at high concentrations in these systems. For the calculation of micellar weight, the part of the τ - c curve between the CMC and the maximum was used.

The S_{90} concentration graphs for the other compounds are conventional and are shown in Figures 31 and 32. The results are summarised in Table XVI

The first member of both straight and branched chain series (C_4n_6 and Me_2n_6) have low aggregation numbers and the "micelles" formed by these detergents are extremely small and probably represent only loose aggregations of monomers. As the alkyl chains are lengthened the micellar weights and the aggregation numbers increase. Differences between straight and branched series are however, not marked although the latter appears to form slightly larger aggregations.

The observed micellar weight of C_8n_6 at 20° (13,300) agrees well with that found by Goodman _et al._ at 18°C (12,800).

Increase in aggregation number occured with increase in temperature (15° - 25°C) in Bu_2n_6 solution, but the system could not be investigated at higher temperatures because of its low cloud point (27°C).

Table XVI

Light-Scattering Results

Compound	dn/dc	ρ	M	Temp. °C	Aggregation no.
C_4n_6	0.134	0.0611	1,200	20	∼4
C_6n_6	0.132	0.0649	4,800	20	13
C_8n_6	0.130	0.0593	13,300	20	34
Me_2n_6	0.135	0.0697	1,500	20	∼4
Et_2n_6	0.133	0.0433	4,970	20	14
Pr_2n_6	0.133	0.0319	15,900	20	40
Bu_2n_6	0.132	0.0420	22,000	15	53
Bu_2n_6	0.132	0.0456	28,700	20	69
Bu_2n_6	0.132	0.0561	38,200	25	91
Bu_2n_9	0.134	–	36,300	20	65

dn/dc in ml/g. ρ = depolarisation · M = micellar weight Z_{45} values were in the region of 1.00 to 1.04.

Bu_2n_9 forms micelles at 20°C with fewer monomers (65) than does Bu_2n_6 at 20° (69) as would be expected by the more hydrophilic character of the former compound.

CMC's determined from light scattering (C_L) are compared with CMC's found from surface tension (Co) and interferometry in Table XVII. The interferometric method of determining CMC, from the change in slope of refractive index with concentration, has been described by Donbrow and Jan.[278] In systems with low aggregation numbers the method is insufficiently accurate as the change slope above the CMC is often hardly discernable. This was so in the case of Me_2n_6 and C_4n_6. Where the CMC is high the specific refractive index increment has to be measured against another solution and further inaccuracies are thus introduced. In systems with extremely low CMC's, on the other hand, it is difficult to obtain readings below the CMC and adsorbtion of detergent on to the cell walls can result in anomalous readings.[278]

In most cases agreement between C_L and Co is good and in no case does any discrepancy approach the region of "several times" as reported for the hexadecane series.[13] The larger concentration has in the past been found to be C_L. It has been suggested by Balmbra *et al.* that this is due to a second association limit. Although the differences between C_L and Co in this series are not great it may be that C_L exceeds Co significantly as the hydrocarbon chain increases, and the results show a tendency in this direction although, because C_L is subject to a significant error, no real conclusions can be drawn at this stage.

Viscosity results are given as plots of $\eta_{sp}/(C - Co)$ vs. C - Co (Figures 35 and 36) for the micellar systems. Systems with high CMC 's exhibited a break in relative viscosity - concentration plots at CMC (Figure 37).

Table XVII

Critical Micelle Concentrations (Moles/litre)

Compound	Temp. °C	S.T Value (C_o)	L.S Value (C_L)	Value Interferometric
C_4n_6	20	7.9×10^{-1}	5.9×10^{-1}	
C_6n_6	20	7.4×10^{-2}	8.56×10^{-2}	9.4×10^{-2}
C_8n_6	20	1.0×10^{-3}	1.45×10^{-3}	1.0×10^{-3}
Me_2n_6	20	9.1×10^{-1}	10.6×10^{-1}	
Et_2n_6	20	1.0×10^{-1}	0.8×10^{-1}	1.0×10^{-1}
Pr_2n_6	20	2.3×10^{-2}	2.28×10^{-2}	
Bu_2n_6	15	3.36×10^{-3}	3.50×10^{-3}	
	20	3.10×10^{-3}	3.50×10^{-3}	
	25	3.00×10^{-3}	3.40×10^{-3}	
Bu_2n_9	20	3.20×10^{-3}	4.10×10^{-3}	

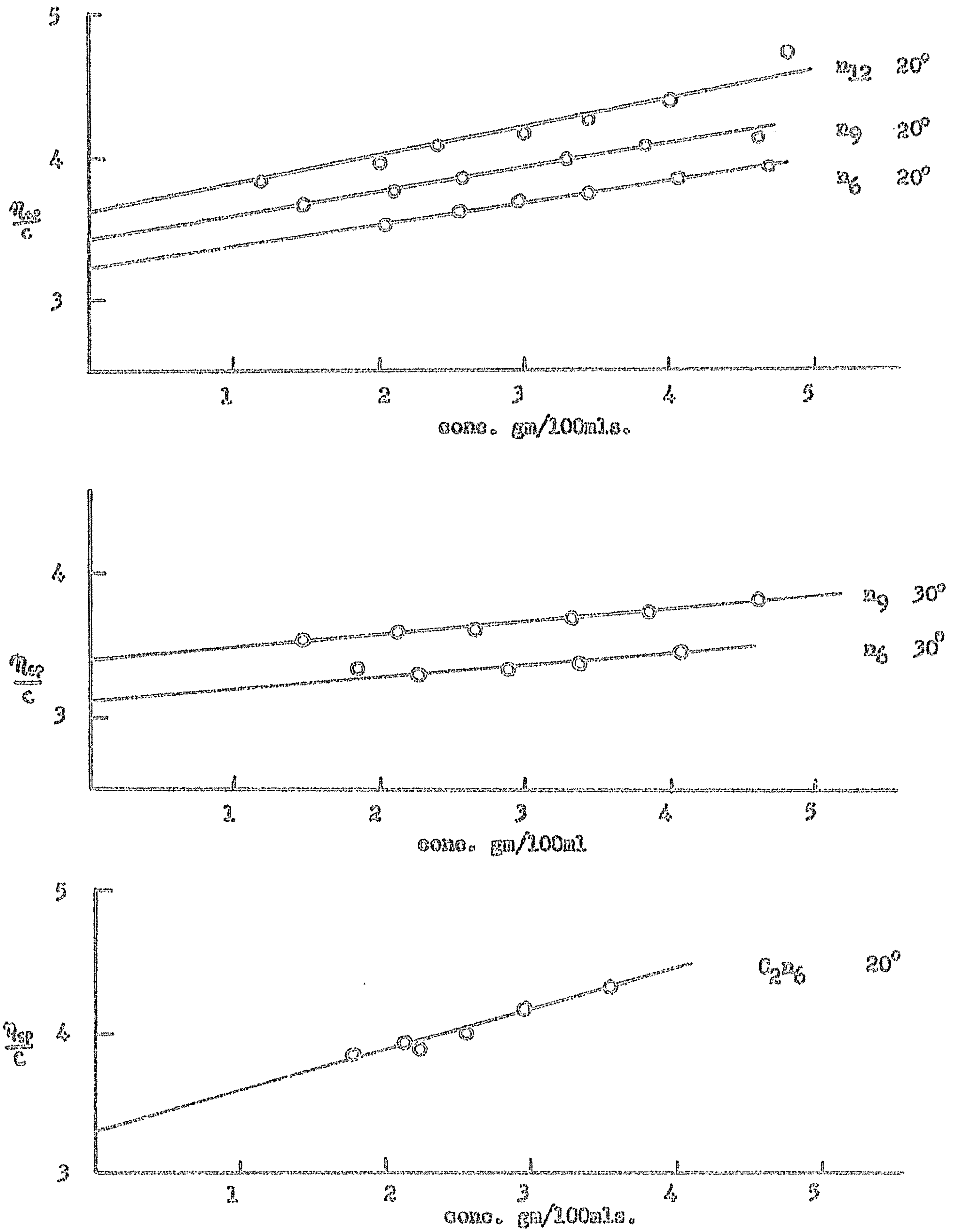


Figure 35: Viscosity plots at 20° and 30° for the glycols and at 20° for 20°. (c in η_{sp}/c is concentration in gm/ml.)

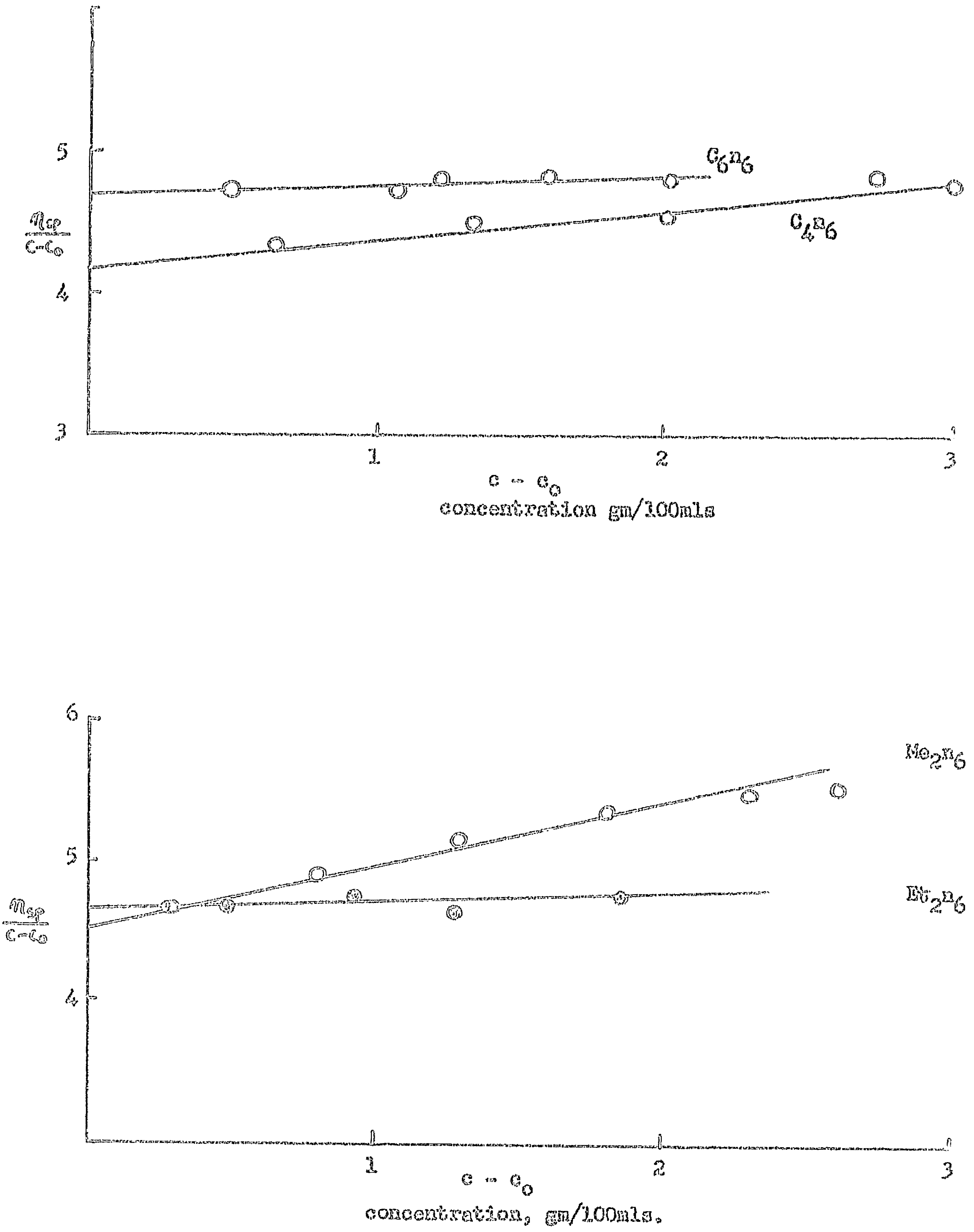


Figure 36: Viscosity plots for C_4n_6, C_6n_6, Me_2n_6 and Et_2n_6 at 20°. Concentration in calculation of $\eta sp/(c - c_0)$ is in gm/ml.

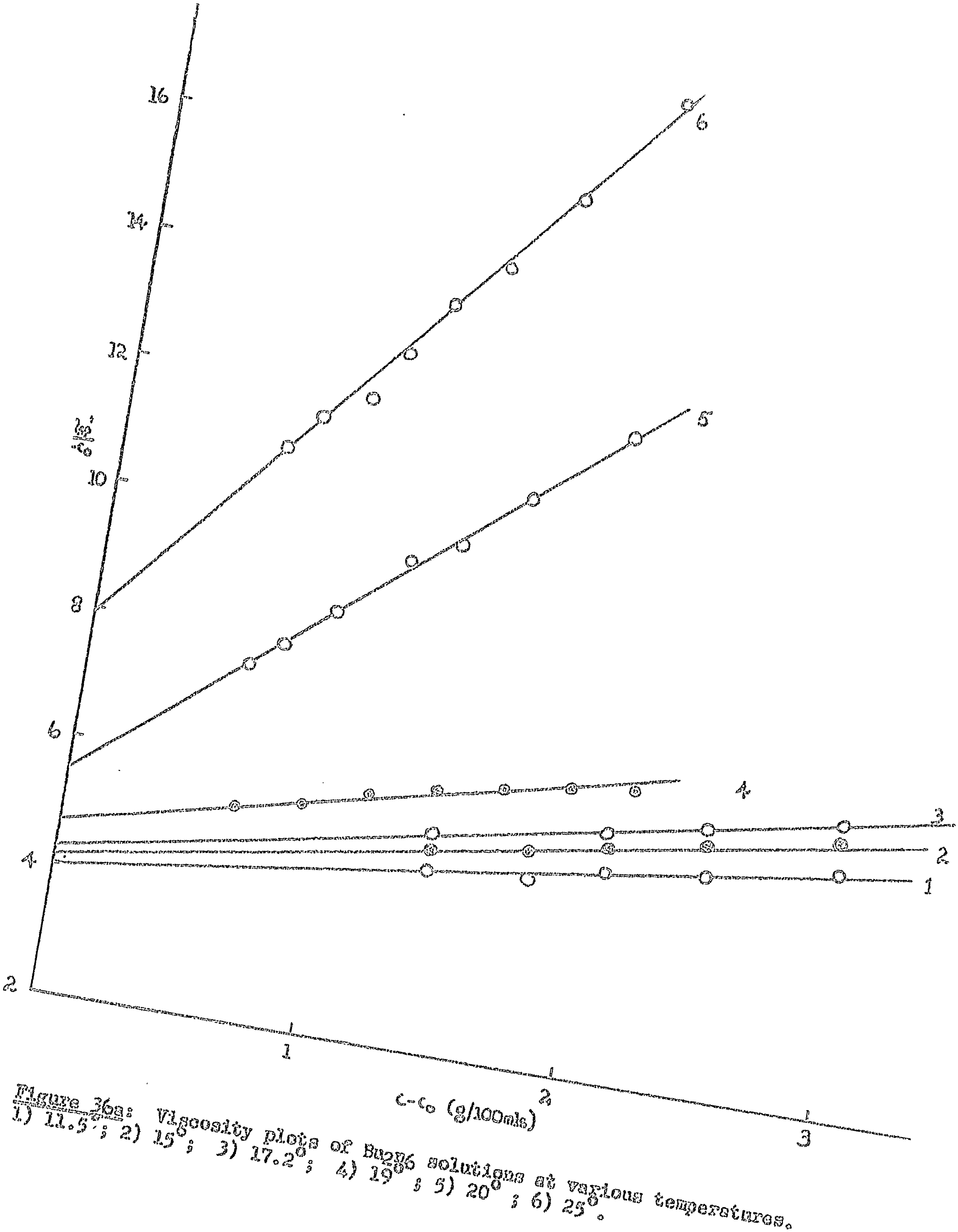


Figure 36a: Viscosity plots of Bu_2E_6 solutions at various temperatures. 1) 11.5°; 2) 15°; 3) 17.2°; 4) 19°; 5) 20°; 6) 25°.

