MICELLAR PROPERTIES IN AQUEOUS SOLUTION OF A SERIES OF SYNTHESISED NON-IONIC DETERGENTS.

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SUMMARY.

Part 1.

In the first part of the thesis a review of the chemistry of the polyoxyethylene type non-ionic detergents is given.

The preparation by ethylene oxide polymerisation and other synthetic routes of the polyoxyethylene glycols and their monoalkyl ether condensates is reported, and a resumé made of the existing work on the formation and structure of the micelles of these detergents in aqueous solution, the effects of temperature, electrolytes, and solubilisates on these properties, and their surface activity.

The theory of the determination of molecular weights of both large and small particles by light-scattering, and the relationship between the viscosity of solutions of macromolecules and solute shape and solvation, is outlined.

Part 2.

The synthesis of a series of non-ionic detergents, based on hexadecyl alcohol, containing a definite oxyethylene chain length is described. The series has the general formula $CH_3(CH_2)_{15}(OCH_2CH_2)_nOH$, and six members,

having n = 6, 7, 9, 12, 15, and 21 respectively, have been prepared (for ease of handling the names of these compounds have been abbreviated to Hn_6, Hn_7, ...Hn_{21}). Some of their physical properties are reported.

The critical micellar concentrations (cmc's.) of these materials in aqueous solution have been investigated using the Wilhelmy plate method for measuring surface tension; cmc's. were determined from plots of surface tension vs. log. concentration. Very small critical micellar concentrations were obtained.

A light-scattering photometer has been constructed and calibrated. Using the Hn_9 detergent and the results from the calibration of the photometer, a statistical analysis of most of the errors in the measurement of molecular weight by light-scattering has been carried out, and it is shown that the largest part of the error arises in the measurement of the turbidities of the solutions rather than from the measurement of the specific refractive index increment or depolarization.

A study of aqueous solutions of the synthesised detergents has been made at 25°. Results obtained from viscosity measurements have been used in conjunction with data from light-scattering to elucidate the micellar structures of the various members of the series.

In general the micellar weight and aggregation number falls as the series is ascended; the micellar weight of Hn$_6$ is 1.23 x 10^6; of Hn$_{21}$, 0.82 x 10^5. The first two members of the series, Hn$_6$ and Hn$_7$, formed asymmetric micelles and showed aggregation of the smaller micelles, formed at low concentrations, into larger micelles as the concentration was increased; a mass action law has been applied to this aggregation to give an idea of the size of the aggregated species. The other four members of the series appeared to form reasonably spherical micelles. Using the viscosity results possible micellar shapes and hydration are discussed.

As disentanglement of the effects of asymmetry and hydration on the intrinsic viscosity is very difficult without an independent determination of one of these properties, an attempt has been made to develop an empirical method for determining micellar hydration using vapour pressure measurements of concentrated solutions and gels of the detergents. This method gave values of hydration which agreed well with values calculated from viscosity results for the higher members of the series which appeared to give spherical micelles. Results showed micellar hydration increased as the polyoxyethylene chain became longer.

Calculations of micellar dimensions have been made and it appears that in the micelle the polyoxyethylene chain exists in a curled up form, as its measured length was significantly less than that of the fully extended chain.

The effect of temperature between 20° and 30° on solutions of one of the compounds, Hn_7, has also been investigated; results indicating that both micellar size and hydration increase with increasing temperature.

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PART 1.

THE PREPARATION AND PROPERTIES OF POLYOXYETHYLENE TYPE NON-IONIC DETERGENTS.

THE THEORY OF LIGHT-SCATTERING.

THE INTERPRETATION OF VISCOSITY RESULTS.

INTRODUCTION

Synthetic detergents, as we know them today, are of fairly recent innovation but the value of naturally occurring substances exhibiting surface active properties was realised in prehistoric times. When puddling clay primitive man added various organic compounds to his slurry to facilitate handling, and gums, saponins, and proteins have been used empirically for centuries. The first preparation of soap is shrouded in the anonymity of time, yet the basic principles by which it is made have never fundamentally changed, although refinements in starting materials and methods have resulted in end products barely comparable with the earlier efforts.

The coming of the Industrial Revolution, focussing attention on the instability of soap in acid solution and the insolubility of its calcium and magnesium salts, stimulated the development of synthetic detergents to overcome these deficiencies. From these first detergents, prepared by the action of sulphuric acid on castor oil, there has arisen, particularly in the last half century, the vast array of synthetic detergents available on the market today.

Generally, surface active agents are classified into three main groups according to whether the surface active unit in aqueous solution is an anion, cation, or an unionised molecule. There are exceptions to these generalisations and some compounds contain both cationic and anionic groups, or ionic and non-ionic groups.

It is with some of the properties in aqueous solution of a series of compounds of the non-ionic type that this thesis is concerned i.e. the monohexadecyl ethers of polyoxyethylene glycols of various chain lengths.

As their name implies, non-ionic detergents do not ionise in aqueous solution, and thus have many advantages both in detergent properties and for physical-chemical studies. Furthermore, in a series of compounds as has been studied, a range of compounds with a constant hydrophobic portion, but a varying hydrophilic moiety, can be obtained without fundamentally altering the chemical structure of the detergent, thus enabling a fuller and more comprehensive study to be made than is possible in an ionic series, where the hydrophilic portion can only be altered by changing the ion with the consequent inherent disadvantages of such a step.

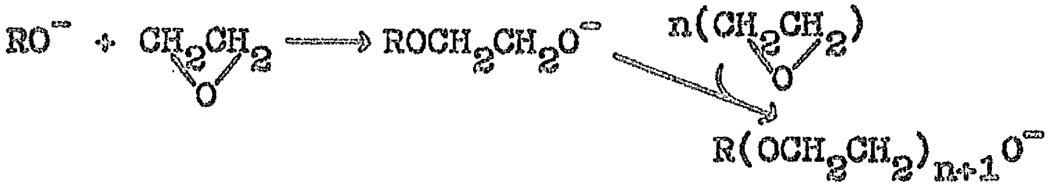
Although polymers of ethylene oxide of up to six units were first synthesised over one hundred years ago[1,2] it was not until around 1930 that their commercial potential (and particularly that of their derivatives) was realised. Since then a wide range of compounds incorporating the polyoxyethylene glycols have been produced for a multitude of purposes, ranging from aids in drilling to pharmaceutical preparations, where their wetting, detergent, foaming, dispersing, or emusifying properties are utilised.

Even to this day much of the knowledge of the usefulness and properties of these compounds has been obtained empirically, and, until a more complete insight to their behaviour, structure, and orientation in solution has been procured, a more rational scientific approach to their use will remain difficult.

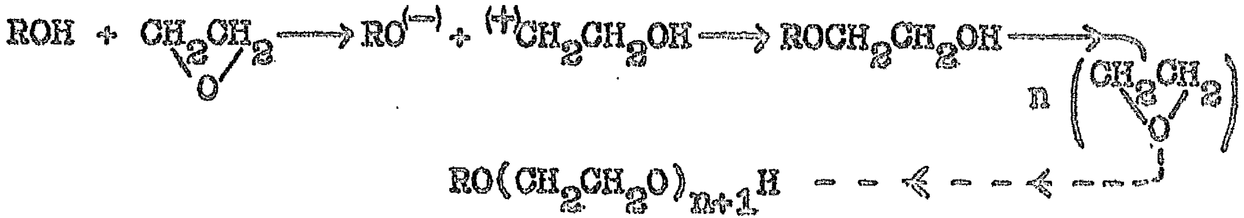
Preparation of Ethylene Oxide Adducts.

Ethylene oxide is a colourless gas with an ether-like odour, prepared on a small scale by heating 2-chloroethyl acetate with potassium hydroxide[3], on a commercial scale by the chlorohydrin process[4], or by direct oxidation of ethylene. Highly inflammable, liable to undergo exothermic reaction with itself, and of a toxicity similar to carbon monoxide, it is however the fundamental unit in the production of polyoxyethylene polymers and herein lies its value in the chemical industry. Although early polyoxyethylene glycols were made as a byproduct of diethylene glycol syntheses, all ethylene oxide adducts made on a commercial basis today are prepared by the polymerisation of ethylene oxide in the presence of a suitable catalyst.[1,2,5-13]

Various schemes have been suggested for the polymerisation mechanism; several of which appear to be influenced by the type of catalyst used. Gee[14] suggested the following reaction sequence when an alkoxide ion e.g. sodium methoxide is used as initiator:-



Various other catalysts, alkaline and acid, have been mentioned in the literature; as a general route for the polymerisation Fine[5] proposed that the epoxide ring of the ethylene oxide opened, combined with an active hydrogen atom contained in a functional group of the second reactant then combined with the latter to form its hydroxyethyl derivative.



The active hydrogen of the hydroxyethyl group was then available for reaction with an additional epoxide group, and, by repetition of this process, the polyoxyethylene compound was built up; the degree of polymerisation being controlled by the amount of ethylene oxide made available.

Alcohols, phenols, carboxylic acids, amines, amides, alkyl and aryl sugar derivatives, and mercaptans are among the compounds most commonly combined with a polyoxyethylene chain; the properties and stability of the resulting compounds being influenced by the choice of hydrophobe, the type of linkage, and the extent of polymerisation.

When polyoxyethylene chains are built up ideally, from a fixed number of propagating units by a sequence of kinetically identical additions of monomer, size distribution of chain lengths has been shown [15] to be described by Poisson's formula.[16]

Although the conditions producing Poisson distribution are found in the reaction of ethylene glycol with ethylene oxide[17], complications are encountered when the rate of the initial step of the reaction is different from that of further steps, or the subsequent additions themselves vary in rate with chain lengthening. Complex formulae have been derived for reactions where all steps are kinetically different[18], but are very cumbersome to use. As a compromise, Weibull and Nycander[17] produced a simplified formula based on the assumption that the rate of ethylene oxide additions were equal, but differed from that of the initial reaction of ethylene oxide with the parent hydrophobe.

Fractional distillation of compounds prepared by Wrigley, Smith, and Stirton[19] showed a distribution of chain lengths which agreed with Weibull and Nycander's equation, rather than with the Poisson distribution. This work was however limited to long chain fatty alcohol adducts. On the other hand, the Flory-Poisson distribution has been found valid for the oxyethylation of ethylene glycol[17], phenols[20,21] and stearic acid[22]; in the last case presumably because of preferential combination of the parent compound with ethylene oxide before significant further reaction of the ether alcohols took place.[10,12,23]

Industrially an alkaline catalyst seems to be preferred[24] although the reaction may also be catalysed by acid, or even proceed uncatalysed[25]. Acid catalysts are used if low temperature conditions are required[26]. The choice of catalyst and the purity of the starting materials have quite a striking effect on the end product. For obvious reasons manufacturers do not disclose their particular routes, but work by Drew, Howard, and Schaeffer[11] illustrates this point. In their experiments they found acid catalysed reactions gave rise to byproducts, the amount of which increased with the degree of polymerisation, and the presence of traces of water (either by contamination or by formation during the reaction) resulted in the formation of glycols. The concentration and type of catalyst, and the reaction conditions affected the distribution of chain lengths,[14,27,28] and in practice, variation of these is often used to obtain the type of product most suitable for the purpose to which it is to be applied.

It would therefore appear that there is a great variation in the possible distribution of the ethylene oxide chain lengths in a glycol or detergent; the properties identified with the various commercial products are influenced by this distribution as well as the average molecular ratio of ethylene oxide to hydrophobe.[21,29]

In an attempt to obtain a clearer view of the properties of this type of compound various means have been tried to obtain a homogeneous preparation, i.e. one which did not contain a distribution of chain lengths. Fractionation of the polymerised products by distillation[21] and chromatographic [30,31] techniques have been tried, but as yet has only succeeded in narrowing the chain length distribution. Alternative routes of building up the chains have also been investigated. As mentioned previously, short length polyoxyethylene glycols were first described by Laurenco,[1], and by Wurtz,[2] the former prepared them by reacting ethylene glycol with either ethylene dibromide or ethylene bromohydrin, the latter by reacting ethylene oxide with ethylene glycol or by hydration of ethylene oxide, whereas Mohr,[32,33] at a slightly later date, heated ethylene glycol monoacetate with the monosodium derivative of ethylene glycol.

Although certain early workers suggested a cyclic structure[3] for the polyoxyethylene glycols, much of the data supporting this was of a negative nature, and the detection of hydroxyl groups was taken as evidence of an open chain.[34,35]

The first direct method of synthesising a single polyoxyethylene glycol, devised by Perry and Hibbert,[36] used a Williamson type ether reaction of the α,ω-dichloro derivative of a pure lower glycol with two molecules of the monosodium salt of another or the same glycol.

$$ClCH_2CH_2(OCH_2CH_2)_nOCH_2CH_2Cl + 2NaO(CH_2CH_2O)_xH$$
$$\Downarrow$$
$$HO(CH_2CH_2O)_{n+x+2}H$$

Using this procedure Fordyce, Lovell, and Hibbert[35] synthesised glycols containing up to 186 ethylene oxide units. The compounds containing up to six ethylene oxide units were distilled, but the longer ones had to be purified by extraction and crystallisation; the final purity being assessed by time/temperature cooling curves. Examination of these synthesised polyoxyethylene glycols by Xray diffraction[37] showed, that as far as could be detected by that technique, there was no essential difference between them and products of ethylene oxide polymerisation, substantiating the claims of other workers as to the identity of the two end products.[26,34]

Synthesis of homogeneous glycol derivatives presents an even more formidable problem, particularly when a compound with a hydrophobic radical at one end only is required. Certain workers have ducked round this problem by using a short sodium alkoxide,[38,39] e.g. sodium methoxide, to initiate the polymerisation reaction, obtaining a methoxypolyoxyethylene glycol, fractionating this, and converting the required fraction to its sodium salt. Thence, by the Williamson reaction with the hydrophobe halide, they obtained the desired compound. Such a compound is based on the product of the polymerisation reaction, and hence a uniform chain length is extremely difficult to obtain.[21,30] Moreover the compound must be used as its methoxy derivative; removal of this group without breaking the hydrophobe-glycol link is virtually impossible.

A few reports have appeared in the literature describing synthesised compounds,[40-49] but the majority have contained short polyoxyethylene chains of up to six ethylene oxide units. Lange[50] has reported a monohexadecyl ether of decaoxyethylene glycol, but as his melting point is some six degrees lower than that generally accepted for the monohexadecyl ether of hexaoxyethylene glycol, it would appear that the purity of the former is in doubt.

For detergents the synthetic route used has also been via Williamson ether synthesis type reactions, two ways being available:-

a) building up the glycol by the method of Perry and Hibbert, converting it to its monosodium salt and by reacting this with the hydrophobe halide.

$$Na + HO(CH_2CH_2O)_nH \longrightarrow NaO(CH_2CH_2O)_nH$$

$$RX + NaO(CH_2CH_2O)_nH \longrightarrow RO(CH_2CH_2O)_nH$$

b) by preparing a short chain compound as above, chlorinating the terminal hydroxyl group with thionyl chloride, then reacting this compound with a monosodium derivative of a glycol.

Yields by either route are not particularly good and side reactions such as dehydrohalogenation of the chloro compound have been reported.[45] Alkyl tosylates have also been described as intermediates,[51] and recently, the stepwise synthesis of the monodecyl ethers of mono to tetra oxyethylene glycols by acid catalysed addition of ethylene oxide has been reported.[42]

The difficulties encountered in the purification and separation of the end products from the reaction mixture has been one of the main causes of delaying the syntheses of longer chain compounds. A relatively short oxyethylene chain compound, such as the monohexadecyl ether of hexaoxyethylene glycol, forms the limit for normal distillation, and, even under high vacuum, the conditions required are rather rigorous for an organic compound of this nature (b.p. $235^\circ/10^{-3}$mm.). Neither do the actual distillation procedures used seem to produce an entirely satisfactory compound, as oxidised byproducts have been[43,45] reported in the distillate, and subsequent chromatography on silica was required to remove them. Traces of glycols are one of the most common contaminants and crystallisation and other purification techniques are hampered by the similarity of their properties to those of the adduct, particularly when the glycol chains become large. Further complications are encountered due to the surface active properties of the derivatives causing emulsions when partition techniques are used. To overcome this partition between ethyl acetate and saturated sodium chloride solution[52] has been used, or heating an aqueous solution of the mixture to about 100° and separating the detergent-rich phase[39]; in both cases the glycol and any other water soluble products of the reaction were retained in the aqueous phase.

Analysis

In estimating the purity of synthesised compounds it has been shown that although standard analyses (percentages of C, H, and O) gave figures indicating satisfactory purity, such analyses were not sufficiently sensitive to detect impurities in this type of compound as minima occurred in the surface tension/concentration curves.[45] Estimation of the hydroxyl group by acetylation or other techniques also loses its sensitivity when only small samples are available and the hydroxyl group is only equivalent to some 1-2% of the molecular weight.

Various assays have been developed to estimate the ethylene oxide content of the adducts. Most of these have been dependent on degradation of the chain, or a complex formation; the complexes being formed by reacting the ethylene oxide derivatives with heteropoly inorganic acids, such as silico-tungstic,[53-55] or phosphomolybdic[56,57] acids, or with tannins, potassium ferrocyanide, or other suitable reagents.[58-62] These complexes were then quantitatively estimated either by gravimetric, volumetric, or absorptiometric techniques, and a direct relationship could be established with the particular surfactant being determined.

Dichromate oxidation has been advocated by Edkins[63,64] and others, but lacked the specificity for ethylene oxide units desired. Morgan,[65] using a modified alkoxyl apparatus, decomposed the ethylene oxide residue to ethylene iodide and ethylene with constant boiling hydriodic acid. The latter method has been developed by Siggia et al.[66] by refluxing the polyoxyethylene adduct with excess hydriodic acid under an atmosphere of carbon dioxide, and titrating the liberated iodine with sodium thiosulphate.

This reaction has the advantage over the other chemical methods that it is an absolute method; no standard curve need be prepared for a given compound under specified conditions.

All the above methods estimate the total amounts of ethylene oxide present, thus the presence of glycols will affect the result. Several methods of estimating the amount of glycol present have been devised,[27,52,67] generally involving the separation of the glycol from the detergent, but recently correlation of total ethylene oxide content, obtained by the hydriodic acid analysis, with the percentage of hydroxyl groups found by acetylation, has been used to calculate the quantity of glycol in the adduct.[68]

Properties in Aqueous Solution.

The Formation of Micelles.

In contrast with the copious work on ionic detergents, e.g. references 69-79, the number of papers on the micellar structure in aqueous solution of non-ionic detergents is relatively small, no doubt influenced by the discovery of soap micelles some twenty-five years[80-83] before the first work advocating that micellisation was exhibited by the non-ionics was forthcoming. Using the Scatchard[84] method of determining freezing point depressions, Gonick and McBain[85] found results obtained for both Triton X 100, a commercial octyl-phenyl oxyethylene adduct, and a monolaurate of nonaoxyethylene glycol, in aqueous solution bore a striking resemblance to those obtained for colloidal electrolytes. Correlating this work with previous results on solubilisation of benzene and various dyes by the lauryl adduct,[86] and Xray diffraction[87] in aqueous solution, they concluded that non-ionic detergents also formed micelles. This deduction has since been confirmed by other workers using Xray and solubilisation techniques, and by viscosity and turbidimetric data.[12,88-92]

Many theories have been put forward for the formation of ionic surfactant micelles[69,71,93-108] and on the thermodynamics entailed, mostly based on two standpoints:- the law of mass action, and the phase rule (the micelles are considered as a separate phase). In one of the simpler theories, Debye[71] proposed that as the number of long chain ions aggregated to form a droplet or core of hydrophobic tails, the number of charges per aggregate increased. The charge density at the periphery rose and with it the electrostatic free energy of the growing aggregate. An equilibrium was reached when the drop in energy due to aggregation of hydrophobic groups was balanced by the rise in energy due to electrostatic repulsion. Criticism has been levelled at Debye's treatment as it was based on minimising the free energy of the micelle rather than the entire system.[93,94]

It is evident from knowledge of the non-ionics that other factors must also be at work in the process of micelle formation; these factors may be operational for micelles of ionic, as well as non-ionic detergents and may play a large part in micellisation over and above the more readily understood electrostatic repulsion. Such additional factors stabilising an equilibrium size distribution of micellar aggregates, must be of the nature of forces resisting the decline in particle-solvent contact and the concomitant dehydration and entropy changes.

The necessity of looking for additional opposing additional opposing factors which could balance the drop in energy due to aggregation of hydrophobic groups, and thus the need to look at the behaviour of all other components has been stressed by Reich,[93] who calculated the equilibrium micellar size from energy and entropy changes taking place during micelle formation. His calculation was based on a simple model of coalescence of hydrocarbon tails to a liquid droplet, and fitting the ethylene oxide chains over their surfaces. On the basis of his theory, Reich also postulated that micelle formation of non-ionic surfactants occurs at a distinct critical micellar concentration (cmc.), the cmc. decreases with increasing hydrocarbon chain, and increases with increasing the ethylene oxide chain.

Kushner, Hubbard, and Doan[109] have pointed out that the sharpness of the micelle appearance forecast by Reich was dependant on the values assigned to the entropy and energy change associated with micelle formation; his assignment of a high negative value (-20 kcal.) for the entropy change was probably unwarranted since it was based primarily on considerations of the heat of vaporisation of dodecane, and neglects the positive contribution of the total entropy change which results from the uncurling of the hydrocarbon portion of the molecule when it enters the micelle. Choice of a smaller value for ΔS would have reduced the predicted sharpness of micelle formation. Calculation of the entropy of micellisation[97,98] for a synthesised monododecyl ether of hexaoxyethylene glycol,[45] and for a series of commercial surfactants,[110] from measurements of cmc. as a function of temperature appears to support Kushner's criticism, as values of + 5.9 kcal. mol.$^{-1}$ deg.$^{-1}$, and 7.6 to 18.4 kcal. mol.$^{-1}$deg.$^{-1}$, were obtained. This, according to the authors, was unlikely to be caused by the molecules being less restricted in the micelles than in water, the magnitude of ΔS strongly suggesting that the energetics of micellisation of these compounds was governed almost entirely by the partial desolvation of the monomer as it entered the micelle. Thus it was possible that the gain in entropy resulted from the orientation of some or all of the water molecules in the vicinity of a single monomer, changing to a freer orientation on micelle formation.

Hoeve and Benson,[103] in an extensive statistical mechanical treatment, extended Reich's approach and also pointed out that dehydration phenomena had to be taken into account. The simple shielding of hydrocarbon tails from water by ethylene oxide used in Reich's calculation accounted for only "complete micelles" i.e. where the hydrocarbon core was entirely covered by ethylene oxide chains. It has also been pointed out that, unfortunately, undefined parameters in Hoeve and Benson's theory makes comparison with practical results somewhat difficult.[111,112]

A theory, postulated by Nakagawa and Kuriyama,[113] considered the main factors preventing association are the heat of hydration and the configurational entropy terms of the flexible hydrophilic chain. It gave quantitative predictions for the cmc., micellar weight and other properties in solution, but could not reasonably explain temperature effects and clouding phenomena.

A recent paper by Mukergee[108] has come down heavily in favour of the mass action approach and attempted to point out some of the difficulties and inaccuracies of the two phase theory; but the latest paper[107] on the thermodynamics of micelle formation reanalysed Reich's model from the two phase approach and developed a theory of micellar statistical mechanics from the extended theory of dilute solutions,[114] the dielectric continuum model of the solvent, and the statistical mechanical treatment of physical clusters at constant pressure,[115] and formulated a more general theory by elimination of the first two.

Critical Micellar Concentration.

Formation of micelles causes abrupt changes in many of the physical properties of a solution of a surfactant[116] and measurement of the concentration where these changes take place is generally taken as indicative of the coalescence of the monomers. Philips[95] has proposed that the cmc. could conveniently be defined mathematically as the total concentration (c) at which some colligative property ϕ gave $\frac{d\phi^3}{dc^3} = 0$ but the choice of the colligative property for defining the cmc. generally depended on factors of convenience. The exact location of the cmc. is thus to some extent subjective, but can be recorded with sufficient meaning in most cases.

Absence of electrical effects, although advantageous in many ways, has its disadvantages when obtaining a cmc., as it precludes the use of any method based upon these properties e.g. conductivity; moreover, due to the absence of electrostatic repulsion, non-ionics tend to form micelles at much lower concentrations[117,118] than their ionic counterparts,[119,120] thus other common methods are not sufficiently sensitive. Techniques have therefore been developed in an effort to overcome these difficulties.

Ross and Olivier[121] have reported a photometric method for the determination of the cmc. of polyoxyethylene adducts in both aqueous and nonaqueous solutions, based on the formation of a molecular complex between iodine and the non-ionic micelle which showed an absorption maximum at 360 mμ, and Becher[122] has shown good agreement between the results of this method and values obtained from light scattering with a range of commercial non-ionic detergents. Elworthy[123] followed up this work using cetomacrogol, a commercial polyoxyethylene monocetyl ether containing an average of 22 ethylene oxide units, and obtained consistent results for three methods:- the iodine method, solubilisation of a dye (dimethyl yellow), and a surface tension technique. Japanese workers,[119,124,125] as well as using conventional surface tension and solubilisation methods, have suggested polarographic and other techniques. Surface potential measurements,[126] showing similar results to those obtained from surface tension,[110] have been described recently.

As already mentioned, the absence of electrostatic repulsive forces results in the formation of micelles at very low concentrations, and figures down to 10^{-6} molar[45] appear in the literature. The cmc., as might be expected, has been interpreted as a function of the hydrophobe-hydrophile balance of the molecule, and Reich's suggestion,[93] that for a given hydrophobic moiety the cmc. will increase with increasing ethylene oxide chain length, has been demonstrated by several workers.[122,126-132] Formulae for their relationship, on lines parallel to that of Klevens[133] for a homologous series of ionic surfactants, have been published[122,129] i.e.

$$\log \text{cmc.} = A + Bn$$

where A and B were constants for a given hydrophobe and n = the number of ethylene oxide units per molecule. This equation may only hold over a limited range of ethylene oxide chain lengths, as comparison of octadecyl ethers containing fourteen and one hundred ethylene oxide units per molecule, respectively, have shown an unpredictably lower cmc. for the latter;[110,116,126] while with short compounds Mulley[134] has claimed that increasing the glycol chain lengths had little effect on the cmc. (up to six ethylene oxide units per molecule).

As far as alteration of the hydrophobic group was concerned the number of carbon atoms, even in a saturated hydrocarbon chain, did not necessarily directly influence the hydrophobic weighting of that moiety as far as cmc. was concerned. The overall number of carbon atoms in a straight chain appeared to be the main factor as comparison of the cmcs. of branched tridecyl[110] and n-dodecyl adducts, with the same number of ethylene oxide units, showed the latter to be approximately half that of the former. Experiments with synthesised,[45] and commercial compounds,[110,129] have shown that for a given ethylene oxide chain the cmc. decreased with increased length of the hydrophobic moiety. Schick,[110] however found little difference in the cmcs. of fractionated octadecyl and dodecyl monoethers containing fourteen ethylene oxide units, and Lange found the generally accepted behaviour was invalid with polyoxyethylene ethers of paraffin chain alcohols greater than dodecyl, but his compounds were by no means pure.

Attempts at correlation between the values of cmcs. for different commercial alcohol adducts[122] showed the slopes of graphs of log cmc. vs. ethylene oxide content decreased with increase of the number of carbon atoms in the straight chain of the hydrophobic group, and the series had a common intercept at a hypothetical zero ethylene oxide content. Unlike the majority of other published cmc. results concentrations in this work were based on % $^{W}/_{V}$; conversion of these results to the more common moles/litre designation of concentration have shown that the cmcs. for the lauryl and stearyl adducts now decreased with ethylene oxide chain length, although those of the oxo-process produced tridecyl alcohol adducts still increased. Despite this, for a given ethylene oxide chain, the cmc.(moles/litre) decreased with lengthening of the aliphatic chain. Such results further stress the unsatisfactory nature of working with heterogeneous compounds.

The presence of a sharply defined cmc. has been assumed in the majority of the previous mentioned work on this subject, but Kushner et al.[90] claimed, from turbidimetric results on a sample of Triton X 100, that there was no well defined cmc. but a gradual increase in the fraction of added detergent forming micelles up to a concentration of about 0.3 G/dl, where virtually all of each increment added to the solution became micellar. The authors suggested that this may have been caused by the effects of the chain length distribution; the shorter ethylene oxide adducts forming micelles at lower concentrations. Later work[109] in molecularly distilled fractions still showed no sharp cmc. The concentration where the concentration/turbidity vs. concentration graph settled to a straight line was lower in the case of the fraction with the shorter mean ethylene oxide chain length. When considering these latter results it must be borne in mind that molecular distillation does not give a series of clear cut chemical entities, but at the best merely increases the incidence of molecules having an ethylene oxide content close to that of the mean. It has been suggested that this monomer saturation concentration is an artifact arising from non-equilibrated solutions,[135] but this time dependance of micellar breakdown has in turn been attributed to the presence of impurities,[45] and did not occur when chemically pure synthetic compounds were studied. Recent work on a synthetic dodecyl ether of hexaoxyethylene glycol[136] gives yet another angle on this problem. Comparison of the cmc. obtained from surface tension plots (C_o) with that apparent from turbidity (C_1) showed the latter to be much higher. The constant value for the surface tension observed at concentrations greater than C_o was taken to indicate that the activity of the monomers in equilibrium with the surface phase remained constant, C_1 being caused by the micellar units between C_o and C_1 having such low aggregation numbers that the solution turbidities are too small to be distinguished experimentally from the solvent turbidity, and only at concentrations greater than C_1 does the micellar weight become appreciable and constant.

Size, Shape, and Hydration.

The fundamental properties of detergents in solution of most interest are obviously their surface and micellar behaviour, and the factors which affect them. Aqueous solutions of the non-ionics are colloidal in nature and thus the techniques applied in their study have been similar to those generally used in colloid science.

Surface tension, viscosity, and light-scattering procedures have perhaps been used most commonly to date, but sedimentation, diffusion, and other techniques appear in the literature.[111,137-142]

It has now been generally accepted that, provided the polyoxyethylene chain is sufficiently large to produce water solubility of a given hydrophobe, non-ionic surfactants of this type orientate themselves in micelles, with the hydrophobic moiety internally and the glycol chains to the outside. The glycol chain confers water solubility by trapping water molecules in some way.[88,143] The exact amount and method of this trapping is however subject to conjecture, as, as yet, no independant method of measuring the aqueous co-volume of the micelle has been published. Hydroxonium ions, hydrogen bonding and various types of arrangement of the water molecules around the ether oxygens or within the glycol structure have been suggested.[53,126,129,144-149] From viscosity and micellar studies, Kushner and Hubbard[90] calculated 43 molecules per polyoxyethylene chain in a micelle of Triton X 100 (n = 10). Of this, they suggested 20 molecules of water were held by hydrogen bonding to the ether oxygens, with the rest physically trapped by the chain. Nakagawa and Inoue[142] showed the number of hydrated water molecules per oxygen atom increased with chain length, and other papers,[93,147,148,150-152] using data from viscosity, polarimetry, and heat of hydration, have given 1, 2, 3, or 4 water molecules per ether oxygen, depending on the chain length and the workers concerned.

As with most of the work on non-ionics, the majority of the studies of micellar structure has been carried out on commercial detergents, and much of the conflicting data which has appeared in the literature can be blamed on the batch variation of the nominally similar compounds.[137,138,153,154] (See Table 1). As already discussed, the polymerisation syntheses result in products containing a range of ethylene oxide chain lengths; a range which even varies depending on the experimental conditions used, and, despite what certain workers claim concerning "reproducible heterogeneity"[156] such compounds are not ideal for physical-chemical study.

The effect of fractionation of these materials has been studied and further illustrated this point.[109,156] Molecular distillation of a sample of Triton X 100 gave two fractions one of which gave a clear solution in water, the other was classed as "insoluble". Further redistillation of the two fractions gave one insoluble and one soluble subfraction from each. Consequent molecular weight studies by light-scattering of the two soluble subfractions gave the micellar weights tabulated.

	M	$\bar{\bar{n}}$	Aggregation Number
Lower Distilling Fraction	208×10^3	8	373
Undistilled	90×10^3	10	139
Higher Distilling Fraction	53×10^3	12	73

(Where M, is the micellar weight and $\bar{\bar{n}}$, the mean number of ethylene oxide units per molecule.)

Recombination of the soluble and insoluble fractions gave a molecular weight the same as that of the undistilled compound.

These values, although obtained by some rather naive assumptions, indicate a trend which has been shown to occur with all polyoxyethylene type surfactants at a

Table 1.

Micellar Weights of Various Non-ionic Surface Active Agents in Aqueous Solution.

Hydrophobic group	n	Temp.	10^{-4}M	Agg.No.	Ref.
C_8	6	18	1.25	32	45
C_{12}	6	18	7.80	178	45
C_{12}	6	18	8.40	191	136
C_{12}	6	25	18.0	411	136
C_{12}	6	30	32.0	730	136
C_{12}	8		6.82	123	155
C_{12}	9	25	4.03	67	181
C_{12}	9	25	5.16	86	287
C_{12}	9.5		3.85	63	156
C_{12}	12		3.20	45	156
C_{12}	12		5.89	81	155
C_{12}	14	25	10.0	125	111
C_{12}	18		5.06	51	155
C_{12} †	20.8	25	6.17	56	210
C_{12}	23		4.88	40	155
C_{12}	30	25	8.20	55	111
C_{18}	14	25	33.0	370	111
C_{18}	100	25	46.5	465	111

given temperature:- the micellar aggregation number for a given hydrophobic group decreases with increasing polyoxyethylene chain length,[39,109,111,155-157] and similarly, with a standard polyoxyethylene chain length, the aggregation number increases with increasing the length of the hydrophobic part of the molecule e.g. by the increasing the length of the paraffin chain.[38,45,158] (See Table 1).

Straight line relationships between the aggregation number and the reciprocal of the number of ethylene oxide units per molecule have been obtained for the former series, which would appear to predict an aggregation number of unity for a given hydrophobe. Whether this in fact happens has not been proved as little work has been done on detergents with ethylene oxide chains around the hypothetical length for monomer dispersion, but it has been shown for some larger[111] compounds that, although still showing a decreased aggregation number, the micellar weight had risen appreciably over that of the shorter compounds. This, coupled with a lower cmc. than expected, has been attributed to a decreasing solubility of the ethylene oxide portion as its molecular weight was increased in this region, or may be caused by a steric hindrance of micellar packing. Unfortunately

Table 1 (contd.).

Hydrophobic group	n	Temp.	10^{-4}M	Agg.No.	Ref.
C_8Ph.	8	25	20.8	373	109
C_8Ph.	9	25	8.13	135	181
C_8Ph.	9	25	6.67	111	287
C_8Ph.	9.5	25	6.31	100	138
C_8Ph.*	10.0	25	9.00	139	109
C_8Ph.	10.0	30	10.5	162	158
C_8Ph.	12.0	25	5.35	73	109
C_9Ph.*	9.5	25	16.9	265	138
C_9Ph.	10.0		6.63	100	155
C_9Ph.	10.0	25	18.2	276	111
C_9Ph.*	10.3	25	8.50	125	138
C_9Ph.*	10.3	25	7.95	117	137
C_9Ph.	15	25	7.00	80	111
C_9Ph.	15		4.50	52	155
C_9Ph.	20	25	6.80	62	111
C_9Ph.	30	25	6.70	44	111
C_9Ph.	30		2.97	19	155
C_9Ph.	50	25	4.80	20	111

there is insufficient data to show whether a graph of aggregation number vs. ethylene oxide units per molecule passes through a minimum or merely flattens.

To correlate data obtained by different techniques the shape of the micelle is a further factor which has to be determined. Three models most frequently referred to for micellar aggregates in the concentrations being studied are spheres, discs, or rods. It has been put forward that, in dilute solution, small micelles of ionic detergents with molecular weights in the region of 10 to 50 x 10^3 [73,79] are spherical, whereas large micelles, with aggregate molecular weights of greater than 500 x 10^3, are rod shaped.