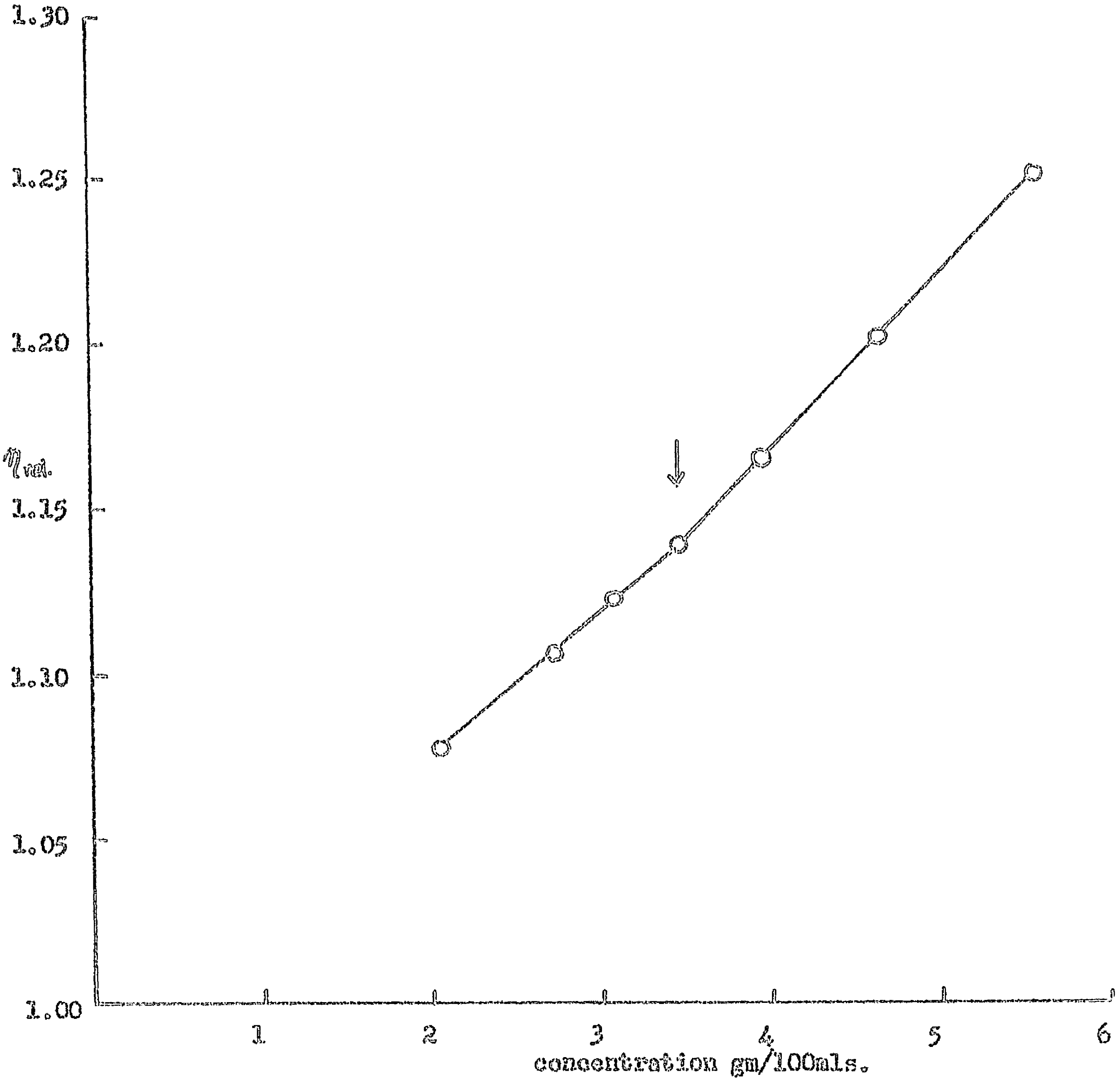


Figure 37: Plot of relative viscosity, $\eta_{rel.}$, against concentration for Et_2n_6, showing the break at the critical micelle concentration.

For the determination of micellar characteristics η_r was calculated relative to the solution at the CMC and η_{sp} was obtained from this value. ω_1, the hydration in gms/gm of detergent was evaluated assuming micellar sphericity from,

$$[\eta] = 2.5\ (V_2 + \omega_1 V_1^{\circ})$$

where $[\eta]$ is $\left(\frac{\eta_{sp}}{c-c_0}\right)_{c-c_0 \to 0}$ and V_2 = specific volume of the solute and V_1° the specific volume of the solvent. In Table XVIII, h is the number of water molecules associated with each monomer in the micelle. The Simha shape factor, ν, and axial ratios for prolate ellipsoids are listed and derived on the assumption that the deviation of $[\eta]$ from 2.5 was due to asymmetry and not hydration. In Table XVIII there are, therefore, values of maximum hydration and maximum asymmetry.

The intrinsic viscosities of Br$_2$n$_6$ at 20° and 25° were 5.41 and 7.98 respectively, and the results are discussed later.

Huggins constants, K_H, were derived from viscosity plots using the relationship,

$$\frac{\eta_{sp}}{c} = [\eta'] + [\eta']^2 K_H . c$$

where η_{sp}' and $[\eta']$ are the values recorded in Table XVIII x 10^{-2} as C is in this case gm/100mls. These values are listed in Table XIX.

The high critical micelle concentrations of the C_4 and C_6 detergents has allowed viscosity measurements to be made on premicellar solutions to determine hydration. These results are given in Table XX and may be compared with the viscosity results of three glycol solutions in Table XXI.

Discussion

Because of the small size of the micelles in this series, light scattering gives no indication of micellar shape; Z_{45} values were all close to unity. Before discussing micellar structure we thus have to decide which micelles

Table XVIII

Detergent Viscosity Results

Compound	Temp. °C	$[\eta]$	ω_1[1]	h[2]	ν	a/b
C_2n_6	20	3.40	0.43	7.3	3.65	2.95
C_4n_6	20	4.20	0.74	13.9	4.38	3.72
C_6n_6	20	4.70	0.89	18.1	4.76	4.10
Me_2n_6	20	4.49	0.84	15.8	4.71	4.05
Et_2n_6	20	4.65	0.88	17.8	4.73	4.08
Pr_2n_6	20	5.32	1.12	24.5	5.29	4.56
Bu_2n_6	11.5	4.02	0.59	13.8	3.95	
	15	4.16	0.64	14.2	4.09	
	17.2	4.30	0.71	16.6	4.22	
Bu_2n_9	20	4.14	0.63	19.4	4.06	3.41
	25	4.40	0.74	22.8	4.37	3.72

C_2n_6 did not form micelles in aqueous solution over the concentration range studied (up to 3 molal).

[1] ω_1: in g. water per g. detergent. [2] no. of water molecules per monomer.

Table XIX

Huggins Constants

Compound	Temp.	K_H	Compound	Temp.	K_H
C_2n_6	20	2.7	Bu_2n_6	11.5	3.6
C_4n_6	20	1.1	"	15.0	3.8
C_6n_6	20	0.3	"	17.2	3.9
Me_2n_6	20	1.8	"	19.0	5.0
Et_2n_6	20	0.3	"	20	11.6
Pr_2n_6	20	1.3	"	25	7.3
Bu_2n_9	20	2.2	Bu_2n_9	25	3.2

Table XX

Some Pre-Micellar Viscosity Results

Detergent	Temp. °C	$[\eta]$	ω [1]	h
Me_2n_6	20	3.25	0.35	6.5
Et_2n_6	20	3.30	0.34	6.85
C_4n_6	20	3.40	0.43	7.3
C_6n_6	20	3.26	0.35	6.5

1. g. water per g. detergent, assuming sphericity of units in solution.

Table XXI

Glycol Viscosity Data

Glycol	Temp. °C	$[\eta]$	ω [1]	h	h'	ν [2]	a/b
Hexagol	20	3.21	0.38	6	(6.9)	3.61	2.90
	30	3.11	0.35	5.5	(3.8)	3.49	2.79
Nonagol	20	3.41	0.48	11.0	(12.8)	3.85	3.18
	30	3.28	0.42	9.7		3.70	3.02
Dodecagol	20	3.60	0.56	17.0	(18.7)	4.08	3.41

Values of h in brackets (h') were obtained using the relationship, $\log \eta_{rel.} = A \cdot c/(1-Q'c)$ where $Q' = QV$ is an arbitrary constant. V is the molar volume of solute including any water of hydration.
$A = 2.5V/2.303$.
1. Calculated assuming sphericity 2. calculated assuming no hydration.

are symmetrical and which micelles are not on other evidence available.

Previous work by Elworthy and McDonald[22] on the hexadecyl series $C_{16}n_7$, $C_{16}n_8$ and $C_{16}n_9$ has given some clues as to how one may detect assymmetry. In this series micellar asymmetry developed as the temperature was raised above a certain threshold temperature, T_h, specific for each system. Systems with asymmetric micelles gave large viscosity intercepts. Calculation of the Huggins constants from the results of Elworthy and McDonald[32] showed that, in the region of T_h, K_H increased greatly. Table XXII contains some values for the hexadecane series. It is evident from these values that when asymmetric micelles are present there is a large Huggins Constant. For solid, uncharged spheres K_H is approximately 2.0, both in theory and in practice.[247,279] K_H values above about 6 are due to two-dimensionally expanded particles.[247] Alexander and Grey,[280] for example, obtained a Huggins constant of 10 for flat aluminium soap micelles.

From Table XIX it can be seen that only Bu_2n_6 at 19°, 20° and 25° has large K_H values (11.3, 7.3 at 20° and 25° respectively), the values at lower temperatures being in the region of 3.8. From this one may tentatively conclude that asymmetry is present at 20° and 25°.

There is other evidence. The viscosity intercept of Bu_2n_6 at 20° is greater than that of Bu_2n_9 at the same temperature. As micellar hydration increases with PEG chain length, it seems likely that the greater intrinsic viscosity of Bu_2n_6 must be attributed to micellar asymmetry.

A third indication of asymmetry is given by the sign of the second virial coefficient, B. It has been found that, as the temperature in non-ionic detergent systems was raised, B decreased and became negative when asymmetric micelles were present.[22,72.] There may be reservations about using the value

Table XXII

Huggins Constants of the Hexadecyl Series

Compound	Temp. °C	25	35	45	50	55	59.8	65
$C_{16}n_9$	$[\eta]$	0.043	0.045	0.047	0.06	0.101	0.187	0.35
	K_H	2.6	1.9	3.7	13.7	19.5	10.9	5.3
		← spherical →			← asymmetric →			
$C_{16}n_8$	Temp. °C	15	25		35	38	40	45
	$[\eta]$	0.036	0.038		0.042	0.059	0.085	0.22
	K_H	3.0	2.8		19.3	34.8	27.0	7.2

At Constant Temperature
(25°)

Compound	Huggins Constant	
$C_{16}n_{21}$	1.39	(spherical)
Cetomacrogol 1000	1.52	"
$C_{16}n_{15}$	1.70	"
$C_{16}n_9$	2.70	"
$C_{16}n_7$	34.30	(asymmetrical)

of B as an indication of asymmetry, as a rod-shaped molecule has a higher second virial coefficient than a spherical particle of the same volume. The situation is different in non-ionic systems, however, as factors other than the excluded volume affect the chemical potential of the solute.[22] Nevertheless, on a purely empirical basis, negative values of B can be correlated with the existence of asymmetrical micelles. In the present series, as the hydrophobe is lengthened, B decreases and is negative for Bu_2n_6 at 20° and 25° (Figure 34).

From the above arguments it seems likely that Bu_2n_6 forms asymmetric micelles at 20° and 25°. There is a possibility that Pr_2n_6 micelles at 20° are on the borderline of becoming asymmetric, for this system has a slightly negative second virial coefficient - but it has a low Huggins constant. The value of B is subject to considerable experimental error, and, because of this, no specific values are quoted. In view of this the micelles of Pr_2n_6 and of the remainder of the series, except Bu_2n_6 above T_h, 18.5°C, are likely to be spherical.

Spherical Micelles

At 20°C the micellar aggregation number increases as the hydrocarbon chain is lengthened, for a constant polyoxyethylene chain length. In order to gain further insight into the structure of the micelle, use of a model can be instructive. Knowing the aggregation number from light-scattering and the density of the alkane portion of the molecule, one can determine the radius of the hydrocarbon interior of the micelle (r_h) if it is assumed to be liquid. There is much evidence to bear out this assumption.

$$r_h = \sqrt[3]{\frac{(\text{molecular volume of alkane}) \times 3}{4\pi}}$$

The total volume of the micelle (V_m) was calculated by adding the total volume of the detergent monomers and the total volume of hydrating water, the latter being deduced from Table XVIII.

$$V_{water} = h \times n \times 30 \text{ Å}^3$$

$$V_{detgt.} = n \times \text{molecular volume of monomer,}$$

$$V_{micelle} = V_{water} + V_{detergent}$$

$$\text{and} \quad r_m = \sqrt[3]{3 . V_m / 4\pi}$$

The radial length occupied by the glycol chain (r_e) may be obtained from

$$r_e = r_m - r_h$$

This is a very simple model, but one which seems to be useful in explaining micellar behaviour. The dimensions calculated according to the model are collected in Table XXIII.

The figures (Table XXIII) show that an increase in aggregation number is accompanied by an increase in the radial length occupied by the polyoxyethylene chain (at constant temperature). This is the same trend as was noted in the hexadecyl series,[13] which was explained on steric grounds when large numbers of monomers had to be packed into a spherical shape.

The area per monomer at the hydrocarbon surface of the micelle was calculated by dividing the surface area of the micellar interior by the aggregation number. The area is seen to decrease with increasing aggregation number - again emphasising the packing effect. Constriction of the monomer forces the glycol chain to expand in the micelle. r_e is 6.73 Å in Et_2n_6 micelles and 9.82 Å in Pr_2n_6 micelles. At the air/water interface the area per monomer was generally greater for the branched-chain detergents, but the differences are lost in the micelle - which would appear to suggest the fluid nature of the micelle interior.

Table XXIII

Micellar Volumes, Radii and Surface Areas for Spherical Micelles (20°)

Compound	$V_m \times 10^3 (Å^3)$	Å			%max.[1]	Area/monomer ($Å^2$)	
		r_m	r_h	r_e		Hydrocarbon Surface	Air/H_2O
C_4n_6	3.93	9.71	5.35	4.36	20	89.9	92
C_6n_6	15.02	15.27	8.70	6.57	30	73.2	62
Me_2n_6	4.07	9.90	5.40	4.50	20.5	91.6	75
Et_2n_6	16.16	15.68	8.95	6.73	30.6	71.9	77
Pr_2n_6	54.96	23.59	13.77	9.82	44.6	59.6	66
Bu_2n_6	(15°)63.99	24.81	15.81	9.00	40.9		
Bu_2n_9	88.07	27.6	17.03	10.57	31.1	56.0	71

---

1. %max. is the percentage of the extended chain length of glycol, based on 22.0 Å for hexagol

It has been proposed before$^{e.g.13}$ that the PEG chain is most likely arranged as an expanding spiral in the micelle, and this arrangement would be consistent with the present results, at least as far as the spherical micelles are concerned. For the smaller aggregates of C_4n_6 and Me_2n_6 another arrangement of the monomers is possible. Examination of molecular models shows that 4 or 5 monomers can be arranged with the polyoxyethylene glycol chain wrapped around the hydrocarbon chains, as depicted in Figure 38. The width of an extended PEG chain is 4.3 - 4.5 Å (Catalin models). This figure agrees well with the values of r_e quoted in Table XXIII for Me_2n_6 and C_4n_6 aggregates. The extended length of a monomer of Me_2n_6 is 27.0 Å. Two of these monomers, placed end to end can circumscribe a spherical hydrocarbon interior of radius 5.4 Å. So one can picture these small aggregates as being rather less ordered than the larger micelles, with the PEG chain not in a spiral form but rather draped around the hydrophobe. The values of r_m, r_e and r_h, in any case, seem to be quite realistic.

C_2n_6 did not form micelles in aqueous solution over the concentration range studied, which was up to 40% w/w.

The micelles appear to be heavily hydrated, the hydration increasing with increasing aggregation number and extension of the glycol chain, the latter resulting in an increased capacity for the physical trapping of water molecules. The results in Tables XX and XXI on the glycol and monomers indicate that thehydration of these units is much lower - in the region of 6 - 7 water molecules per monomer. This is borne out by the hydration number of 7.3 for C_2n_6. It appears that the glycol chain is hydrated along its length, and that the attachment of an alkyl group to one end does not decrease the hydration. In interpreting the results for both monomers

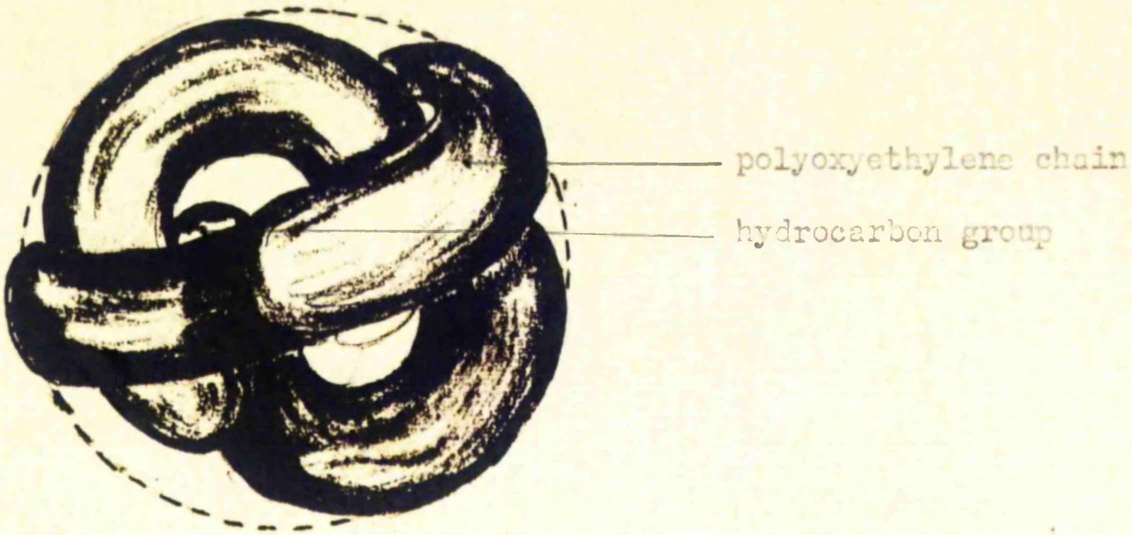


Figure 38: Drawing of the possible configuration of the monomers in an aggregate of Me_2n_6. The hydrocarbon groups, which are relatively short, are enveloped by the polyoxyethylene chains. In this arrangement there are numerous sites for trapping water molecules.

and glycols on the basis of hydration it has been assumed that they act as spherical entities in aqueous solution. This is reasonable as the hydration values obtained for both hexagol and nonagol agree with the estimates of hydration by the vapour pressure method (section 4), and as the effect of temperature is to reduce the intercept. If asymmetry was the primary determinant of the viscosity intercept, an increase in temperature would tend to increase this value. We can thus draw two conclusions: i. the hydration calculated per ethylene oxide unit increases as the chain lengthens, ii. the hydration of the monomers decreases with increase in temperature. This will be discussed later in the vapour pressure section of the thesis.

Asymmetric Micelles

Bu_2n_6, nearing its limit of solubility at 20° and 25°, might be expected to form asymmetric micelles if only by analogy with the case of $C_{16}n_6$ which, being almost insoluble, formed rod-like micelles with high aggregation numbers at normal temperatures.

A plot of $[\eta]$ against temperature for Bu_2n_6 (Figure 39) shows a pronounced break at 18.5° C, which may thus be considered to be the threshold temperature, T_h. Below T_h, $[\eta]$ increases slowly with temperature, this being most likely due to an increase in micellar hydration.[22] Thus values of $[\eta]$ may be extrapolated to 20° and 25° to determine ω_1 and h for the micelles, uncomplicated by shape factors. Below T_h, K_H is low. Above the threshold temperature, $[\eta]$ increases rapidly and K_H is large, following the trend of results for the hexadecyl series. The increase must be due to the sudden development of asymmetry at T_h. The decrease in the Huggins constant which may be seen after it has reached its maximum at the threshold temperature is probably due to the elongation of the micelles and the approach of polymer dimensions. (The Huggins constant for long rod-like

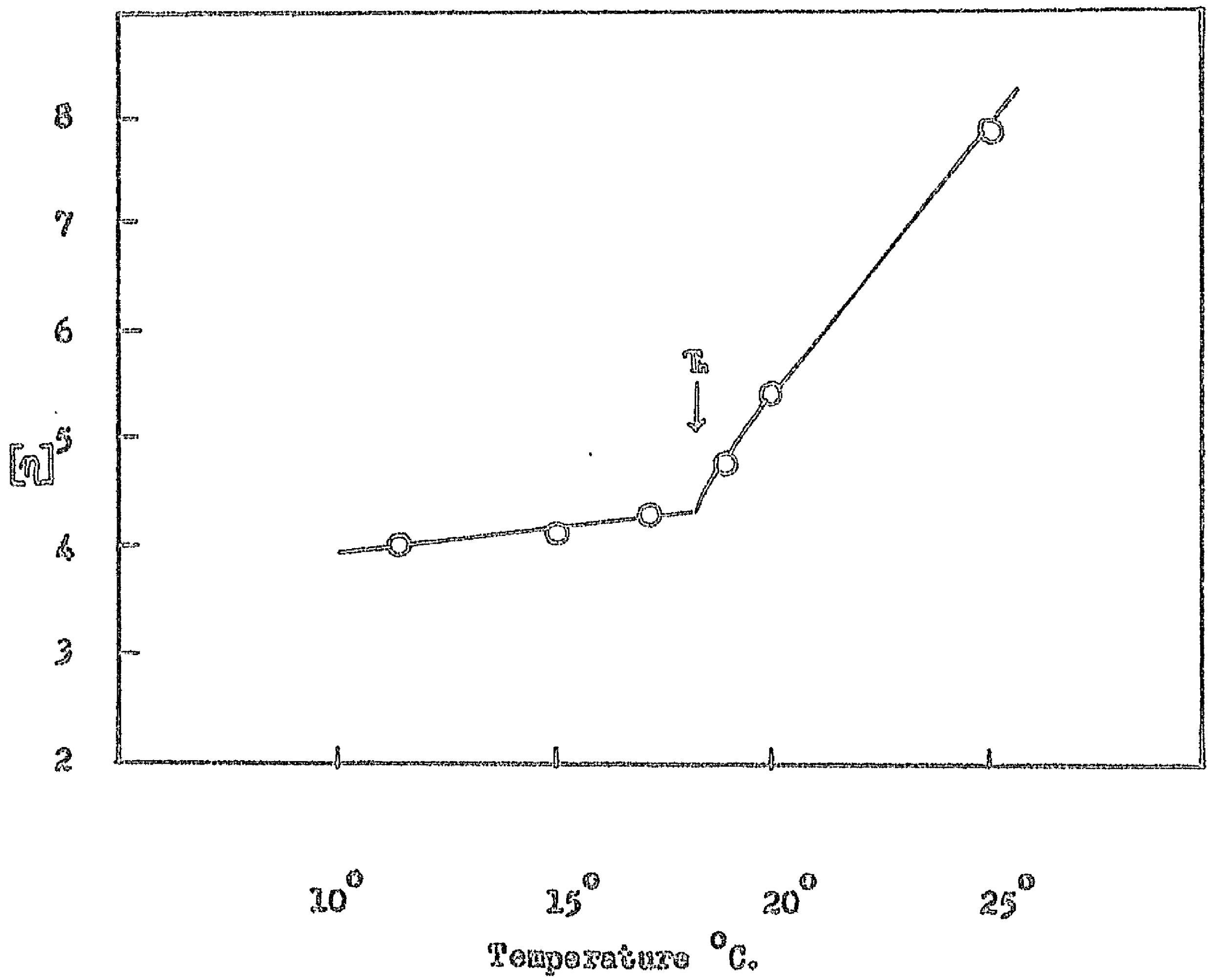


Figure 39 : Diagram showing variation of intrinsic viscosity of Br_2n_6 with temperature. Sharp break (T_h) is threshold temperature.

molecules should fall to the region of 0.5.) A plot of log$[\eta]$ against log(micellar weight) for Bu_2n_6 has a slope of 1.4, i.e. $[\eta] = K'M^{1.4}$. Such a value is consistent with the existence of rod-shaped particles.

The method of Elworthy and Macfarlane, devised for the empirical determination of hydration without the complication of micellar shape probably depends on the presence of large micelles, such as are present in the hexadecyl series, and it was not applied to Bu_2n_6 solutions. However, using the extrapolation mentioned above, hydration was estimated at 20° and 25° and various dimensions of the micelles of Bu_2n_6 at these temperatures were calculated, on the basis of a prolate ellipsoid model. The results are summarised in Table XXIV.

The volume of the micelle, V_m, was computed as before, by adding the volume of monomers and volume of hydrating water. The shape factor, ν, was obtained from

$$[\eta] = \nu (V_2 + \omega_1 V_1^o)$$

ω_1 was the extrapolated value and the axial ratio a/b was obtained from the tables of Mehl, Oncley and Simha.[240] The semi-axes a and b were then calculated from $4.189\, ab^2 = V_m$ or, where R is the axial ratio,

$$4.189\, Rb^3 = V_m$$

as $\underline{a} = Rb$. The volume of the hydrocarbon interior was taken to be n X the molecular volume of the alkane, and the values of r_e were adjusted so that the volume of the ellipsoid's interior was equal to this value. It seems reasonable to assume that the polyoxyethylene chain has an equal extension over the whole micelle; r_e was taken to be constant. The volume of the hydrocarbon interior was given by

$$V_h = 4.189\,(a - r_e)(b - r_e)^2 = n \times (\text{mol.volume alkane})$$

The results in Table XXIV show that r_e is nearly constant at 20° and 25°, in spite of the b axis becoming smaller. It is, therefore, the hydrocarbon interior which is thinning or lengthening more quickly as the temperature is raised, and it seems that it is the hydrophobe and its interactions with the solvent which are the primary cause of the development of asymmetry and eventual cloud point development.

The axial length occupied by the glycol chains (9.2 – 9.3 Å) compares well with the value of r_e obtained for the spherical micelles of Bu$_2$n$_6$ (9.0 Å), the slight increase in r_e being due to the temperature increase, and consistent with the explanation of increased hydration by trapping of water molecules in the region of the PEG chains.

Table XXIV

Dimensions of Bu$_2$n$_6$ micelles above T_h

Temp.	C	$[\eta]$	w_1*	h	ν	a/b	a	b	r_e	$V_m \times 10^3$
20		4.41	0.74	17.4	3.07	2.20	46.4	21.1	9.20	86.20
25		4.60	0.82	19.2	4.33	3.68	72.7	19.8	9.30	118.70

* extrapolated from results for spherical micelles at lower temperatures
r_e is the axial length occupied by the PEG, assumed to be constant over whole micelle.

Tentative Picture of Cloud Point Formation and Occurrence of Micellar Asymmetry

The sharp appearance of asymmetry depends to a large extent, as mentioned in the introduction, on the hydrophobe-hydrophile balance which, of course, governs the aggregation number. For a particular hydrocarbon chain, there is a maximum number of monomers which can be packed into a a spherical shape. This number increases as the hydrocarbon chain length increases, from simple geometric considerations. For a straight chain dodecanol derivative, Reich gave the number as 64 monomers.[132] For the hexadecyl series it appears to be in the region of 274-292.[22] If the area per monomer at the hydrocarbon-polyoxyethylene boundary in the micelle is calculated, one obtains for radius of each monomer the values listed in Table XXV.

Table XXV

Compound:	Me_2n_6	Et_2n_6	Pr_2n_6	Bu_2n_6 (15°)	(20°)'	C_6n_6	$C_{16}n_8$
Radius(Å)	5.2	4.8	4.4	4.35	4.18	4.8	3.85

': if spherical.