From intrinsic viscosity numbers, sedimentation constants, and light-scattering dissymmetry ratios on a range of compounds, Schick et al.,[111] claimed a similar pattern for non-ionics i.e. in the range 45 - 100 x 10^3 spheres appear the most probable, with discs or rods for large micelles. For Triton X 100 (M = 90,000), Kushner and Hubbard[90] suggested a spherical micelle from light-scattering and viscosity work, and Nakagawa and Inoue,[142] the same for a series of compounds of micellar weight from 40 - 60 x 10^3 on the basis of constant effective specific volume. Becher,[155] on the

Table 1 (contd.).

Hydrophobic group	n	Temp.	$10^{-4}M$	Agg.No.	Ref.
C_{10}—Me	8	30	4.31	83	39
C_{10}—Me	11	30	4.21	65	39
C_{10}—Me	12	29	3.71	53	175
C_{10}—Me	12	30	3.72	53	158
C_{12}—Me	12	20	5.67	80	38
C_{12}—Me	12	30	6.11	86	174

$C_8n_9 \equiv C_8H_{17}O(CH_2CH_2O)_9H$

$C_8Phn_{10} \equiv C_8H_{17}C_6H_4O(CH_2CH_2O)_{10}H$

$C_{10}n_8Me \equiv C_{10}H_{21}O(CH_2CH_2O)_8CH_3$

M = Micellar Weight

Agg.No. = the number of monomers in the micelle

synthesised compounds

All micellar weights in the table were determined by light-scattering except those marked:

† - diffusion-viscosity

* - ultracentrifuge

other hand, pointed out that these micelles are so small that the light-scattering dissymmetry values of one which are obtained do not give much clue as to the shape of the micelles. His calculations, based on surface area measurements and the hydrated volume of the micelle, suggested that, for micelles containing molecules with fairly short ethylene oxide chain lengths, the assumption of a rod-like micelle was to be favoured. It is to be noticed however that he made no allowance for variance of the hydrophobic group and based his deductions on certain rather disputable assumptions:-

a) the molecule was in the fully extended state.
b) the hydrophobes in the core did not overlap.
c) the cross-sectional area of the molecule in the micelle was the same as that at the air-water interface.
d) the co-volume of water was the same as that obtained by Kushner[90] for Triton X 100 - a figure itself obtained on the assumption that the micelle was spherical.

The use of viscosity studies in the determination of micellar shape is complicated by the presence of the co-volume of water in the micelle, and, until a method of disentangling the two effects is found, no deductions from data obtained by this method can be made without making certain assumptions about one property or the other. Viscosity has therefore been mainly used in conjunction with other techniques but, despite this, work done[159] did at least indicate a trend, as, though the viscosity of a given molar concentration of an adduct decreased with the decreasing ethylene oxide chain length, (presumably due to decreased micellar hydration), it passed through a minimum, after which an increased asymmetry and micellar size outweighed these effects of hydration causing an increase in viscosity.

Configuration of the Ethylene Oxide Chains.

Due to the lack of knowledge of micellar dimensions much of the early speculation as to the configuration of the oxyethylene chain in the micelle was based on viscosity and X-ray diffraction data of the glycols themselves. Lower molecular weight chains i.e. with not more than ten ethylene oxide units, appeared to exist in the regular extended "zig-zag" or trans structure, whereas longer chains occured as the more condensed "meander" or gauche form.[160] Coils, and "crumpled helical" and"highly convoluted" structures, particularly for very long chains, have been suggested as well.[37,148,149,161-164]

Rosch[164] has claimed the meander form is the most likely in aqueous solution; a spiral chain being formed due to carbon-oxygen dipoles (forces which are said to be accentuated in water due to the presence of an onium structure) where each oxygen approached closely and was attracted to a carbon atom separated from it by three other carbon atoms and one oxygen atom. Despite its steric possibility, the meander form has been described as somewhat "crowded"[165] and may require stabilisation by a chain of hydrogen bond linked water molecules between the adjacent chain oxygens. The polyoxyethylene chain might even be a random mixture of both configurations, (trans or gauche) as found in dioxane solution by dipole and infra-red measurements.[47,166-168]

An expanding coil structure has been described from measurements of micellar volume[111] but the dimensions of the coils were dependant on the volume assigned to the hydrophobic core of the micelle; that of an oil droplet being considered the most probable.

Although not strictly comparable with micellar structure, application of the Gibbs equation to surface tension data has shown that the size of the polyoxyethylene oxide chain was the controlling factor in the packing of the molecules in the interface,[110,126,129,165] but the increment of area per ethylene oxide unit decreased as the number of ethylene oxide units increased. Coupled with a similar effect for surface potential measurements,[126] this has been interpreted as a coil formation of the polyoxyethylene chain in the aqueous phase, the size of the coils increasing as the chain lengthened without reaching complete randomness even with the longest chains studied by this technique, (containing up to one hundred ethylene oxide units).

The Effects of Temperature.

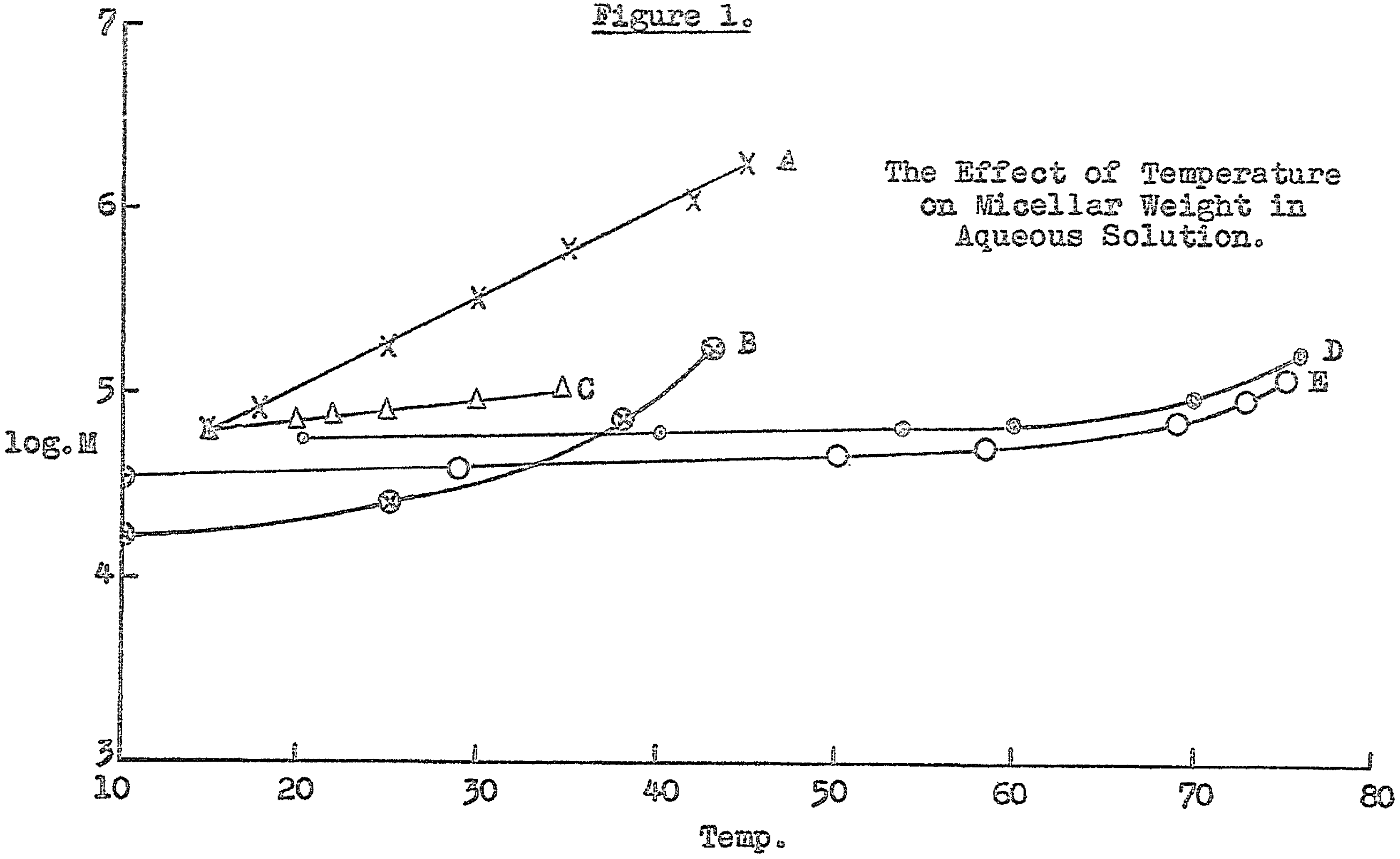
Solubility of surfactant compounds, even in dilute solutions, is often limited to certain temperature ranges i.e. only between a lower "Krafft Point" and an upper "Cloud Point" can a solution exist without phase separation. Thus, outwith these temperatures, the detergent loses many of its most important properties.[169] Little work appears to have been done on the Krafft point as few illustrate this phenomenon but the cloud point has been studied extensively.

As has been discussed, micellar properties are influenced by the hydrophilic properties of the molecule, which, in turn, appear to be a function of the length of the polyoxyethylene chain and the amount of water "trapped". The cloud point has generally been assumed as being caused by a thermal dehydration of the micelle reaching a stage where the hydrophilic properties of the micelle were reduced to such a level that the surfactant was thrown out of solution. Above the cloud point a phase, rich in surfactant, separated out of solution,[170,171] leaving a concentration of surfactant in the co-existing aqueous phase in the region of the cmc.; the detergent, in the latter phase, appearing to be dissolved as a monomer dispersion with virtually no micelles present.

Here, as with the other solution properties, altering the length of the polyoxyethylene chain for a given hydrophobe affected this behaviour; the cloud point rising on increasing the number of ethylene oxide units in the chain.[159,172] For ether linked adducts of constant glycol chain length it fell with increasing the size of the hydrophobic group by ascending a homologous series. Though cloud points are reasonably constant over a fairly wide range of concentration,[171] some have been shown to vary with concentration,[136] and certain discrepancies in the literature have been blamed on not taking results from comparable parts of the curves of cloud point vs. concentration.[142]

Provided the compound is pure, the cloud point of polyoxyethylene ether adducts appears as a sharp change in turbidity, but as the hydrophilic chain is lengthened, the cloud point reaches a stage where it is greater

Figure 1.



The Effect of Temperature on Micellar Weight in Aqueous Solution.

A $C_{12}H_{25}O(CH_2CH_2O)_6H$ Ref. 136.
B $C_9H_{19}C_6H_4O(CH_2CH_2O)_{10.3}H$ Ref. 176.
C $C_7H_{15}COO(CH_2CH_2O)_{7.6}CH_3$ Ref. 137.
D $C_{12}H_{25}O(CH_2CH_2O)_{12}CH_3$ Ref. 158.
E $C_{10}H_{21}O(CH_2CH_2O)_{10}CH_3$ Ref. 175.

than 100°. To measure these higher cloud points increase in pressure has been used to obtain higher temperatures, or addition of a range of concentrations of a substance which lowered the cloud point to a more easily measured temperature, followed by extrapolation of the values obtained to zero additive concentration.[171]

Clouding for non-ionic surfactants is a reversible procedure, a clear solution being re-obtained when the temperaure is allowed to drop below the critical one. It is of use in following the polymerisation of ethylene oxide onto a hydrophobic group as it can be adapted to give a quick idea of how far the reaction has progressed. Steele and Berger[173] have used cloud points as a means of characterising non-ionic detergents from plots of cloud points vs. apparent density. These showed values for a particular type of surfactant fell into a characteristic band on the plots which could be used as a method of identification.

In direct contrast to many ionic detergents,[158,174] it has been shown that the micellar weights of polyoxyethylene type non-ionic detergents increase with rising temperature,[136,137,176] the rate of increase becoming greater as the cloud point is approached.[38,158,175] (See figure 1.) It is therefore obvious that one must also consider the effects of temperature on micellar weight and structure in conjunction with the original ideas of micellar dehydration when seeking an explanation of clouding.

Kuriyama[158] analysed micellar weights and apparent second virial coefficients (obtained from light-scattering of a methoxydodecyl polyoxyethylene glycol over a range of temperatures up to the cloud point)[130] and of phase separation. He found the solute-solvent interaction decreased with temperature elevation, the rate of decrease increasing as the cloud point was approached, and concluded that the phase separation occurred not as a simple dehydration of small micelles but rather as a result of the decreased interaction between water and micelles which have grown very large.

Diffusion-viscosity experiments on a methoxy-polyoxyethylene octanoate[176] showed the increase in micellar weight with temperature was accompanied by an increase in micellar radius and a decrease in hydration, with the development of asymmetry near the cloud point. Balmbra et al.[136] have also postulated an increase in micellar asymmetry with temperature and micellar weight increase; their compound, a synthesised monododecyl ether of hexaoxyethylene glycol, giving an exponential increase in micellar weight over the range studied.

Critical micelle concentration followed a complementary trend to micellar behaviour and decreased as the temperature was raised.[45,110] On the assumption that the micellar phase could be treated as a separate phase and its composition remained constant over the range of temperature studied, this effect has been used to calculate the partial molal heats of micelle formation[45,110,175,176] by use of an equation of the Clapeyron-Clausius type;[96,97,177,178]

$$\frac{d \ln \text{cmc.}}{dT} = -\frac{\Delta H_m}{RT^2}$$

and thence, from $\Delta S_m = \Delta H_m/_T$ the corresponding values of the partial molal entropy change were obtained.

Effect of Electrolytes.

One of the advantages often quoted for non-ionic detergents is their stability even in relatively high electrolyte concentration: this however does not mean by any manner of speaking that they are unaffected by the presence of electrolytes.[158,171,179] Early work by Doscher et al.[180] showed that sodium chloride strikingly raised the viscosity and turbidity of aqueous solutions of non-ionic detergents, whereas calcium chloride had a much smaller effect. Similarly the surface tension increased gradually with increase of the ratio of calcium chloride to surfactant, whereas it decreased with sodium chloride. These effects, were interpreted as sodium chloride "salting out" the non-ionic detergent whereas calcium salts "salted in" i.e. hydrated calcium ions co-ordinated in some way with the ether oxygens. Further substantiation of this theory was the isolation of a surfactant-calcium chloride complex. Macley,[171] and others,[179] in an examination of the factors affecting solubility of non-ionic adducts, showed that in dilute solution the lowering of the cloud point by electrolytes is a linear function of the ionic strength, and the observed salting out effect for alkali metals and multivalent cations is roughly in the order of decreasing ion hydration. Kuriyama,[158] on the other hand, pointed out that although calcium chloride exhibited a smaller effect on the cloud point when compared with sodium chloride at the same ionic strength, if compared at the same molar strength they are virtually equally effective. The effect of electrolytes on the cloud points is obviously integrated with the complex network affecting micellar structure, hydration, and aggregation number at different temperatures, but whether one can obtain an indication of the effects of electrolytes at lower temperatures from their effects on cloud points is doubtful, particularly in the light of studies on the effects of salts on micellar weights at different temperatures.[581] At 30°, addition of sodium chloride to a methoxy polyoxyethylene dodecyl ether ($n = 12$) gave a linear increase in micellar weight with increase of salt concentration whereas with calcium chloride, although the micellar weight increased initially, it was nearly constant over a range of 0.5 – 1.0 molar. At 50° C, the effect of sodium chloride was greater than at the lower temperature, but at this higher temperature addition of equimolecular concentrations of calcium chloride was equal or more potent in its effect on micellar weight than sodium chloride. A further complication of the issue is that other workers have claimed that addition of electrolytes at a given temperature does not necessarily give an increase in micellar[111,165,181] weight. Becher,[165] working on a series of commercial dodecyl ethers showed that although a slight increase in micellar weight was found for the lower members of the series, the larger molecules showed, if anything, a slight decrease in micellar weight. Schick et al.[111] have shown similar effects with an octadecyl ether series but the decrease in micellar weight with added salt did not appear until a much longer polyoxyethylene chain was present in the adduct (n = 100). It has been suggested that the increased length of the polyoxyethylene chain enhanced the adsorption of electrolyte to such an extent that it increased the overall solubility[111] of the detergent, but it would appear that much depends on the particular series being studied.

In a further attempt to elucidate salting out, the effect of added electrolyte on the cmc. has been studied, and here the order of effectiveness in lowering the cmc. was in line with a decrease in lyotropic number;[110,129,165] being more pronounced with the more hydrophilic longer oxyethylene chains. A change in the lyotropic number of the anions had a larger effect than that of the cations. Surface moment and surface tension studies have suggested a collapse of the ethylene oxide coil structure on the addition of sodium chloride in a manner similar to that observed for the glycols by Bailey and Callard.[163] Addition of a proton donor or acceptor also affects the cmc.[126] e.g. for a nonylphenyl adduct (n = 15).

Solvent	cmc.
0.86M HCl	150 micro-mol/litre
Water	110 micro-mol/litre
0.86M NaOH	80 micro-mol/litre

Hsaio[129] et al. have attributed this shift to oxonium ion formation in the polyoxyethylene chains, added protons increase the ionic character of the non-ionic detergents and consequently the cmc. is increased, and vice versa. This has been taken by the authors to indicate that non-ionics are weakly cationic in aqueous solution, and, by Becher,[165] to explain the electrolyte effects in the terms of a positive double layer in the outer layer of the micelle. Recent conductivity experiments[182] to try to clear up this last point appear to be somewhat masked by the presence of polymerisation catalysts in the substance. Strangely, no attempt was made to remove this beforehand.

A theory has been put forward[181] that the lowering of the cmc. in the presence of electrolyte does not occur due to any specific electrical property of the electrolyte but rather to its effect on the solvent. On the basis that sucrose would markedly lower the activity without affecting the electrical properties, experiments have been carried out measuring cmc. in different concentrations of sucrose solutions.[182] These however showed little variance, and coupled with the magnitude of the effects at given electrolyte concentrations, and the apparent specificity of the anions, did not point to the activity effect as a likely explanation.

Perhaps the most complete picture of this topic was that obtained from micellar and surface studies by Schick et al.,[110,111,126] and, on the basis of their results, they have postulated the following mechanism for "salting out" of non-ionic detergents:- salting out of neutral molecules depends on the concentration and ionic radii of the eletrolyte, and the dielectric constant of the nonelectrolyte.[149] Small hydrated ions (low lyotropic number) are more effective in salting out than large hydrated ions (high lyotropic number). This was shown to follow with the non-ionic surfactants studied; the salting out increased with increasing electrolyte concentration and with decreasing radii of hydrated ions. The hydration of the anions was more important than that of the cations. Thus, they claimed, there is firstly the removal of hydrogen bonded water molecules[92,183] from the ether oxygens of the ethylene oxide chain by the increased electrolyte concentration, and secondly, the extent of the dehydration of the ethylene oxide chain is then determined by the closeness of approach of the cations to the ether oxygens, but is partially counteracted by the tendency of the counter anions to be hydrated.

Solubilisation.

The ability of detergent solutions to dissolve organic compounds which are insoluble, or only slightly soluble in water, is one of their most striking properties, and is termed solubilisation. For ionics, it is generally believed that with non-polar hydrocarbons uptake occurs into the interior of the micelle; partially miscible polar compounds, such as octanol and phenols, by adsorption on the micelle surface with the hydrocarbon inside and the polar group of the solubilisate in the aqueous phase. Water soluble polar substances, such as glycerol and certain dyes, which are insoluble in hydrocarbons, are thought to be adsorbed onto the exterior of the micelles.[184,185] With non-ionic surfactants of the polyoxyethylene type there is an additional possible mode of incorporation i.e. into the polyoxyethylene chain part of the micellar structure.

In the study of solubilisation, as with electrolytes, much of the work and conclusions obtained have been based on the effects of solubilisates on cloud points.[171,179,186,187] The cloud point of Triton X 100[171] has been shown to be significantly raised by anionic detergents and aliphatic hydrocarbons, but, as the polarity of the solubilisate was increased by the introduction of double bonds or polar constituents, the effects on cloud points was much less marked. Aromatic and polar aliphatic additives caused the cloud points to be sharply decreased.[171]

The mode of incorporation may account for the difference in the effects on cloud points of such compounds. Dodecane is insoluble in a polyoxyethylene glycol and will be taken into the hydrophobic core of micelle; benzene however, is miscible with the hydrophobic moiety, with polyoxyethylene glycols, and with concentrated aqueous solutions of the glycols, and may thus be partially present in the glycol structure, thereby decreasing the hydrophilic properties of the micelle.

Weiden and Norton[186] attributed the lowering of the cloud point by benzene and phenol to decreasing of the hydrophilic properties of the micelles, but Livingstone[187] suggested pH might also play an important part in the effect of phenols although this latter idea was refuted by later work.[171] Such effects have been used in attempts to develop methods of assay for non-ionics in aqueous solution, either to ascertain the length of the oxyethylene chain of the adduct or to gain an idea of its properties in solution.[188,189]

The solubilisation of phenol and its analogues has also been said to occur by binding of the phenolic hydroxyl groups with the ether oxygens of the polyoxyethylene chains by hydrogen bonding.[190,191] Higuchi et al.[192,193] have reported complex formation of phenolic substances with polyoxyethylene groups, and it has been observed that many phenolic substances were readily dissolved in concentrated solutions of polyoxyethylene glycols.[194,195]

The solubilisation of iodine[196-200] and various dyes,[201-205] with their concomitant spectral changes, have similarly been the subject of much varying opinion.

Examination of phase changes[207] and construction of phase diagrams[87,134,136,208,209] in the presence of different solubilisates have also been carried out to try to obtain a clearer insight to this problem, but, as far as can be seen, no work on perhaps one of the most suitable techniques for such a problem i.e. diffusion has been carried out.

Light-scattering measurements have been made in a study of the effect of n-decane and n-decanol on the micellar weights of two methoxypolyoxyethylene glycol monodecyl ethers by Kuriyama et al.[39] These have shown that the micellar weights increased with the addition of solubilisates within the saturation limit of the solubilisate, the increase originating not only from the simple incorporation of solubilisate molecules into the existing micelle, but also from the number of surfactant molecules in the micelle increasing with added solubilisate. The solubilisation process was therefore accompanied by a reconstitution of the micelles in a manner analogous to that concluded from other techniques.[210,212] The rate of increase in micellar weight being more rapid with shorter oxyethylene chain compounds.

The concept of "no solubilisation when there are no micelles" (though addition of a third component may lower the concentration at which micelles are formed), is also illustrated by this work. Peaks in the plots of R_{90} (Rayleigh's ratio) vs. concentration below the cmc. (c_1) for the pure compound, which increased as the ratio of solubilisate to surfactant was raised, were interpreted as being caused by solubilisate or a solubilisate-surfactant complex, ejected into the aqueous phase by dilution below the cmc., forming small droplets which increased the amount of scattered light. The concentration at which this peak started to develop gradually decreased with the addition of solubilisate in a manner similar to that found for ionic detergents.[213,215]

Increasing the temperature of ternary systems, such as n-decane or n-decanol[38] in an aqueous non-ionic solution, showed the micellar weights to increase with temperature, but the patterns of increase varied from each other, reflecting the different effects on the cloud point of the two compounds.

Addition of an anionic detergent[174] to a non-ionic gave a mixed micelle, the micellar weight showing virtually a straight line relationship between the micellar weights (at 30°) of the two pure compounds in aqueous solution, and increase of micellar weight with temperature elevation of the non-ionic was progressively suppressed by increasing addition of ionic surfactant, until a stage was reached when the micellar weight decreased on heating.

Surface Activity.

The adsorption of surface active agents at an interface causes a reduction in the surface tension; the surface tension dropping rapidly with increasing concentration until a constant minimum value is reached at the cmc. The general theory of adsorption of such compounds at the interfaces is that it is due to the opposing tendencies of the hydrophobic and hydrophilic groups, the former tending to escape from the surface of the water, provided the external phase is sufficiently sympathetic, the latter group tending to pull the molecule into solution.

With non-ionic detergents of the type under consideration it has been shown for a given hydrophobe group that the surface tension at the air-water interface above the cmc. increases with increasing glycol length, the actual value of the surface tension being a property of the hydrophobe in question,[9,110,113,159,169,216-218] and the temperature; the surface tension decreasing with rise in temperature over moderate ranges.[45]

Measurement of the surface tension has been employed for the determination of the cmc.,[45,119,123,219] having the advantage that the solution may be examined without the need for the addition of any extra component which may itself effect the value obtained, and application of the Gibbs' Equation to measurements below this concentration have been used to calculate the area per molecule at the interface.[110,128,129] These measurements have shown that the ethylene oxide chain is the determining factor in the packing of the interface, the area per molecule increased with the length of the glycol chain, but the increment per ethylene oxide decreased. Similar results, obtained from surface potential studies, have been used in an attempt to discern the orientation of the glycol chain.[126]

Surface aging, though said to be absent with shorter compounds,[134] has been reported by Schick,[110,126] Ottewill,[45] and others,[128,129,220] particularly as the concentration of the solution came near the cmc. Times alloted for attainment of equilibrium vary vastly with different workers and although up to three hours at 10^{-6} molar can be expected from consideration of diffusion of the molecules to the air-water interface,[221,222] several days were required for a monohexadecyl ether of hexaoxyethylene glycol at concentrations less than the cmc.,[45] which, in conjunction with other results,[126] suggest further factors are involved.

Other methods of observing adsorption have been reported[220,223,224] but with a great deal of variance occuring in the results, depending on the interfacial conditions and the mode of analysis; selective adsorption of shorter length ethylene oxide chain adducts often influencing the results to different extents.

Interfacial tensions of aqueous solutions of polyoxyethylene ether adducts against such substances as vegetable oils,[10,159,218] benzene, and toluene, gave minima with ethylene oxide contents of 14-20 units,[10,159] and 7-12 units[218] respectively, but hexane followed a pattern similar to the air-water interface. Lipophilic substances, such as carbon black,[224] gave a Langmuir type adsorption for a range of nonyl-phenol adducts, but for a hydrophilic powder, such as calcium carbonate,[223] the type of adsorption depended on the compound examined and was very sensitive to change in chain length. Compounds with less than four and more than nine ethylene oxide units per molecule showed no adsorption onto calcium carbonate, those with five and six gave Langmuir type, whereas seven and seven point five ethylene oxide units showed multi-layer adsorption.

Conclusion.

The present lack of published work on pure synthesised compounds makes correlation of the information appearing in the literature extremely difficult. The use of polymerised mixtures, prepared under varying conditions, sometimes fractionated, coupled often with inadequate definition of the experimental conditions and varying methods of interpretation, have led to the widely diverging results for nominally similar compounds.

It would appear at the present stage that the formulation of generalised rules for the colloidal properties of polyoxyethylene mono alkyl/aryl ethers would present a formidable task as their behaviour in solution is not merely a simple effect of varying the ethylene oxide content but the product of a much more complex combination of the effects of many variables, both physical and chemical on the hydrophilic and hydrophobic moieties.

Light-Scattering by Particles whose Dimensions are small compared with the Wavelength of Light. ($<\lambda/20$).

Rayleigh's Equation for Dilute Gases.

(i.e. for non-interfering, optically isotropic, randomly located particles).

If any particle in space is subjected to an electric field of strength $\mathcal{E}$, its constituent electrons become subjected to an electric force in one direction and its constituent nuclei to a force in the opposite direction; a dipole moment, p, is thus induced in the particle, which, if the particle is optically isotropic, will be parallel to the direction of the electric field. The magnitude of the dipole moment is proportional to the electric field strength; the proportionality constant, α, known as the polarizability of the particle, represents the degree to which the electrons and nuclei respond to the field:

$$p = \alpha\mathcal{E} \qquad (1)$$

A periodic electric field, such as is produced by a parallel beam of plane-polarized light (the general equation for which is given by:-

$$\mathcal{E} = \mathcal{E}_0 \cos 2\pi(\nu t - x/\lambda) \qquad (2)$$

where $\mathcal{E}_0$, is the maximum amplitude; ν, the frequency; λ, the wavelength measured in the medium of propagation; t, the time; and x, the location along the line of propagation) will thus induce an oscillating dipole in any particle in its path such that

$$p = \alpha \mathcal{E}_0 \cos 2\pi(\nu t - x/\lambda) \qquad (3)$$

The oscillating dipole produces an oscillating magnetic field, in turn accompanied by an oscillating electric field;[226] the combination of both constituting an electromagnetic wave (scattered light).

The scattered radiation is a spherical wave extending in all directions with a field strength proportional to:-

a) d^2p/dt^2. (The first derivative represents an electric current).

b) $\sin\theta_1$; where θ_1 is the angle between the dipole axis and the line joining the point of observation to the dipole.

c) $1/r$; where r is the distance between the dipole and the observer and must be large. (The total energy flux per unit area must vary as $1/r^2$ but since the intensity is proportional to $\mathcal{E}^2$, $\mathcal{E}$ must vary with $1/r$.[226]

Differentiating equation 3. to obtain d^2p/dt^2, introducing this and the other proportionality factors, and dividing the product by the square of the velocity of light (c^2), for dimensional correctness, one obtains

$$\mathcal{E}s = \frac{4\pi^2\nu^2\alpha\mathcal{E}_0 \sin\theta_1 \cos 2\pi(\nu t - x/\lambda)}{c^2 r} \qquad (4)$$

where $\mathscr{E}_s$ is used to designate the field strength of the scattered radiation.

The experimental measure of the energy in a light wave is the intensity, (the energy which falls on 1 cm.^{2} of area per second) and, as mentioned on the previous page, by Poynting's theorem,[226] this quantity is proportional to $\mathscr{E}^2$, averaged over a period of the vibration, hence, from equation 4. the intensity of the scattered light, i_s, is given by

$$i_s = \mathscr{E}_s^2 = \frac{16\pi^4\nu^4\alpha^2\mathscr{E}_0^2\sin^2\theta_1\cos^2\left[2\pi(\nu t - x/\lambda)\right]}{c^4 r^2} \qquad (5)$$

and from equation 2. the intensity of the incident beam, I_0,

$$I_0 = \mathscr{E}^2 = \mathscr{E}_0^2\cos^2\left[2\pi(\nu t - x/\lambda)\right] \qquad (6)$$

may be calculated. Substituting $1/\lambda$ for ν/c, the ratio of the two intensities then gives

$$\frac{i_s}{I_0} = \frac{16\pi^4\alpha^2\sin^2\theta_1}{\lambda^4 r^2} \qquad (7)$$

This equation was first derived by Rayleigh,[225] its most significant feature being the inverse fourth power dependance on the wavelength of the incident light. A factor which has been used in the explanation of several natural phenomena including the blueness of the sky.

As everything in equation 7. can be evaluated except the polarizability, α, a substitution for this in terms of measurable quantities is indicated.

The polarizability of a medium is related to its dielectric constant, ϵ,[227] which is, in turn, equal to the square of the refractive index at the same frequency, i.e. if the molecules are in a vacuum:-

$$\epsilon - 1 = 4\pi N\alpha \qquad (8)$$

where N is the number of particles per cc., and as $\epsilon = n^2$;

$$\therefore\ n^2 - 1 = 4\pi N\alpha \qquad (9)$$

Now, $n^2-1 = (n+1)(n-1)$, and as n is close to unity in the systems under consideration;

$$n^2 - 1 \simeq 2(n-1) \qquad (10)$$

$$\therefore\ n - 1 = 2\pi N\alpha \qquad (11)$$

Dividing by c (concentration in gms./cc.) gives

$$\frac{n-1}{c} = \frac{2\pi N\alpha}{c}$$

but $\frac{n-1}{c}$ represents the change in refractive index with addition of gas molecules from zero concentration to concentration c, i.e. dn/dc.

$$\frac{dn}{dc} = \frac{2\pi N\alpha}{c} \qquad (12)$$

or, by rearrangement and squaring,

$$\alpha^2 = \frac{c^2(dn/dc)^2}{4\pi^2 N^2} \qquad (13)$$

Rayleigh's equation (7) was only calculated for one particle, so for N particles, provided they are entirely independant of one another and randomly located.

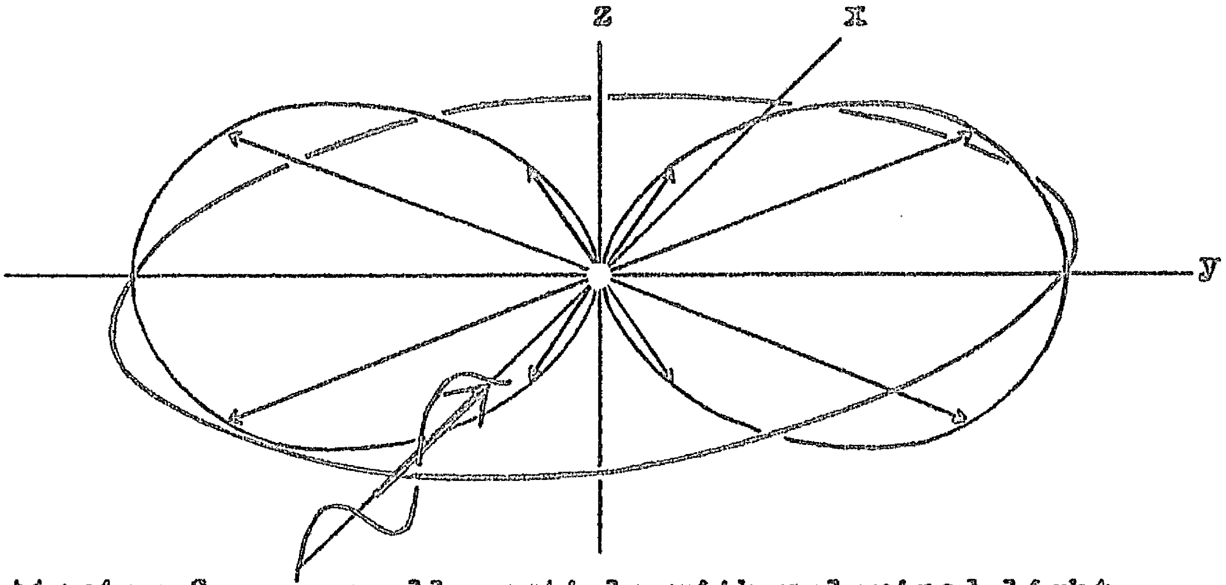
$$\frac{i_s}{I_o} = \frac{16\pi^4 \alpha^2 \sin^2\theta_1 N}{\lambda^4 r^2} \qquad (14)$$

Combination of equations 13. and 14. with substitution of $\frac{c\mathcal{N}}{M}$ for N (where $\mathcal{N}$ is Avagadro's number and M is the molecular weight of the particle) gives

$$\frac{i_s}{I_o} = \frac{4\pi^2 (dn/dc)^2 Mc \sin^2\theta_1}{r^2 \lambda^4 \mathcal{N}} \qquad (15)$$

As the angular dependance of scattering is given by the term $\sin^2\theta_1$, it can be seen that if vertically polarized light is used and observations are made in a horizontal plane the scattered intensity will be constant (θ_1 is constant) but in any other plane the intensity will be dependant on $\sin^2\theta_1$.

Figure 2.



Scattering from a small particle with polarized light. The scattered intensity is indicated by the length of the vectors.

In practice, an unpolarized beam is generally used as the source of the incident beam; this may however be taken as equivalent to two superimposed plane-polarized beams, independant in phase, and of equal intensity, with their planes of polarization perpendicular to one another. The intensity of scattering, i_θ, is therefore the sum of terms of the two forms of equation 15.

For the vertical component:-

$$\frac{i_{s(V)}}{\frac{1}{2}I_o} = \frac{4\pi^2 \sin^2\theta_1 (dn/dc)^2 Mc}{\mathcal{N} \lambda^4 r^2} \qquad (16)$$

and for the horizontal component:-

$$\frac{i_{s(H)}}{\frac{1}{2}I_o} = \frac{4\pi^2 \sin^2\theta_2 (dn/dc)^2 Mc}{\mathcal{N} \lambda^4 r^2} \qquad (17)$$

where θ_1 and θ_2, are the angles made by the line of observation with the y and z axes, respectively.