The minimum radius at the air-water interface for the branched-chain non-ionic is in the order of 4.4Å, while for the straight-chain detergents it is considerably less, being about 3.5 Å. One may tentatively state that, if packing of the monomer into the micelle is to cause the monomer to occupy less than this minimum, then a spherical shape will not suffice, and the micelle will become asymmetric. It is perhaps significant that Bu_2n_6 at 20°, considered by the earlier arguments to be asymmetric, occupies, in the spherical model, an area significantly less than the minimum. ($r = 4.18$Å compared with the considered minimum of 4.4 Å.). $C_{16}n_8$ - at its threshold temperature-occupies an area just greater than the minimum for the straight chain series.

The extension of the PEG chain also plays some part in the onset of asymmetry, as Elworthy and McDonald have suggested.[22] Increasing temperature will result in an extension of the PEG chain and a reduction in the area of hydrocarbon surface "protected " until at some stage (T_h) water

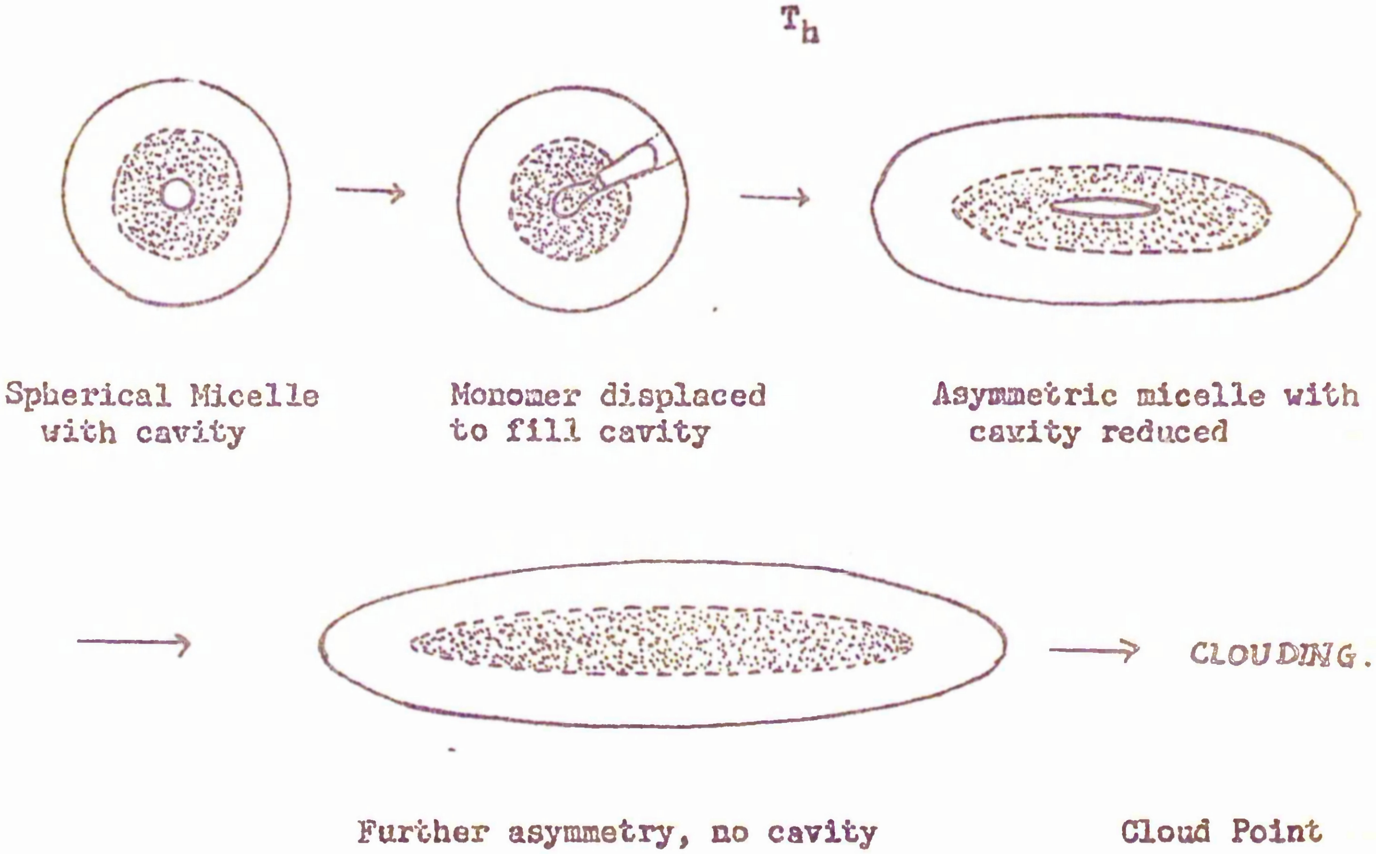


Figure 40: Diagrammatic representation of asymmetry and cloud point formation in solutions of non-ionic detergents.

comes into contact with the hydrocarbon chains and results in a change of shape. It seems, however, that the geometric argument is more likely, for, as the temperature is increased, the hydration of the monomer decreases rendering it less hydrophilic and inducing in it a greater tendency to micellise. The aggregation number will thus increase with temperature until the aggregation limit is reached. The micelle then becomes asymmetric.

Another possibility is this: the calculated radial lengths for the hydrocarbon core of the micelles are, not infrequently, greater than the extended lengths of the alkane groups, which means that there is a tendency to form a "hole" in the centre of the micelle. The space occupied by this hypothetical hole must be filled by the displacement of one or more monomers into the micelle interior. This necessitates the contact of hydrated ethylene oxide chains and hydrocarbon, which is not energetically favourable. Increased temperature militates against this and the micelle will tend to elongate to reduce the tendency to cavity formation. Examination of prolate ellipsoid models shows that the cavity is much reduced; elongation of the micelle will completely eliminate it. (Figure 40)

Branched-chain non-ionic detergents become asymmetric at lower temperatures than do straight-chain detergents ($C_{10}n_6$ is spherical at 20° and 25° whereas Bu_2n_6 is not) probably because of the bulky head groups and the consequent difficulty in packing a large number of monomers into a spherical shape.

Section 4:

VAPOUR PRESSURE

Vapour Pressure Studies

Introduction: The vapour pressure of water in equilibrium with an aqueous solution can be determined directly by either static or dynamic methods. The direct static method is illustrated by the method of Gibson and Adams[281] and Shankman and Gordon[282] whose measurements of water activity could be reproduced to one part in 2000. The transpiration method of determining water activity involves the saturation of an inert gas by water from an aqueous solution. Measurements by Becktold and Newton[283] indicate a probable error of one part in 10,000. Recently, a method depending on the temperature difference between solvent and solution has been employed, the temperature effect compensating for the vapour pressure difference.[284] A very sensitive differential manometer was used to observe the null point. The isopiestic method[285,286] is a simple, indirect method involving the attainment of equilibrium of a solution with a solution of known water activity (e.g NaCl or sucrose solutions), but up to four days are sometimes required before equilibrium is attained.

In using water activity measurements to determine the activity of the solute, it is necessary, especially in dilute solutions, to have a high degree of accuracy, for the activity of the solvent may not differ greatly from unity while that of the solute does. The osmotic coefficient, ϕ, defined earlier, has been introduced to express the deviation of solvent activity from ideal behaviour. For an ideal solution, ϕ is unity. Extrapolation can thus be made from finite concentrations to $\phi = 1$ at $m = 0$, thereby minimising the effect of experimental error on the scatter of results.

For very dilute solutions other methods must be used. There are a number of experimental difficulties still unresolved in measuring accurately the osmotic effect or water activity at low solute concentrations. Frazer and Patrick[211*] overcame the difficulty of finding a suitable semi-permeable membrane for osmotic pressure measurements by equilibrating solution and solvent through the vapour phase, with a porous disc supporting the pressure difference. The temperature must be controlled to fine limits, and this has been achieved by Williamson[211*] within millionths of a degree. It is probably with such an apparatus that further progress will be made, enabling studies to be undertaken in detergent solutions above and below the CMC, even where the CMC is very low.

Apparatus and Method

In the present investigation, an apparatus based roughly on the design of Gibson and Adams[281] was set up. The systems to be studied were, in general, to be over 0.2 molal in concentration, and this apparatus seemed to combine accuracy in this region with ease of operation. The apparatus is depicted in Figure 41.

The manometer is approximately 100 cms. long, this being essential to give the larger displacements envisaged for water at higher temperatures. Water, at 25°C, gave a displacement of 36.49 cms of oil (Edwards "Hyvac", density at 25° = 0.8868.).

A mirrored scale was attached to the manometer to facilitate readings. These were obtainable to ± 0.01 cm. oil. The manometer was joined to the main ring of the apparatus by means of flexible rubber joints. The side arms carrying the solution flasks and solvent flasks were also attached by flexible joints. Difficulty was experienced initially from the leakage of volatile substances from the rubber, but boiling in water and subsequent use under vacuum remedied this fault.

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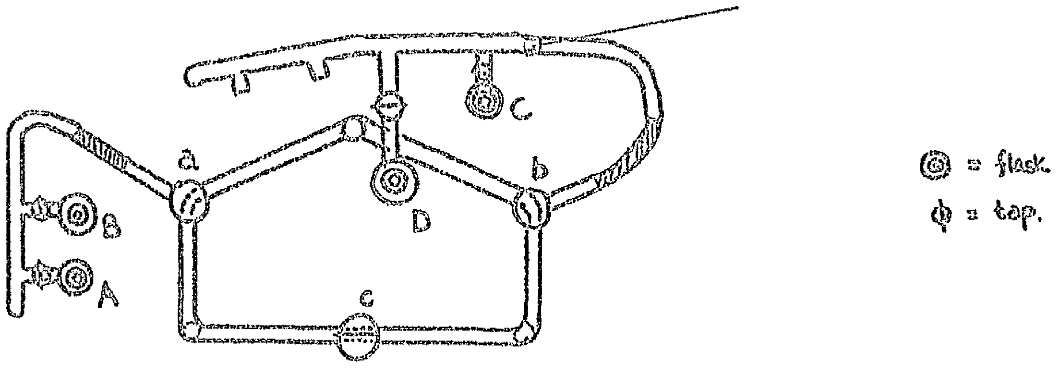


plan view of ring : not to scale.

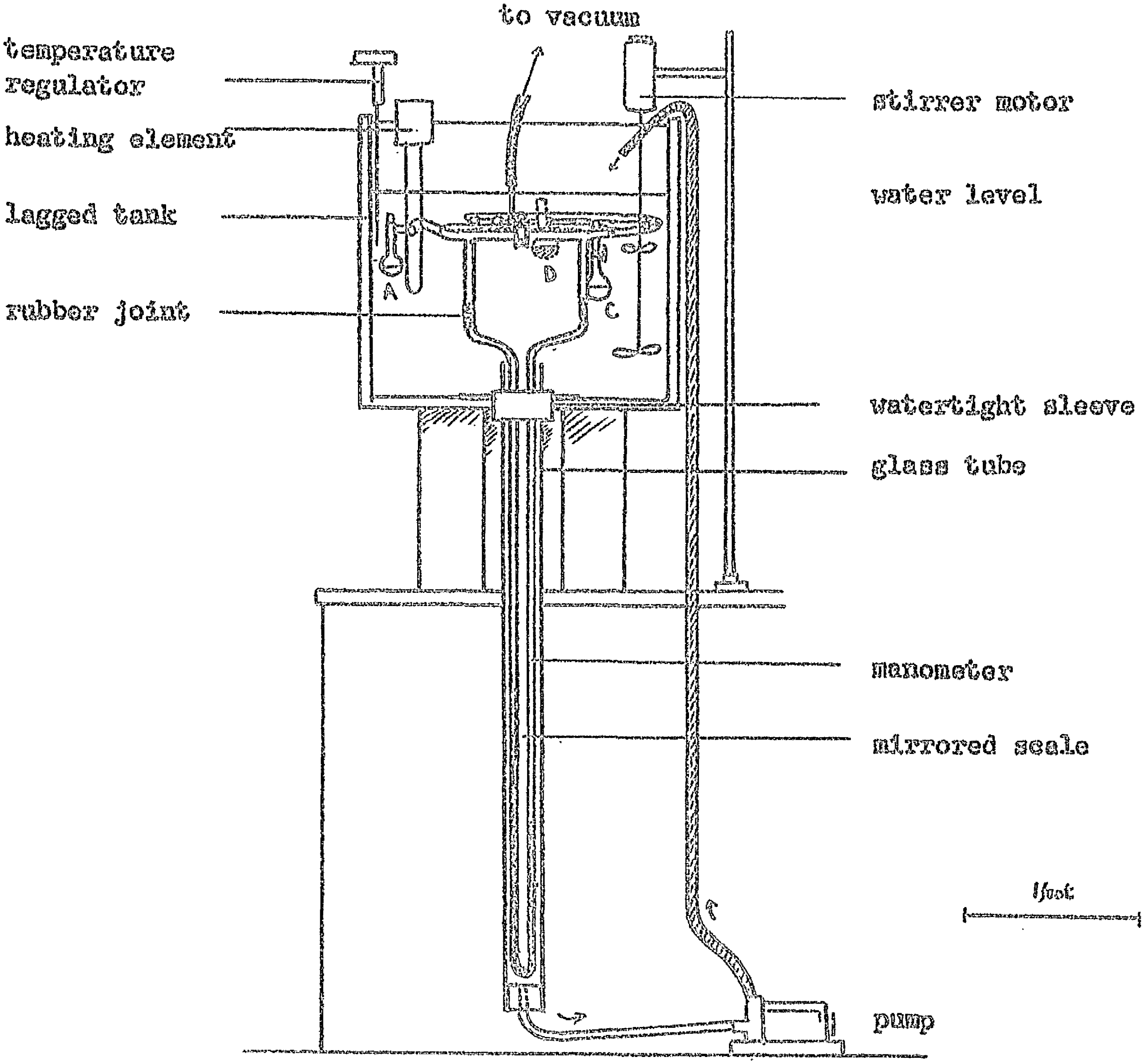


Figure 41: Vapour Pressure Apparatus (drawn to scale).

Accurate control of temperature was an essential feature of the technique. The whole apparatus was immersed in a thermostat tank - which was well lagged - heated by an element controlled by a mercury-toluene thermoregulator, a valve relay and a proportionating head. A cooling coil and stirrer were present in the tank; the water was circulated by means of a pump through the tube containing the manometer back into the tank (see diagram.) A Beckmann thermometer, standardised against an N.P.L thermometer, was used, and the temperature could be controlled to ± 0.001°C over long periods. Final readings of vapour pressure were always made at the same temperature on the Beckmann to minimise errors.

The ground glass joints of the apparatus were treated with Apiezon grease.