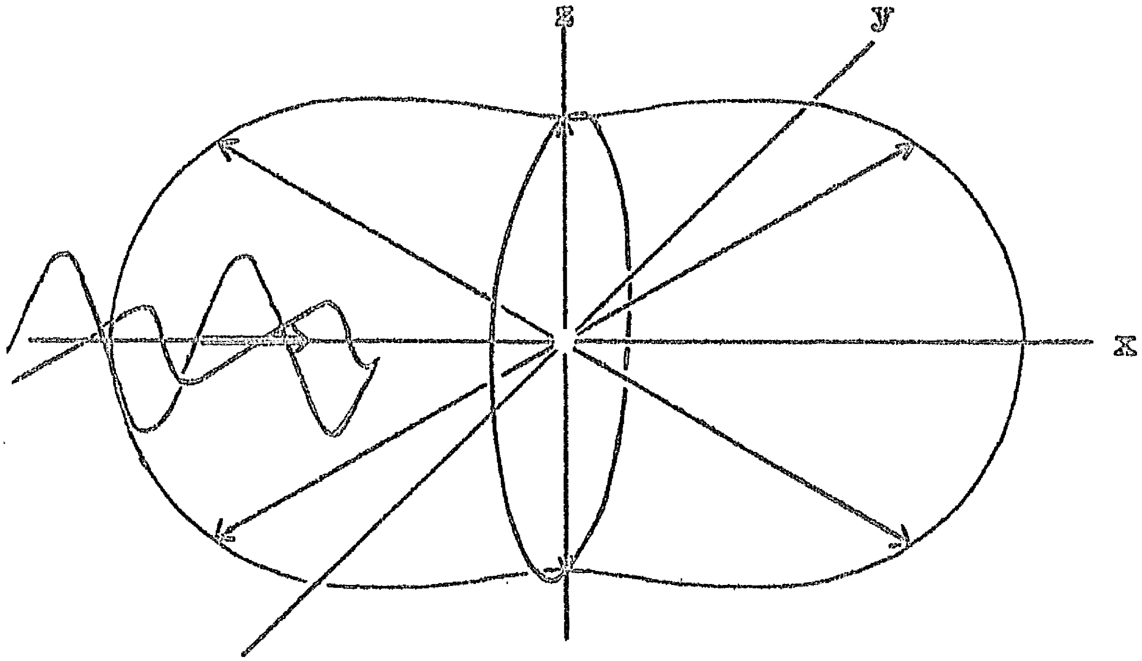
Thus
$$\frac{i_\theta}{I_o} = \frac{2\pi^2 (dn/dc)^2 Mc(\sin^2\theta_1 + \sin^2\theta_2)}{\mathcal{N} \lambda^4 r^2} \qquad (18)$$

But the resultant of $\sin^2\theta_1 + \sin^2\theta_2 = 1 + \cos^2\theta$, where θ is the angle between the line of observation and the direction of the light beam (in the xy plane). Thus equation 18. may be expressed in the simpler form of

$$\frac{i_\theta}{I_o} = \frac{2\pi^2 (dn/dc)^2 Mc(1 + \cos^2\theta)}{\mathcal{N} \lambda^4 r^2} \qquad (19)$$

The angular dependance of the intensity of scattered light, for an unpolarized incident beam is given in figure 3.

Figure 3.



Scattering from a small particle (unpolarized incident light). The intensity of the scattered light, indicated by the lengths of the vectors, is symmetrical about the x axis.

Scattering of Transparent Crystals.

Unlike the conditions considered in the previous section, where random location and complete independance of the scattering points was assumed, in a crystalline solid the opposite situation prevails. The individual scattering particles are rigidly fixed in space relative to one another resulting in destructive interference between the light scattered from individual particles. The interference being complete when the wavelength of light used is considerably greater than the interparticle distance, as the particles in the crystal can always be paired off in such a way that the light paths from the two particles to an observer at any particular value of θ will differ by half a wavelength.

Scattering by Liquids.

A liquid, though ordered to a greater extent than a gas, is not completely so, the molecules being continually on the move. Thus if a liquid is treated as a series of small, equal volume elements,[228-229] (dimensions $\ll \lambda$) and one considers two such elements separated by the right distance for the light paths to an observer to differ by half a wavelength, whereas in a crystal one would get complete destruction of the scattered light, in a liquid the number of scattering particles in each volume element is the same only when averaged over a period of time. At any given instant the partially random motion of the particles in the liquid gives rise to fluctuations in the density at any particular point so that the number of particles in the first volume element differs from that of the second. There is thus an excess of scattering of light from the one which is not cancelled by the other element.[230]

Scattering from Solutions of Macromolecular Substances.

The Ideal Solution.

On the assumption that the scattering by the solute is ideal i.e. the effects of the molecules, and the molecules themselves, are quite independant, a derivation similar to that used for calculating the scattering from a gas can be used, the main difference being the molecules are now immersed in a medium of refractive index, n_o, instead of the free space for which the refractive index is unity.

Corresponding to equation 19. one obtains from this:-

$$\frac{i_\theta}{I_o} = \frac{2\pi^2(1 + \cos^2\theta)(dn/dc)^2 n_o^2 Mc}{\mathcal{N} \lambda^4 r^2} \qquad (20)$$

where M, is the molecular weight of the solute and c, its concentration in gm./cc.

Macromolecular solutions do not, however behave ideally and the preceding equation would only apply at infinite dilutions. A clearer insight to the problem is that developed by the adaptation of Smoluchowski's fluctuation theory to solutions by Einstein[231] and Debye.[232,233]

Fluctuation Theory.

As with pure liquids the solution is considered as being made up of small volume elements, ψ, of dimensions smaller than $\lambda/20$ so that the entire element can be considered a single scattering source but is large enough to contain many solvent molecules and a few solute molecules.

Being a two component system, only a single variable of composition, the concentration of the solute, (gm./cc.) is required; the fluctuating concentration, c, is designated by $c = c' + \delta c$ where c', is the average concentration over the entire solution, and δc, the concentration fluctuation (which may be positive or negative and will occur in a completely random manner).

Corresponding to the fluctuations in concentration there are fluctuations in polarizability and refractive index. Thus if α' is the average polarizability of a volume element, $\alpha = \alpha' + \delta\alpha$ represents the polarizability of a given element at any instant, $\delta\alpha$ being the contribution due to the concentration fluctuation, δc.

From equation 7. the light scattered by a single volume element at a particular instant is

$$\frac{i_s}{I_o} = \frac{16\pi^4(\alpha' + \delta\alpha)^2\sin^2\theta_1}{\lambda^4 r^2} \qquad (21)$$

and for N volume elements (where $N = \frac{1}{\psi}$)

$$\frac{i_s}{I_o} = \frac{16\pi^4(\alpha' + \delta\alpha)^2\sin^2\theta_1 N}{\lambda^4 r^2}$$

But as $(\alpha' + \delta\alpha)^2 = \alpha'^2 + 2\alpha'\delta\alpha + (\delta\alpha)^2$ (22)

the contribution of α'^2 is zero for the same reason as the scattering of a perfect crystal is zero and any terms in $\delta\alpha$ must cancel out each other as there is an equal chance of their being positive or negative, one is thus left for the scattering per unit volume containing N volume elements

$$\frac{i_s}{I_o} = \frac{16\pi^4(\overline{\delta\alpha})^2\sin^2\theta_1}{\lambda^4 r^2 \psi} \qquad (23)$$

where $(\overline{\delta\alpha})^2$ is the average value for a large number of elements at any instant.

Temperature, pressure, and concentration will also affectα, thus the fluctuation, $\delta\alpha$, can be expressed in terms of fluctuations of these variables:-

$$\delta\alpha = \left(\frac{\partial\alpha}{\partial P}\right)_{T,c}\delta P + \left(\frac{\partial\alpha}{\partial T}\right)_{P,c}\delta T + \left(\frac{\partial\alpha}{\partial c}\right)_{T,P}\delta c \qquad (24)$$

For dilute solutions, the first two terms on the right hand side of equation 24. can be assumed to be the same as for the solvent, and, as in practice the solvent scatter is deducted from that measured for a solution, these two terms may be ignored.

In a manner analagous to equation 8. one can obtain $\partial\alpha/\partial c$ in terms of $\partial n/\partial c$:-

$$n\left(\frac{\partial n}{\partial c}\right)_{T,P} = 2\pi N\left(\frac{\partial\alpha}{\partial c}\right)_{T,P} \qquad (25)$$

or

$$\left(\frac{\partial\alpha}{\partial c}\right)_{T,P} = \frac{\gamma n}{2\pi}\left(\frac{\partial n}{\partial c}\right)_{T,P}$$

Hence, by squaring the remnants of equation 24. and substituting this into equation 23. gives

$$\frac{i_s}{I_o} = \frac{4\pi^2\gamma n^2(\partial n/\partial c)^2\sin^2\theta}{\lambda^4 r^2}(\overline{\delta c})^2$$

where $(\overline{\delta c})$ is the average value for the concentration fluctuation.

Similarly for unpolarized light:-

$$\frac{i_\theta}{I_o} = \frac{4\pi^2\gamma n^2(\partial n/\partial c)^2(1 + \cos^2\theta)}{\lambda^4 r^2}(\overline{\delta c})^2 \qquad (27)$$

Calculation of $(\delta c)^2$

In a system at equilibrium, the change in a thermodynamic quantity from its mean value, $\bar{x}$, to any other value, x, must involve some sort of change in free energy, i.e. $\Delta G = f(x) - f(\bar{x})$; the probability of this change occurring is given by $e^{-\Delta G/kT}$. As large fluctuations in concentration are not expected to occur one can expand δG in a Taylor series and retain only the first two terms.

$$\delta G = \left(\frac{\partial G}{\partial c}\right)_{T,P}\delta c + \frac{1}{2!}\left(\frac{\partial^2 G}{\partial c^2}\right)_{T,P}\delta c^2 \qquad (28)$$

but the average concentration about which fluctuations are occurring is the equilibrium concentration at constant pressure, therefore $\frac{\partial G}{\partial c} = 0$.

The probability of a given value of δc then becomes

$$e^{-\frac{\delta G}{kT}} = e^{-\left(\frac{\partial^2 G}{\partial c^2}\right)(\delta c)^2/2kT} \qquad (29)$$

which makes positive and negative values of δc equally probable. The expression for the average value of $(\delta c)^2$ is obtained from equation 29. and gives on integration

$$\overline{(\delta c)}^2 = \frac{kT}{(\partial^2 G/\partial c^2)_{T,P}} \qquad (30)$$

Calculation of $\partial^2 G/\partial c^2$.

Taking n_1 and n_2 as the number of moles of solvent and solute respectively, in a volume element,

$n_1\bar{V}_1 + n_2\bar{V}_2$ = the total volume of the element $= \psi$,

or $dn_1 = -(\bar{V}_2/\bar{V}_1)dn_2$, where $\bar{V}_1$ and $\bar{V}_2$ are the partial molal volumes of solvent and solute.

At constant temperature and pressure any free energy change accompanying change in concentration is

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

$$= dn_2\left[\left[-\bar{V}_2/\bar{V}_1\right]\mu_1 + \mu_2\right] \qquad (31)$$

where μ_1 and μ_2 are the chemical potentials of solvent and solute respectively.

The number of solute moles per cc. is $n_2/\psi = c/M$:

$$dn_2 = (\psi/M)dc$$

$$\therefore \left(\frac{\partial G}{\partial c}\right)_{T,P} = \left(\frac{\psi}{M}\right)\left[\mu_2 - \left(\bar{V}_2/\bar{V}_1\right)\mu_1\right] \qquad (32)$$

Differentiation of equation 32, with respect to c gives

$$\left(\partial^2 G/\partial c^2\right)_{T,P} = \left(\frac{\psi}{M}\right)\left[\left(\frac{\partial\mu_2}{\partial c}\right)_{T,P} - \bar{V}_2/\bar{V}_1\left(\frac{\partial\mu_1}{\partial c}\right)_{T,P}\right] \qquad (33)$$

But by the Gibbs-Duhem Equation

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

so equation 33. becomes

$$\left(\partial^2 G/\partial c^2\right)_{T,P} = -\frac{\psi}{M}\left(\frac{n_1\bar{V}_1 + n_2\bar{V}_2}{n_2\bar{V}_1}\right)\left(\frac{\partial \mu_1}{\partial c}\right)_{T,P}$$

and since $n_2 M/\left(n_1\bar{V}_1 + n_2\bar{V}_2\right) = c$

$$\left(\partial^2 G/\partial c^2\right)_{T,P} = -\psi/c\bar{V}_1\left(\frac{\partial \mu_1}{\partial c}\right)_{T,P} \tag{34}$$

Introducing this into equation 30. and hence into equation 27. produces;

$$\frac{i_\theta}{I_o} = \frac{2\pi^2 n^2 (dn/dc)^2 (1 + \cos^2\theta) c}{\lambda^4 r^2 \left[-\left(1/\bar{V}_1 kT\right)\left(\partial\mu_1/\partial c\right)_{T,P}\right]} \tag{35}$$

The dependance of the chemical potential of the solvent on the concentration of the solute can be expressed as

$$\left(\frac{\partial \mu_1}{\partial c}\right)_{T,P} = -RT\bar{V}_1\left(1/M + 2Bc + 3Cc^2 \ldots\ldots\right)$$

where B and C are the second and third virial coefficients respectively.

But as $k = R/\mathcal{N}$

$$-\frac{1}{\bar{V}_1 kT}\left(\frac{\partial \mu_1}{\partial c}\right)_{T,P} = \mathcal{N}\left(1/M + 2Bc + 3Cc^2 \ldots\ldots\right) \tag{36}$$

Introducing this into equation 35.

$$\frac{i_\theta}{I_o} = \frac{2\pi^2 n^2 (dn/dc)^2 (1 + \cos^2\theta) c}{\mathcal{N}\lambda^4 r^2 \left(1/M + 2Bc + 3Cc^2 \ldots\right)} \tag{37}$$

For dilute solutions the difference between 'n' and the refractive index of the solvent becomes negligible, so that n^2 may generally be replaced by n_o^2. At infinite dilution this equation reduces to the theoretical equation (20). B can be related to molecular size and shape.[234]

Equation 37. has also been calculated by the exact molecular theory of Fixman.[235]

As 'r' (experimentally the distance between the centre of the solution cell and the light detector unit) varies with the apparatus used, a more suitable method of determining a comparable value for the light scattered is by Rayleigh's ratio, $r^2 i_\theta / I_o$, or more conveniently by the ratio :

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

giving,

$$R_\theta = \frac{Kc}{1/M + 2Bc + 3Cc^2 \ldots.} \qquad (38)$$

K, being an optical constant given by

$$K = \frac{2\pi^2 n_o^2 (dn/dc)^2}{N\lambda^4}$$

An alternative experimental procedure is to interpret the light scattered as the turbidity, τ, of the substance; the relationship between τ and i_θ being found by integrating the scattered light, i_θ, over the area of the surface of a sphere of radius, r, giving:

$$\tau = \frac{16\pi}{3} R_\theta \tag{39}$$

One thus obtains, analagous to equation 38,

$$\frac{Hc}{\tau} = \frac{Kc}{R_\theta} = \frac{1}{M} + 2Bc + 3Cc^2 \ldots\ldots\ldots \tag{40}$$

where

$$H = \frac{32\pi^3 n_0{}^2 (dn/dc)^2}{3\mathcal{N}\lambda^4} \tag{41}$$

The quantity, τ, is ordinarily too small to be measured but experimental results are frequently reported in the form of $\frac{Hc}{\tau}$, when $\frac{Kc}{R_\theta}$, has actually been measured.

Experimentally, for particles with dimensions less than $\lambda/20$, it is necessary to determine i_θ as a function of θ only in so far as to show there is no asymmetry in the scattering envelope. Subsequent measurements are generally made at 90° to the incident beam and the turbidity at this angle determined for various concentrations of the solute, and the solvent; a plot of $\frac{Hc}{\tau - \tau_s}$ vs. c, (where τ, is the turbidity of the solution at concentration, c gm./ml. and τ_s, the turbidity of the solvent), extrapolated to zero solute concentration giving an intercept equal to 1/M and the limiting slope a measure of the second virial coefficient.

Anisotropy and Depolarization.

In the preceding derivations it has been assumed that the scattering particles in all cases were optically isotropic, and, as discussed, when the incident beam is unpolarized, there is induced in the particle two independant oscillating dipoles, both perpendicular to the direction of the incident beam; one at 90° to the horizontal plane and one at 90° to the vertical plane. The former will obviously contribute nothing to the radiation in the line $\theta = 90^\circ$ in the horizontal plane (see figures 2. and 3.) , thus the light viewed along this line will be completely polarized in the vertical plane and the ratio of horizontally to vertically polarized scattered light will be zero.

In an anisotropic particle the induced dipole moment is not necessarily parallel to the electric vector of the incident light, thus the ratio of horizontally to vertically polarized light will not be zero. This ratio is known as the depolarization ratio, ρ_u.

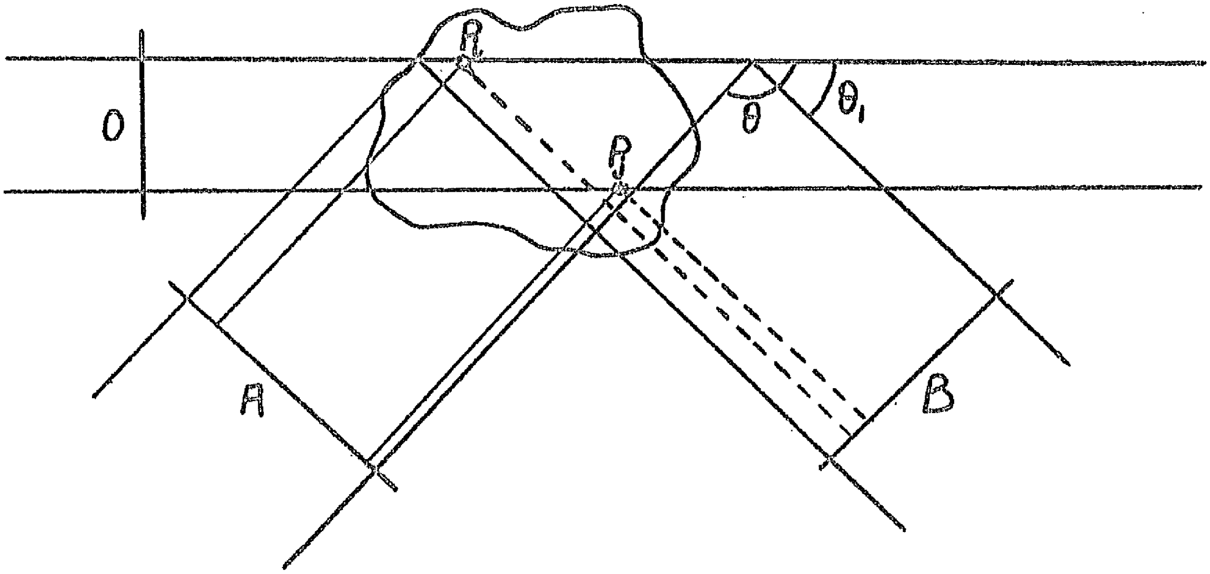
Where anisotropic effects are present the value of i_θ observed is therefore greater than the theoretical value obtained from concentration fluctuations as there is also the possibility of additional scattering due to fluctuations in the orientation of the scattering particles. This excess scattering can however be related to the depolarization ratio,[236] and a correction factor,[237] calculated from the latter, $\frac{6 + 6\rho_\mu}{6 - 7\rho_\mu}$ applied to the observed value for the light scattered.

Caution must be exercised in the interpretation of depolarization, as it may also arise from secondary scattering, and this does not affect the intensity of scattering appreciably; Geiduschek,[238] has gone so far as to say that in most cases where non-zero values of ρ_μ have been reported, it is not at all certain whether the measured values of ρ_μ really reflect anisotropy at all.

Light-Scattering by Larger Particles.

Particles of dimensions less than $\lambda/20$ have been considered as point scatterers or, in other words, equivalent to single dipoles, whereas in reality, they are made up of a series of dipoles. For these particles the separation between the dipoles is small compared with the wavelength of the incident light, and the combined radiation is coherent because the phase differences between the individual contributions are too small to cause interference. When one dimension of the particle under examination exceeds $\lambda/20$, the particle can no longer be considered a single scattering source as the differences in phase between the scattering of dipoles in various parts of the particle has become large enough for destructive interference to occur. This is illustrated in figure 4.

Figure 4.



P_i and P_j are two points on a large scattering particle. O,is a reference plane where all of the incident light is in phase, and A, a second reference plane perpendicular to the scattered beam at viewing angle, θ. The distance OP_iA is clearly considerably less than the distance OP_jA, so that light scattered from P_j, will reach the observer out of phase with that scattered from P_i, thus causing interference and diminution of the scattered intensity. Comparison with a third reference plane, B, perpendicular to the viewing angle, θ_1, a smaller angle than θ, shows that the difference between OP_iB and OP_jB is less than the difference between OP_iA and OP_jA; consequently there will be less interference and less diminution of intensity at the smaller angle. The path difference, and subsequent interference, disappears altogether at the zero angle. (See figure 5.)

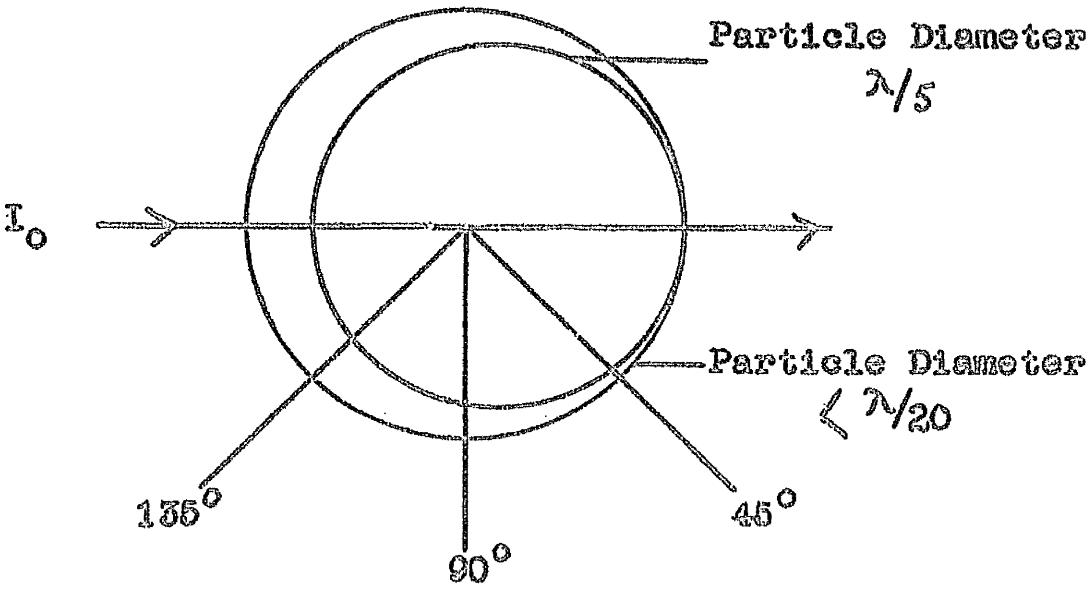


Figure 5. The angular distribution of the vertically polarized component of spherical particles.

The effect of decreased scattered intensity is generally described by a function $P(\theta)$ where

$$P(\theta) = \frac{\text{Scattered intensity for a large particle at angle } \theta}{\text{Scattered intensity without interference at angle } \theta}$$

This function has been derived[239] by dividing the particle up into σ scattering elements and thence evaluating it in terms of the distance between two scattering elements, r_{ij}, and a function of the angle of observation and the wavelength;

$$\mu = \frac{4\pi}{\lambda_1}\sin\theta/2 \qquad (42)$$

where λ_1, is the wavelength in the scattering medium. This gives a value for $P(\theta)$ based on random orientation of the scattering particle which may be used for both polarized and unpolarized light.

$$P(\theta) = \frac{1}{\sigma^2} \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} \frac{\sin \mu r_{ij}}{\mu r_{ij}} \qquad (43)$$

where r_{ij} is the distance from the i-th to the j-th scattering points.

One of the most important results of equation 43., first recognised by Guinier,[240] is that, although the behaviour of $P(\theta)$ as a function of angle depends upon the shape of the particle, it becomes independant of particle shape as θ approaches zero and, under these limiting conditions, becomes a measure of the radius of gyration.

By expansion of the sine term under the summation sign of equation 43. in terms of a power series, and since $\sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma} 1 = \sigma^2$, on retaining only the first two terms of the expansion one obtains

$$\mathcal{L}_{\theta \to 0}\, P(\theta) = 1 - \frac{\mu^2}{3!\,\sigma^2} \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} r_{ij}^{\;2} \qquad (44)$$

From calculations on the configurations of particles divided in σ elements it can be shown that,[241,242]

$$\sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} r_{ij} = 2\sigma^2 R_g^{\;2} \qquad (45)$$

where R_g is the average radius of gyration.

Substituting equations 42. and 45. into equation 44. gives:

$$\mathcal{L}_{\theta \to 0}\, P(\theta) = 1 - \frac{16\pi^2}{3\lambda_1^{\;2}} R_g^{\;2} \sin^2 \theta/2 \qquad (46)$$

As the usual notation for this function is $P^{-1}(\theta)$, and as 1/1-x for small values of x can be taken as equal to 1+x

$$\underset{\theta \to 0}{\mathcal{L}} \frac{1}{P(\theta)} = 1 + \frac{16\pi^2}{3\lambda_1^2} R_g^{\,2} \sin^2 \theta/2 \qquad (47)$$

For large particles the decreased turbidity due to interference upsets the values obtained for molecular weights if the results are analysed by equation 40. From the definition of $P(\theta)$ the measured value may be corrected by introducing this function into the equation

$$\underset{c \to 0}{\mathcal{L}} \frac{Hc}{\tau} = \frac{1}{MP(\theta)} \qquad (48)$$

or in the fuller form, from equation 47.;

$$\underset{c \to 0}{\mathcal{L}} \frac{Hc}{\tau} = \frac{1}{M}\left(1 + \frac{16\pi^2}{3\lambda_1^2} R_g^{\,2} \sin^2 \theta/2 + \ldots\right) \qquad (49)$$

but as the equation for $P(\theta)$ is only valid at very high dilution it is necessary to extrapolate the data at each angle to zero concentration before one can perform the extrapolation indicated by equation 49. At the same time it is necessary to extrapolate the data at each concentration to zero angle so that M_w and B can be determined by equation 40. (this equation is only valid for large particles at zero angle, see page 71).

Zimm's method for analysis of light-scattering results[243] achieves this by plotting $\frac{Hc}{\tau}$ vs. $\sin(\theta/2) + kc$, where k, is an arbitrary constant chosen to give the plot a convenient spread.

From the extrapolations to zero angle one obtains a plot of $\frac{Hc}{\tau}$ vs. kc, which, on extrapolation to $c = 0$, gives an intercept of $\frac{1}{M}$, with 2Bk as the limiting slope; and, from the extrapolations to zero concentration, a plot of $\frac{Hc}{\tau}$ vs. $\sin^2 \theta/2$, which (from equation 49.) gives the same intercept as $\theta = 0$ plot. The limiting slope is a measure of R_g.

It should be noted that the extrapolation method is applicable only over a limited range of dimensions i.e. $0.05 \leqslant R_g/\lambda \leqslant 0.5$. If R_g falls below the lower limit $P(\theta)$ becomes too small for accurate estimation, and above the upper limit, it is impossible to measure values of θ small enough to give an accurate extrapolation.

The radius of gyration can be interpreted in terms of molecular dimensions by comparison with standard models; the dimensions of the models being related to the radius of gyration by:-

Sphere: $R_g^2 = 3D^2/20$ (50)

Rod: $R_g^2 = L^2/12$ (51)

Coil: $R_g^2 = r^2/6$ (52)

where D, is the diameter of the sphere; L, is the length of the rod; and r, is the root mean square distance across the coil.

The correct choice of model can often be made by fitting the zero concentration line of the Zimm plot, and using the observed radius of gyration actually obtained as the basis for calculating the theoretical values for $P(\theta)$ from equations which have been developed for the various models:-

Spheres[244,245] $$P(\theta) = \left[\frac{3}{x^3}(\sin x - x\cos x)\right]^2 \qquad (53)$$

$$\text{where } x = \frac{2\pi D}{\lambda_1}\sin{}^{\theta}/_{2}$$

Coils[233] $$P(\theta) = \left(\frac{2}{w^2}\right)(e^{-w} + w - 1) \qquad (54)$$

$$\text{where } w = \mu^2 R_g{}^2$$

Rods[246] $$P(\theta) = 1 - \frac{x^2}{9} + \frac{2x^4}{225}\cdots\cdots \qquad (55)$$

$$\text{where } x = \left(\frac{2\pi L}{\lambda_1}\right)\sin{}^{\theta}/_{2}$$

By comparing the limiting line of the Zimm plot with the lines obtained from the theoretical values, an idea of the most suitable model can be gained. The appropriate dimensions can then be calculated from equations 50-52.

A second means of treating data is by the dissymmetry method. In addition to measuring the light scattered at 90°, measurements are also made at two angles symmetrical about 90°, e.g. 45° and 135°. The values of the dissymmetry, $Z = \frac{i_{45^{\circ}}}{i_{135^{\circ}}} = \frac{P(45^{\circ})}{P(135^{\circ})}$ have been tabulated[247] as a function of $P(90^{\circ})$ and of the ratio of characteristic particle dimensions to the wavelength of the light used. From measurements of Z, and choice of a suitable model for the particle, i_{90} may be corrected for internal interference to enable M, to be calculated, and the characteristic dimension of the particle determined. This procedure involves preconceived ideas as to the type of model which best fits the particle, but for small values of Z (< 1.2), little error is introduced in calculation of M, as the values of $P(90^{\circ})$ for the different models in this region are similar.

Polydispersivity and Molecular Weight.

The extrapolation method from equations 40. and 49. is limited to molecular dimensions below $\lambda/2$.

These equations give, within their limits, a weight average molecular weight, $M_w = \sum c_i M_i / \sum c_i$ whereas the radius of gyration is a z average. Developments from investigations of molecular weight distribution for polydisperse samples, where the radius of gyration becomes large ($R_{gz} > 800$Å),[248] introduced into the light scattering equations have evolved, for large coiled molecules[249]

$$\frac{Hc}{\tau_{(c=0)}} = \frac{1}{M_n}\left[\frac{1}{2} + \frac{\mu^2 R_{gn}^{\;2}}{3}\right] \qquad (56)$$

and for large rod molecules[250]

$$\frac{Hc}{\tau_{(c=0)}} = \frac{1}{M_n}\left[\frac{2}{\pi^2} + \frac{2}{\pi}\left(\frac{2\pi}{\lambda_1}\right) L_n \sin \theta/2\right] \qquad (57)$$

Thus if the molecules are large enough a number average molecular weight and particle dimensions are obtained; this condition occurring on the asymptote to the limiting line to the Zimm plot which, for these large particles, may be a curve. The lower part (assuming that measurements could be made at very low angles) giving M_w, and the upper part a function of M_n.

The Interpretation of Viscosity Results.

The increase in viscosity accompanying the solution of a macromolecule, soap, or other substance forming a colloidal solution is a fairly readily measured effect, and consequently has been the focus of considerable effort to derive information as to the nature of the solution and the solute.[278]

On the basis that the increase in viscosity arose from distortion of flow lines around the particles, Einstein[251,252] calculated for a suspension of rigid, completely wetted spheres, sufficiently far apart so as to prevent overlap of the distortion of the flow lines produced by each individual particle:

$$\eta' = \eta\ (1 + 2.5\phi) \qquad (58)$$

where η', is the viscosity of the suspension; η, the viscosity of the solvent; and ϕ, the volume fraction of the disperse phase.

This approach has been adapted for use in the interpretation of viscosity of colloidal or macromolecular solutions on the assumption that such a solution can be taken as equivalent to a suspension of particles within the limits defined by Einstein.

Extension of Einstein's treatment to asymmetric particles leads to complications due to orientation of the particles with the stream lines, but at sufficiently low velocity gradients, this effect is negligible and Simha[253,254] derived for particles which are ellipsoids of revolution:

$$\eta' = \eta(1 + \nu\phi) \quad \text{or} \quad \eta_{sp} = \nu\phi \qquad (59)$$

where η_{sp}, the specific viscosity is equal to $(\eta'/\eta - 1)$ and ν, Simha's factor, is a function of axial ratio and shape.

The Einstein and Simha equations take no account of solvation of the particles, i.e.

$$\phi = \frac{\text{Volume of Solute}}{\text{Total Volume of Solution}} = c\bar{V}_2$$

where c, is the solute concentration in gm./ml.; and $\bar{V}_2$, the specific volume of the solute = the reciprocal of its density. If however the particle is hydrated its effective volume is increased by the co-volume of water associated with it:-

Hydrated Volume of Solute = Volume of Solute + Volume of Hydrating Water

$$= c\bar{V}_2 + \omega c\bar{V}_1$$

where ω, is the water of hydration expressed as gm. water/gm. solute; and $\bar{V}_1$, the specific volume of the water (assumed to have the same value as the unbound water).

The volume fraction of a hydrated solute, ϕ_H, is thus:-

$$\phi_H = \frac{\text{Volume of Hydrated Solute}}{\text{Total Volume of Solution}}$$

$$\begin{aligned}\phi_H &= c\bar{V}_2 + \omega c\bar{V}_1 \\ &= cV_2\left(1 + \omega\bar{V}_1/\bar{V}_2\right) \\ &= \phi\left(1 + \omega\bar{V}_1/\bar{V}_2\right) \qquad (60)\end{aligned}$$

which, on introduction into Simha's equation gives

$$\eta_{sp} = \nu\left[\phi\left(1 + \omega\bar{V}_1/\bar{V}_2\right)\right] \qquad (61)$$

Equations 61, 59, and 58, can only be applied to infinitely dilute solutions to satisfy the conditions of non-interference specified by Einstein, thus for practical purposes the form suggested by Oncley[255] has been adopted:

$$\mathop{\mathcal{L}}_{\phi \to 0} \frac{\eta_{sp}}{\phi} = \nu\left(1 + \omega\bar{V}_1/\bar{V}_2\right) \qquad (62)$$

This treatment can be used for colloidal particles which can be considered as fairly compact entities but for such things as flexible polymers other interpretations must be used.[277]

Further, in the Oncley equation, as the volume fraction used is the unhydrated value, the intercept $\left(\frac{\eta_{sp}}{\phi}\right)_{\phi=0}$, obtained by extrapolation of a plot of $\frac{\eta_{sp}}{\phi}$ vs. ϕ is a function of both particle shape and hydration; one of which must be known before the intercept can be fully analysed.

PART 2.

EXPERIMENTAL, RESULTS,

AND

DISCUSSION.

Materials, Methods of Synthesis and Analysis.

Fractionation of commercial adducts of ethylene oxide has, as yet, only produced compounds with a narrower chain length distribution[21,30,31] but likewise, attempts at synthesis of a pure compound of this type, with an unambiguous number of ethylene oxide units per molecule, have been fraught with difficulties, stemming from the very nature of the compounds concerned. Similarity of linkages throughout the compound, and similarity of the chemical properties and solubilities of the desired product, the starting materials, possible contaminants, and products of side reactions, coupled with a strong tendency to form emulsions and the fact that most of the compounds wanted are beyond the range of distillation by normal procedures, have made the isolation and purification of synthesised detergents a very difficult problem. This, without doubt, accounts for the lack of published results on this topic.

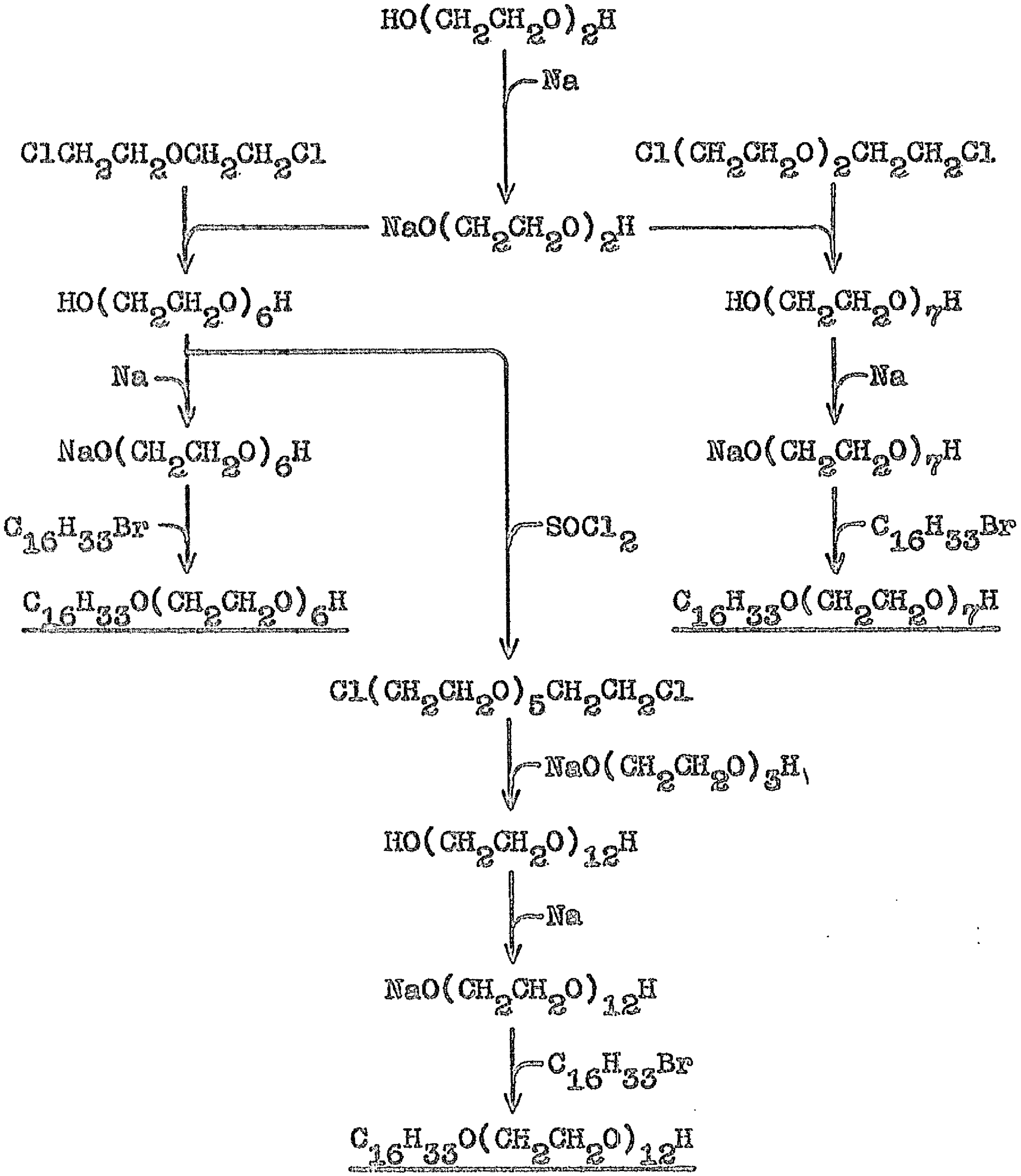
Preliminary Experiments.

As mentioned in the introduction, the route for synthesis mainly used has been a Williamson Ether reaction of an alkyl halide with the monosodium salt of a glycol; the latter compound being prepared by dissolving metallic sodium in a four molar excess of the appropriate glycol.[35,36] Using this method the syntheses of monohexadecyl ethers with up to six ethylene oxide units have been described by direct or stepwise addition of the glycol units.[45,49]

In an attempt to bypass the rather tedious build up of oxyethylene glycols from di- and tri- ethylene glycols, samples of P.E.G. 300 (a Shell, polymerised polyoxyethylene glycol with a mean molecular weight equivalent to about 6.4 ethylene oxide units) were fractionally distilled, several times, up a six inch fractionating column packed with Dixon gauze rings. From physical characteristics and hydroxyl analyses the appropriate cuts appeared to have been reasonably fractionated, but conversion of the apparent hexaoxyethylene glycol to its monohexadecyl ether by the Williamson reaction synthesis, and subsequent purification by published methods,[45,49] gave a compound with a melting point some 3° - 5° lower than that described by other workers.[45,49] The presence of glycol was initially suspected as causing the depressed melting point but the application of published,[52] and other techniques for its removal had little effect on the end product.

Diagrams of the Reaction Routes followed in Synthesising the Detergent Series.

Figure 6.



Several variations on the mode of distillation and redistillation of the glycol, reaction conditions, and purification were tried but the final compounds were always unsatisfactory. Efforts to produce a long chain compound by building it up from the fractionated glycols met with a similar lack of success.

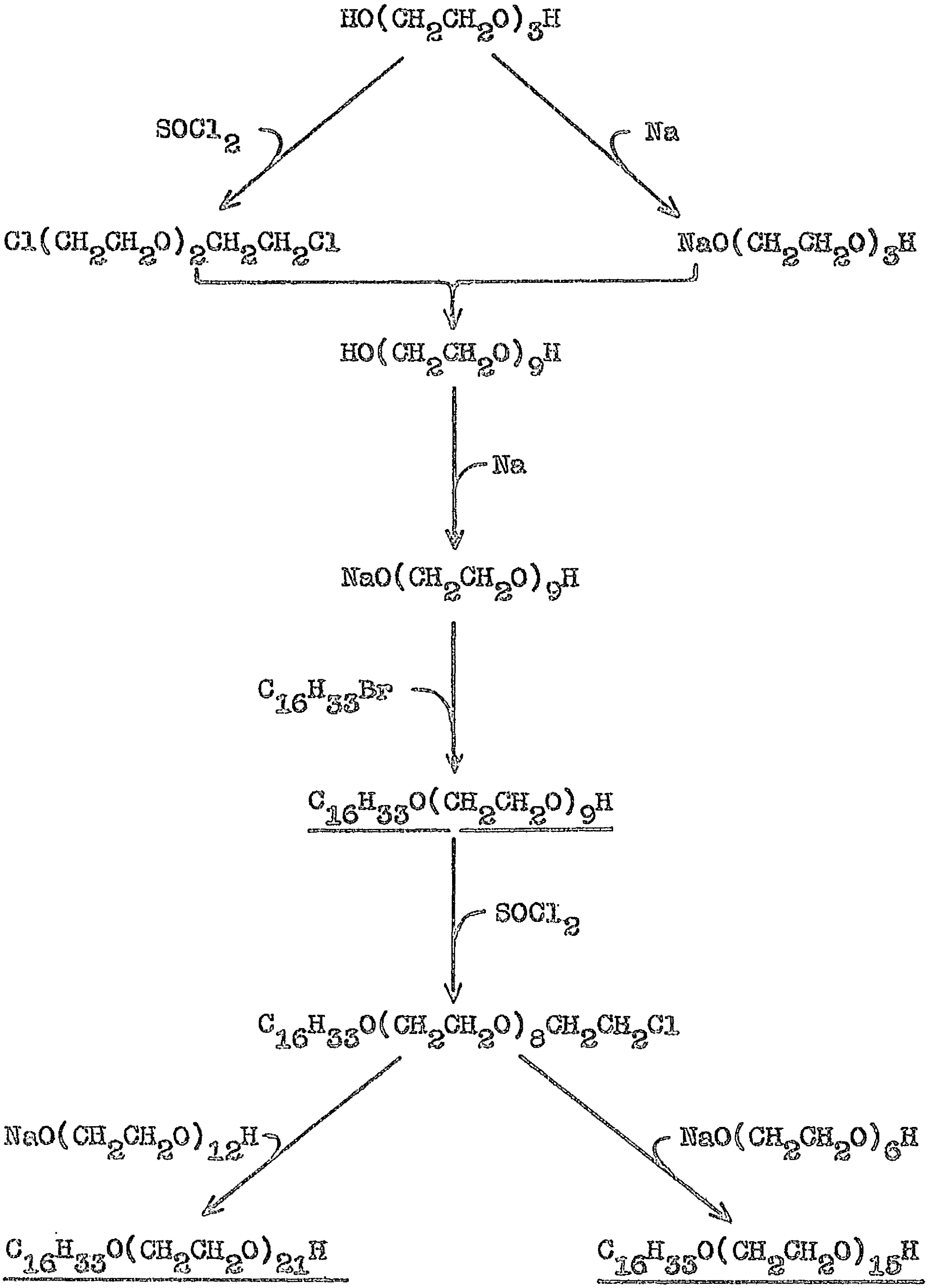
It was therefore necessary to fall back on the alternative route from short length glycols.

Reaction Routes.

The routes used in synthetic work are shown in Figures 6 and 7. Glycols of up to twelve units were synthesised by reaction of one mol. of the $\alpha\omega$-dichloro derivative of one glycol with two mols. of the monosodium salt of the same or another glycol. The subsequent glycol was then converted to its monosodium derivative (by dissolving 1 mol. sodium in 4 mols. glycol) and condensing this compound with hexadecyl bromide to give the appropriate monohexadecyl ether.

Dodecaoxyethylene glycol forms the limit for distillation, even in a molecular still, thus longer compounds were prepared by condensation of the monosodium derivative of the glycol with the monochloro derivative of Hn_9 (obtained by chlorinating the

Figure 7.


$HO(CH_2CH_2O)_3H$
$SOCl_2$
Na
$Cl(CH_2CH_2O)_2CH_2CH_2Cl$
$NaO(CH_2CH_2O)_3H$
$HO(CH_2CH_2O)_9H$
Na
$NaO(CH_2CH_2O)_9H$
$C_{16}H_{33}Br$
$C_{16}H_{33}O(CH_2CH_2O)_9H$
$SOCl_2$
$C_{16}H_{33}O(CH_2CH_2O)_8CH_2CH_2Cl$
$NaO(CH_2CH_2O)_{12}H$
$NaO(CH_2CH_2O)_6H$
$C_{16}H_{33}O(CH_2CH_2O)_{21}H$
$C_{16}H_{33}O(CH_2CH_2O)_{15}H$

terminal hydroxyl group of Hn_9 with thionyl chloride).

Initial runs were made using the compounds shown in the diagrams but yields were not particularly good, especially with the final addition of glycol to the alkyl halide, and, in an attempt to produce better yields, substitution of the other halogens, except fluorine, in the various reactants, in place of those primarily tried, was investigated. These however did not improve the yields in any way, nor did attempts at reversing the position of the alkali metal and halogen radicals in the reactants. Thus, comparing the labour involved, the route first explored, being the most easily handled, was adopted.

It is of interest to note that when making glycols although $\alpha\omega$-dichlorodiethyl ether reacts quite satisfactorily with the monosodium derivatives of other glycols, 1:2-dichloroethane under similar experimental conditions, although giving the theoretical amount of salt, did not show any sign of formation of a higher glycol; and various unsaturated compounds were produced.

Extraction and Purification.

Glycols.

Unlike polymerisation products synthetic glycols have a gap of at least two ethylene oxide units between possible contaminants, and the incidence of these compounds is much less than in the commercial product, hence effective fractional distillation is much easier. Hexa and hepta oxyethylene glycols presented no problem as they could be fractionally distilled by normal vacuum techniques. Nona and dodeca oxyethylene glycols would have required excessively high temperatures for a similar treatment and were therefore molecularly distilled, after removal of lower distilling glycols by normal procedures; the end products being pale straw coloured liquids which solidified at room temperature to form needle like clusters.

Detergents.

Hn_6, the only compound of interest in this series so far described was purified by distillation,[45,49] but the temperature of distillation (235° at 0.01 mm.) does not seem to improve the compound and subsequent chromatography was required. It was therefore clear that another means of isolation of the detergents was required for the longer compounds.

Extraction.

Over and above any products of side reactions, the mixture contains the desired product, excess glycol, and salt. Comparison of the properties of the glycol and its hexadecyl ether showed that, of the commoner organic solvents only with two, diethyl and petroleum ethers, did they show any variation in solvent properties; the former being slightly soluble in ether and virtually insoluble in petroleum ether. Partition between organic solvents and water is baulked by emulsion formation and although various suggestions have been made to overcome this,[52,127] practical disadvantages outweigh their usefulness.

Diethyl ether was more efficient for extracting the detergent from the reaction mixture but at the same time tended to extract some glycol. The method used was therefore to extract the reaction mixture with successive portions of diethyl ether, evaporate off the ether and re-extract the residue with petroleum ether. The second extraction effectively getting rid of much of the glycol.

Purification.

Crystallisation.

Crystallisation from ether, methyl and ethyl alcohols, acetone, and other solvents, mixtures, and series of solvents was examined but although a pure compound could be obtained the number of crystallisations required, with losses incurred, did not leave a reasonable quantity of product for physical-chemical measurements.

Chromatography.

The use of silica for fractionation of comparable compounds has been described,[30,45,127] but application of similar systems to the compounds under examination did not give satisfactory separation, nor did other solvent systems investigated.

Alumina showed more promise, and eventually, after trying several solvent systems, the most suitable conditions for the various compounds were found and are detailed in the appropriate synthetic descriptions.

Materials and Syntheses.

Diethylene Glycol.

Redistilled Digol B.D.H., b.p. 126°/10 mm., n_D^{20} 1.4470
Curme and Johnston[144] give: b.p. 128°/10 mm., n_D^{20} 1.4472
Found: CH_2CH_2O, 82.8. Calc. for $C_4H_{10}O_3$: CH_2CH_2O, 83.0%

Triethylene Glycol.

Redistilled Trigol B.D.H., b.p. 164°/10 mm., n_D^{20} 1.4553
Curme and Johnston[144] give: b.p. 162°/10 mm., n_D^{20} 1.4559
Found: CH_2CH_2O, 87.8. Calc. for $C_6H_{14}O_4$: CH_2CH_2O, 88.0%

Hexadecyl Bromide.

Redistilled B.D.H. material, m.p. 14°, n_D^{20} 1.4622

Heilbron and Bunbury[206] give: m.p. 15°, n_D^{20} 1.4620

Gas chromatographic examination on a column of silicone oil distributed on Celite showed only one peak.

3,6,9,12,15-Pentaoxaheptadecane-1,17-diol (hexaoxyethylene glycol), n_6.

This was prepared by the method of Fordyce et al.[35] from redistilled diethylene glycol (848 g.; b.p. 106°/0.1 mm., n_D^{20} 1.4470,) sodium (46 g.), and 2,2 - dichlorodiethyl ether (143 g.; b.p. 76°/15 mm.). The glycol and dichlorodiethyl ether were redistilled immediately before use. After removal of the excess of glycol, the hexaoxyethylene glycol was distilled; it (140 g.) had b.p. 182°/0.01 mm., n_D^{38} 1.4589 (Found: C, 50.9; H, 9.1; CH_2CH_2O, 93.5. Calc. for $C_{12}H_{26}O_7$; C, 51.1; H, 9.3; CH_2CH_2O, 93.6%).

1, 8-Dichloro-3, 6-dioxaoctane (αω-dichlorotriethylene glycol).

This was prepared by chlorinating the terminal hydroxyl groups of triethylene glycol (300 g.) by reaction with excess thionyl chloride (600 g.) in the presence of pyridine (350 g.). After the reaction was complete the excess thionyl chloride was removed by distillation under reduced pressure, followed by distilling 3 x 50 ml. portions of benzene from the residue. The reaction mixture was neutralised with saturated sodium bicarbonate solution and solid sodium bicarbonate, and the dichlorotriethylene glycol extracted into chloroform. This extract was washed with hydrochloric acid, water, sodium carbonate solution, and water, dried, and the chloroform distilled off. Vacuum distillation of the residue gave the dichloro compound (250 g.); b.p. 124°/18 mm., n_D^{38} 1.4528. (Found: C, 38.7; H, 6.5; Cl, 37.8. $C_6H_{12}O_2Cl_2$ requires: C, 38.5; H, 6.5; Cl, 38.0%).

1, 17-Dichloro-3,6,9,12,15-pentaoxaheptadecane (α,ω-dichlorohexaoxyethylene glycol).

Hexaoxyethylene glycol (140 g.) and thionyl chloride (160 g.), in the presence of pyridine (95 g.) gave, by the method described for α,ω-dichlorotriethylene glycol, a product (80 g.) which had b.p. 164°/0.1 mm., n_D^{38} 1.4598. (Found: C, 45.5; H, 7.7; Cl, 23.1. $C_{12}H_{24}O_5Cl_2$ requires: C, 45.2; H, 7.6; Cl, 23.4%).

3,6,9,12,15,18-Hexaoxaeicosane-1,20-diol (heptaoxyethylene glycol), n_7. Sodium (46 g.) was slowly dissolved in redistilled diethylene glycol (848 g.) by stirring under a layer of light petroleum (b.p. 100-120°) at 70°. Ethylene bis-(2-choroethyl ether) (187 g.) was added and the mixture stirred at 115° until neutral (4 hr.). Precipitated salt was filtered off and the excess of triethylene glycol removed by distillation. Vacuum-distillation of the residue gave heptaoxyethylene glycol (103 g.), b.p. 201°/0.01 mm., n_D^{38} 1.4600. (Found: C, 51.6; H, 9.3; CH_2CH_2O, 94.5. $C_{14}H_{30}O_8$ requires C, 51.5; H, 9.3; CH_2CH_2O, 94.5%).

3,6,9,12,15,18,21,24-Octaoxahexacosane-1,26-diol (nonaoxyethylene glycol, n_9).

Sodium (46 g.) was dissolved slowly at a temperature not exceeding 75° in redistilled triethylene glycol (1200 g.); by stirring under a layer of light petroleum (b.p. 100-120°). αω-Dichlorotriethylene glycol (187 g.) was added, and stirring continued at 115° until the reaction mixture was neutral (4 hr.). Precipitated salt was filtered off, and the excess of triethylene glycol removed by distillation under reduced pressure. The residue was distilled in a short-path still, giving nonaoxyethylene glycol (185 g.), m.p. 16°, n_D^{38} 1.4612. (Found: C, 52.0; H, 9.1; OH, 8.1; CH_2CH_2O, 95.4. $C_{18}H_{38}O_{10}$ requires C, 52.2; H, 9.2; OH, 8.2; CH_2CH_2O, 95.6%).

3,6,9,12,15,18,21,24,27,30,33-Undecaoxapentatriacontane-1,35-diol (dodecaoxyethylene glycol, n_{12}).
The dodecaoxyethylene glycol was prepared from sodium (23 g.), redistilled triethylene glycol (600 g.), and αω-dichlorohexaoxyethylene glycol (159.5 g.) by the method described on the previous page for n_9. Short-path distillation gave 123 g. of product, m.p. 24°, n_D^{38} 1.4615. (Found: C, 52.6; H, 9.4; OH, 6.1; CH_2CH_2O, 96.5. $C_{24}H_{50}O_{13}$ requires C, 52.7; H, 9.2; OH, 6.2; CH_2CH_2O, 96.7%).

3,6,9,12,15,18,21,24,27-Nonaoxatritetracontan-1-ol (nonaoxyethylene glycol monohexadecyl ether, Hn_9).
Sodium (2.3 g.) was dissolved in the nonaoxyethylene glycol (166 g.) as before, hexadecyl bromide (30.7 g.) added, and the mixture stirred at 135° until neutral (1 hr.). After cooling it was extracted with ether (3 x 150 ml.), and the residue after evaporation of the ether re-extracted with warm dry light petroleum (b.p. 60-80°; 3 x 50 ml.). This procedure removed the unchanged glycol present in the original extract. The residue (21 g.) obtained on evaporation of the petroleum was recrystallised from ether, then from acetone.

This material (1.5 g.) was adsorbed from benzene on alumina (25 g.), and the column washed with 1 : 4 acetone-benzene until no further material was eluted (200 ml.). About 15% of the initial column load was removed in this step, the eluate being a water-insoluble fraction, possibly the dihexadecyl ether of the nonaoxyethylene glycol. Further elution with acetone-methanol-benzene (300 ml.; 25 : 1 : 24) gave the monohexadecyl ether (0.9 g.) which, recrystallised from ether, then from acetone had m.p. 43° (Found: C, 63.4; H, 10.9; OH, 2.7; CH_2CH_2O, 62.2. $C_{34}H_{70}O_{10}$ requires C, 63.9; H, 11.0; OH, 2.7; CH_2CH_2O, 62.1%).

3,6,9,12,15,18-Hexaoxatetratriacontan-1-ol (hexaoxyethylene glycol monohexadecyl ether, Hn_6).

Sodium (2.3 g.), hexaoxyethylene glycol (112 g.), and hexadecyl bromide (30.5 g.) gave, by the method described earlier for Hn_9, a product (18 g.) that, crystallised and chromatographed in the same way, had m.p. 37° (Found: C, 66.1; H, 11.5; CH_2CH_2O, 52.3. Calc. for $C_{28}H_{58}O_7$: C, 66.4; H, 11.5; CH_2CH_2O, 52.2%).

3,6,9,12,15,18,21-Heptaoxaheptatriacontan-1-ol (heptaoxyethylene glycol monohexadecyl ether, Hn_7).

Sodium (1.55 g.), heptaoxyethylene glycol (88 g.), and hexadecyl bromide (20.6 g.) gave, by the method described for Hn_9, a product (14 g.) that, crystallised and chromatographed in the same way, had m.p. 39°. (Found: C, 65.4; H, 11.3; CH_2CH_2O, 56.0. $C_{30}H_{62}O_8$ requires C, 65.4; H, 11.3; CH_2CH_2O, 55.9%).

3,6,9,12,15,18,21,24,27,30,33,36-Dodecaoxadopentacontan-1-ol (dodecaoxyethylene glycol monohexadecyl ether, Hn_{12}). Sodium (1.15 g.), dodecaoxyethylene glycol (110 g.), and hexadecyl bromide (15.35 g.) gave, by the method described for Hn_9, a product (11 g.) that, crystallised and chromatographed in the same way, had m.p. 45.5°. (Found: C, 62.1; H, 10.5; OH, 2.0; CH_2CH_2O, 68.6. $C_{40}H_{82}O_{13}$ requires C, 62.3; H, 10.7; OH, 2.2; CH_2CH_2O, 68.6%).

1-Chloro-3,6,9,12,15,18,21,24,27-nonaoxatritetracontane. The monohexadecyl ether of nonaoxyethylene glycol was prepared as described previously. This compound (10 g.) was heated under reflux with an excess of thionyl chloride (2.25 g.) for 4 hrs. The volatile by-products of the reaction and excess of thionyl chloride were removed by heating the mixture under reduced pressure, and then by distilling three 15 ml. portions of benzene from the residue. The final residue was dissolved in benzene (25 ml.) and washed with water (3 x 5 ml.). The washings were shaken with ether (10 ml.), and this ethereal layer was added to the benzene extract. After removal of the solvents, the residue (10 g.) was dried over phosphorus pentoxide. This material (5 g.) was adsorbed from benzene on to alumina (100 g.), and the column washed with 1 : 5 acetone-benzene until no further material was eluted (600 ml.). Evaporation of the eluate and recrystallisation of the residue from ether gave the chloro-derivative (4.55 g.), m.p. 39.5° (Found: C, 62.0; H, 10.7; Cl, 5.5. $C_{34}H_{69}ClO_9$ requires C, 62.1; H, 10.6; Cl, 5.4%).

3,6,9,12,15,18,21,24,27,30,33,36,39,42,45-Pentadecaoxaheneihexacontan-1-ol (pentadecaoxyethylene glycol monohexadecyl ether, Hn_{15}).

Sodium (0.46 g.) was dissolved in hexaoxyethylene glycol (22.6 g.) under a layer of light petroleum (b.p. 100-120°) at $\not> 90^\circ$, the above-mentioned chloride (13.1 g.) was added, and the mixture was stirred at 125° until neutral (3 hrs.) and extracted with ether and light petroleum. The residue from the extract was recrystallised twice from ether and twice from acetone. The substance (2 g.) was adsorbed from 1 : 20

acetone-benzene on to alumina (50 g.) and the column washed with 1 : 1 acetone-benzene (600 ml.). This removed 1.3 g. of the initial load. Elution with 1 : 12 : 12 methanol-acetone-benzene (300 ml.) and recrystallisation of the eluted material from acetone gave the ether, Hn_{15} (0.45 g.), m.p. 47° (Found: C, 60.9; H, 10.7; CH_2CH_2O, 73.1. $C_{46}H_{94}O_{16}$ requires C, 61.2; H, 10.5; CH_2CH_2O, 73.2%).

3,6,9,12,15,18,21,24,27,30,33,36,39,42,45,48,51,54,57, 60,63-Heneicosanoxanonaheptacontan-1-ol (heneicosanoxyethylene glycol monohexadecyl ether, Hn_{21}). Sodium (0.23 g.) was dissolved in dodecaoxyethylene glycol (22 g.), and the above-mentioned chloride (6.6 g.) was added. The mixture was heated, extracted, and chromatographed as for Hn_{15}. Here a better percentage of the initial column load was obtained as Hn_{21}, possibly because of better separation owing to the increased difference in chain length. The product had m.p. 49° (Found: C, 59.3; H, 10.2. CH_2CH_2O, 79.4. $C_{58}H_{128}O_{22}$ requires C, 59.6; H, 10.2; CH_2CH_2O, 79.2%).

C.P.G.E. 24.

The C.P.G.E. 24 used was a commercial sample of a polyoxyethylene glycol monoalkyl ether based on cetyl alcohol. Before use, the sample (5 g.), dissolved in methanol, was run down a 10" long by 1" diameter column of mixed anion and cation exchange resins (Biodeminrolit) which had been previously well extracted with methanol. The detergent was washed off with 200 mls. of methanol, the eluate concentrated, and the residue thoroughly dried in a vacuum oven over phosphorus pentoxide. A 0.5% solution of this material had the same conductance as distilled water ($\approx 1 \times 10^{-6}$ mho.), and the material, a mean molecular weight (ethylene oxide assay) of 1295 (theory; 1300).

Benzene, Toluene, and Carbon Tetrachloride.

"AnalaR" materials were used for light-scattering measurements. The solvents were dried and freshly distilled before use, having:-

n_D^{25}	Measured	Timmermans[256]
Benzene	1.4979	1.4981
Toluene	1.4940	1.4941
Carbon Tetrachloride	1.4604	1.4603

Ludox.

A fresh commercial sample was used.

Purity of Compounds.

Carbon and Hydrogen analysis are not particularly sensitive to traces of impurity, nor are acetyl values as only small quantities are available for the larger detergents, therefore, as a further test, a modification of Siggia[66] and Morgan's[65] hydriodic acid assay for the oxyethylene content of detergents was carried out on the synthesised compounds. This assay is quite sensitive to differences in ethylene oxide content[153] or the presence of glycol.[68]

The principle of the assay is the break-down of the ethylene oxide structure by refluxing a sample of the detergent with excess of hydriodic acid for 1½ hours at 135° in an inert atmosphere (CO_2). The suggested mechanism is illustrated by the following equations:[66]

$$-(CH_2CH_2O)_{\overline{n}} + 2n\ HI \longrightarrow n\ ICH_2CH_2I + n\ H_2O$$

$$\begin{tikzcd}
 & CH_3CH_2I + I_2 \\
ICH_2CH_2I \arrow[ur, "\text{excess HI}"] \arrow[dr] & \\
 & CH_2{=}CH_2 + I_2
\end{tikzcd}$$

As may be seen, no matter which route the 1,2-diiodoethane breaks down by, we are in effect obtaining two atoms of iodine for every ethylene oxide unit in the chain.

By addition of potassium iodide solution, after destruction is complete, and by running a blank assay, the amount of iodine released was obtained by titration with sodium thiosulphate. The assay was tested using compounds of known ethylene oxide content and conditions arranged until satisfactory results were obtained. Use of the assay on the synthesised compounds gave excellent agreement with theoretical results (See syntheses of compounds).

Despite precautions taken to try to ensure pure compounds and the fact that analyses performed indicated that the material was at least 99% pure, Ottewill et al.[45] when synthesising a similar series of compounds, still obtained small minima in the surface tension vs. log. concentration plots near the cmc. of some of their compounds; a factor often indicative of traces of impurity. This effect, as will be seen later, did not occur with the compounds just described nor could any trace be found, either in the glycols or the detergents, of the carbonyl peaks in infra-red spectra mentioned by other workers.[45]

Determination of Critical Micelle Concentration (cmc.).

The majority of the published methods for investigating the concentrations at which micelles are formed by non-ionic detergents depend on either solubilisation or interfacial tension measurements. A method based on the latter, having the advantage of not requiring the introduction of a third component into the system, and at the same time producing further information as to the properties in aqueous solution of the synthesised compounds, was employed in the determination of the cmcs. of the six surfactants.

With increasing detergent concentration, the surface tension at the air-water interface first fell rapidly, until, at a concentration characteristic of the given detergent, a sharp transition occurred; subsequent increase in the concentration of the solute caused little further effect on the surface tension. The concentration at which this transition took place was taken as the cmc.

As surface aging, particularly around and below the cmc. has been reported,[45,110,128] a method of determining surface tension was chosen which allowed a series of readings to be taken over a period of time

Figure 8.

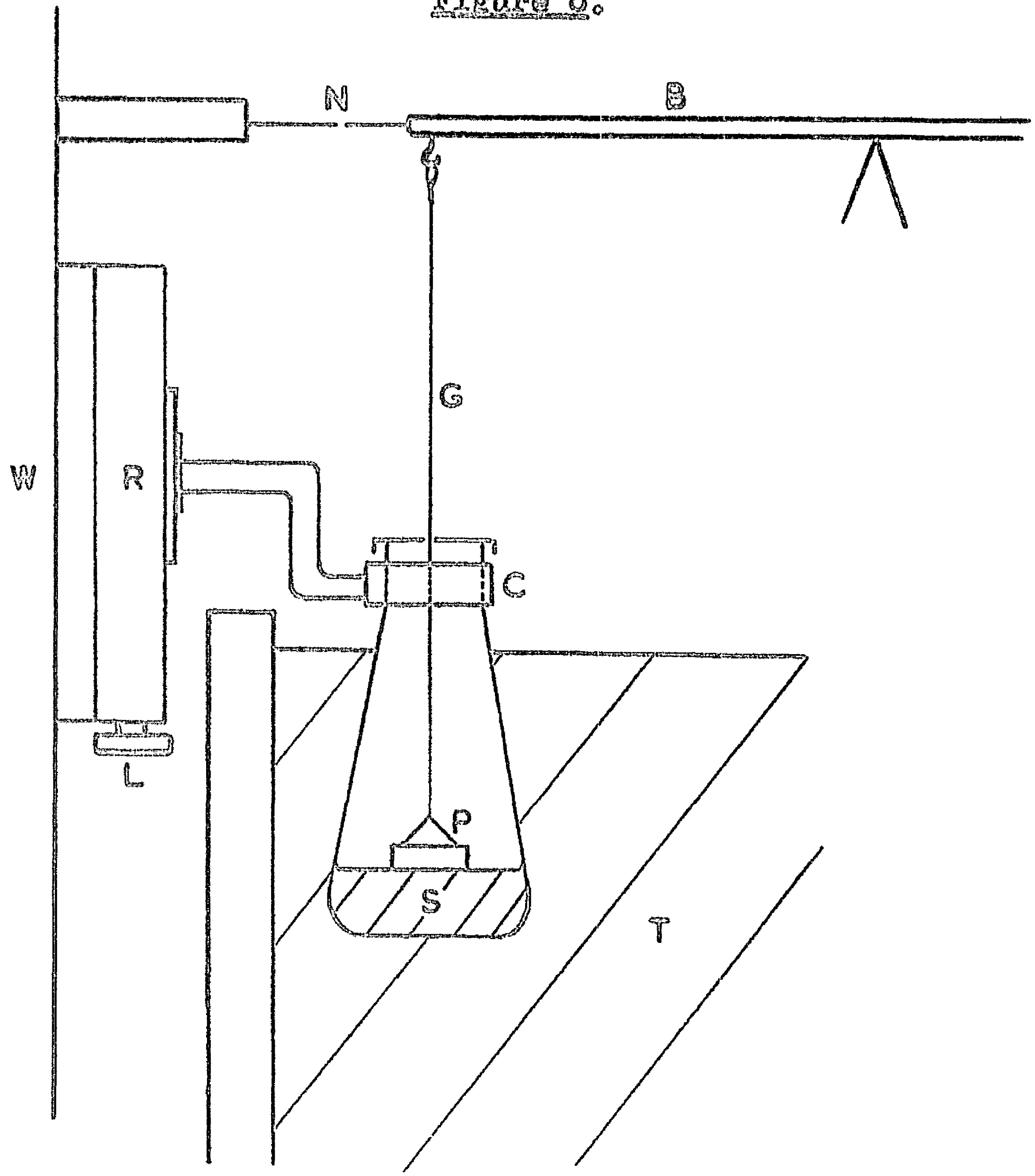


Diagram of Surface Tension Apparatus.

B - Balance	P - Platinum Plate
C - Clamp	R - Rack and Pinion
F - Flask	S - Solution
G - Gut	T - Thermostat
N - Levelling Needles	W - Wall

L - Flask Level Adjusting Screw

until equilibrium was reached, yet produced minimal disturbance of the interface.

Apparatus and Method.

Surface tension measurements were made using the Wilhelmy plate method as described by Harkins and Anderson.[257] A depolished platinum plate, perimeter, $l = 6.045$ cm., was suspended from the arm of a torsion balance, sensitivity ± 0.2 mg. The flask containing the solution was lifted by a rack and pinion device until the plate just touched the surface of the solution. The weight required to lift the plate from the interior of the liquid to this point in the surface was determined. To ensure zero contact angle, all measurements were made by lifting the plate in this manner. A saturated atmosphere was maintained above the solution. The apparatus is shown in figure 8.