Flasks A, B and C held de-gassed distilled water. Flask D contained the solution under study. The side arm connecting D and C to the main ring could be removed and the solution and water de-gassed by cooling and thawing under vacuum, outside the apparatus. After the last traces of gas were removed, the tap between the side arm and flask was closed, the arm attached to the apparatus, and the whole apparatus evacuated. The water level was then raised and brought to temperature.

For direct measurements of the vapour pressure of the solution, the tap between D and the side arm was opened, tap "b" was turned to connect the side arm to the ring, tap "a" was turned to shut off A and B and tap "c" was closed. In this way, one arm of the manometer was connected to the flask and the other to the vacuum. Agitation of flask D resulted in shortened equilibration times.

When the vapour pressure was little different from that of water, the solvent flask C was opened momentarily to the manometer before opening the solution flask, this partially filling the system with water vapour. This procedure speeded up equilibration by lessening the degree of cooling in the solution flask when this was opened.

In concentrated solutions, or in solutions where the difference in vapour pressure between solvent and solution was large, the "difference" method was employed. In this method, flask A or B was opened to one side of the manometer through tap "a" — with the solution flask D open to the other side. The reading obtained was thus the difference in vapour pressure, $p^o - p = \Delta p$. Equilibration times by this method tended to be excessively long, often being in excess of 12 hours.

Most of the measurements were made by the direct method. Readings of vapour pressure were made at intervals and plotted against time until no further increase in vapour pressure was evident. After this point had been reached, several further readings were taken at intervals to check that equilibrium had, in fact, been achieved. At 20° , 3 - 5 hours were generally required for equilibration.

After the vapour pressure had been measured, the concentration of each solution was determined by removing 3 X 1 ml. samples of solution, weighing them and drying to constant weight in a vacuum oven over phosphorus pentoxide.

The activity of water, a_1, is the ratio of the vapour pressure of solution to the vapour pressure of water. Tests were made with calcium chloride solutions of known activity, and the following readings were obtained at 25°C: For a 1.375 molal solution,

	mm. oil
Water(p^o)	36.49
Solution(p):	33.54
"Difference"	2.94

$a_1 = \frac{p}{p^o} = \frac{p^o - \Delta p}{p^o} = \frac{p}{p + \Delta p}$; these three alternatives gave 0.9192, 0.9194, and 0.9194 respectively (Mean 0.09193) The literature value[191] is 0.9193. A 6.261 molal solution of calcium chloride gave 0.3678, 0.3672 and 0.3676 for the three readings, a mean of 0.3675 - identical with the literature figure.[191]

The values for water were as follows:

Temperature	mm. Oil	mm. Hg.	Lit. mm Hg
20.0°	26.89	17.51	17.515
25.0°	36.48	23.75	23.734
30.0°	48.18	31.82	31.797

Preparation of Solutions: Solutions of polyoxyethylene glycols and detergents were found to have a significant electrical resistance, even after the starting material had been distilled twice. Solutions of purified hexagol had aresistance of 91,120Ω in a cell of cell constant 1.1. Because electrolyte would have affected the activity measurements, dilute aqueous solutions were run down columns of "Bio-demineralit" until the specific resistance approached that of distilled water (440,000Ω). The solution was then concentrated to the region desired, and out-gassed prior to use. The likely source of the electolyte contamination is the sodium chloride or bromide produced in the synthesis of the compounds.

Results: Vapour pressure measurements were made on hexagol and nonagol solutions at 20° and 30°, on dodecagol at 20° and on C_2n_6 , C_4n_6, Me_2n_6 and Et_2n_6 at 20° and on Me_2n_6 and C_4n_6 at 30°.

Water activity - concentration (molality) curves were obtained for all systems. These are reproduced in Figures 42 and 43.

From the water activity values, values of ϕ were calculated (ϕ = $-1000 \ln a_1/18.01m$) and the activity coefficients of the solutes were

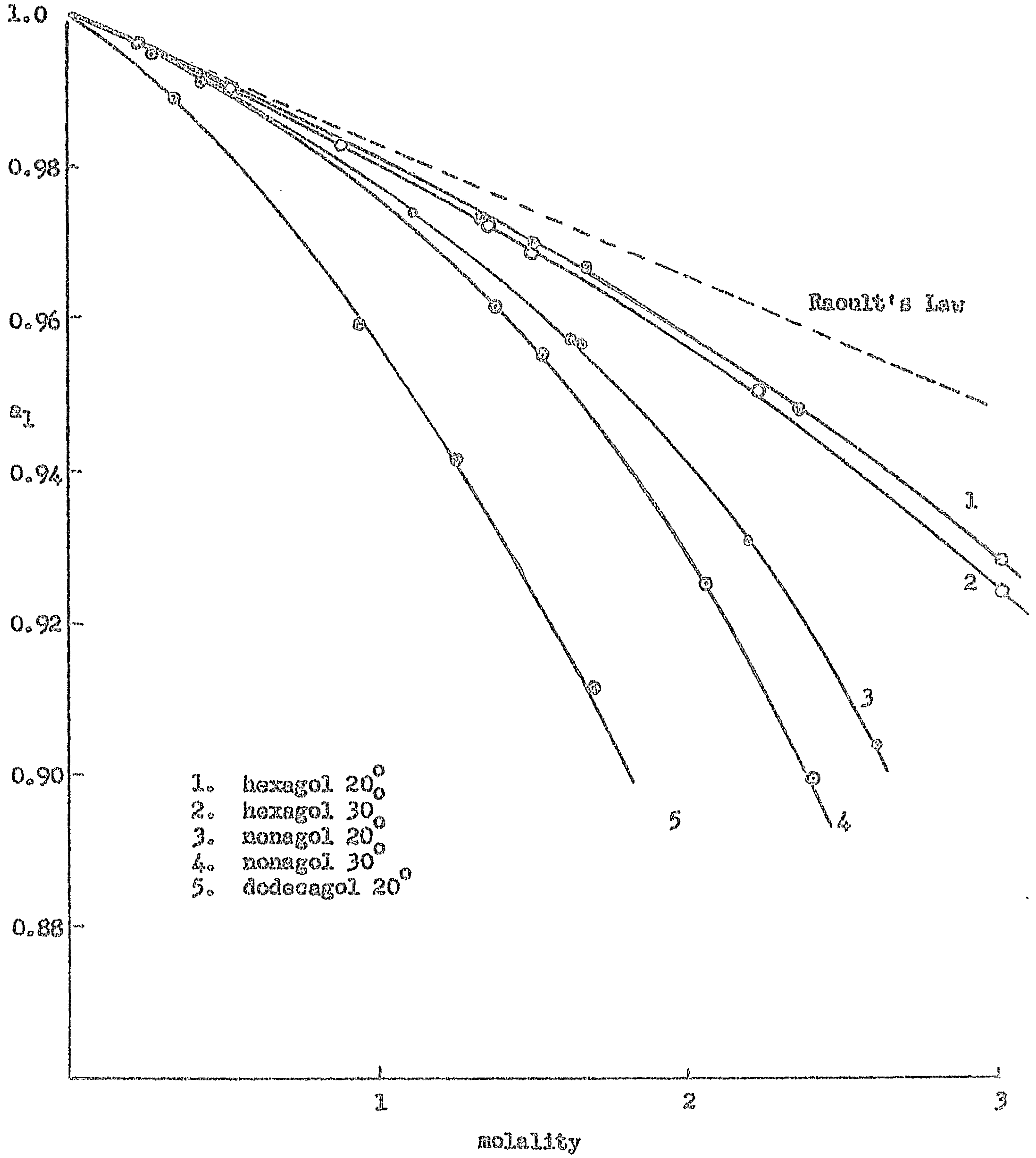


Figure 42: Plots of water activity vs. molalities for three glycols at 20° and 30° for hexagol and nonagol and at 20° for dodecagol.

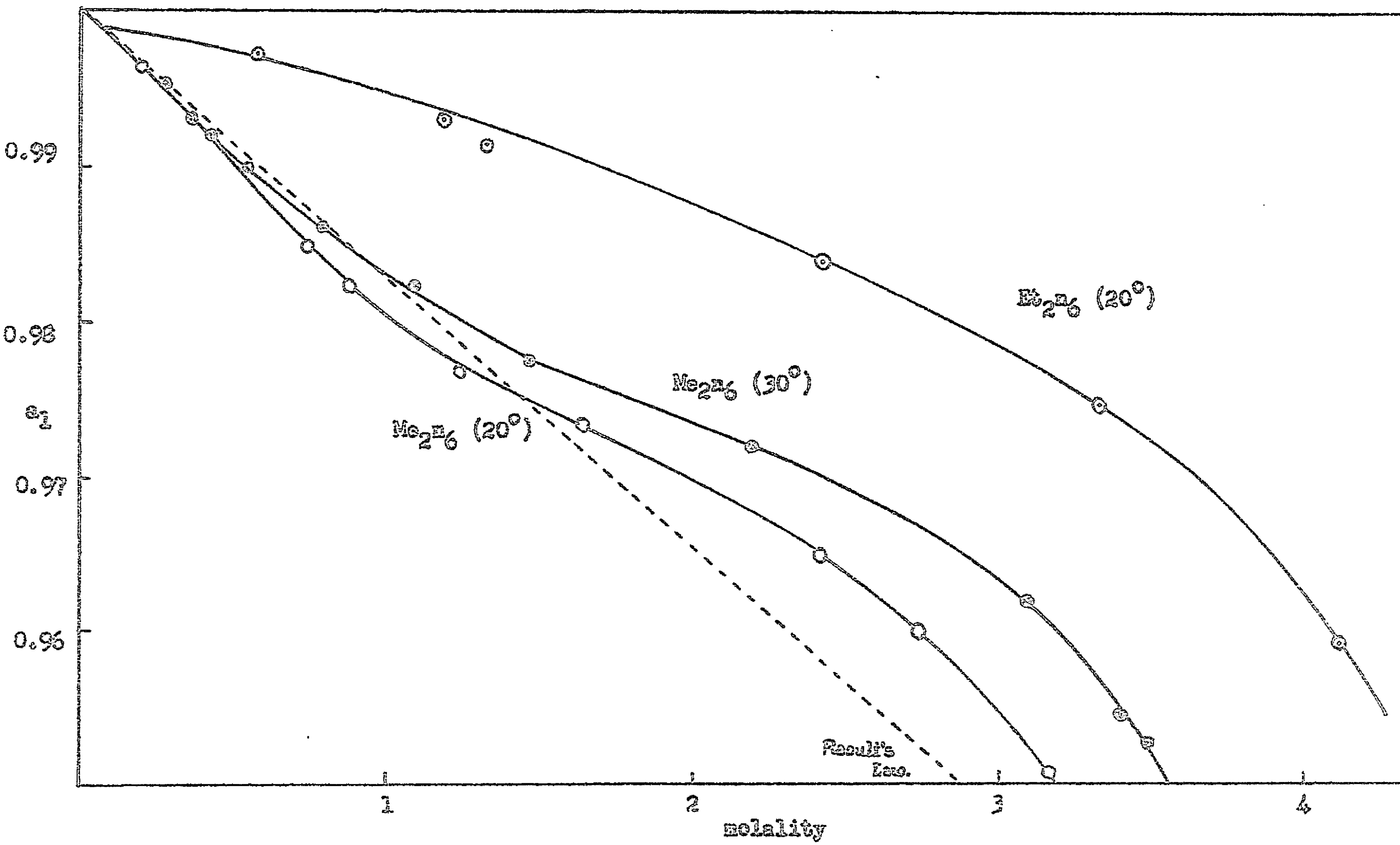


Figure 42a: Water-activity - molality curves for Me$_2$m$_6$ and Et$_2$m$_6$.

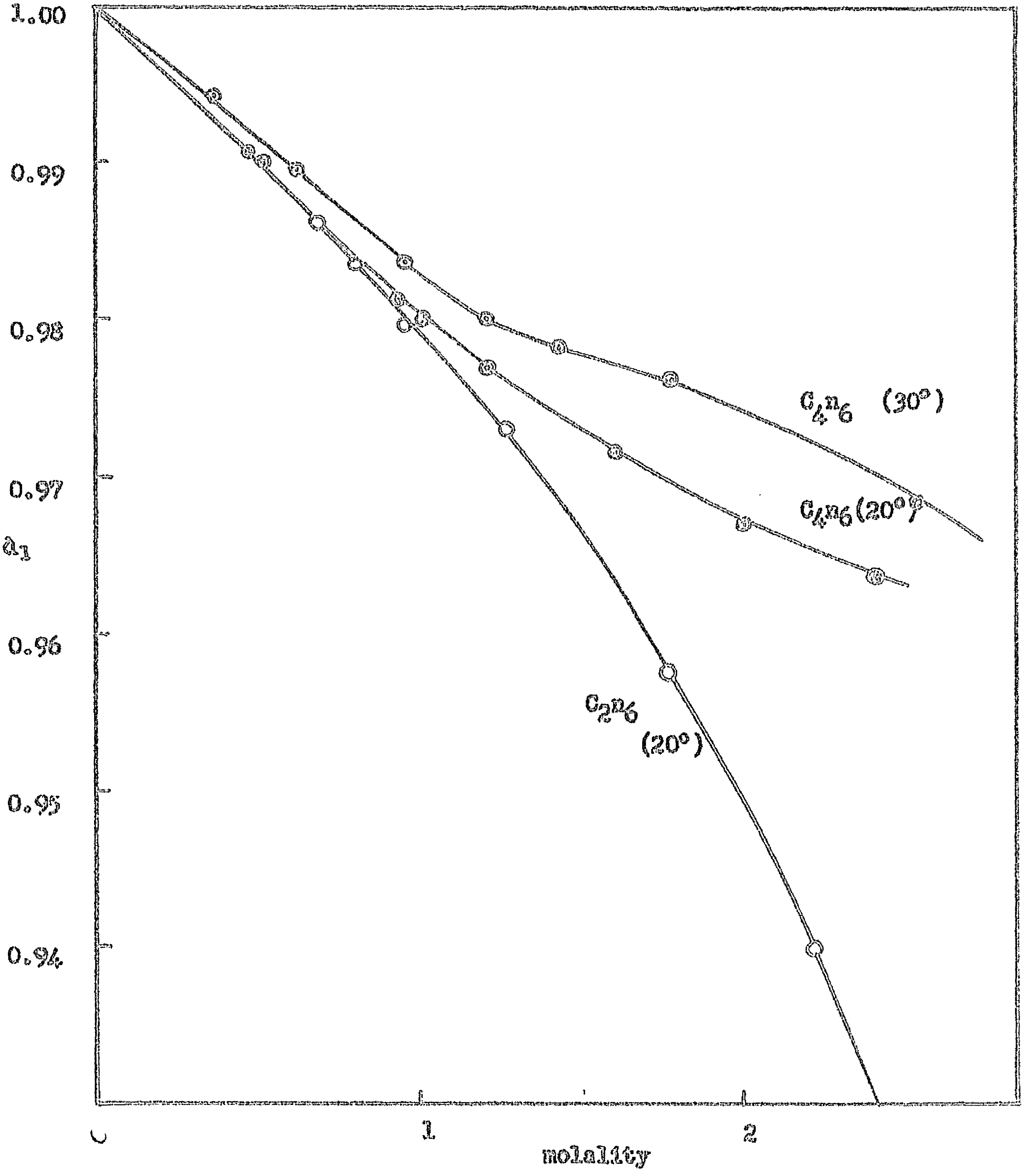


Figure 43: Water activity - molality curves for C_2n_6 (showing typical behaviour of hydrated solute) and C_4n_6 at 20° and 30°C.

obtained using the Gibbs-Duhem relationship in the form,

$$\ln \gamma_2 = (\phi - 1) + \int_{m=0}^{m=m} (\phi - 1)\, d\ln m.$$

The area, $\int_0^m (\phi - 1)\, d\ln m$ was obtained from plots of $(\phi - 1)$ vs. ln m by graphical integration. Experimental values of ϕ were plotted as a function of molality, and smoothed curves were drawn through the experimental points. The values of ϕ from the "smoothed" curves were used in the evaluation of activity coefficients. Some representative plots of osmotic coefficient are shown in Figures 44 and 45. The activities and activity coefficients obtained are listed in Tables XXVI and XXVII.