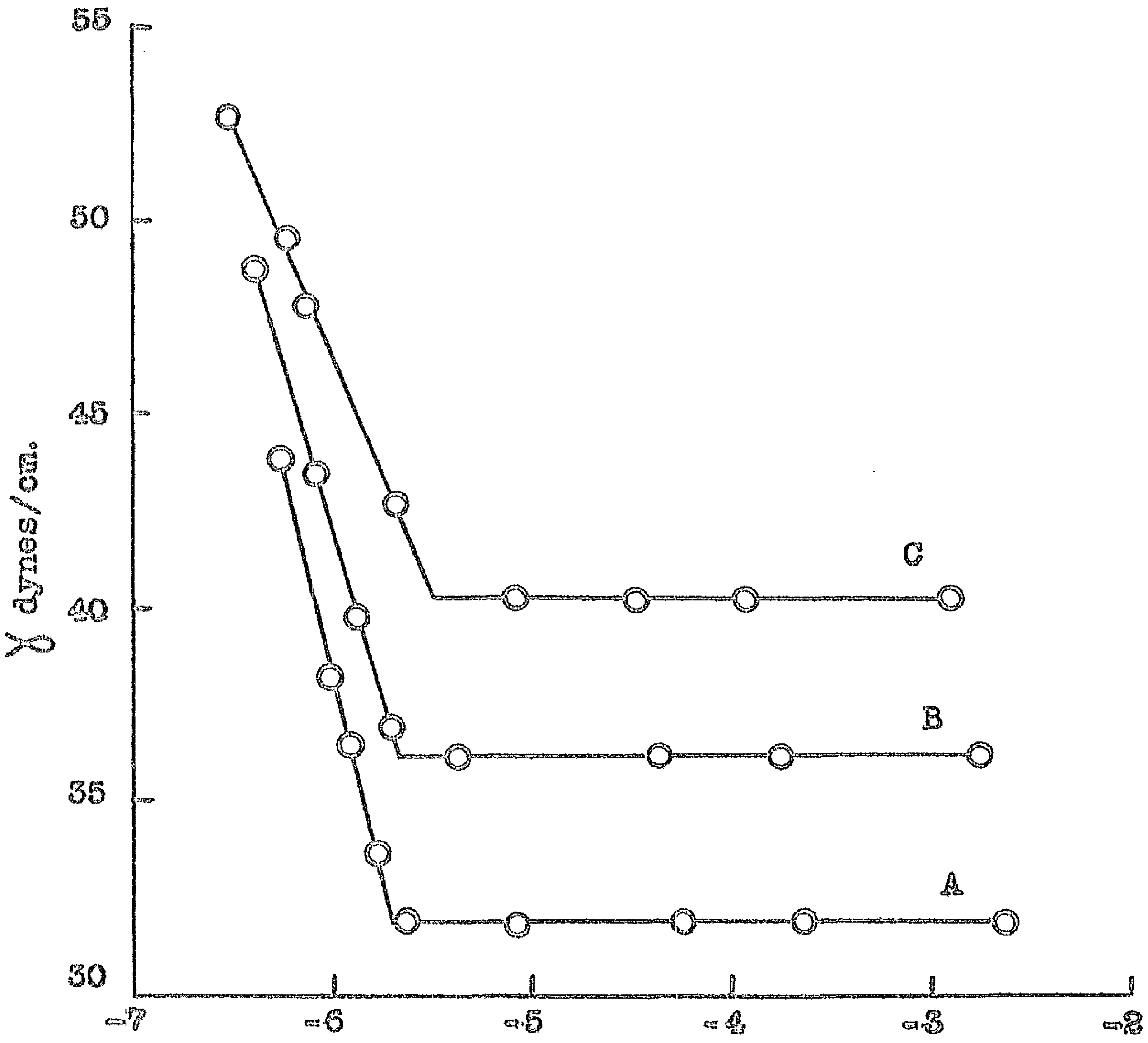
The difference between the weight of the plate in air and in the surface, W, is related to the surface tension, γ, by

$$\gamma = Wg/l$$

Measurements were made at $25 \pm 0.01^\circ$.

A check of the apparatus was carried out by measuring the surface tension of water;

Figure 9.



Log. conc. (moles/litre).

Surface Tension/log. Concentration Plots.

A = Hn_6 B = Hn_9 C = Hn_{15}

γ = 72.0, 72.1 dynes cm.$^{-1}$ (Harkins[258] gives 72.0 dynes cm.$^{-1}$) and methanol, 22.3 dynes cm.$^{-1}$ (Timmermans[256] gives 22.2 dynes cm.$^{-1}$).

All glass ware and the plate were cleaned between measurements with chromic acid, followed by thorough rinsing in distilled water.

As the critical micellar concentrations were very small, very dilute solutions had to be handled with the consequent risk of appreciable adsorption of detergents from solution. To compensate for this a method similar to that described by Pethica[259] was followed: all flasks containing solutions were set aside for three hours, the flasks thoroughly drained, and fresh solutions made up in the same flasks.

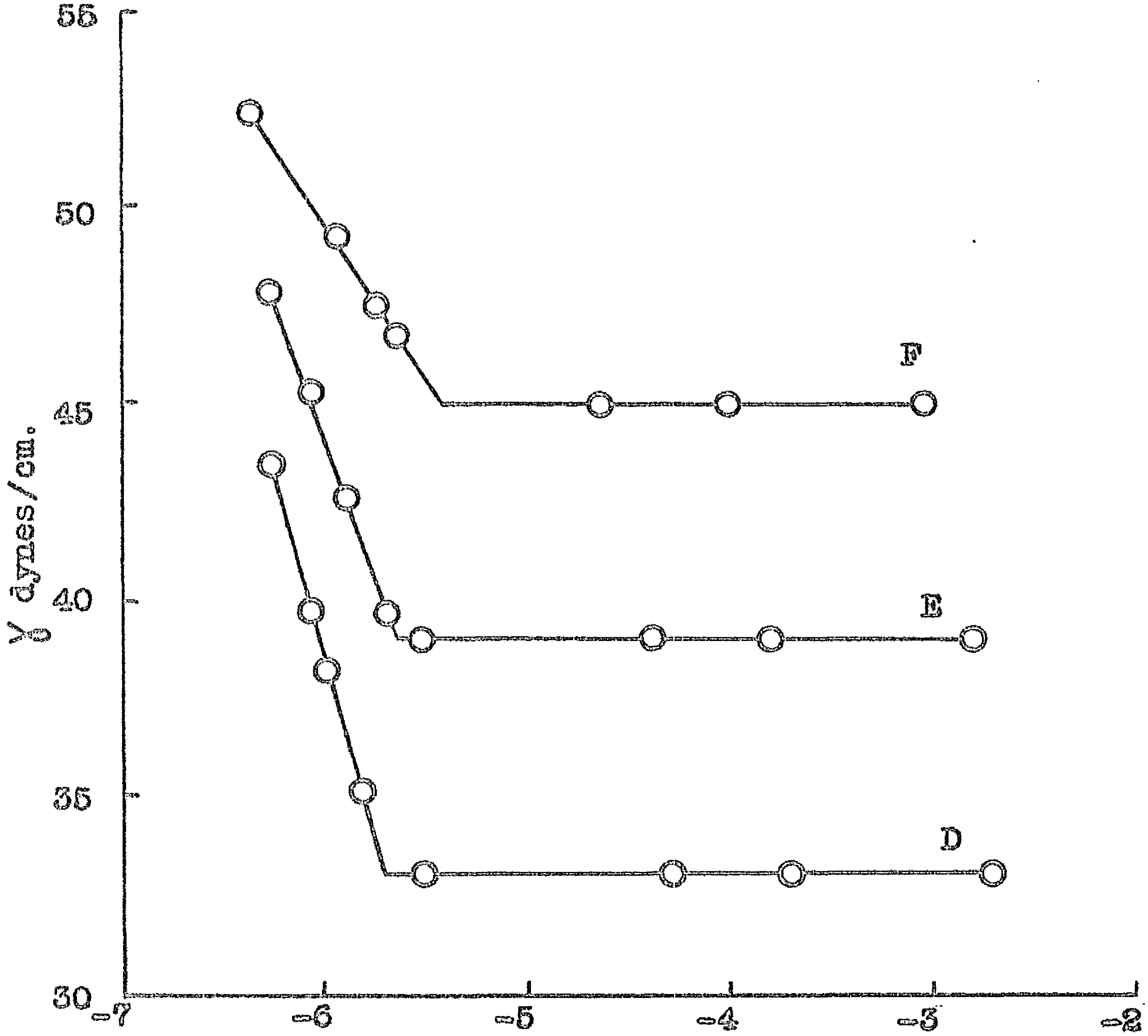
Results.

Aging effects were noted for all but the most concentrated solutions studied; for a 9.59 x 10^{-7} mole/litre solution of Hn_6 the results were:

Time, hr.	0	1	2	3	4
γ, dynes/cm.	71.1	61.2	49.7	44.4	41.1
Time, hr.	5	7	9	10	26
γ, dynes/cm.	39.7	38.5	38.3	38.3	38.3

This effect would appear to be due to a slow

Figure 10.



Log. conc. (moles/litre).

Surface Tension/log. Concentration Plots.

D = Hn_7 E = Hn_{12} F = Hn_{21}

diffusion from the bulk to the surface together with the possibility that considerable orientation of the molecules had to take place in the surface layer before equilibrium was reached.

In figures 9. and 10. the surface tension of the detergents have been plotted against log. concentration (moles/litre) and from these graphs the cmcs. were determined (see table 2.). From these results it was seen that a lengthening of the polyoxyethylene chain, with the concomitant increase of the hydrophilic powers of the molecule, increased the cmc. and this effect could be represented by the equation:

$$\log.\ \text{cmc.} = -5.93 + 0.0245n$$

where n, is the number of ethylene oxide units in the detergent molecule.

The cmc. was thus more than doubled on adding fifteen ethylene oxide units to the molecule. This trend agreed with the findings of other workers on compounds of a similar nature.[125-132]

The value obtained for Hn_6 is near that given by Ottewill et al.[45] but comparison of the cmc. obtained for Hn_{21} with those published for cetomacrogol, a commercial product with $n = 20$ to 24, showed the cmc.

Table 2.

Detergent	10^6cmc.	γ	Area/ molecule	Area/ CH_2CH_2O
Hn_6	1.6_6	31.9	38	6.3
Hn_7	1.7_4	33.2	44	6.3
Hn_9	2.0_9	36.2	53	5.9
Hn_{12}	2.3_4	39.2	72	6.0
Hn_{15}	3.0_9	40.3	81	5.4
Hn_{21}	3.8_9	45.0	120	5.7

γ is the surface tension above the cmc.; cmc's are in moles/l.; and areas in Å^2.

of the latter[123,260] to be much higher than the synthesised material (cetomacrogol 8 to 50 x 10^{-6} moles/litre). This difference may be due to the polydisperse nature of the commercial product.

Area per Molecule.

Having measured the surface tension as a function of concentration (figures 9. and 10.) it was also possible to obtain the surface excess and hence the area per molecule adsorbed at the interface by application of a simplified form of the Gibbs equation.

In dilute solutions of non-electrolyte colloidal substances this equation may be reduced to[261]

$$\Gamma = -\frac{1}{RT}\,\frac{d\,\gamma}{d\,\ln . a} \qquad (1)$$

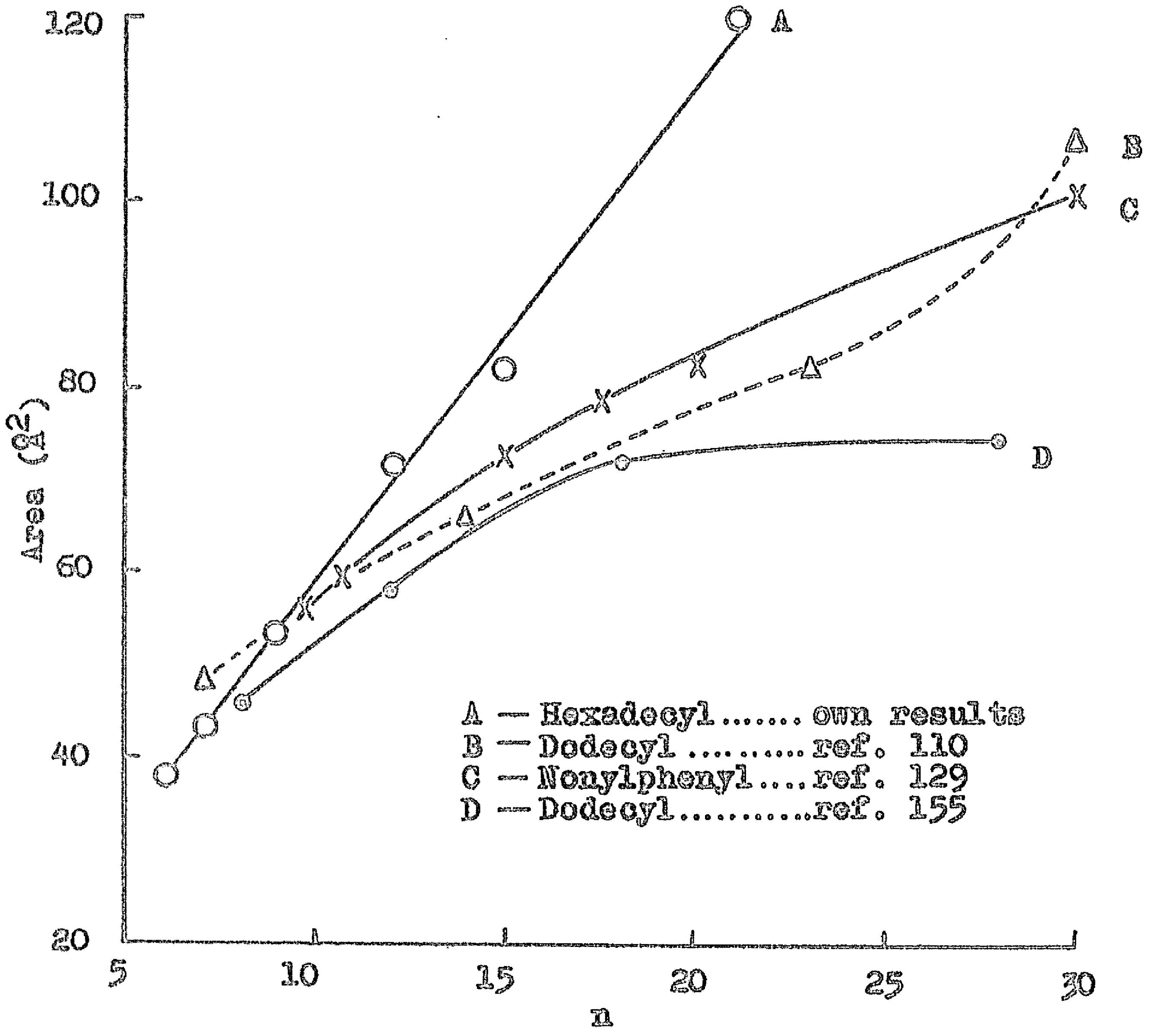
where Γ, is the surface excess of the solute ; and a, is its activity.

Moreover for solutions of unionised surface active compounds such as were being investigated, it was sufficiently accurate to replace activities by concentrations so that equation 1. then became

$$\Gamma = -\frac{1}{2.303RT}\,\frac{d\,\gamma}{d\,\log . c} \qquad (2)$$

By measuring the gradients of the plots of γ against log.c just below the cmc., values for

Figure 11.



Plots of Surface Area per molecule against the no. of ethylene oxide units in the molecule for various non-ionic detergents.

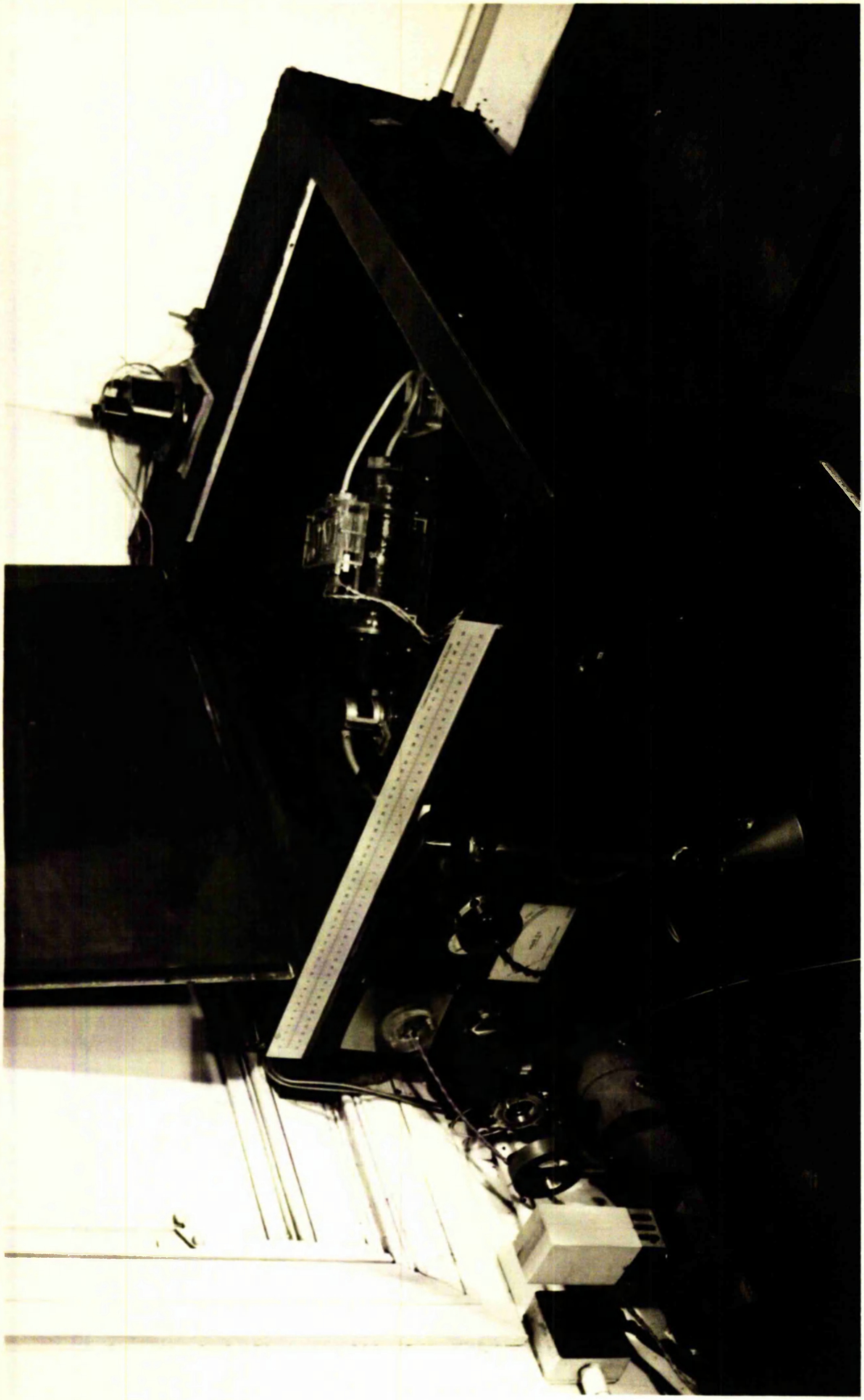
$d\gamma/d \log_e c$ were obtained for each system. The surface excess was calculated from equation 2. and hence the area/molecule determined.

Discussion.

As the areas/molecule (table 2.) were all larger than the cross-sectional area of the hydrocarbon chain (20.5 Å^2) and as the area/molecule increased with increase of the ethylene oxide content, it appeared the polyoxyethylene chain was the determining factor in the packing at the interface. It was also shown from the parts of the graphs parallel to the concentration axes in figures 9. and 10. that the compounds with the shorter ethylene oxide chains were more efficient in lowering the surface tension than the longer ones.

The areas/molecule measured gave reasonable agreement with other published results (figure 11.) particularly for the shorter compounds but tended to be larger for the compounds with longer oxyethylene chains. It may be however that these upper results for the commercial materials are affected by the selective adsorption of shorter length molecules into the interface; these smaller compounds exerting a greater influence on the calculated area/molecule as the mean ethylene oxide content increased.

The actual arrangement of the oxyethylene chains at the interface is a matter for conjecture. Comparison of the measured areas with the dimensions of the fully extended chains suggested the hydrophilic parts may well have been in a curled up form analagous to that suggested by measurements on micelles (see final section), further the areas/ethylene oxide unit, (see table 2) showed a tendency to decrease as the chain length was increased. One end of the glycol chain would be anchored in the surface by the presence of the hydrocarbon moiety while the other, being less strongly adsorbed, may have found it possible to tend away from the surface giving this effect on the area.



Description of the Light-Scattering Photometer.

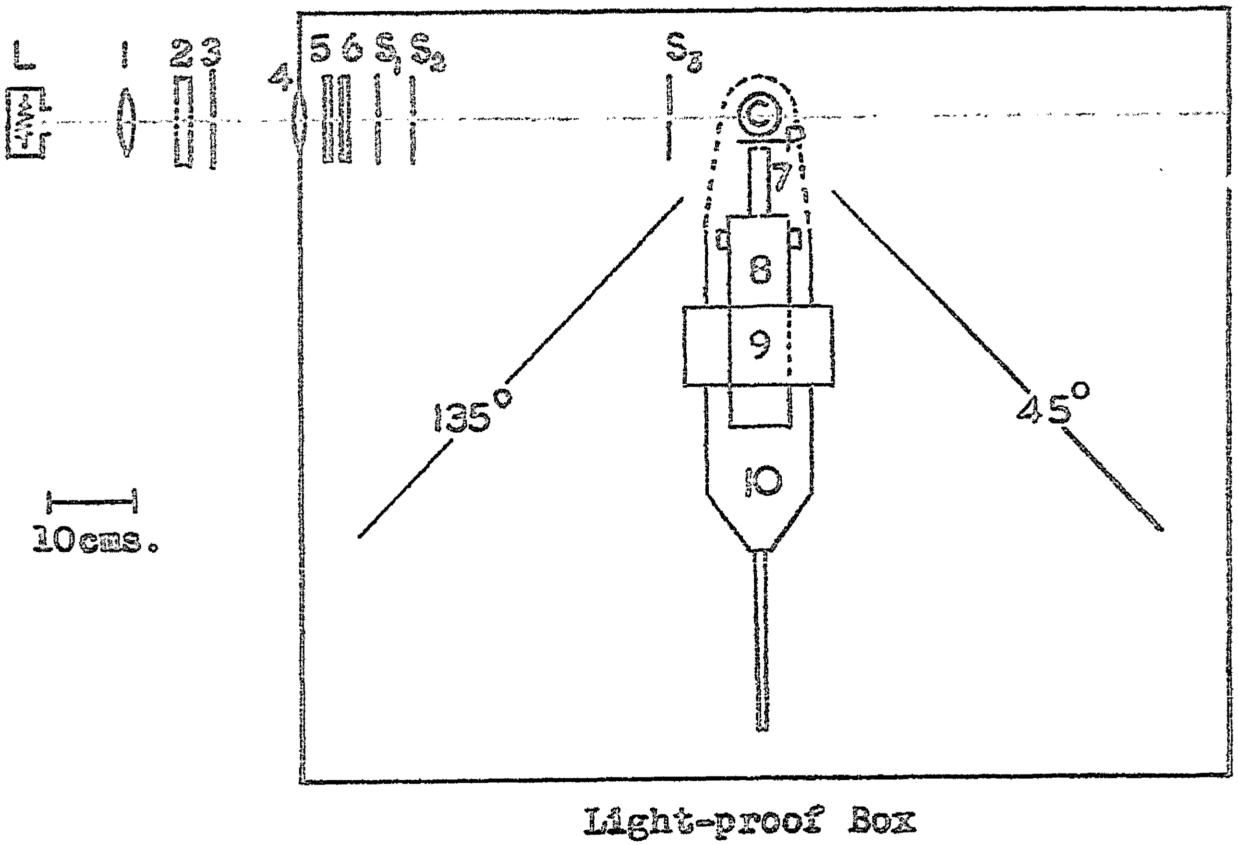
A light-scattering photometer has been constructed on a similar basis to previously described models,[262,263] but incorporating a considerable number of modifications in its design.

The three main factors which had to be considered in assembling an apparatus of this type were: the production of a suitable, collimated beam of incident light, the design of a cell to contain the liquid under examination, and a method of measuring the amount of light scattered over a range of angles to the incident beam. Although there must obviously be some overlap between such headings, the description of the apparatus has been arranged to follow a similar pattern to illustrate how the various difficulties encountered in each section have been met.

The Incident Beam.

Normally, scattered light was of very low intensity thus a powerful light source of the correct wavelength was necessary; mercury vapour lamps, giving much of their output concentrated in the green, yellow, and blue lines have been considered the most suitable. By

Figure 12.

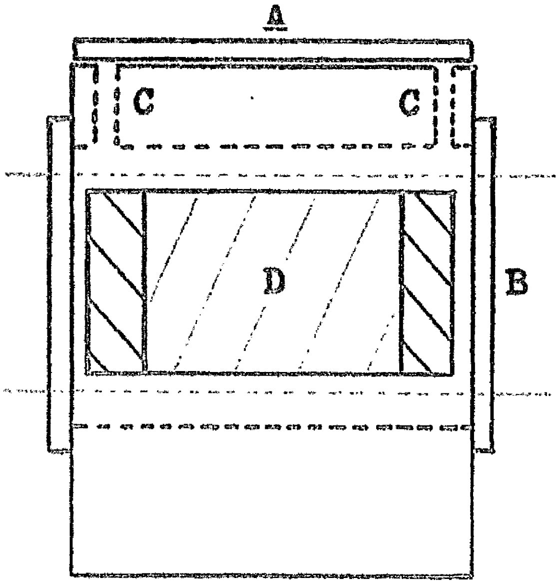


1.	Condenser Lens
2.	Shutter
3.	Slit
4.	Collimating Lens
5.	Interference Filter
6.	Neodynium Glass Filter
7.	P.M. Slit Holder
8.	Photomultiplier
9.	Resistance Chain
10.	Tufnol Arm
C.	Cell
L.	Mercury Vapour Lamp
P.	Polaroid Filter
S.	Slits

Diagram of Planar View of Light-Scattering Photometer using a lamp of this type (Osram, 250W. ME/D. compact source mercury vapour lamp) and passing its emission through the lens and slit system illustrated (figure 12.), a parallel beam of light of known dimensions (transverse section 2 mm x 25 mm) was obtained. The required wavelength (green line, 5461 Å) was isolated by introducing an interference filter (Barr and Stroud) into the optical system immediately after the collimating lens; this position giving maximum protection to the filter from deleterious effects of heat from the lamp. Any residual traces of yellow light were removed by a neodymium-glass filter, mounted immediately after the interference filter.

As the consistency of the intensity of a narrow beam of light of the type produced is very susceptible to any fluctuations in the light source, a voltage stabilising unit was incorporated in the lamp circuit (Advance, 250W). Further, in addition to measuring scattered light, simultaneous measurement of the incident light by deflection of part of the beam into a photocell (E.M.I.,type 25110) could be used to produce a compensatory circuit which helped to balance out variations in beam intensity.

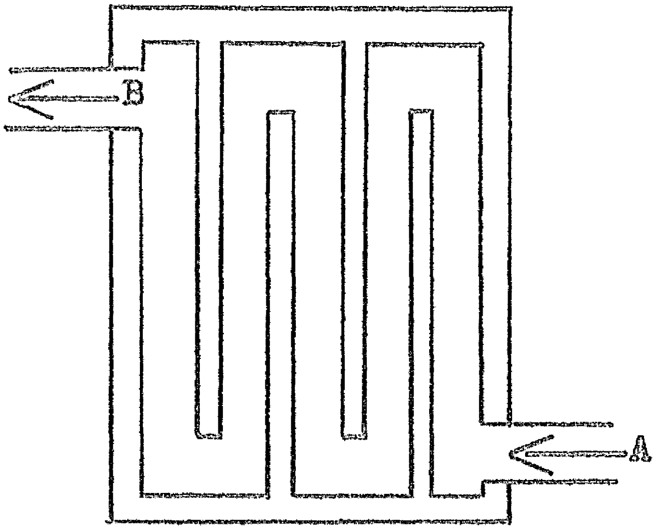
Figure 13.



A	Lid
B	Side Windows
C	Air Outlet Channels
D	Viewing Window

Light-scattering Cell : Front View.

Figure 15.



A	Water Inlet
B	Water Outlet

Light-scattering Cell : Thermostating Channels

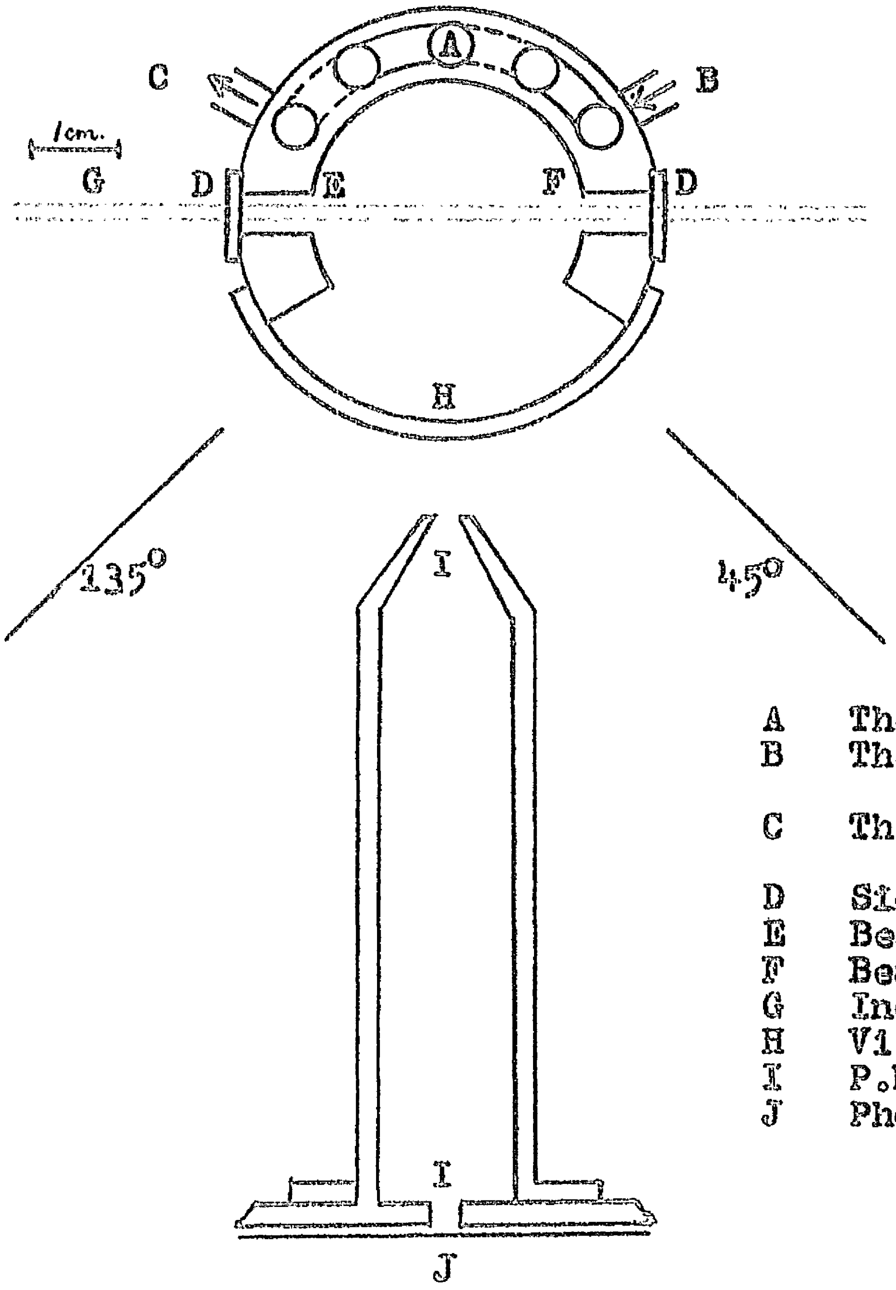
The Cell.

A cell similar to that mentioned by Elworthy and MacIntosh[264] has been used. Cylindrical in shape, (figure 13.) except for two, parallel, diametrically opposite, flattened faces, (to accomodate the windows of the incident beam entrance and exit slits) the cell was constructed of brass, blackened by the Relonol process. The curved observation window was made from a cylinder of glass of a suitable radius to allow it to be fitted concentrically to the cell. Araldite resin, cured at 37° to minimise strains and cracking of the glass from differences in coefficients of expansion, was employed as the adhesive for the windows.

As may be seen from figure 14. the cell has been designed to allow scattering envelopes to be measured between 45° and 135° to the incident beam. The channel surrounding the exit and entry ports of the beam in and out of the cell, prevented stray light from the points of entry and exit being viewed through the curved window. The significance of this is discussed later.

Thermostatic control of the liquid in the cell was achieved by circulation of water through the pipe system (figure 15.) between the inner and outer faces of the back wall of the cell.

Figure 14.



A	Thermostating Channels.
B	Thermostating Water Inlet
C	Thermostating Water Outlet
D	Side Windows
E	Beam Entrance Channel
F	Beam Exit Channel
G	Incident Beam
H	Viewing Window
I	P.M. Viewing Slits
J	Photomultiplier Tube

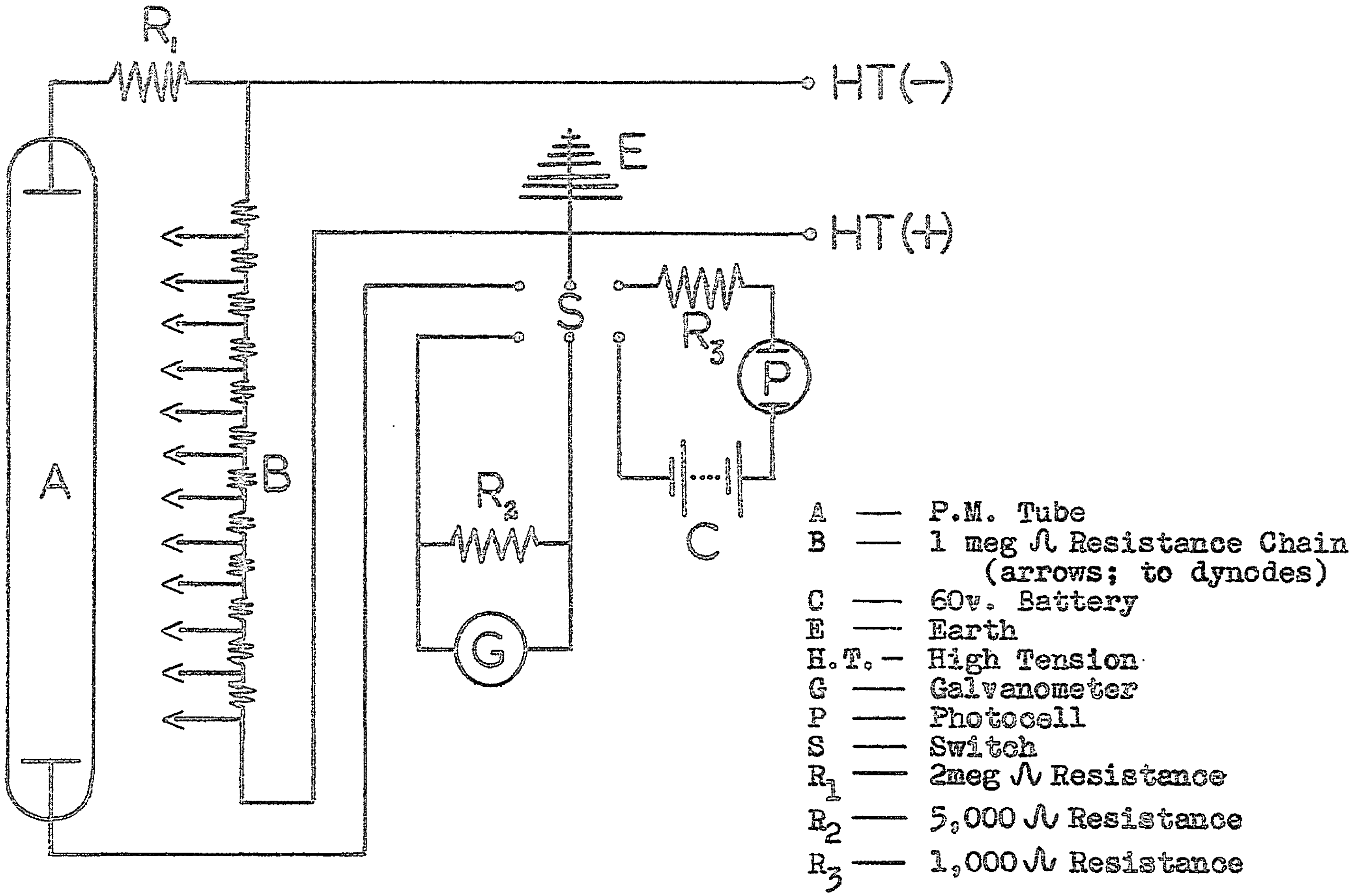
Light-Scattering Cell : Planar View.

For reproducibility and comparability of results it was important that the cell was replaced in exactly the same position for each set of readings. To ensure this a 7 mm. deep seating, into which the cell fitted neatly, was built into the apparatus. Final adjustments in alignment to the incident beam were made by rotating the cell in its seating until the reflections of the incident beam from the entrance and exit slit windows coincided with the final slit of the optical system (Slit 3, figure 12.). A slotted piece of perspex for maintaining the reference block in a constant position was incorporated into the cell seating.

Measurement of Scattered Light.

Scattered light was detected by an eleven stage photomultiplier tube (E.M.I., type 6097B) and the signal it produced measured on a Cambridge d'Arsonval galvanometer (type 41148/2, F.S.D. at 0.5 μ amp.).

The photomultiplier tube and its resistance chain were mounted on a tufnol arm, fixed to, and rotating round, a point immediately below the centre of the cell; allowing the detector unit to sweep round the viewing window at a constant distance from the centre of the cell. A system of two 3 mm. wide by 10 mm. high slits,



A — P.M. Tube
B — 1 meg Ω Resistance Chain
(arrows; to dynodes)
C — 60v. Battery
E — Earth
H.T. — High Tension
G — Galvanometer
P — Photocell
S — Switch
R_1 — 2meg Ω Resistance
R_2 — 5,000 Ω Resistance
R_3 — 1,000 Ω Resistance

Wiring Diagram - Light-Scattering Photometer.

set 8 cm. apart, mounted in front of the photomultiplier tube (see figure 14.) controlled the area of the beam seen by the photomultiplier.

The sensitivity or overall gain of a photomultiplier tube increases with the voltage across the dynodes. This gave a means of controlling the signal to the galvanometer to within the limits of the scale used, but increase in the voltage was accompanied by increased dark current and sensitivity to stray electromagnetic effects, and a general decreased stability within the tube itself. To combat this all electrical leads near the photomultiplier tube were of screened cable, the resistance chain encased in a plastic box, and the side walls of the photomultiplier tube were painted with conducting aluminium paint and brought to cathode potential. The tube itself was mounted in a metal cylinder and kept clear of the walls of this cylinder by layers of parafilm.

The voltage across the photomultiplier was controlled and stabilised by two Siemen-Ediswan Power Packs (type R1184) joined in series. These were capable of producing up to 2,200v. but in practice not more than 1,700v. were ever used as above this voltage the stability of the readings showed rapid deterioration.

Rapid response of the galvanometer to varying voltage pulses, with concomitant jumping of the galvanometer spot, was damped down by joining a 5,000 ohms. resistance in parallel with the galvanometer.

Stray Scattering.

Stray reflections and other sources of unwanted light form a very significant source of error in light-scattering measurements, particularly at low turbidities when the apparatus is working at full sensitivity. Their elimination was therefore paramount. Preliminary precautions such as enclosing the cell, photomultiplier, etc. in a light proof box, (see figure 12. and photograph) painting the box internally with matte black paint and erection of a light opaque shield between the photomultiplier and the incident beam, minimised the chance of any source of stray light from outside the cell.

The presence of dust, air bubbles, scratches, or marks on the glass at the air/glass, metal/liquid, or glass/liquid interfaces tend to cause pinpoints of light, stray scattering, and distortion of the beam. The matte black internal surface of the cell in itself reduced stray reflections, and air bubbles, trapped when filling the cell, could escape via the two small holes drilled in the roof of the cell beam channels (figure 13.). Moreover as previously mentioned, the design of the cell and scanning set-up was such that the photomultiplier, even at its widest angles, (45° and 135° to the incident beam) never saw the beam as it entered or left the cell.

Preparation of Materials for Light-Scattering.

The complete removal of extraneous matter from liquids used in light-scattering experiments is extremely important as traces of unwanted suspended particles can wreak havoc on results.

Organic solvents cleaned fairly easily but aqueous solutions, particularly of surface active compounds with their inherent suspending powers, were the most difficult. Various methods of cleaning solutions have been suggested, mostly based on centrifuging or filtering.[265-268] Both techniques were investigated and from an evaluation of ease of handling coupled with efficiency in cleaning, filtration through a seasoned, No.5, scintered glass disc in the form of a gas filter tube, using positive pressure of up to 8 cm., appeared the best. Criticism has been levelled at this technique on the grounds of adsorption of the solute onto the filter pad, but, as solution concentrations were determined interferometrically after scattering, such effects did not apply in the experiments reported.

Clarification and Cleaning Techniques.

Solvents.

Organic solvents were dried, carefully redistilled, and filtered twice through a No.5 scintered glass disc before examination.

Water, for making up solutions, was distilled three times from potassium permanganate solution via a standard Quickfit splash-head. Only freshly distilled water was used for making solutions.

A sample prepared in this way, and filtered three times through a No.5 disc, gave an R_{90} of 1.01×10^{-6} cm.$^{-1}$ (c.f. Goring and Napier,[269] 1.02×10^{-6} cm.$^{-1}$; and Fessenden and Stein,[270] 0.973×10^{-6} cm.$^{-1}$).

Solutes.

Before the final crystallisations, the ethereal solutions were filtered through a No.5 glass filter.

Solutions.

Solutions were clarified by passing them three times through a No.5 disc; final filtrates being collected directly into the scattering cell. Tests on dilute solutions of potassium chloride in water, prepared in this way, gave a Z_{45} of 1.03.

Cells.

Cells were scrubbed periodically with a detergent solution then washed out with copious volumes of water. Between each solution the cells were cleaned by blowing a stream of acetone vapour through the cell and rinsing with the condensed vapour.

Filters.

Filters were cleaned after every six solutions with potassium permanganate and sulphuric acid followed by acidified hydrogen peroxide, washed free of acid with redistilled water, and dried, either in an oven or by percolation of redistilled acetone and ether through the filter. The latter solvents being removed by sucking filtered air through the disc.

Measurement of dn/dc.

Accurate measurement of the change of refractive index between solution and solvent (dn/dc) was necessary as it appeared as a squared term in the light-scattering equation. A Hilger Interference Refractometer (type M154), thermostated to the appropriate temperature, ± 0.01°, was employed.

This apparatus is based on two intersecting light beams from the same source made to produce a set of interference bands in the plane of intersection. If a transparent substance of refractive index, n, is placed in the path of one beam and an equal length of another substance with a different refractive index, n_o, in the path of the other beam, there is a displacement of the interference bands. The interferometer provides a method of obtaining the difference in refractive index, $(n - n_o)$, by measuring the shift in position of the interference bands.

Water, used here as the reference liquid, was put into both compartments of the cell and, after temperature equilibration, the interference patterns (the reference pattern and that through the liquids) were aligned using white light to a position where the zero order bands were coincident. An interference filter was introduced into the optical system of the apparatus to isolate the green line before final adjustments to the alignment were made. A mean value of six scale readings was taken, r_1. Substitution of a solution, concentration, c g./ml., in one of the compartments displaced the upper pattern; realignment of the zero order bands, using the green line as before, gave the second scale reading, r_2. The scale was then screwed back to a position, r_3, where the bands coincided within one band width of r_1, and the number of bands displaced between r_2 and r_3 counted (a).

From $\frac{r_2 - r_3}{a}$, the mean band width, d, was calculated and hence the exact number of bands displaced by the solution, f, was obtained from:

$$f = \frac{r_3 - r_1}{d} + a$$

Repetition of this procedure at various concentrations, and plotting the number of bands displaced against concentration, gave a straight line. From this graph the number of bands displaced, f_1, at the concentration, c_1, could be determined and the specific refractive index increment was calculated from:

$$\frac{dn}{dc} = \frac{\lambda(f - f_1)}{l(c - c_1)}$$

where f, is the number of bands displaced at concentration, c g./ml.; and l, is the thickness of the cell.

Calibration of the Light-Scattering Photometer.

As values obtained from readings of the detector unit for scattered light were only relative to the conditions of a given experiment, calibration of the apparatus to a known standard was required. A polished perspex block was chosen as the secondary standard for experimental purposes. Being solid, it did not have the inherent disadvantages of a liquid standard, gave a scatter in a similar range to the majority of systems under investigation and, provided the block was kept clean and scratch free, gave a constant intensity of light scattered at 90° to the incident beam. Absolute values for scattering at other angles in the envelope were found by reference to the 90° scatter.

An absolute method of calibration, being preferable to a comparative one, Ludox, a colloidal suspension of small silica spheres, was used for determining the calibration constant: these measurements on Ludox being carried out jointly with D.S.McIntosh.[271]

Organic solvents of known turbidity were used to check the value obtained.

Experimental.

A fresh sample of Ludox was spun for twenty minutes at 54,000 g., the supernatant suspension decanted off and a series of solutions made from it. Each solution was, in turn, filtered through a No.5 scintered glass disc until dust free, and its optical density and the amount of light it scattered at 90° to the incident beam determined: the former in 4 cm. cells in an S.P.600 spectrophotometer, using the same wavelength as that for light-scattering, the latter with reference to the perspex block. Scattering envelopes and depolarization of the Ludox were also measured.

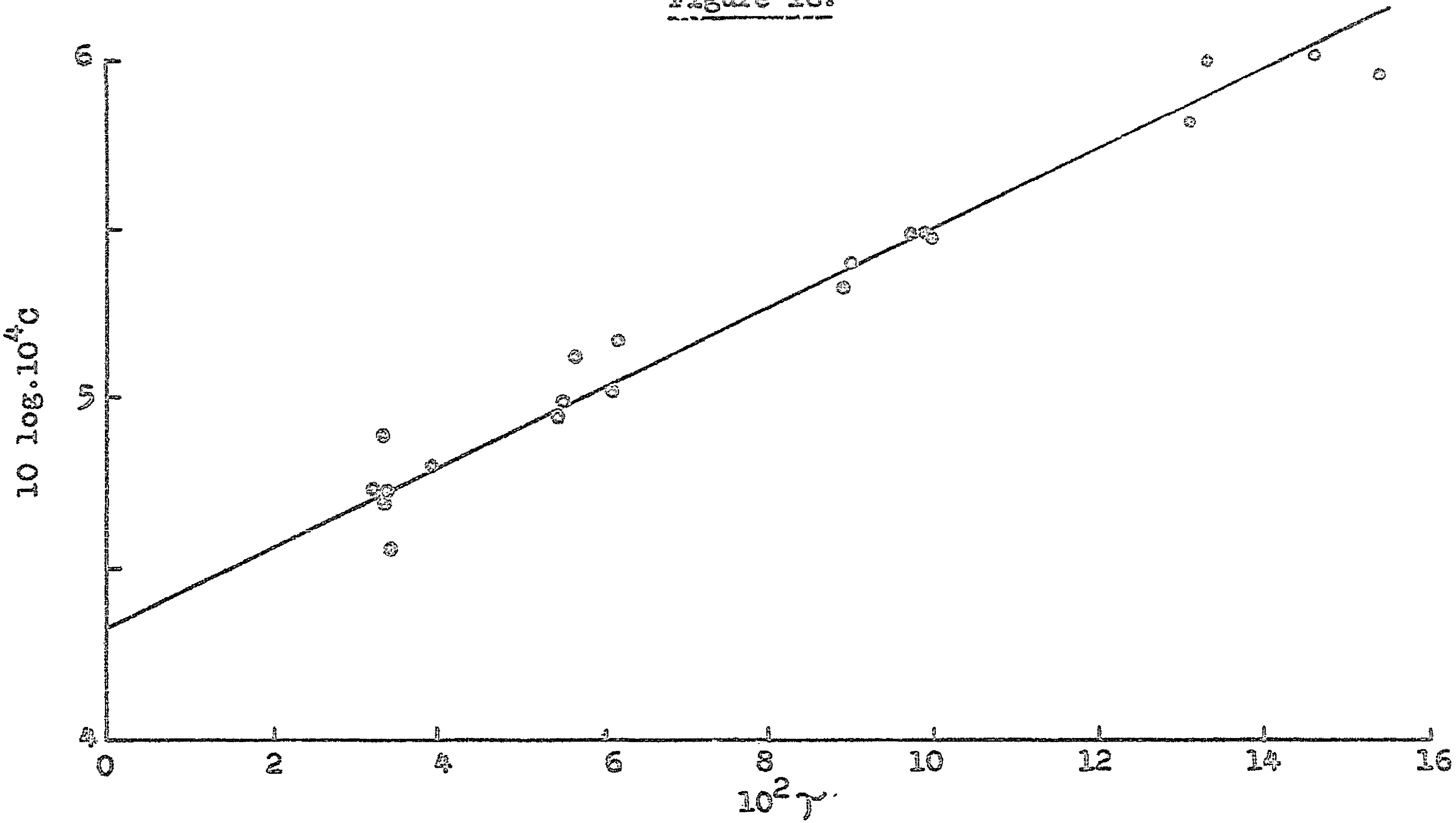
Values for C_D were then calculated for each solution from:

$$\tau = \frac{16\pi}{3} R_{90} = \frac{2.303\ D}{L} = C_D S_{90}$$

where C_D, is the value obtained for the calibration constant from a solution of Ludox of optical density, D; τ, is the turbidity of the solution; R_{90}, is Rayleigh's ratio; L, is the length of the optical density cell; and S_{90}, is the ratio of the light scattered by the solution at 90° to the incident beam to that scattered by the perspex block at the same angle.

Due to the high optical density of Ludox and other factors interfering with the light beam, as the concentration of Ludox increases, the S_{90} measured becomes

Figure 16.



Plot of Calibration Constant against Turbidity.

less than the true value, hence values of C_D obtained from the equation on the previous page increase with concentration (and optical density). Maron and Lou's[272] procedure of extrapolation to zero concentration to obtain the true calibration constant was therefore used (figure 16.): giving $C = 2.71 \times 10^{-4}$ cm.$^{-1}$ with a Z_{45} of 1.04 and a depolarization of 0.011.

Although Ludox is perhaps the most commonly used method of calibration the procedure did involve several practical difficulties. The Ludox had to be carefully handled, it tended to degenerate if not stored under the correct conditions, and left deposits on glass surfaces which had to be scrupulously cleaned to avoid affecting the results. A solution where the optical density was readily measured gave an excessively high scattering for accurate comparison with the perspex block, but optical densities, being a function of the path length through the solution, could only be increased by increasing the length of the cell. This however was limited by the apparatus used, 4 cm. cells being the longest available.

The light scattering problem was overcome by the use of a series of three standards, made of thin perspex, or of glass partly coated with aluminium paint, each giving a scatter some six times greater than the one lower in the series, and comparing the Ludox solutions with the most suitable standard. Comparison of the standards with each other gave conversion factors to the perspex block, which, on analysis of some twenty results, showed limits of error of only ± 0.2% (P = 0.95): a value giving a considerably smaller source of error than would have been produced by direct comparison of the perspex block with the more concentrated solutions.

Measurements of the turbidities of benzene, toluene, and carbon tetrachloride, cone angle corrected for interfacial refraction,[274-276] were used to check the calibration constant obtained from Ludox. The values from the solvents showed excellent agreement with the best literature figures.

	Measured		Published		
Solvent	τx10^5	ρ	τx10^5	ρ	Ref.
Benzene	27.2	0.41	27.4	0.40	262
Carbon Tetrachloride	9.6		9.4		273
Toluene	29.6	0.42	29.5	0.40	262

Measurement of Depolarization.

Depolarization was measured by inserting a polaroid filter between the photomultiplier tube and the curved window of the cell (see figure 14.) and determining the intensity of the vertical and horizontal components of the scattered light. The degree of depolarization was calculated from the ratio of these two quantities.

To obtain the depolarization due to micelles required further measurements as contributions of solvent and free monomers had to be removed. The horizontal (S_{Hc}) and vertical (S_{Vc}) components of the light scattered by a solution of a concentration, c, greater than c_1, were measured, this time with reference to the vertical component of the light scattered by the standard perspex block (B_V). Similar measurements were made for a solution of concentration, c_1. Thus, by subtracting the latter values from the former, the depolarization ratio (ρ) due to micelles alone was obtained.

$$\frac{S_{Hc}}{B_V} - \frac{S_{Hc_1}}{B_V} = H \qquad \frac{S_{Vc}}{B_V} - \frac{S_{Vc_1}}{B_V} = V \qquad \rho = \frac{H}{V}$$

As unpolarized light was used in the incident beam the appropriate correction factor for the light-scattering equation was then calculated from Cabannes formula,[237] $\left(\frac{6 - 7\rho}{6 + 6\rho}\right)$

Errors in the Estimation of a Micellar Molecular Weight by Light-Scattering.

(Hn_9 at 25°)

In the determination of the micellar weight in a system such as has been studied, it appeared that the most probable sources of error in the value obtained, originated in the measurement of the concentration/turbidity ratio, $(c - c_1/\tau - \tau_1)$; the depolarization, ρ; the specific refractive index increment, dn/dc; the dissymmetry, Z; and the calibration constant, C.

Dissymmetries observed in the majority of systems investigated were slight, giving only a small correction to $H(c - c_1)/\tau - \tau_1$, hence the error in these measurements was not assessed. The other four factors have been considered.

All calculations were determined to 95% confidence limits and, in the analysis of measurements of detergent solutions, as the concentration of the detergent could be accurately determined, errors in the value of concentrations were assumed to be negligible.

Concentration/Turbidity Ratio.

Examination of graphs of $(c - c_1/\tau - \tau_1^{*})$ vs. $(c - c_1)$

* (τ calculated from the mean value of the calibration constant)

Table 3.

Depolarizations of Hn_9 Solutions.

$10^3(c-c_1)$, g. ml.$^{-1}$	ρ
1.101	0.015_2
1.790	0.006_4
1.905	0.023_1
2.187	0.051_2
2.351	0.010_8
2.617	0.012_5
2.777	0.026_9
2.995	0.017_2
3.165	0.005_2
3.178	0.011_0
3.285	0.022_2
3.860	0.020_2
3.895	0.012_4
4.595	0.017_0
6.384	0.086_0

of Hn_9 (see figure 18; facing page 131) showed a significant correlation between these two quantities, thus to assess the limits of error in the concentration/turbidity ratio estimate it was necessary to calculate the variance of both the mean value of $(c - c_1/\tau - \tau_1)$ and that of the slope of the graph. The calculation for this is given in Appendix 1.

This gave a value for the intercept on the ordinate $\left(\text{where } (c - c_1) = 0\right)$ of 3.506 with limits of error of $\pm$ 0.284 ($\pm$ 8.1%).

A figure similar to this ($\pm$ 7%) for the assessed error in c/τ for lysolecithin sols has been given by Robinson and Saunders.[279]

Depolarization.

The results obtained for this (table 3.) were tested for correlation between concentration and depolarization; the calculated correlation coefficient, r_c, came to 0.27, while the theoretical $r_t = 0.50$. No correlation exists between ρ and $(c - c_1)$.

The mean value of ρ was $0.016_7 \pm 0.004_8$.

Specific Refractive Index Increment.

Table 4.

Values of dn/dc for Hn_9 solutions.

$10^3(c - c_1)$.....	1.624	1.842	2.460	2.613	2.944
dn/dc*...........	0.1386	0.1341	0.1351	0.1340	0.1367
$10^3(c - c_1)$.....	3.884	4.398	4.852	5.425	6.384
dn/dc*...........	0.1350	0.1347	0.1344	0.1337	0.1366

where c is in $g.ml.^{-1}$; and dn/dc in $ml.g.^{-1}$

*(The refractive index at c_1 was subtracted from the refractive index of each solution in the calculation of dn/dc.)

A test on the above results (table 4.) showed no correlation between dn/dc and $(c - c_1)$: $r_c = -0.23$; $r_t = 0.63$.

The mean value of dn/dc was 0.1353 ± 0.0011 $ml.g.^{-1}$

Calibration Constant.

As both variables in the estimation of C are subject to error, the analysis was performed by dividing the results into three nonoverlapping groups and analysing as described by Davies.[280] The calculation is given in Appendix 2.

This gave the limits of error of C as ± $0.10 \times 10^{-4} cm.^{-1}$ or ± 3.8%.

Micellar Weight.

A summary of the errors and their influence on the components of the Debye equation is given in table 5.

Table 5.

	Mean Value.	Limits of Error.	% Error about mean.
$c - c_1/\tau - \tau_1$	3.506	± 0.284	± 8.1
ρ	0.0167	± 0.0048	± 28.7
Cabannes factor.	0.964	± 0.011	± 1.1
dn/dc	0.1353	± 0.0011	± 0.81
H	2.008×10^{-6}	$\pm 0.032 \times 10^{-6}$	± 1.6
C	2.71×10^{-4}	$\pm 0.1 \times 10^{-4}$	± 3.8

The observed dissymmetry, Z_{45}, for the Hn_9 was 1.03, giving, after consideration of the calculated limits of error, a value for the micellar weight of 140,000 ± 18,700 (± 13.4%).

This error was much larger than expected and the main part of it came from the measurement of the turbidity of the detergent solutions.

In spite of the great care taken in cleaning cells and filters, and in filtering solutions, traces of dust may have been responsible for this variation, but there was certainly not an excessive amount present as observed dissymmetries were close to unity. It is possible that the tendency of the detergent to suspend extraneous matter, and also its non-ionic character, could have been responsible for the variations in $(c - c_1)/(\tau - \tau_1)$; Stacey states that aqueous solutions containing salt are relatively easy to clarify,[283] and it may be that errors of this size are inherent in the study of this class of compound by light-scattering.

The calibration constant is the other large contributor to the error in the micellar weight and the limits of error for this could perhaps be reduced by a more precise determination of the optical densities using longer absorptiometer cells.

The Measurement of Viscosity.

Apparatus.

Viscosities of solutions relative to water were determined in a suspended level dilution viscometer (Polymer Consultants Ltd.) and in the case of Hn_6, a Couette apparatus[281,282] was used to check that Newtonian flow was obtained.

Estimation of Limits of Error of the Intercept $\eta_{sp}/\phi_{(\phi=0)}$.

The limits of error of the viscosity intercepts were calculated in a similar manner to that used for the error in $c - c_1/\tau - \tau_1{}_{(c - c_1 = 0)}$ for Hn_9. Again the errors in concentration, and consequently ϕ, were taken as negligible.

At 25° the limits of error for Hn_9 and longer compounds were around ± 3%, but shorter chain compounds, due to the greatly increased gradient of the plot η_{sp}/ϕ vs. ϕ, had a somewhat larger error (± 10%).

At 20°, Hn_7 showed a very slight increase of η_{sp}/ϕ with ϕ, hence results near zero concentration were difficult to obtain. The consequent long extrapolation raised the limits of error of this intercept to ± 18%.

Densities.

Densities of the ethers Hn_{15}, and Hn_{21}, were determined by the displacement of pure dry n-hexane; neither of these compounds being appreciably soluble in this. The shorter chain detergents on the other hand tend to dissolve to a larger extent in n-hexane, thus for compounds between Hn_6 and Hn_{12}, the densities of the respective glycols were measured and those of the detergents calculated from the molar volumes of the glycols, water, and cetyl alcohol.

No. of ethylene oxide units per molecule.	Density (g./ml.) 25°	
	Detergent	Glycol
6	0.971	1.124
7	0.982	1.125
9	1.001	1.128
12	1.037	1.133
15	1.078	
21	1.142	

Temperature.

With the exception of Hn_7, all measurements were made at 25°. Thermostating was to within ± 0.01°, other than the light-scattering measurements where the uncertainty was ± 0.1°.

Table 6.

Detergent	dn/dc*	$10^2\rho$	$10^{-5}M$	1	Z_{45}	$(\eta_{sp}/\phi)_\phi$	10^6cmc.	10^4c_1
Hn_6	0.135	1.3	12.3	2430	1.02	22.0	1.6_6	3.0
$Hn_7(20^\circ)$	0.135	1.2	1.3_7	249	1.00	2.8_6		3.6
$Hn_7(25^\circ)$	0.135	1.5	3.2_7	594	1.02	9.5_3	1.7_4	3.0
$Hn_7(30^\circ)$						29.4		
Hn_9	0.135	1.7	1.4_0	219	1.03	4.3_1	2.0_9	2.0
Hn_{12}	0.134	0.9	1.1_7	152	1.03	4.9_7	2.3_4	1.8
Hn_{15}						5.8_1	3.0_9	
Hn_{21}	0.135	1.9	0.82	70	1.03	7.8_1	3.8_9	†

* dn/dc in ml./g.; ρ = depolarization; M = molecular weight, corrected for depolarization and dissymmetry; 1 = number of monomers in the micelle; cmc. in moles/l.; c_1 in g./ml.; † no visible c_1, $c_1 \approx c_0$

Light-Scattering.

Results.

In the interpretation of the light-scattering of micelle forming solutes, where the micellar dimensions are $< \lambda/20$, the procedure generally adopted is to use Debye's equation:

$$\frac{H(c - c_0)}{\tau - \tau_0} = \frac{1}{M} + 2Bc$$

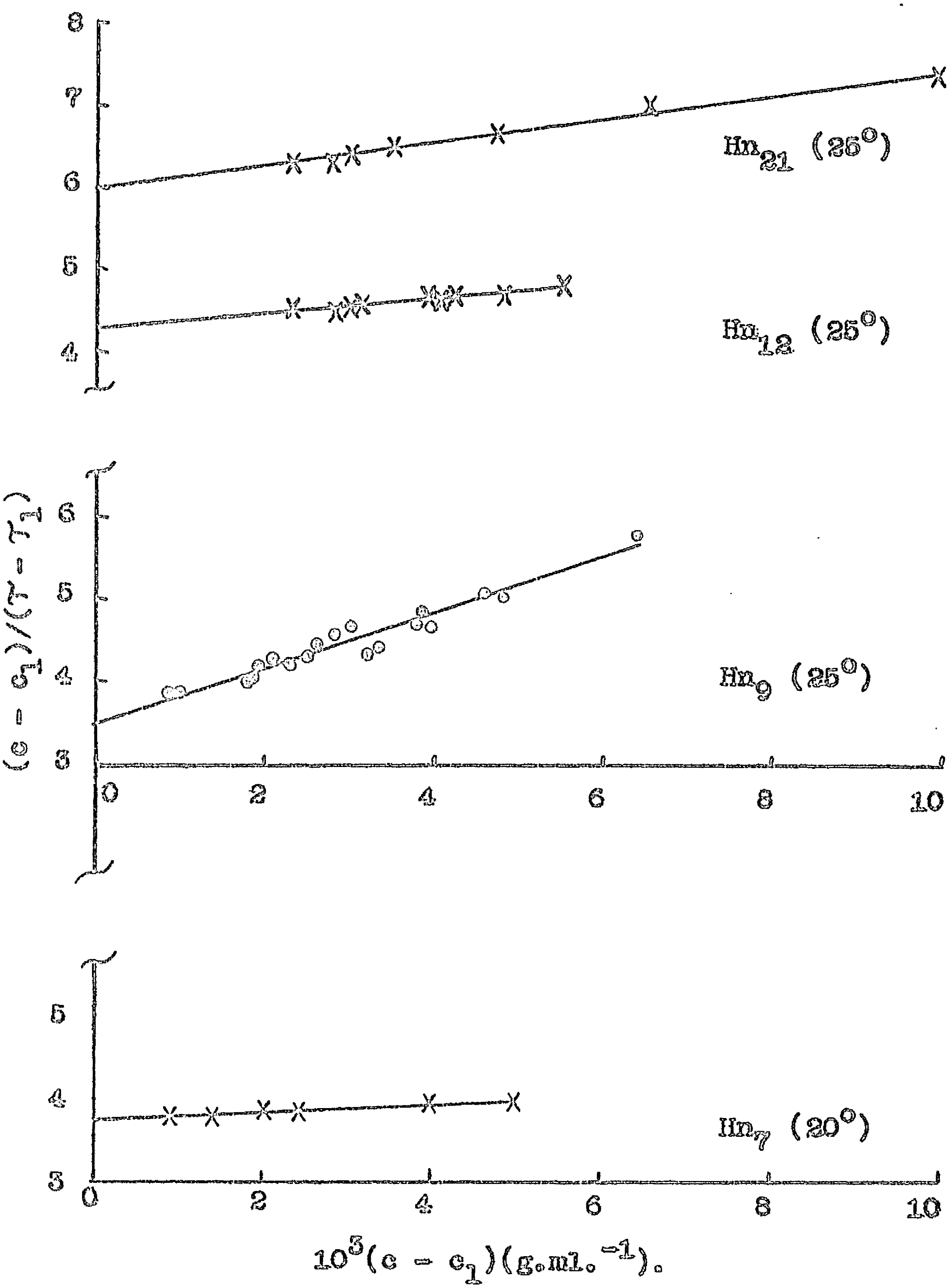
where τ, is the turbidity at concentration, c g./ml.; and τ_0, the turbidity at c_0, the cmc.

The measurement of the cmc. by a surface tension technique has been described, but the plots of $H(c - c_0)/\tau - \tau_0$ vs. $(c - c_0)$, where c_0, is the cmc. from surface tension showed a slight upswing of the line at low concentrations, particularly as the oxyethylene chain length of the detergent was decreased.

Examination of $\tau - \tau_0$ vs. $c - c_0$ graphs for Hn_9 and Hn_{12} showed that the plot was linear over the concentrations studied but the intercept of the concentration axis was not through the origin but at a value several times greater than c_0. This larger concentration has been designated, c_1.

For Hn_9, Hn_{12}, and Hn_{21}, the turbidities around the

Figure 18.



Plot of $(c - c_1)(\tau - \tau_1)$ against $(c - c_1)$.

c_1 region were too small for any quantitative interpretation of this effect, and, as the observed dissymmetry (1.03) indicated that no dimensions of the micelles exceeded $\lambda/20$, the micellar weights were consequently calculated from:

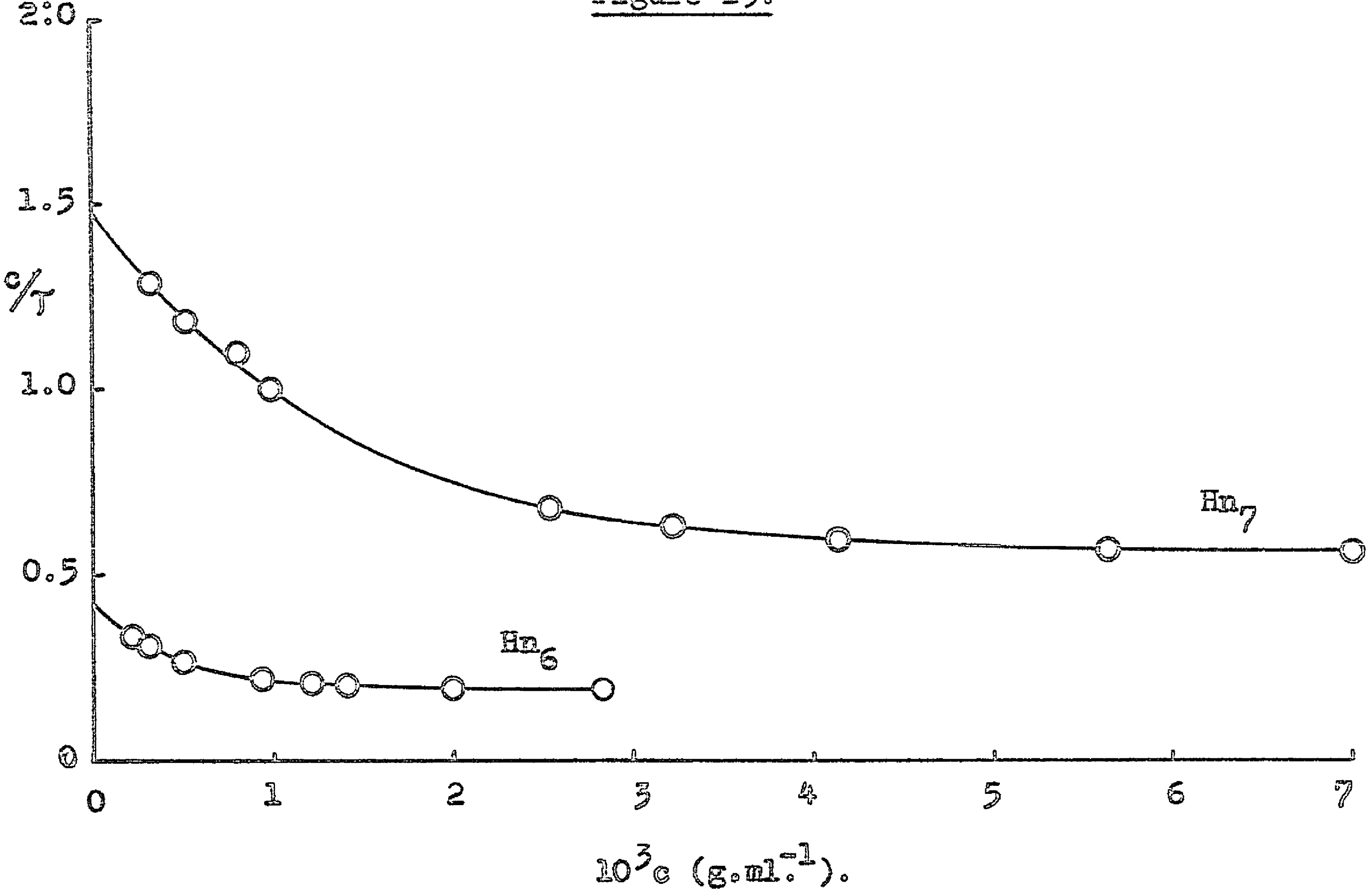
$$\mathcal{L}_{(c - c_1)\to 0} \frac{H(c - c_1)}{\tau - \tau_1} = \frac{1}{M} + 2B(c - c_1) \qquad \text{(A)}$$

with the intercept $H(c - c_1)/\tau - \tau_1$ corrected for depolarization and the particle scattering factor (obtained from the mean Z_{45}).

The results for these compounds are shown as plots of $c - c_1/\tau - \tau_1$ vs. $c - c_1$ (figure 18.) and in table 6.

The two smallest compounds, Hn_6, and Hn_7, behaved somewhat differently to Hn_9 and above; plots of $c - c_0/\tau - \tau_0$ vs. $c - c_0$ (figure 19.) showed a considerable upswing of the line at lower concentrations. The position of the intercept $c - c_0/\tau - \tau_0$ was fixed by making a large scale c vs. τ plot, which must pass through τ_0 at c_0, and interpolating values of the two quantities at very low concentrations, converting them to $c - c_0/\tau - \tau_0$, and plotting on the graph of $c - c_0/\tau - \tau_0$ vs. $c - c_0$; this procedure gave a reasonably accurate measure of the intercept. Solutions of Hn_6 and Hn_7 also developed appreciable Z_{45} values at higher concentrations, (figure 20)

Figure 19.



Plot of c/τ against c for Hn$_6$ and Hn$_7$ at 25°.

indicating that some dimension of the micelle had become larger than $\lambda/20$. The micellar weights for Hn_6 and Hn_7, given in table 6 are those obtained by extrapolation of the light-scattering results to the critical micellar concentrations, but the fall in the $c - c_0/\tau - \tau_0$ figures, and the development of Z_{45} values represent an aggregation of these units into larger ones as the concentration increases. The amount of light scattered by these systems over this range ($c_0 \rightarrow c_1$) was however sufficiently large to give a measure of the micellar sizes.

An attempt to analyse these results for the two shorter detergents has thus been made on the assumption that the mass-action law, without activity coefficients, applies to the aggregation:

$$\log . c_2 - m \log . c_1 = K \qquad \text{(B)}$$

where c_2, is the concentration of large micelles; and c_1 is that of small micelles; m, is the number of small micelles aggregating to give one large one; and K, is a constant. The fraction, x, of small micelles aggregated will equal $c_2/c_1 + c_2$.