Increase of ϕ above 1 is due to solvation and decrease below 1 to association. Hutchinson et al.[151] found the osmotic coefficient of various glucosyl alkyl benzene surfactants below the CMC to be greater than unity, attributing this to experimental error. The glucose portion of the monomers, however, will be solvated and this will result in the observed values of ϕ, though the values quoted by these authors are probably exaggerated through experimental error.

The experimental water activities of the glycol solutions (hexagol and nonagol) can be fitted using an equation

$$a_1 = \frac{1 - 0.018\, hm}{1 - 0.018(h-1)m}$$

with h = 6 for hexagol and h = 14 for nonagol. In Table XXVIII, experimen-al water activites are compared with those calculated using this equation The relationship appears to hold well, even up to 2 molal concentration.

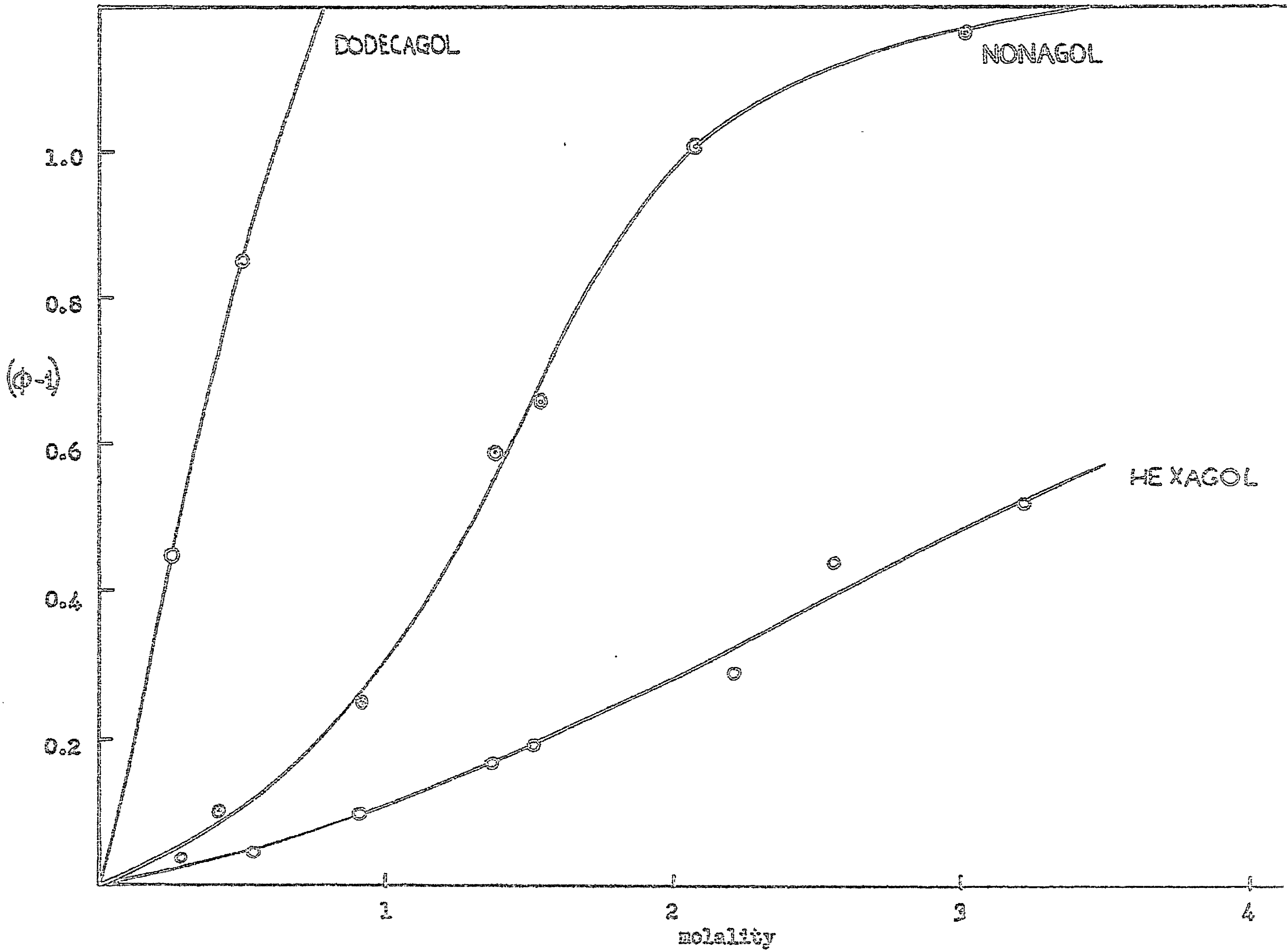


Figure 44. Experimental values of ($\phi - 1$) vs molality for the glycols at 20°C.

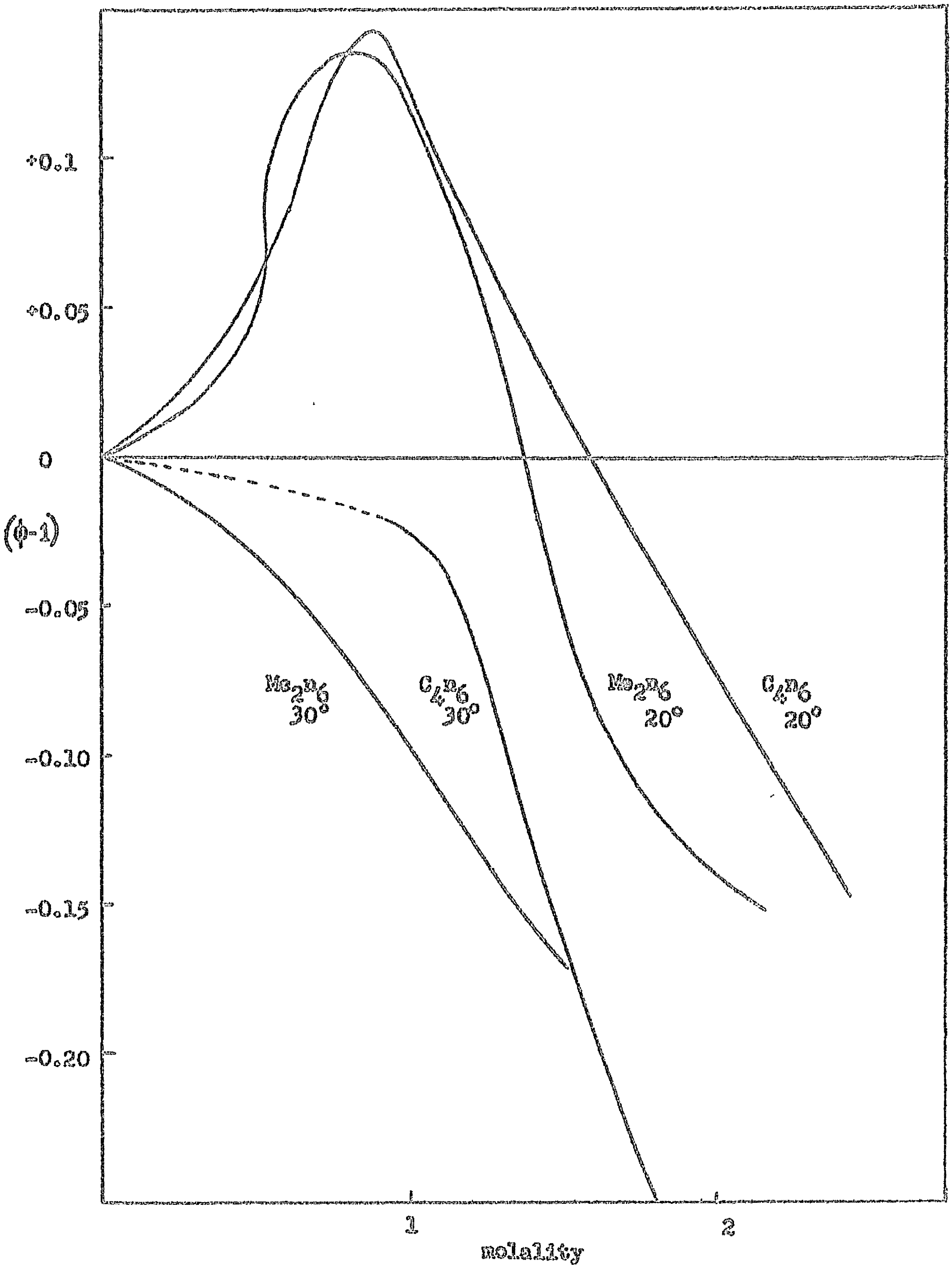


Figure 45: Variation of the osmotic coefficient with concentration and temperature for the two detergents Me_2n_6 and C_4n_6. Smoothed curves.

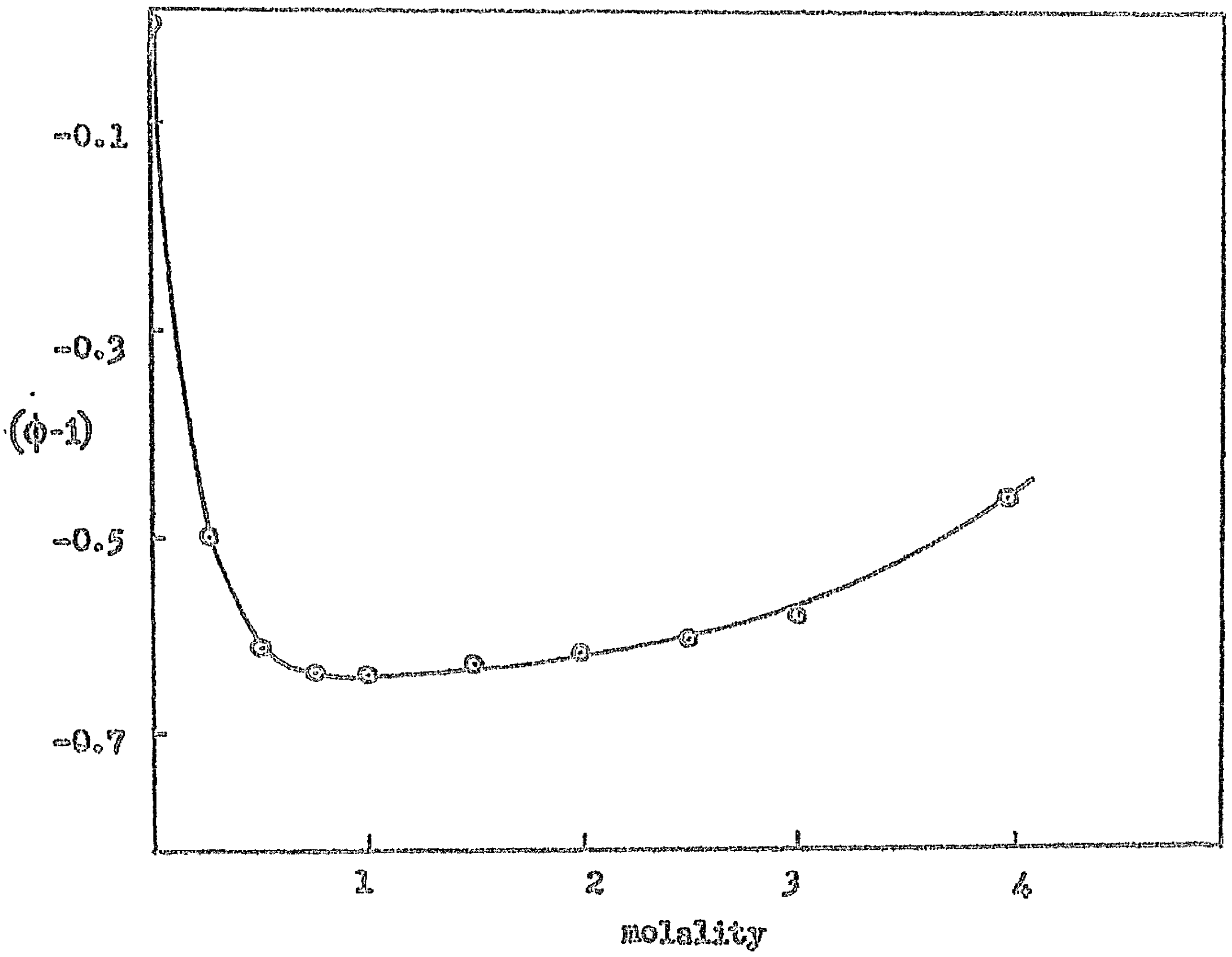


Figure 45a: Variation of osmotic coefficient with concentration for the detergent Et_2n_6 at 20°. Experimental points.