A solution of small micelles will have a turbidity, $\tau_1 = HM_1c_1$, while for a solution of large micelles, $\tau_2 = HM_2c_2P(\theta)$, where $P(\theta)$ is the particle scattering

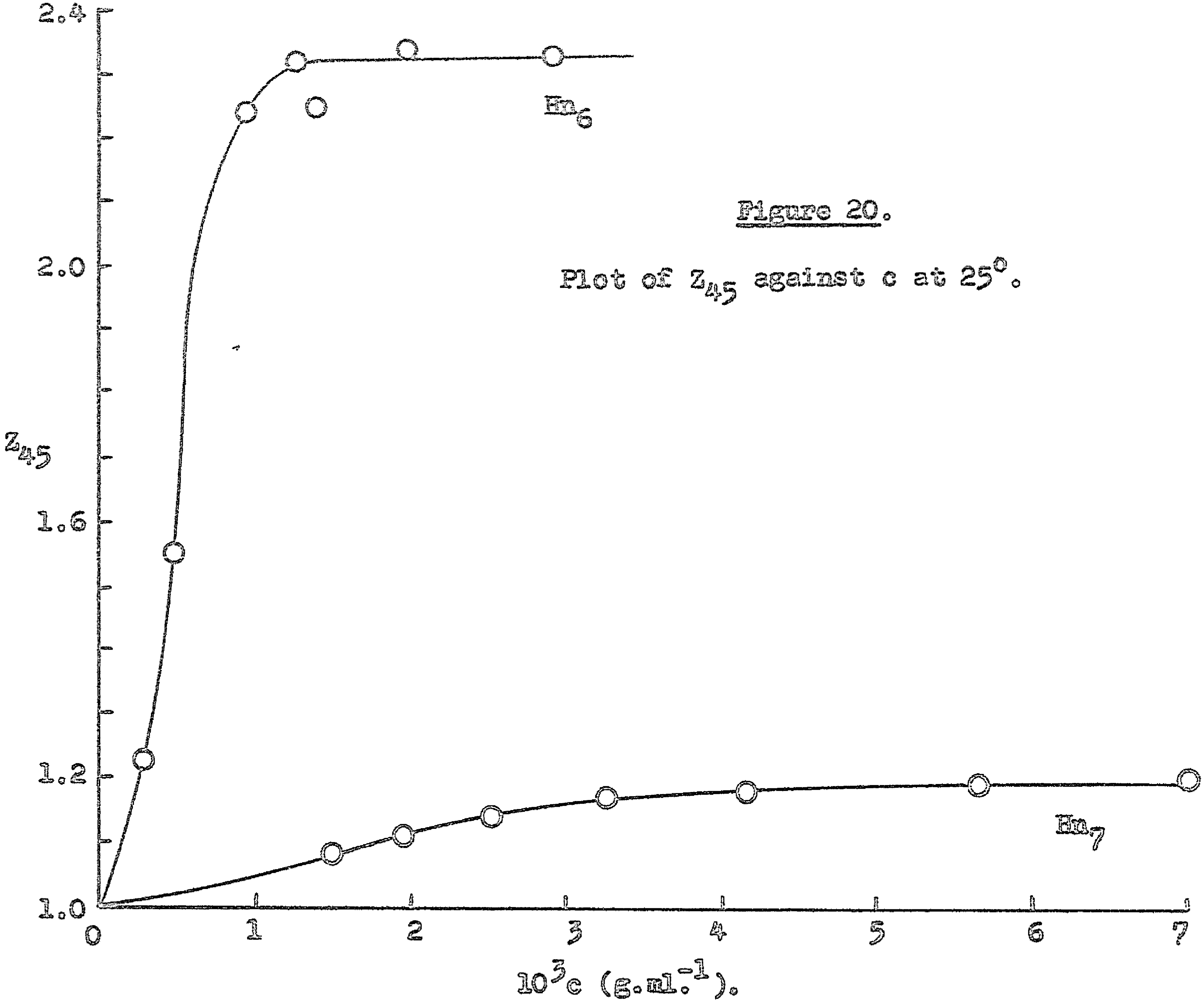


Figure 20.

Plot of Z_{45} against c at 25°.

factor; and M_1 and M_2, the micellar weights of the small and large micelles respectively. The Z_{45} values for small micelles were so close to unity that $P(\Theta)$ has been neglected in the expression for τ_1. The same optical constant, H, was used for both species (i.e. that determined experimentally) as the concentrations where small micelles exist in solution were too minute for dn/dc to be measured accurately. M_1 is that obtained from extrapolation of the light-scattering results to c_o. The excess turbidity of a solution of concentration, $c_t = (c_1 + c_2)$, is $\tau_t = \tau_1 + \tau_2$. For the larger micelles, $P(\Theta)$ was obtained from the maximum Z_{45} values (shown in figure 20.).

Two models were explored, a rod, and a coil, and a successive approximation procedure used. A value of m having been chosen (the molecular weight of the aggregated species, M_2, was thus mM_1) suitable values of c_1 were substituted in equation B; K being chosen to give c_2 in the correct region. K and m were adjusted until the total calculated turbidity for a solution agreed as closely as possible with the experimental value when a c_t vs. τ_t (observed) plot was used for comparison.

For Hn_7 an equation of

$$\log. c_2 - 3.5 \log. c_1 = 7.45$$

Table 7.

Association of Small into Large Micelles, Hn_7 at 25°.

10^3c_1	10^3c_2	10^3c_t	x	$10^4\tau_t$ (obs)	$10^4\tau_t$ calc.	Z_{obs}	Z_{calc}
0.30	0.013	0.313	0.042	2.2	2.3	1.02	1.02
0.50	0.082	0.582	0.141	5.0	5.1	1.02	1.06
0.70	0.277	0.977	0.284	9.8	10.6	1.05	1.11
0.90	0.684	1.584	0.432	18.5	20.5	1.09	1.13
1.00	1.000	2.000	0.500	26.6	27.9	1.13	1.15
1.10	1.406	2.506	0.561	36.2	37.2	1.16	1.16
1.30	2.565	3.865	0.664	62.7	63.0	1.17	1.17
1.50	4.310	5.810	0.742	101.0	101.1	1.18	1.18
1.60	5.420	7.020	0.772	125.1	125.4	1.18	1.18
1.65	6.053	7.703	0.786	139.0	139.1	1.18	1.18

was obtained using this procedure, but, when the Z_{45} values were calculated for the flat portion of figure 20., a value of 1.15 instead of 1.18 was obtained. This error was due to the first approximation of taking all the light scattered at 45° and 135° to be due to the large micelles, whereas in fact, some of it is due to the small micelles. The whole procedure was repeated until, with a Z_{45} of 1.21 for the large micelles, a reasonable fit to the experimental Z_{45} and the c_t vs. τ_t curve was obtained; the final equation being:-

$$\log. c_2 - 3.6 \log. c_1 = 7.80 \qquad (C)$$

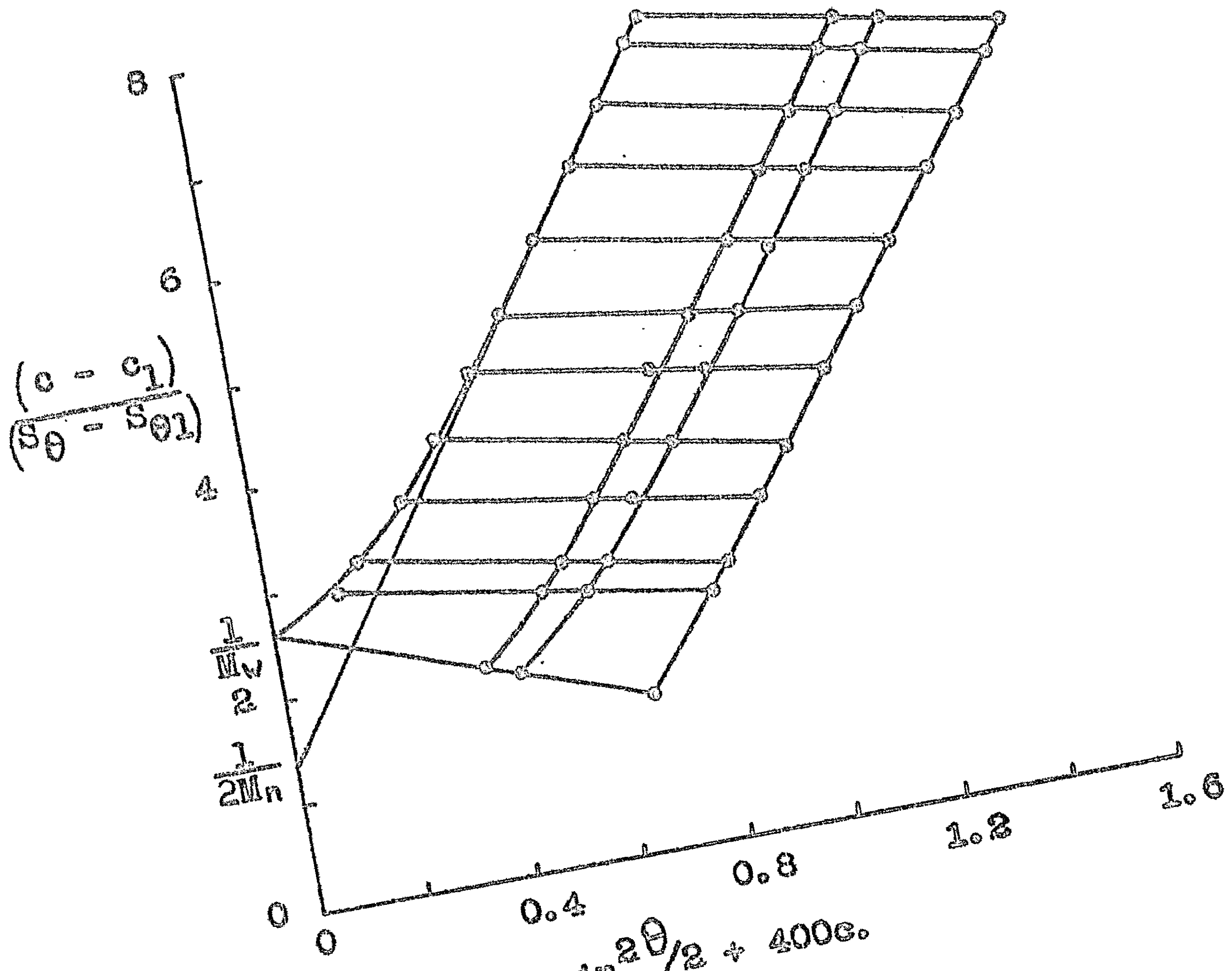
The final value for M_2 is thus 1.2×10^6.

Theoretical and calculated results are given in table 7, and, in view of the approximations of the treatment, e.g. neglect of c^2 terms and virial coefficients in calculating turbidities of the solutions, the aggreement between calculated and observed values is good.

As the $P(\theta)$ values for a rod and coil were almost identical for the theoretical Z_{45}, the fit applied for either model and no differentiation as to the most likely model could be made from these results.

For Hn_6 the analysis was much more difficult for the rod-like model. A small change in Z_{45} caused a large change in $P(\theta)$, and, as the precision of Z_{45} measurements

Figure 21.



Zimm Plot : Hn_6.

was about 1-2%, very large errors in $P(\theta)$ were liable to be obtained. The best fit to the experimental results, calculated in a similar manner to that outlined for Hn_7, was by the equation:

$$\log. c_2 - 18.7\ c_1 = 67.5$$

The length of a rod from the calculated Z_{45} value for the larger micellar species would be 12,000 Å with a micellar weight of 23×10^6. The extreme length of such a rod makes this model seem unlikely.

In order to decide which model was more realistic a crude Zimm plot was made. There is a reasonably sharp break in the c vs. τ plot of Hn_6 representing a critical micellar concentration, (c_1) between the large and small micelles (cf. c_1 for Hn_9 and above), and thus, in a manner analagous to that used for Hn_9 of subtracting the turbidity at this concentration from the total turbidity, and c_1 from the total concentration. By doing this at all angles, affords the information for a Zimm plot for Hn_6. (figure 21.). This procedure is a simplification as the mass-action law governing the aggregation allows c_1 and τ_1 to increase slightly above the critical concentration. The micellar size was so large that the asymptote to the $(Hc/\tau)_{c=0}$ line was obtained down to $\theta = 90^\circ$ giving an intercept of $1/2M_n$, but, for an equilibrium

Table 8.

Association of Small into Large Micelles, Hn_6 at 25°.

10^4c_1	10^4c_2	10^4c_t	x	$10^4\tau_t$ (obs)	$10^4\tau_t$ calc	Z_{obs}	Z_{calc}
2.0	0.68	2.68	0.255	8.9	9.0	1.20	1.44
2.7	3.16	5.86	0.539	24.9	25.0	1.94	1.94
3.0	5.41	8.41	0.643	38.6	38.0	2.20	2.07
3.2	7.52	10.72	0.702	51.2	50.5	2.27	2.14
3.5	11.88	15.38	0.772	77.1	77.3	2.30	2.22
3.7	15.77	19.47	0.810	99.9	99.8	2.30	2.26
4.0	23.48	27.48	0.854	145.0	147.0	2.30	2.30
4.1	26.63	30.73	0.867	163.4	163.0	2.30	2.31

system of this type, $M_n = M_w$, and a micellar weight much smaller than that found for the rod-like model was obtained: $M_n = 5.2 \times 10^6$. An attempt to plot $(Hc/\tau)_{c=0}$ against $\sin\theta/2$, as is required for equation **57** for a large rod, gave a curve which did not give an intercept on its Hc/τ axis.

The results for Hn_6 were then examined in greater detail for the coil model and a much better agreement between τ_t (observed) and τ_t (calculated) for the mass-action law fit was obtained (see table 8) by using the equation:-

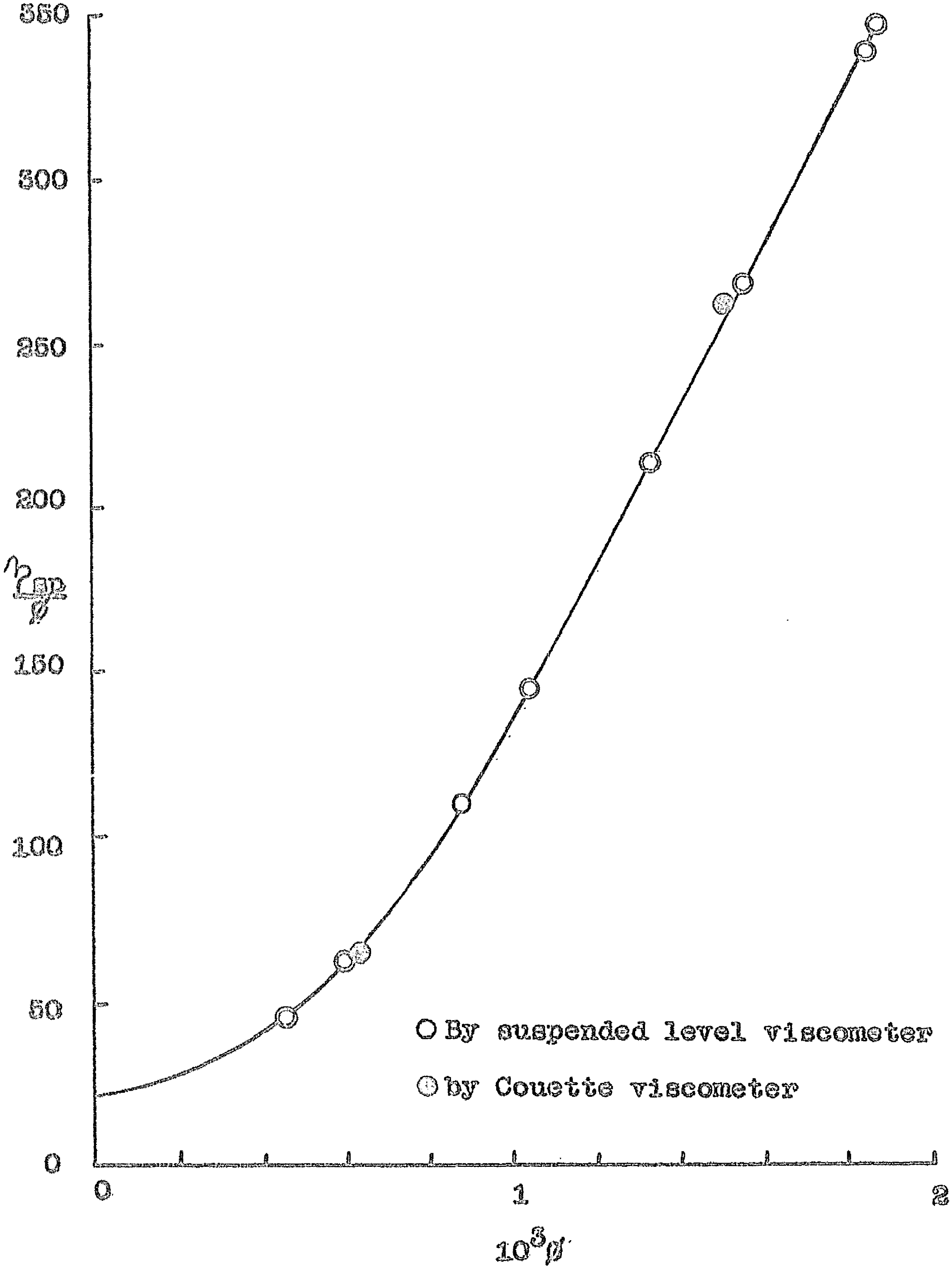
$$\log. c_2 - 5.1 \log. c_1 = 14.7 \qquad (D)$$

The micellar weight for the larger species was thus 6.28×10^6, a reasonable agreement with that from the crude Zimm plot, and from the ratio;

$$\frac{\text{Limiting Slope of Asymptote}}{\text{Intercept of } (Hc/\tau)_{c=0}} = \frac{16\pi^2}{\lambda_1^{2}} Rg_n^{\;2}$$

Rg_n was found to be 786 Å, and the root mean square end to end distance of the coil to be 1925 Å.

Figure 22.



Plot of η_{sp}/ϕ against ϕ for Hn_6 at 25°.

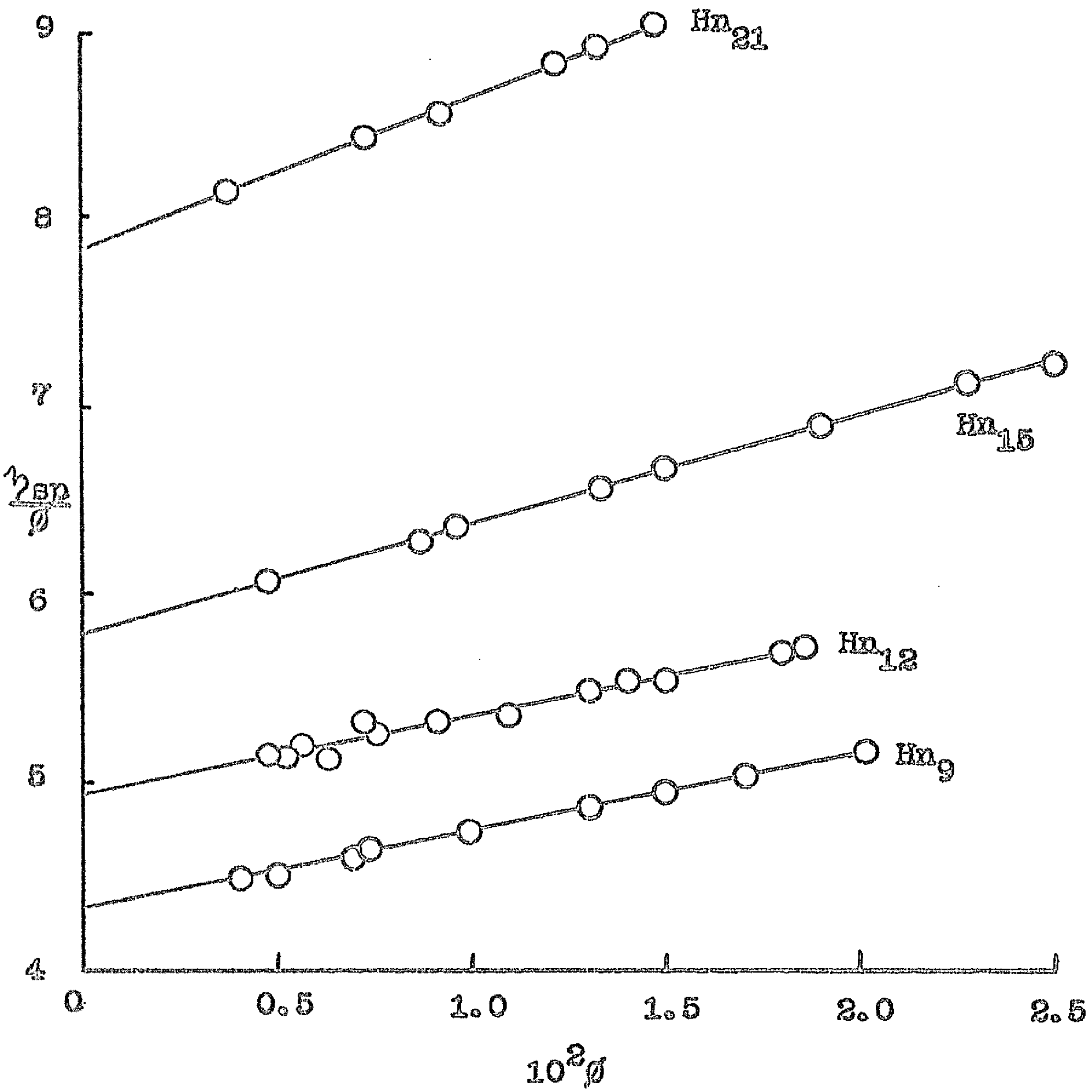
Viscosity.

Results.

The viscosity results are given in figures 22, 23, and 24 as $\eta sp/\phi$ vs. ϕ, where ηsp is the specific viscosity and ϕ, the volume fraction solute. The behaviour of the longer chain detergents followed the expected pattern; the intercept $(\eta sp/\phi)_{\phi=0}$ increasing with chain length between Hn_9 and Hn_{21} (see table 6). Hn_6 and Hn_7 solutions were very viscous, and while a straight line plot resulted for Hn_7 (figure 24) extrapolation for Hn_6 was uncertain under these conditions. The intercept for Hn_6 was obtained from a graph of $\eta sp/\phi$ vs. $(\phi + \phi^2)$, which was linear below $\phi = 0.0010$.

It was thought that the curvature of the original plot for Hn_6 was due to non-Newtonian flow, so several solutions were examined in a Couette viscometer. In all cases the flow was found to be Newtonian, and values of $\eta sp/\phi$ obtained from this instrument, fitted in well with the results found in the capillary viscometer.

Figure 23.



Plot of η_{sp}/ϕ against ϕ at 25°.

Discussion.

It is interesting to note there appears to be two association concentrations for these detergents. The critical micellar concentration, c_o, as determined from surface tension measurements, occurs at very low concentrations; with a second association limit at c_1, in the region of 0.2 - 0.3 x 10^{-3} g./ml. The constant value for surface tension between c_o and c_1 indicates that the activity of the monomeric detergent in equilibrium with the surface phase remains constant, but for Hn_9 and above, using the present techniques, this region is inaccessible for accurate measurement of the arrangement of the solute molecules in the solution bulk. The two shortest detergents studied did however contain large enough aggregates to give some idea of the changes occurring in the micellar structure. The micelles first formed appear to aggregate into larger molecular weight species as the concentration is increased which may indicate that the larger species are more stable. Over what range this larger micellar species may remain constant in size has not, as yet, been investigated but other workers,[138] using ultracentrifugal measurements, have shown a constant micellar size between 0.5 and 1.0 % for three different non-ionic detergents; unfortunately

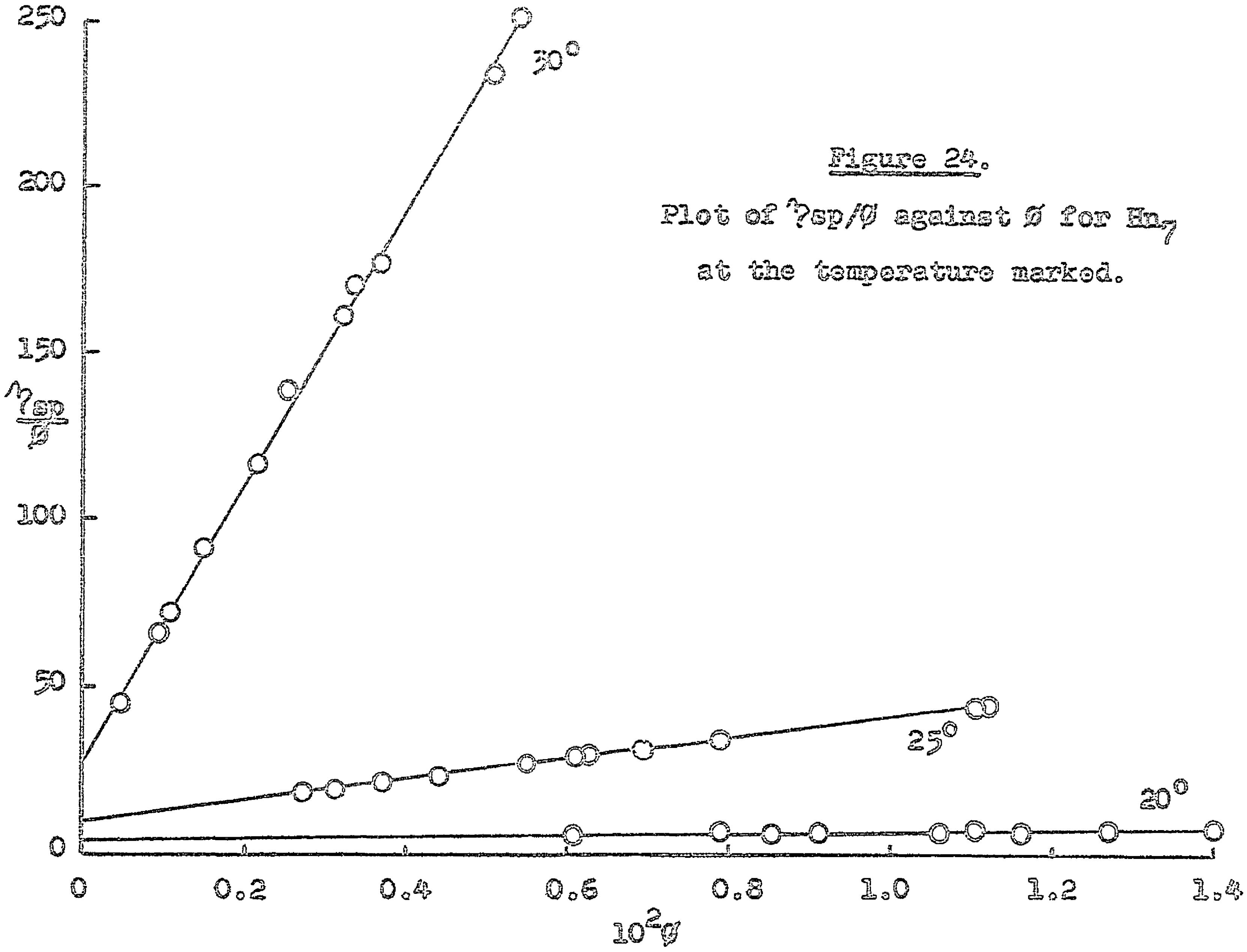


Figure 24.

Plot of η_{sp}/ϕ against ϕ for Hn_7 at the temperature marked.

their technique was not suitable for lower concentrations.

Although c_0 follows the expected pattern of increasing with increase of the length of the hydrophilic moiety, c_1 tends to decrease as the number of oxyethylene units in the molecule is increased. For Hn_{21}, no real indication for c_1 could be obtained i.e. $c_1 \approx c_0$, (see table 6). This decrease in c_1 may well provide a possible answer to the seemingly anomalous results for certain compounds published by Becher[122] and others[128] of a decrease in the critical micellar concentration with the increase of the oxyethylene chain; experiments on Hn_9 and Hn_{12},[286] using the iodine method employed by Becher, have given values very similar to that obtained as the light-scattering c_1, suggesting that it was this higher aggregation point that he was detecting.

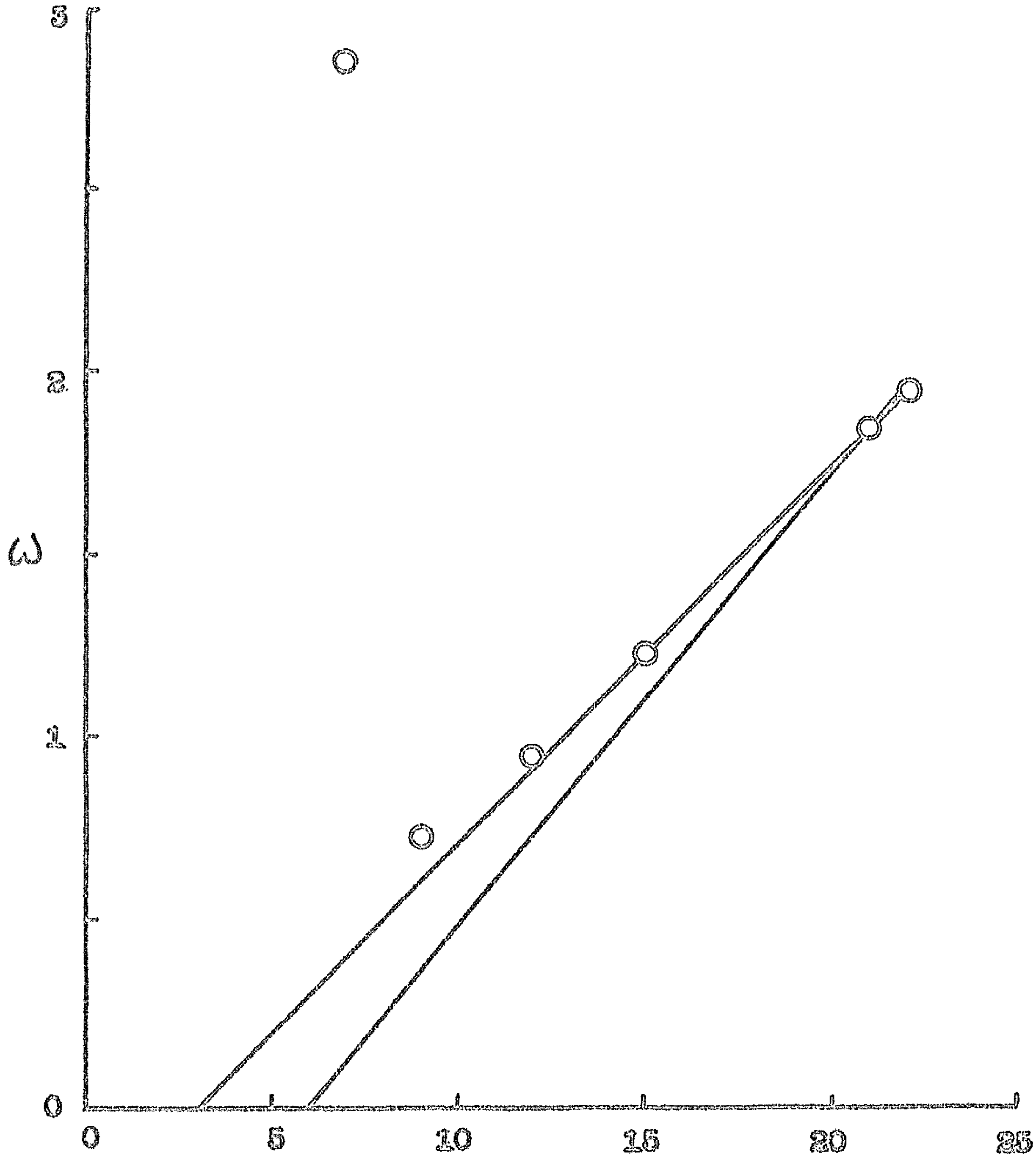
Examination of table 6 shows there is a large decrease in micellar weight as the detergent series is ascended: more than likely due to the increasing hydrophilic powers of the molecule.

Hn_5 is insoluble in water,[49] and Hn_6 is probably in a metastable state; it is soluble only over an 8° temperature range, dissolving at 24° and clouding at 32°. The light scattered by solutions of Hn_6 increased with time after solution until an equilibrium maximum value was attained after about 8 hours. Reproducible values for the light scattered by a solution of a given concentration could however be obtained by equilibrating the solution at 25° for 12 hours before examination. Hn$_7$, equilibrated much more quickly ($\leqslant$0.5 hours after being brought to 25°), and the longer compounds could be used immediately.

Data for both Hn$_6$ and Hn$_7$ suggest the micelles in aqueous solution are asymmetric, but, for Hn$_9$ and above the micellar dimensions are less than $\lambda/20$ and light-scattering does not give much idea of micellar shape.

To disentangle the effects of hydration and asymmetry on the micelles is a complicated problem as the hydration will depend not only on the length of the polyoxyethylene chain but also on the shape of the micelles. If the micelles are spherical, hydration would be expected to be a function of the polyoxyethylene chain length, as this part of the micelle provides the space for trapping water. If the micelles are rod-shaped, the volume per monomer in which water can be trapped is smaller than in the spherical case as the chains must be nearly parallel to one another along the long axis of the rod and the main possiblity for hydration lies around the cross section of the micelle, where the

Figure 25.



Plots of ω against the number of ethylene oxide units in the detergents (see text).

chains occupy a wedge-shaped sector of space. The inherent assumption in such a reasoning is that the degree of extension of the polyoxyethylene chains is the same for a spherical or a rod-shaped micelle.

The viscosity results have been examined in the light of these considerations. If one assumes that the deviation of the viscosity intercept from the value for unhydrated spheres is solely due to hydration, this hydration, ω g. water/ g. detergent can be calculated from:

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

From the very large value for Hn_6 (too large to be included on figure 25) the hydration, calculated in this manner, passed through a minimum, then increased as the polyoxyethylene chain became longer. As the hydration would be expected to decrease with decreasing oxyethylene chain length, the very large values for the hydration obtained for Hn_6 and Hn_7 were considered to be due to asymmetry of the micelles which decreased as the series was ascended; substantiating the conclusions from the light-scattering data. The increase in the calculated hydration with chain length, shown by Hn_9 and above, arose because the effects of hydration on the

Table 9.

Minimum Hydration.

Detergent	$10^{-5}V^{+}$	a/b	a	b	ω
Hn_6	21.10	13.8	458	33	0
Hn_7(20°)	2.61	1.2	45	37	0.13
(25°)	6.24	7.0	193	28	0.13
(30°)	-	15.5	-	-	0.13
Hn_9	3.18	2.3	74	32	0.37
Hn_{12}	3.34	1.7	62	34	0.75
Hn_{15}	-	1.4	-	-	1.11
Hn_{21}	3.73	1.0	45	45	1.86

Maximum Hydration.

Detergent	$10^{-5}V^{+}$	a/b	a	b	ω
Hn_6	27.01	11.8	448	38	0.29
Hn_7(20°)	-	-	-	-	-
(25°)	7.71	5.7	182	32	0.40
(30°)	-	13.5	-	-	0.40
Hn_9	3.74	1.5	57	40	0.61
Hn_{12}	3.68	1.1	47	43	0.92
Hn_{15}	-	1.0	-	-	1.22
Hn_{21}	3.73	1.0	45	45	1.86

$^{+}$ V = the micellar volume ($Å^3$); and a, and b (Å) are the long and short semi-axes, respectively.

micelles of these compounds outweighed any effects of decreasing asymmetry.

There is no physical reason why the longer-chain detergents should give asymmetric micelles and, on the assumption that Hn_{21} was hydrated but not asymmetric, the effects of hydration and asymmetry have been examined by choosing two limiting cases for the hydration. A minimum level was fixed by letting Hn_6 be unhydrated and Hn_{21} be fully hydrated, and an upper limit of Hn_{15} and Hn_{21} fully hydrated, and an asymptote drawn to the curve (see figure 25). Substitution of these values into the generalised form of the Oncley equation:-

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

where ν is Simha's factor, gave the results tabulated (table 9). The micelles have been treated as prolate ellipsoids, as calculation for Hn_6 and Hn_7 showed that, when reasonable values were taken for the cross-sectional area per molecule and molecular lengths, and when the number of monomers in the micelle were those found by light-scattering, the oblate model did not fit the viscosity results.

Although the difference between Hn_6 and Hn_7 is only one ethylene oxide unit this has a most remarkable effect on the micelle indicating that the balance between the hydrophilic and the hydrophobic parts of the molecules is in some critical state in this region.

Whether Hn_6 was treated as hydrated or unhydrated, the cross-sectional area of the micelle was greater than that of Hn_7 at 25° indicating that the molecule, most likely the polyoxyethylene chain, was more extended in the former compound; this may have a bearing on the stability of the micelles in that less of a mesh structure exists to contain the hydrating water than in the other detergent micelles.