Table XXVI

Activity Coefficients and Activities

Compound	molality	γ_2	a_2	γ_2	a_2
		20°		30°	
Hexagol	0.10	1.018	0.1018	1.008	0.1008
	0.20	1.038	0.2076	1.020	0.2040
	0.50	1.102	0.5510	1.042	0.5210
	0.75	1.160	0.8365	1.079	0.7815
	1.00	1.240	1.2400	1.109	1.1089
	1.50	1.408	2.1120	1.212	1.6628
	2.00	1.627	3.2540	1.377	2.7540
	3.00	2.305	6.9150	1.829	5.4870
Nonagol	0.10	1.049	0.105	1.031	0.103
	0.20	1.080	0.216	1.069	0.214
	0.50	1.244	0.622	1.208	0.604
	0.75	1.478	1.109	1.399	1.049
	1.00	1.724	1.724	1.623	1.623
	1.50	2.600	3.900	2.351	3.527
	2.00	4.406	8.812	3.387	6.754
Dodecagol	0.10	1.380	0.138		
	0.20	1.994	0.399		
	0.30	2.500	0.750		
	0.40	3.690	1.476		
	0.50	5.610	3.305		
	0.60	7.400	4.440		
	0.75	11.520	8.640		
	0.80	13.200	10.560		
	1.00	22.241	22.241		

Table XXVII

Activity Coefficients and Activities

Compound	Temperature	Molality	γ_2	a_2
Me_2n_6	20°	0.25	1.029	0.257
		0.50	1.098	0.549
		0.75	1.239	0.929
		1.00	1.248	1.248
		1.50	1.078	1.617
		2.00	0.962	1.924
		2.50	0.885	2.213
Et_2n_6	20°	0.25	0.482	0.121
		0.50	0.306	0.153
		0.75	0.233	0.175
		1.00	0.192	0.192
		1.50	0.151	0.226
		2.00	0.127	0.254
		2.50	0.112	0.279
		3.00	0.102	0.306
C_4n_6	20°	0.20	1.020	0.204
		0.40	1.065	0.426
		0.60	1.133	0.679
		0.80	1.232	0.985
		1.00	1.256	1.256
		1.40	1.185	1.658
		1.60	1.143	1.829
		2.00	1.057	2.113
		2.40	0.972	2.331
C_2n_6	20°	0.25	1.062	0.266
		0.50	1.137	0.569
		0.75	1.225	0.919
		1.00	1.335	1.335
		1.50	1.646	2.469
		2.00	2.137	4.247
		2.50	2.862	7.155

Table XXVII (continued)

Activity Coefficients and Activities

Compound	Temperature	Molality	γ_2	a_2
Me_2n_6	30°	0.20	0.985	0.197
		0.50	0.953	0.471
		0.75	0.894	0.671
		1.00	0.836	0.836
		1.50	0.753	1.129
		1.75	0.695	1.215
		2.00	0.643	1.286
		2.50	0.556	1.389
		3.00	0.494	1.481
C_4n_6	30°	0.20	0.994	0.199
		0.40	0.990	0.396
		0.60	0.983	0.590
		0.80	0.974	0.779
		1.00	0.960	0.960
		1.20	0.926	1.111
		1.40	0.833	1.166
		1.60	0.772	1.236
		1.80	0.715	1.288

Table XXVIII

Calculated and Experimental Water Activities

Compound	Temperature	Molality	a_1(exptl.)	a_1(calcd.)[1.]
Hexagol	20°	0.258	0.9952	0.9952
		0.155	0.9905	0.9903
		0.898	0.9825	0.9824
		1.350	0.9721	0.9723
		1.494	0.9684	0.9689
		2.210	0.9503	0.9505
		2.540	0.9363	0.9398
		3.190	0.9167	0.9193
Nonagol	20°	0.424	0.9917	0.9915
		0.630	0.9874	0.9867
		1.000	0.9762	0.9765
		1.376	0.9613	0.9635
		1.525	0.9554	0.9573
		2.053	0.9256	0.9288
		2.389	0.9013	0.9024

Using the equation relating a , h and m. h = 6 for hexagol and h = 14 for nonagol.

Table XXIX

Calculated and Experimental Activity Coefficients for Glycols (γ_2)

Hexagol	20°	Molality	Exptl.	h = 6	b = -6.62 RT	r = 4.77
		0.1	1.018	1.022	1.022	1.024
		0.2	1.038	1.044	1.045	1.048
		0.5	1.102	1.108	1.115	1.120
		1.0	1.240	1.244	1.240	1.240
		2.0	1.627	1.597	1.517	1.483
		3.0	2.305	2.173	1.825	1.720

Hexagol	30°	Molality	Exptl.	h=4.5	b = - 4.17 RT	r = 4.38
		0.2	1.020			1.038
		0.5	1.042	1.078	1.067	1.094
		0.75	1.079	1.117	1.104	1.140
		1.0	1.109	1.164	1.145	1.186
		2.0	1.377	1.382	1.377	1.368
		3.0	1.829	1.681	1.438	1.545

(calculated values chosen to fit at m=2.0.)

Nonagol	20°	Molality	Exptl.	h=13	b=-15.03 RT	r=6.95
		0.1	1.049	1.047		
		0.2	1.086	1.098		
		0.5	1.244	1.279	1.336	1.294
		0.75	1.478	1.474		
		1.0	1.724	1.725	1.722	1.724
		1.5	2.600	2.514		
		2.0	4.406	4.124	2.631	2.694

Nonagol	30°	Molality	Exptl.	h=11.8	b=-14.33 RT	r=6.62
		0.2	1.069	1.087		
		0.5	1.208	1.247	1.278	1.294
		1.0	1.623	1.621	1.623	1.624
		2.0	3.387	3.349	2.558	2.436

Dodecagol	20°	Molality	Exptl.	h=37.5	b=-89.03 RT	r=16.0
		0.1	1.380		1.374	1.479
		0.2	1.994	1.345	1.884	2.141
		0.3	2.500		2.581	
		0.4	3.690		3.529	
		0.5	5.610	2.471	4.815	5.773
		0.6	7.400			7.770
		0.75	11.520	5.424	10.404	11.802
		1.00	22.241	22.145	22.241	22.202

All values chosen to fit at molality of 1, except hexagol at 30° (m=2)

In the same way experimental activity coefficient - concentration curves have been fitted with data obtained from equations 5, 6 and 7 from the Introduction:

$$\ln \gamma_2 = -h \ln (1 - 0.018hm) + (h-1) \ln [1 - 0.018(h-1)m];$$

$$\ln \gamma_2 = \frac{b}{RT}\left[\frac{1}{(1 + 0.018m)^2} - 1\right] - \ln [1 + 0.018m];$$

$$\ln \gamma_2 = \frac{0.018\ r(r-1)m}{1 + 0.018rm} - \ln [1 + 0.018rm.].$$

The derivation and use of these equations is discussed in the introductory section on non-electrolyte solutions. The results are given in Table XXIX, and a representative diagram, comparing the behaviour of the three equations with h, b and r chosen to fit the experimental results at a molality of 1, is given for hexagol in Figure 46.

Discussion

The first object of this investigation was to obtain some information on the hydration of the glycols and detergent monomers.

Glycols: The glycol water activity - concentration curves all show a negative deviation from the behaviour predicted by Raoult's Law. It can be seen from Figure 46 and Tables XXVIII and XXIX that hydration can best account for the deviation of hexagol and nonagol solutions from ideal behaviour. No reasonable value of b or of r could be found which satisfactorily represented the activity coefficient of the solute throughout the whole concentration range, although at low concnetrations (m = 0.2 or less) there is little to choose between the different approaches. This was the finding, also, of Stokes and Robinson[191] for glycerol and sucrose solutions.

The best values of h, b and r which were found for the three glycols are summarised in Table XXX.

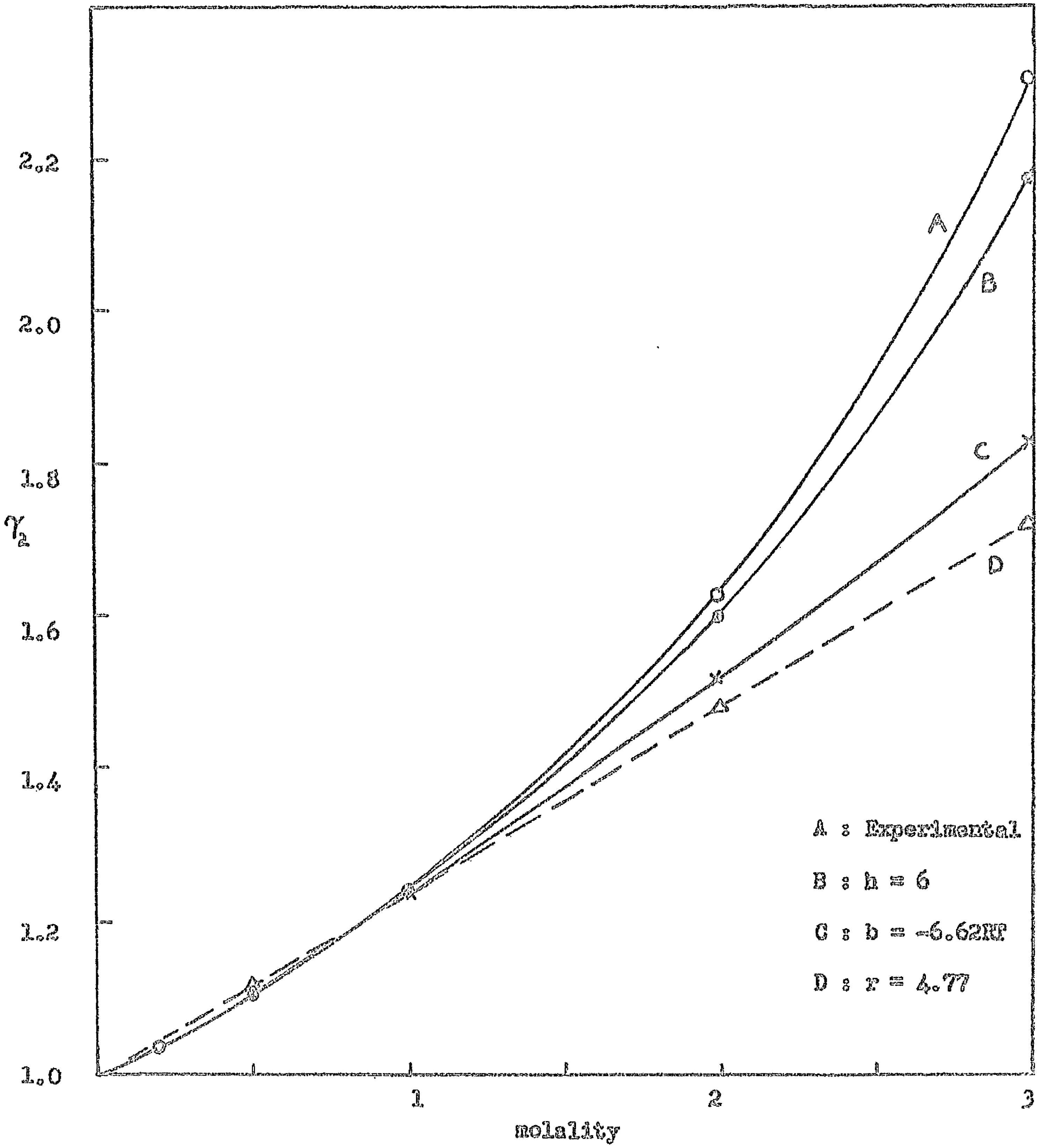


Figure 46: Variation of activity coefficient of hexagol with molality. Experimental results : A. Lines B, C and D drawn from equations 5,6 and 7 (see Introduction); B gives the best fit.

Table XXX

Values of h, b and r

Glycol	Temp.	h	b	r
Hexagol	20°	6	-6.62 RT	4.77
	30°	4.5	-4.17 RT	4.38
Nonagol	20°	13	-15.03 RT	6.95
	30°	11.8	-14.33 RT	6.62
Dodecagol	20°	(37.5)	-89.03 RT	16.00

The hydration value for dodecagol in Table XXX is bracketed because it does not represent the experimental values at all well, although chosen to fit at m = 1. In this case the best fit is obtained with the volume-fraction equation involving "r", the ratio of free volumes of solute and solvent molecules. This is probably because of the size of the dodecagol molecule : $HO(CH_2CH_2O)_{12}H$, Molecular weight 552. Nonaoxyethylene glycol (Molecular weight 419) probably represents the limit for the applicability of the equations used. No value of h fits the water activity - molality curves for dodecagol, although hexagol and nonagol solutions are well represented in this way.

It is interesting to compare the volume ratios of the three glycols with those found to give the best fit i.e with r. These values are compared in Table XXXI, where it will be seen that only in the case of dodecagol does the true ratio of volume of unsolvated species to volume of water molecules agree with r.

Table XXXI

Comparison of True Volume Ratio and "r"

Glycol	MW	$\frac{\text{Volume of unsolvated unit}}{\text{Volume of water molecule}}$	r
Hexagol	282	8.5	4.77
Nonagol	419	13.4	6.95
Dodecagol	552	16.3	16.00

The values of hydration from viscosity and from these vapour pressure measurements agree well in the case of hexagol and nonagol, but do not for the largest glycol, the viscosity result being 17.0 water molecules per molecule of glycol. This is in spite of the fact that the viscosity result would be most likely to be an over-estimate of hydration, because of the possibility of the molecule being asymmetric in solution. The vapour pressure result for n_{12} in terms of hydration alone is, therefore, unrealistic. The increasing hydration per ethylene oxide unit evident for the three glycols (h/n is 1.0, 1.22 and 1.42 respectively from viscosity results) probably reflects the effect of increasing coiling of the chain in solution as the chain length increases.

Monomers: The determination of the hydration of the detergent monomers from activity and activity coefficient data is more difficult because of the limited pre-micellar concentration range available. However, from the results on the non-micellar C_2n_6, and from the experimental data on C_4n_6 and Me_2n_6, with CMC's in the region of 1 molal, one can deduce the number of water molecules associated with the monomers in the same way as for the glycols. The water activity data for C_4n_6 and Me_2n_6 agrees with a value of h=6, a value close to that obtained from the viscosity measurements, described in section 3. The results are given in Table XXXII.

It is obvious from these results, and from the results on micellar hydration (Section 3, Table XVIII) that there is an increase in the hydration of the polyoxyethylene chains on micellisation. In the monomer, the alkyl chains appear to have little influence on the hydration of the PEG chains. The significance of this hydration increase is discussed more fully later.

Effect of Temperature: The results in Table XXX show the effect of temperature on the hydration of the glycol chain. As might be expected, the number of water molecules associated with each chain falls slightly on raising the temperature from 20° to 30°. This contrasts with the effect of temperature on micellar hydration :[22] previous results[22] and the present results for Bu_2n_6 indicate that there is a definite increase in hydration

Table XXXII

Pre-micellar Water Activities for C_4n_6 and Me_2n_6 at 20°.

Molality	a_1 (calculated) [1]	a_1: C_4n_6 [2]	a_1: Me_2n_6 [2]
0.2	0.9963	-	0.9965
0.4	0.9925	0.9921	0.9926
0.6	0.9886	0.9883	0.9881
0.8	0.9845	0.9835	0.9843
1.0	0.9802	0.9799	0.9800

---

1. for $h = 6$
2. from experimental curves

of the micellar units - due to the extension of the glycol chains.

Micellar Solutions : Examination of the water activity - molality plots of the detergents (Figures 42 and 43) reveals that at 20°, before the onset of micellisation at the CMC, the water activity follows the behaviour of monomeric C_2n_6 or hexagol solutions, that is, it shows negative deviation from Raoult's Law. At the CMC the curve alters course and shows a positive deviation from Raoult's Law behaviour. The former type of behaviour is associated with solute - solvent interactions, while the latter is evidence of solute-solute interaction or association.

In non-ionic detergent solutions a complication in any attempt to explain the results is the fact that, above the CMC, there is both solvation and association, the two effects opposing each other in their effect on activity.

Dolezalek attempted in 1908 to account for a number of non-ideal solutions by assuming association and solvation, with all species obeying Raoult's Law.[287] He attempted, according to Hildebrand,[288] to explain too many deviations on this basis and was led to postulate impossible polymerisations to fit the experimental data. In the system aniline-hexane the assumption of extremely complex aniline molecules is insufficient to describe the solution behaviour.[289] The main objection to the so-called "simple chemical theory" of association, which accounts for large positive deviations from Raoult's Law, is that the application of Raoult's Law to the true species in solution is incorrect, due to the non-ideality of the entropy of mixing of multiple molecules and solvent.

In the present case it is obvious that association is occuring, and that this is largely causing the deviations from ideal behaviour above the CMC : by aggregation the number of osmotically active molecules is reduced so that the "true" molality is lower than the measured concentration, and the water activity will correspond to this "true" concentration. Hydration influences the result also, by reducing the number of free water molecules.

From plots of $(\phi - 1)$ vs. molality, the activity coefficients of the solute molecules were calculated (as for the glycols) and the activity (a_2) evaluated at each concentration. See Table XXVII. For the C_4n_6 and Me_2n_6 detergents the solute activity shows a definite increase above the CMC, in agreement with the behaviour predicted by the law of mass action. The detergent Et_2n_6, which has an aggregation number of 14, has a more pronounced break at the CMC and the increase in solute activity above this concentration is less marked. (Figure 47). The results seem to underline the validity of the law of mass action in describing the micellisation process as an equilibrium between monomers and micelles, in preference to the pseudo-phase treatment, which predicts a constant activity in micellar solutions.

A review of the properties of soap solutions by Pethica[153] revealed that the osmotic pressure, and hence osmotic activity, of the water was nearly constant above the CMC for a number of detergents. Other measurements, however, have shown that the vapour pressure decreases with increasing concentration of association colloid in the region where aggregates are present.[290,291,292]. Danielsson[90] found the decrease in vapour pressure of detergent solutions to be slow immediately above the CMC, but more pronounced at higher concentrations. It is obvious from our present results that the degree of vapour pressure lowering above the CMC depends on aggregation number and hydration.

The vapour pressure data of Corkill and co-workers[64,166] for C_6n_6 and

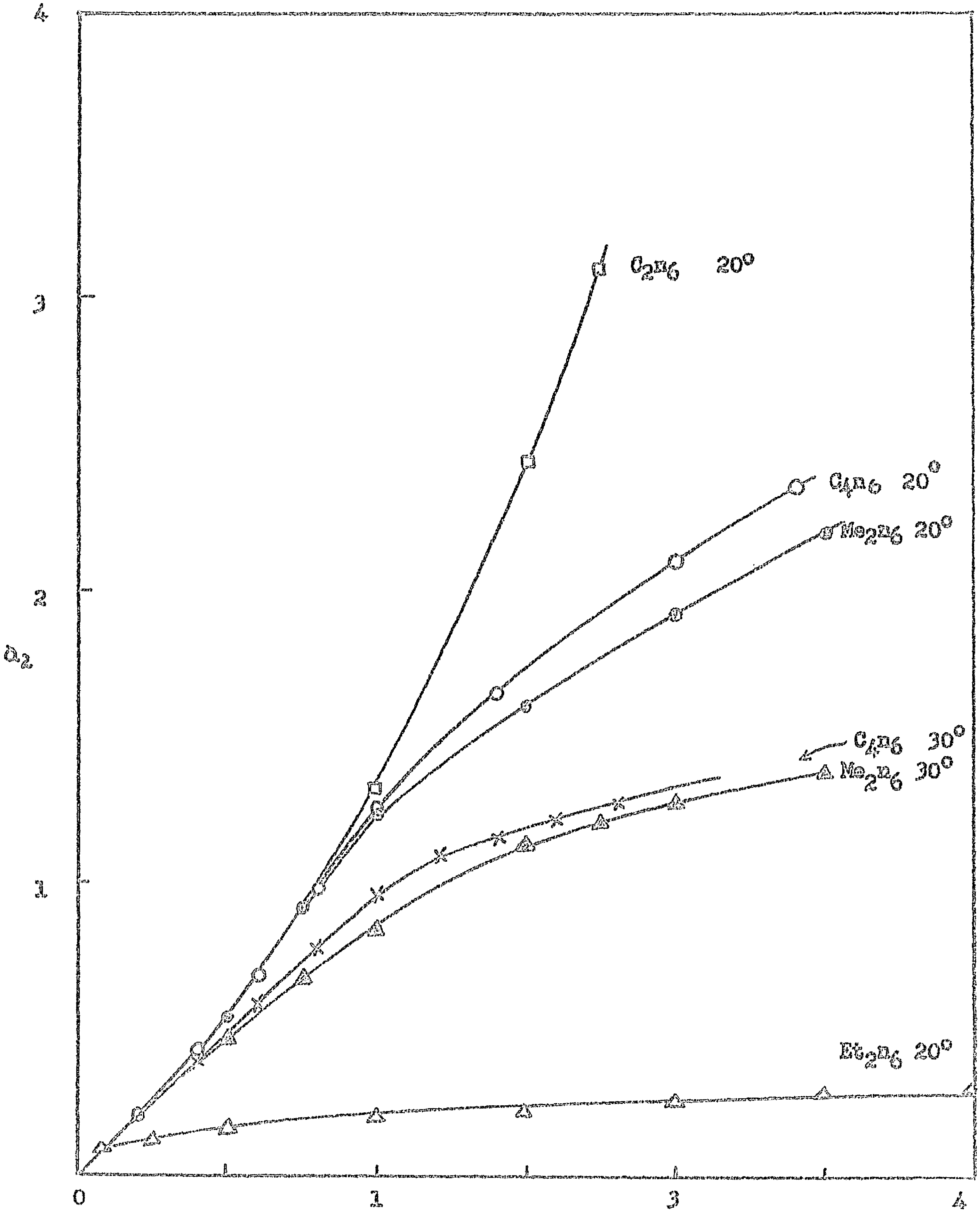


Figure 47: Plots of solute activity vs. concentration for C_2n_6, C_4n_6 Me_2n_6 and Et_2n_6, showing clearly the increase in solute activity above the critical micelle concentration.

C_8n_6 also demonstrates a change in activity of the solute above the CMC, in accord with the present results. However, their surface tension-concentration plots exhibit a constant surface tension above the CMC which implies, if Γ_2 is constant, that the solute activity does not alter above this concentration. The position, then, is obscure. If the solute activity increases above the CMC, as the vapour pressure results indicate, Γ_2 must decrease to keep the surface tension constant. This desorption is unlikely physically and is contrary to the behaviour of other detergents.[147] The discrepancy may more likely be explained by the fact that values of activity are obtained from a bulk property and values of γ from a surface property : trace impurities which may be present would affect the surface properties to a greater extent than the bulk properties and would tend to mask any decrease in surface tension above the CMC.[150] The situation is one which can only be resolved by further experiments such as determination of surface tension after purification of the detergent by extensive foaming. It is essential, also, where there is a discrepancy between bulk and surface properties to be able to determine the CMC by measurement of a bulk property. Experiments of this type are necessary but were outside the scope of this thesis.

It is intended to investigate the application of the law of mass action to the equilibrium between hydrated monomers and hydrated micelles in the near future, using a computer.

<u>Effect of Temperature on Micellar Solutions</u> : The systems C_4n_6 and Me_2n_6 were investigated at 30°. The activity coefficients and osmotic coefficients fall significantly below unity below the CMC. Water activities are extremely difficult to measure at low concentrations, especially at elevated temperatures; ϕ is sensitive to small activity changes .

Therefore the results may be due to experimental error. On the other hand they may be due to dimerisation prior to aggregation at the CMC. Above the CMC, the water activities are higher than those at 20° . Increased hydration results in a more negative deviation from Raoult's Law increased aggregation results in a more positive deviation. As increase in temperature results in larger micelles in other non-ionic detergent systems[22] it is likely that the aggregation number has increased. This may be deduced, also, from Figure 47 for the activity - molality curves for the two detergents at 30° fall between those for an aggregation number of 4 and of 14. Franks and Smith[294] have recently found evidence of dimerisation of sodium dodecyl sulphate in the submicellar concentration region. McBain[295] found deviations from normal behaviour (that is, normal 1-1 electrolyte behaviour) in dilute solutions of ionic surfactants. It is reasonable to suppose that no dimerisation occurs at 20° in the present systems, because of the similarity of the glycol and detergent activity-concentration curves below a molality of 1. Hydrophobic bonding becomes more favourable as the temperature of a system is raised, and, therefore, dimerisation may well be encouraged at higher temperatures. This would explain the activity coefficients below the CMC for the two detergents (Table XXVII)

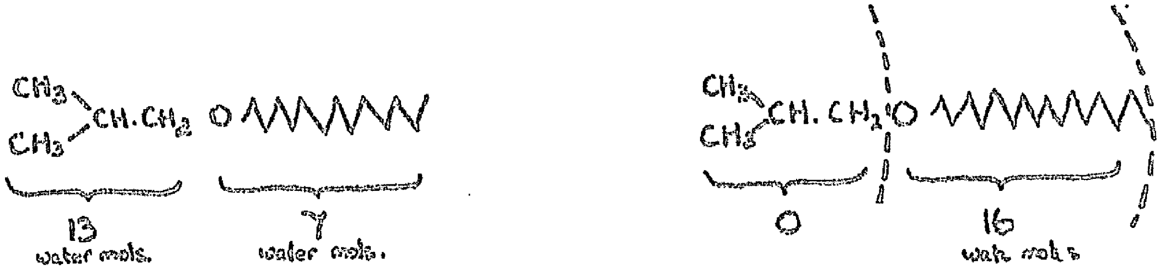
The behaviour of the osmotic coefficient above the critical micelle concentration follows the expected course in both cases, with a sharp downward fall beginning at the CMC.

It would be possible to calculate the partial enthalpies of hexagol, nonagol, C_4n_6 and Me_2n_6 systems from a knowledge of the solute activities at 20° and 30°, but it is felt that, in view of the limited temperature range studied, fuller data over a wider range would be necessary before full use could be made of the information. For this reason the calculations are not presented.

Thermodynamics of Micelle Formation, Part II

Implications of the increase in hydration of the polyoxyethylene chains on Micellisation : The thermodynamics of micellisation have already been discussed in the surface chemistry section whence the experimental results for the enthalpy and entropy changes were derived. The results from the vapour pressure studies throw further light on the problem of explaining these thermodynamic changes.

The viscosity and vapour pressure results for the hydration of the monomeric and micellar species indicate a definite increase in the hydratio of the polyoxyethylene chain on micellisation. This concept of increased hydration in the micellar state is not unreasonable if the hydrating water is considered to be water both associated loosely with the PEG chain and water molecules bound to the chain. It is possible that the bound water remains constant, and that the increase in hydration is due to the trapping of extra water molecules in the micellar state. This has not been entertained by some workers. Hudson and Pethica , for example, speak of the desolvation of the monomer as it enters the micelle. From the thermodynamic evidence it is obvious that there is an *overall* desolvation. It is interesting to consider the process using some experimental values of hydration for both monomer and micellised monomer. Nemethy and Scheraga have listed some values for the transfer of a non-polar side chain from water into a non-polar region based on N, the number of water molecules associated with each hydrocarbon chain lost on bonding. Using these value one may picture the changes on micelle formation as consisting of a) hydrophobic "desolvation" (loss of water structure) and b) increased glycol solvation. For Me_2n_6 for example, the process is envisaged as follows:



(Net reduction on micellisation = 4 H_2O molecules/monomer)

MONOMER MICELLE

Figure 48

Nemethy and Scheraga's results[103-105] show that the enthalpy of transfer is equivalent to 0.18 Kcals. mole^{-1} per water molecule removed from the hydrocarbon. The net reduction depicted in Figure 48 results, therefore, in an enthalpy of transfer of 0.72 Kcals mole,$^{-1}$ which is close to the experimental value for the enthalpy of micelle formation, 0.60 Kcals. mole.$^{-}$ Similar calculations were made to estimate ΔH_{trans} for the other detergents and the results are given in Table XXXIII.

In spite of the assumptions involved, and the experimental error in the estimation of hydration, the correspondence between ΔH_{trans} and ΔH_m is very good. The enthalpy and entropy changes on the formation of a leucine-iso-leucine hydrophobic bond falls with increasing temperature. Experimental evidence shows that ΔH_m and ΔS_m also decrease with increasing temperature.[167] This may be explained on the basis of the ideas above, as increased temperature will result in a reduction of the hydration of the monomer, and an increased hydration of the polyoxyethylene chain in the micellised monomer, resulting in a smaller overall hydration decrease and a lower enthalpy change. Bu_2n_6 gives ΔH_{trans} = 2.7 Kcals mole^{-1} at 20°, which falls to 2.2 Kcals. mole^{-1} at 25° (latter calculated on the basis of h_e(monomer) = 6, h_e (micelle) = 19, as found) which is in line

Table XXXIII

Comparison of calculated enthalpies and experimental enthalpies of micellisation

	monomer[1]		micelle[2]	overall loss[3]	calcd.[4]	
Detergent	h_h	h_e	h_e	$-\Delta h$	ΔH_{trans}	ΔH_m
C_4n_6	14	7	14	7	1.2	0.8
C_6n_6	18	7	18	7	1.2	2.2
Me_2n_6	13	7	16	4	0.7	0.6
Et_2n_6	17	7	18	6	1.1	1.2
Pr_2n_6	21	7	19[5]	9	1.6	2.0
Bu_2n_6	25	7	17	15	2.7	2.9

1. h_h = no. of water molecules associated with hydrophobe, based on Nemethy and Sheraga's estimates. h_e = no. of water molecules associated with ethylene oxide chains.
2. h_h = zero in micelle.
3. $\Delta h = (h_h + h_e)_{mon} - (h_e)_{mic}$
4. $\Delta H_{trans} = \Delta h \times 0.18$ Kcals. mole^{-1}
5. extrapolated value as experimental value seemed too high compared to rest of series.

Assumptions involved in deriving values of Table XXXIII

1. That the value of 0.18 Kcals. per mole of water removed is correct.
2. That the enthalpy involved in losing one water molecule associated with the hydrocarbon chain is the same as that involved in losing one water molecule from the region of the PEG chain. This is reasonable as the change in hydration of the PEG on micellisation must be largely due to the "trapped" – not hydrogen-bonded – water molecules.
3. That the values of h_h are correct.

with the experimental results of other workers.

The above observations, while supporting the importance of the increase in hydration that occurs in glycol portion of the monomers, indicate that the contribution of configurational changes and other subsidiary thermodynamic effects are small.

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