Some further ideas of the structure of the large micelles formed by these two shortest detergents can also be obtained from these results.

The mass-action law treatment showed that for Hn_7 the larger micelles are 3.6 times the size of the small ones, with a volume, on the minimum hydration assumption, of 1.73×10^6 $Å^3$. From the light-scattering results the rod-like model has a length of 1065 Å. If this rod is allowed to approximate to a prolate ellipsoid, $a = 533$ Å so $b = 28$ Å; in agreement with the value of b for small micelles. Although this calculation was crude it did imply that the small micelles grew in the direction of their long axes on aggregation.

The light-scattering results suggested that Hn_6 fitted the coil model better than the rod one; the basic structural unit of the micelle may however be rod-like. If Hn_6 was in a fairly extended state the polyoxyethylene chain would be very flexible and, by taking the b value from table 9 for Hn_6 and the volume of the large micelles ($=10.8 \times 10^6$ Å^3), a value of 4700 Å was calculated for 2a. This length would be great enough for the rod to coil. In contrast, the greater hydration and shorter overall length of the Hn_7 would tend to promote a rod-like micelle, owing, on a mechanical model, to the presence of water molecules driven like wedges between the flexible polyoxyethylene chains.

The calculated micellar dimensions of the larger detergents also indicates a curling up of the monomer in the micelle; the relative degree of overall shortening of length increasing as the series is ascended. This is dealt with in more detail on p. 155 et seq.

The Effects of Temperature on Micellar Structure.

As the effect of temperature was not the main objective of this thesis, only a few measurements have been made (on Hn_7) in an attempt to elucidate the transition between the properties of the longer and shorter detergents; the results are summarised in table 6. Unfortunately Hn_6 could not be studied at lower temperatures than 25° due to phase separation around 23°.

At 20°, the measurements on the Hn_7 solutions tended to follow a pattern more like the longer detergents at 25°; no appreciable dissymmetry was observed at this temperature and the micellar weight was 1.37×10^5, and, if the viscosity intercept is taken as being caused by hydration alone, $\omega = 0.15$ g. water/g. detergent.

Raising the temperature by five degrees more than doubled the micellar weight of the detergent, and, combined with the Z_{45} values obtained (figure 20), the increase in the viscosity intercepts (figure 24) and the general pattern of the plots of $\eta sp/\phi$ vs. ϕ suggested asymmetry of the micelles developed as the temperature was increased.

The Estimation of Micellar Hydration.

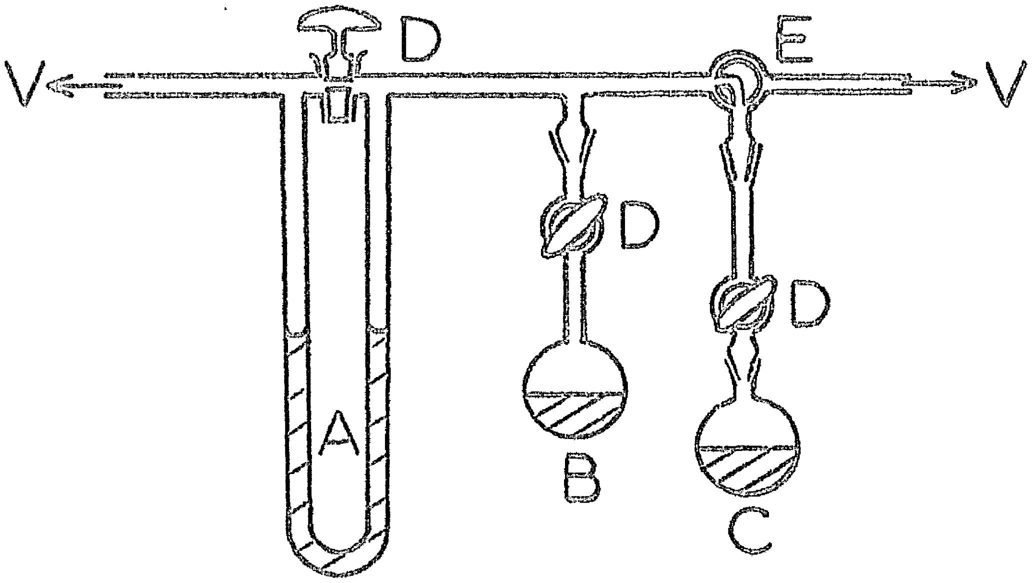
In the previous section light-scattering and viscosity results were combined to calculate the micellar shapes and sizes of the series of detergents under investigation. It appeared from these results that, at a given temperature, the aggregation number and asymmetry of the micelles decreased whereas the hydration increased with increase of ethylene oxide content of the monomer, and for Hn_7 the micellar size and asymmetry increased over the range of temperatures studied (20°- 30°), but, as no independent method of determining micellar hydration was available, the Oncley treatment[255] had to be used. Unfortunately, as discussed, this method only interprets the joint effects of hydration and asymmetry, and although methods of studying hydration using polarimetry, heats of solution, and viscosity maxima have been reported,[93,147,148,150-152] none appeared to be very satisfactory.

A method of assessing the hydration has therefore been investigated in which the vapour pressure over gels and solutions of non-ionics was measured. This procedure is based on the assumption that as water is added to the solid detergent, breakdown of the crystal structure occurs and a gel is formed. The activity of the solvent, which would be expected to be related to the mixing effects by an equation akin to the Flory-Huggins type for gels with low water content, rises as the water content is increased; the concentration of water for this to apply being such that it is only the mixing of water with the polyoxyethylene chains that is occurring at this stage. A concentration is however reached when the polyoxyethylene chains are fully solvated, and further added water no longer mixes with them as before. Above this concentration due to the dual nature of the molecule it is thought that separation into micelles takes place. The system which now exists, in effect consists of very large particles mixed with a solution of concentration equivalent to the cmc., which, for practical purposes can be considered as water. The entropy effects (and hence their influence on the solvent activity) are now very small and the vapour pressure of the system thus becomes, within experimental error, equivalent to that of pure water.

Extrapolation of the relative vapour pressure to a value of one to determine the ratio of water to detergent at which the point of separation of the micelles occurs, should thus give a measure of the water required to hydrate the polyoxyethylene chains.

Figure 26.

Diagram of Vapour Pressure Apparatus.



A - Manometer

B - Solvent Flask

C - Gel Flask

D - Two-way vacuum stopcock

E - Three-way vacuum stopcock

V - To vacuum pump

Experimental.

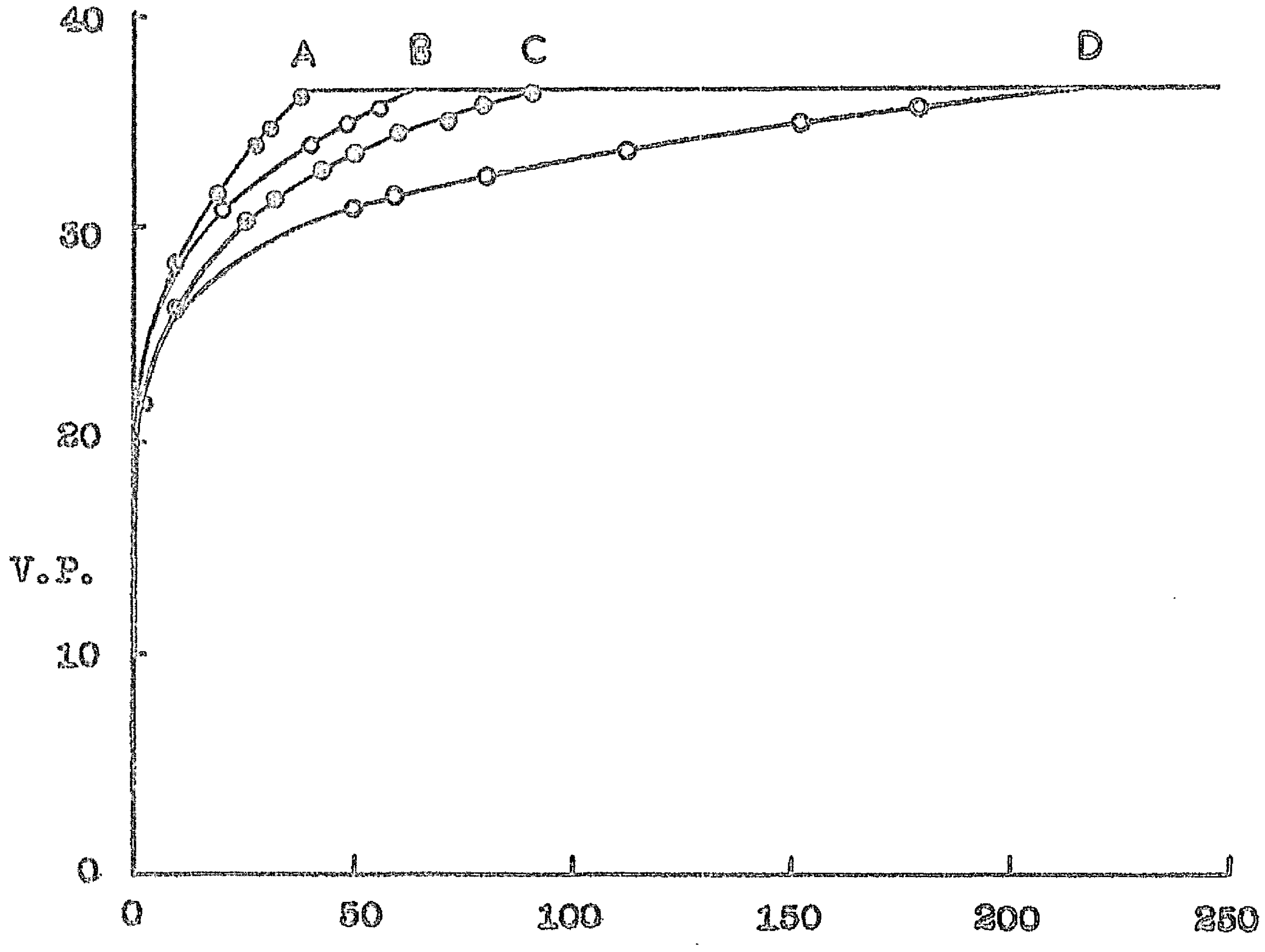
The vapour pressure measurements were made by the direct manometric method in an apparatus similar to that of Gibson and Adams,[283] (figure 26). The manometer liquids used were high vacuum pump oil (Edwards No. 18) when working at 20° and 25°, and mercury at 30°.

Between 5-10 g. of gels or solutions of detergent in water were introduced into the apparatus and outgassed at 0.001 mm. The apparatus was transferred to a thermostat controlled at the desired temperature and left until the gel/water vapour phases had equilibrated (1-3 hours). The vapour pressure of the gel and that of pure water were measured; a sample of the gel removed and analysed for water content by drying to constant weight in a vacuum oven at 50° over phosphorus pentoxide.

The apparatus was tested by measuring the vapour pressure of water at 20°, 25°, and 30° and gave good agreement with literature figures.[284]

	Vapour Pressure (mm. Hg)	
Temperature	Observed	Literature
20	17.50	17.54
25	23.72	23.76
30	31.80	31.82

Figure 27.



Vapour Pressure of Detergent Gels (cms. oil) at 25°.

A = Hn_6

B = Hn_9

C = Hn_{12}

D = Hn_{24}

In practice, after a few readings had been taken for a given system, an approximate idea of the reading could be forecast. Using this, before taking the gel reading, the manometer levels were adjusted to within some two cms. of oil below the expected reading by cautious release of vapour from the water flask, then the tap of the gel flask opened, and the levels read after the system had come to equilibrium (circa 5 mins.). This procedure reduced any local cooling effects due to evaporation from the gel and decreased the time required before the system attained equilibrium after opening of the gel flask tap.

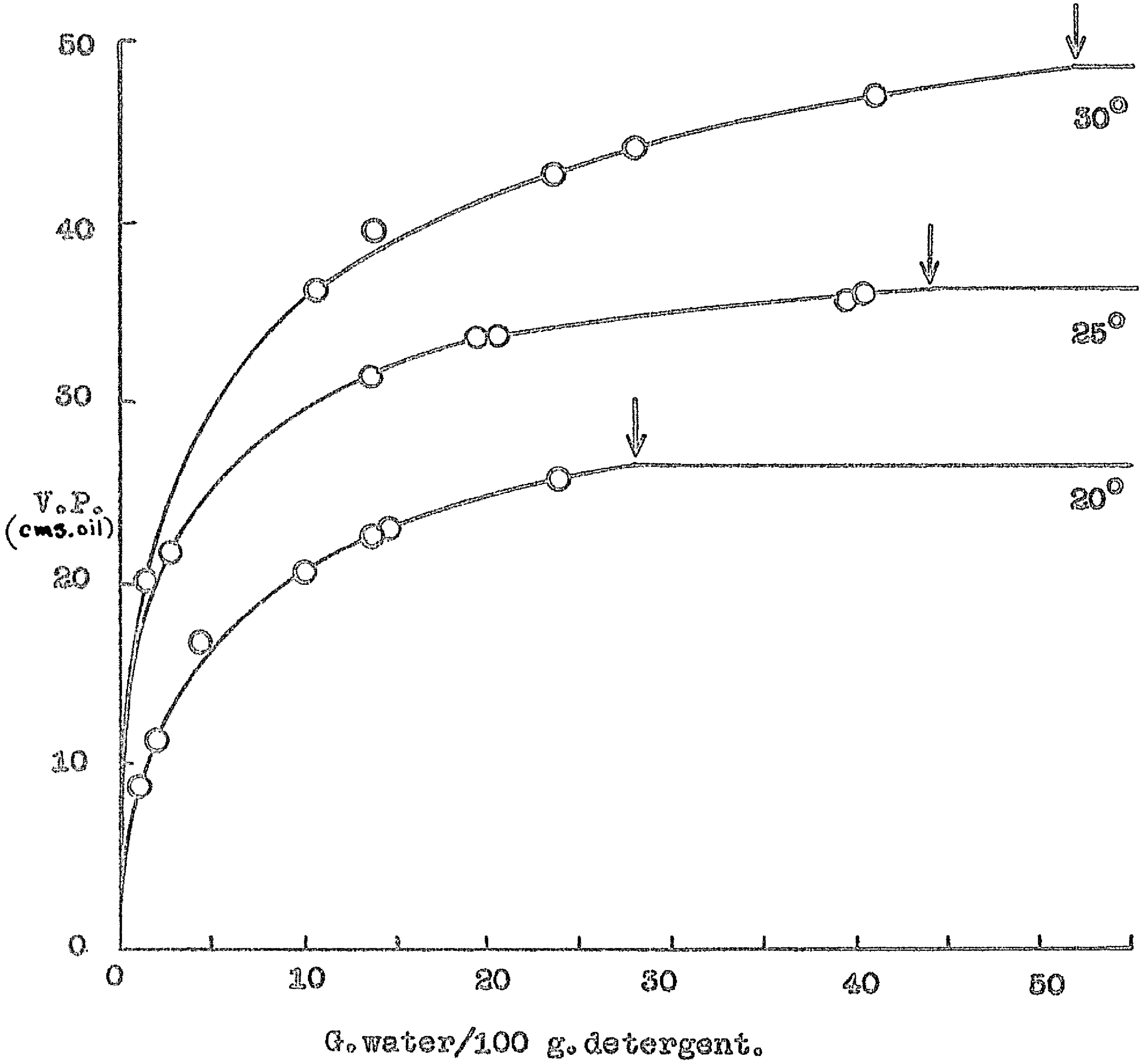
Tests were also carried out on the time taken for the gel/water vapour system to equilibrate after preparation and outgassing to ensure that no variation occurred after the gels had been prepared for some time. In all cases the gels equilibrated within about 2-3 hours.

Table 10.

Vapour pressure against time of a gel of Hn_{24} containing 160 g. water/100 g. detergent.

Time (hours)	0.5	1	1.5	2	3	4	6	8
Vapour Pressure	34.8	35.3	35.4	35.5	35.6	35.5	35.6	35.6
Time (days)	2	3	4	9	10	11	17	28
Vapour Pressure	35.5	35.6	35.6	35.7	35.6	35.3	35.7	35.6

Figure 28.



Vapour Pressure of Gels of Hn_7 at 20°, 25°, and 30°.

Similar tests to the above were made on the other detergents for periods of one week; in all cases equilibrium was reached within 2-3 hours.

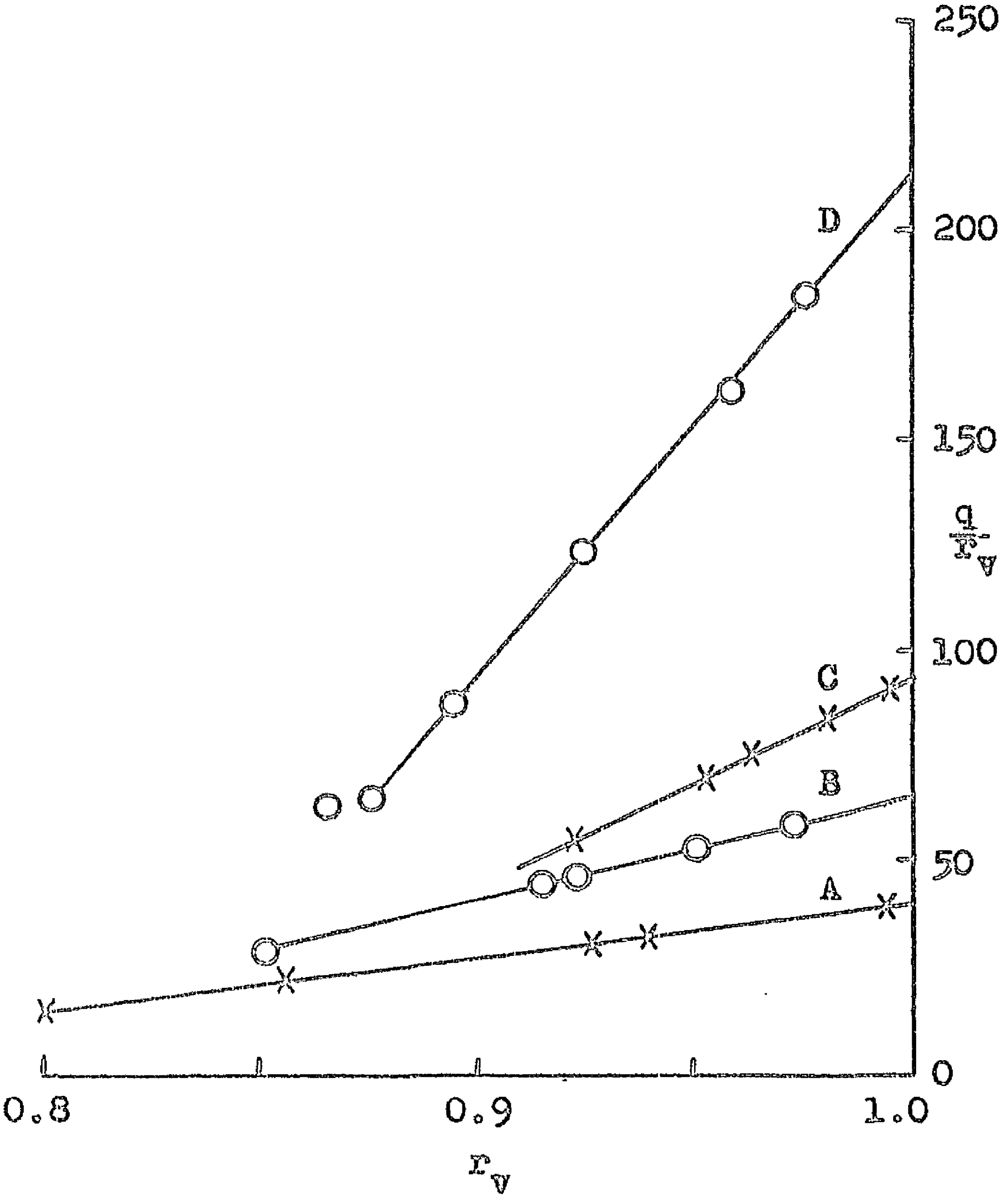
Furthermore, examination of a range of gel concentrations above and below the critical concentration where the vapour pressure of the gel approached that of water, by general physical appearance, and microscopically, using polarized discs, showed no apparent phase change occurring in this region.

Results.

Plots of vapour pressure (p) against g. water/100 g. detergent (q) given in figures 27 & 28 show that the particular concentration, ω, at which the vapour pressure, within experimental error, becomes equal to that of pure water increases steadily with polyoxyethylene chain length. The actual values of ω measured, were obtained by constructing isotherms of q/r_v, against r_v, where r_v is the relative vapour pressure; the isotherms being linear above $r_v = 0.8$, enabling extrapolation to $r_v = 1$. (figures 29 & 30).

The values of ω so obtained are given in the following table.

Figure 29.



Extrapolations of q/r_v to $r_v = 1$ at 25°.

$A = Hn_6$ $B = Hn_9$ $C = Hn_{12}$ $D = Hn_{24}$

Detergent.....	Hn_6	Hn_7	Hn_9	Hn_{12}	Hn_{24}*	Hn_7 (20°)	Hn_7 (30°)
ω.............	0.39	0.44	0.65	0.96	2.18	0.28	0.52

*C.P.G.E.24 was used.

When these results were plotted as g. water per mole detergent x no. of ethylene oxide units^{-1} (y) against the no. of ethylene oxide units in each detergent (x) a straight line was obtained (figure 31) having the equation;

$$y = 4.3 + 4.73x$$

Values of ω for Hn_{15} and Hn_{21} were interpolated from this graph as insufficient of these synthesised compounds remained after the other work.

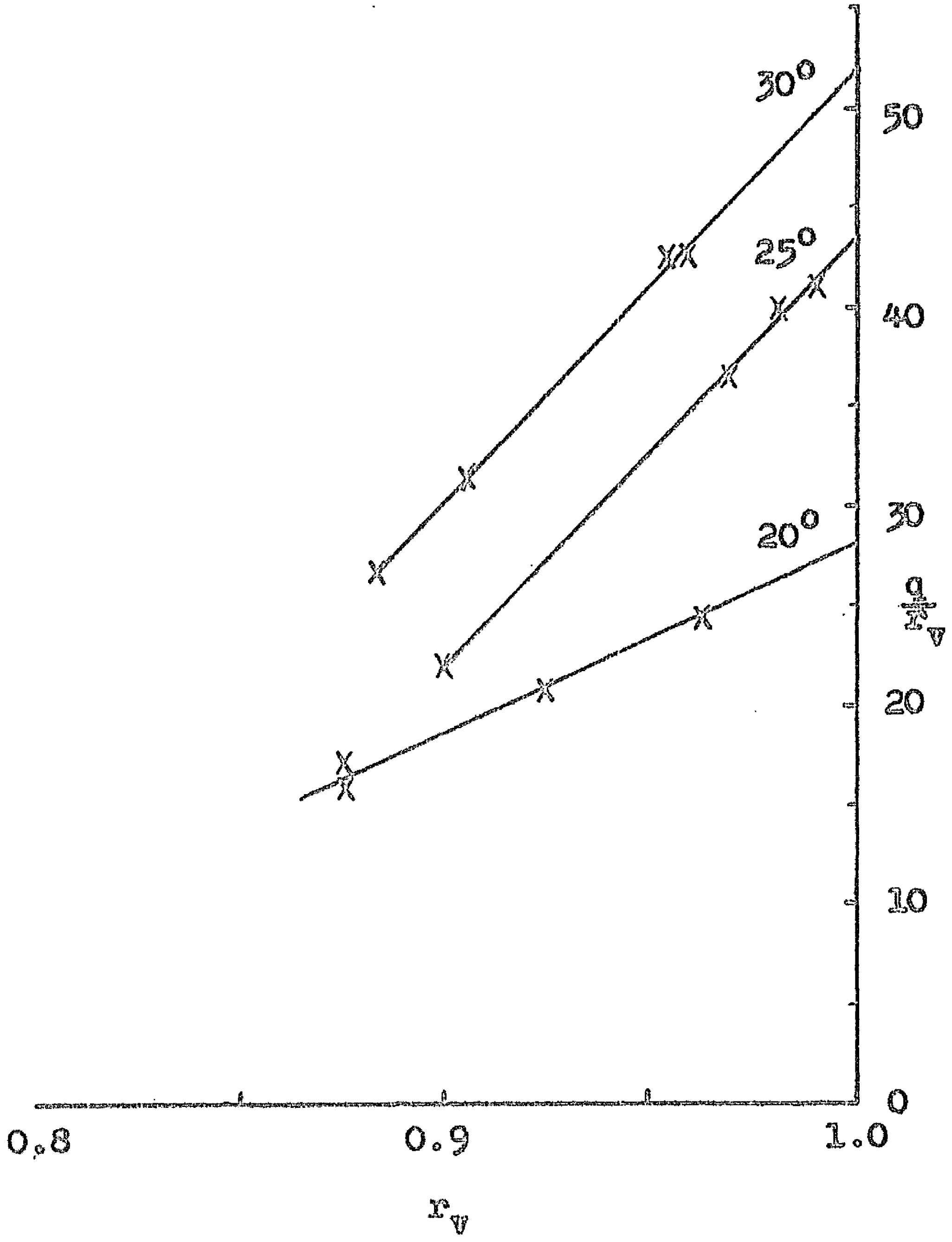
The results for Hn_7 show that hydration increases with temperature. From plots of q against r_v (analagous to "sorption" isotherms) the differential heats of hydration ($\Delta\bar{\bar{H}}$), assumed to be linear over the 20°-30° temperature interval, and the differential entropy of hydration ($\Delta\bar{\bar{S}}$) at 25° were obtained using the equations^{285}:

$$\Delta\bar{\bar{H}} = \bar{\bar{H}}_s - \tilde{H}_1 = R\left(\frac{\partial \ln.(p/p_0)}{\partial(1/T)}\right)_{p,N_1,N_2}$$

and $\quad \Delta\bar{\bar{S}} = \bar{\bar{S}}_s - \tilde{S}_1 = (1/T)\left[\Delta\bar{\bar{H}} - RT\ln.(p/p_0)\right]$

where $\tilde{H}_1$ and $\tilde{S}_1$ are the molar enthalpies and entropies of

Figure 30.



Extrapolations of q/r_v to $r_v = 1$ for Hn_7 at temperatures marked.

water, $\bar{\bar{H}}_s$ and $\bar{\bar{S}}_s$ are the partial molar enthalpies and entropies of the sorbate, and N_1 and N_2 are the number of moles of sorbate and sorbent, respectively.

q (g.H_2O/100g.Hn_7)	5	10	15	20	25	30
$\Delta\bar{\bar{H}}$ (k.cal.mole^{-1})	1.1	1.1	1.3	1.5	1.5	1.5
$\Delta\bar{\bar{S}}$ (cal.mole^{-1})	4.5	4.2	4.6	5.3	5.3	4.9

Discussion.

As there is no apparent physical reason why detergents containing polyoxyethylene chains should form other than spherical micelles at normal temperatures, calculations from the Oncley equation made on this assumption, for the compounds under the conditions which did not show any appreciable light-scattering dissymmetry have been used as a method of comparison of the values of ω from vapour pressure measurements.

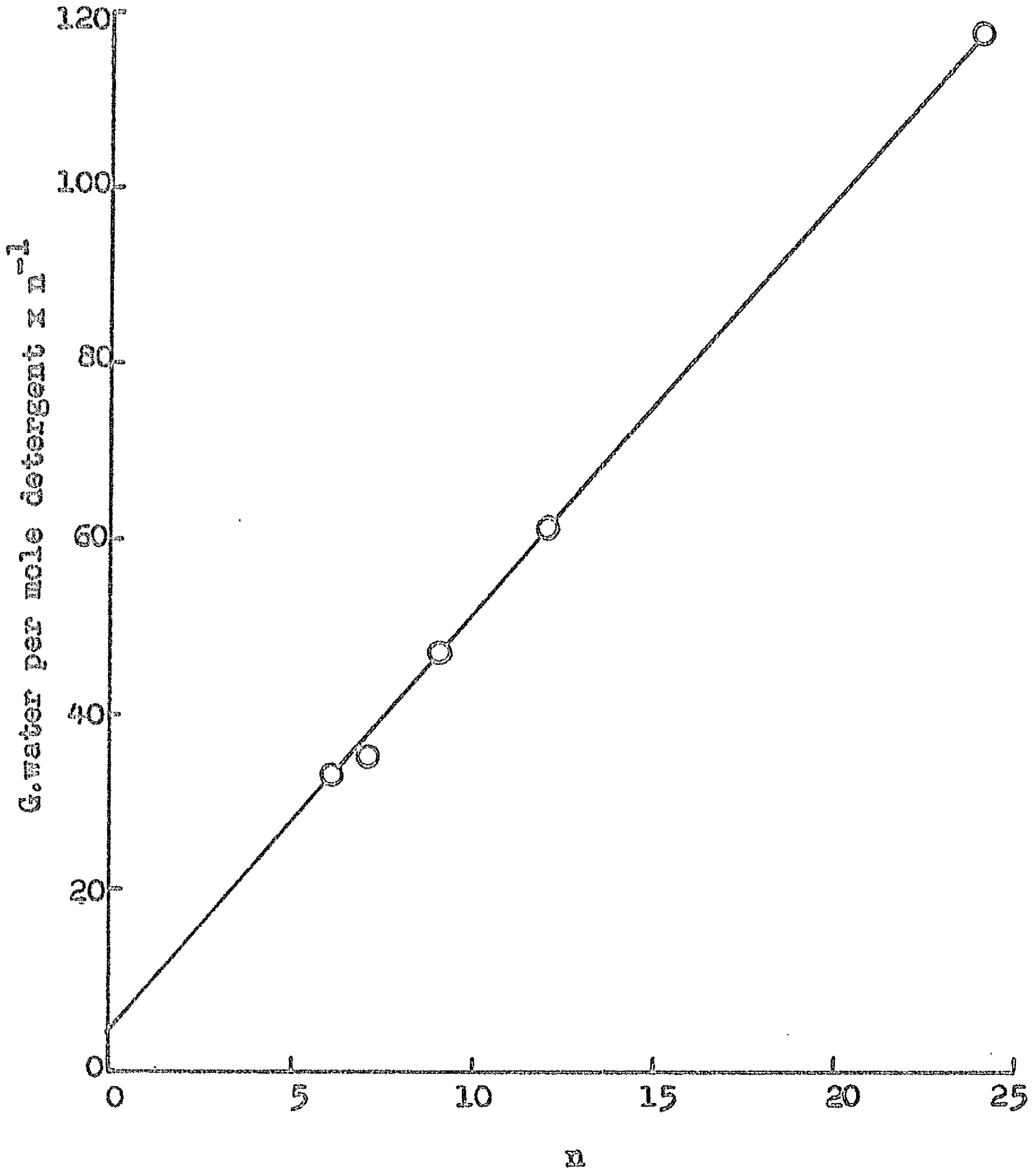
Table 11.

Detergent	Hn_9	Hn_{12}	Hn_{15}^*	Hn_{21}^*	$Hn_{22}^{*\dagger}$	$Hn_7(20^\circ)$
ω(vap. press.)	0.65	0.96	1.24	1.86	1.96	0.28
ω(viscosity)	0.72	0.95	1.23	1.85	1.96	0.15

*ω (vap. press.) are interpolated values from figure 31.

† Hn_{22} was a commercial sample studied previously.[139]

Figure 31.



Plot of g.water per mole detergent x n^{-1} against n.

(n = the number of ethylene oxide units per molecule)

The only system showing a significant difference is Hn_7 at 20°; this system however had a viscosity intercept of 2.86 and from the limits of error calculated for this intercept (p. 128) the error in ω (viscosity) is very high (0.15 ± 0.18 g. water/g. detergent) which satisfactorily accounts for the differences in the results for the two methods.

In spite of viscosities being measured on dilute solutions and vapour pressures on concentrated ones, the overall agreement between the two sets of results appears sufficiently good to support the vapour pressure technique as a method which can be used (if only empirically) to determine the hydration of non-ionic detergents.

Micellar Dimensions.

On the basis of the hydration determined by the water vapour method it would thus appear that the only compounds whose micellar structures are significantly asymmetric at 25° are Hn_6 and Hn_7. Using the value for the hydration obtained by the vapour pressure measurements; the number of monomers in the micelle, N; and the molecular volume of the monomer; the major (a) and minor axes (b) for a prolate ellipsoidal model of the smaller micelles of these detergents are now, at 25°:-

Hn_6: a = 442 Å, b = 40 Å. Hn_7: a = 182 Å, b = 32 Å.

Similarly, using the mean value of ω from table 11 calculations of the total micellar volume and radius, r_m, were made for the four largest synthesised detergents.

The proportion of the radius available to the polyoxyethylene chain obviously depends on the radius of the hydrocarbon moiety. In interpreting this, one has two alternatives; whether the radius of the latter region is taken as the length of the extended hexadecyl chain, which implies an arrangement similar to that of a solid, or whether the radius is calculated from:

$$r_h = \left(\frac{3(\text{molecular volume of hexadecane} \times N)}{4\pi}\right)^{\frac{1}{3}}$$

where r_h, is the radius of the hydrocarbon portion of the micelle. The second method seemed more reasonable, as the hydrocarbon region was most likely to be a liquid phase, and was used to calculate r_h.

Table 12.

	$10^5 M$	$10^5 V$ Å^3	r_m Å	r_h Å	r_e Å	r_e/n Å
Hn_7 (20°)	1.37	3.25	42.7	30.7	12.0	1.71
Hn_9 (25°)	1.40	3.9_2	45.4	29.4	16.0	1.77
Hn_{12} (25°)	1.17	3.7_5	44.7	26.0	18.7	1.56
Hn_{15} (25°)	1.03*	3.7_2	44.6	23.6	21.0	1.40
Hn_{21} (25°)	0.82	3.7_2	44.6	20.1	24.5	1.17

*interpolated from a graph of M against 1/n.

r_e - the radius of the micelle occupied by the polyoxyethylene chain

r_e/n - the radial length occupied per oxyethylene unit

V - hydrated volume of the micelle

Further, using these micellar volumes, and the micellar weights from light-scattering, the second virial coefficients of the various solute systems were calculated using[288]:

$$B = 4V/M^2$$

Comparison of the values from this, and those obtained from light-scattering, showed an agreement between the two sets of results of the correct order (table 13).

Table 13.

	$10^4B_{obs.}$	$10^4B_{calc.}$
Hn_7 (20°)	0.84	0.42
Hn_9 (25°)	3.28	0.48
Hn_{12}(25°)	0.85	0.66
Hn_{21}(25°)	1.40	1.33

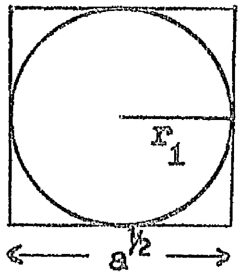
A significant feature which emerges from table 12 is that the volume of the hydrated micelles at 25° is remarkably constant, provided the detergents possess a sufficient number of ethylene oxide units to produce a micelle with a spherical shape. Such a property, if general, suggests the possibility of a quick method of determining the micellar weight of a series of polyoxyethylene detergents. At a given temperature, provided the relevant volume (V) is known, and provided the detergents are within the range which formed spherical micelles, by simply using viscosity measurements to obtain ω, and knowing the density of the detergents, the micellar weight could easily be calculated.

While the radial length of the polyoxyethylene part of the micelle increased with chain length, the length occupied per oxyethylene unit decreased.

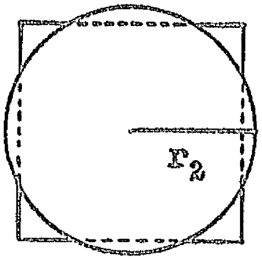
To explain this pattern of behaviour two types of chain orientation have been suggested; a random arrangement and an expanding spiral. Practical difficulties prevented the theoretical calculation of an end to end distance for the former as the chains were not long enough for the application of the statistics of linear polymers and also certain necessary information was lacking. The expanding spiral concept has however been supported by recent papers papers[110,111,126] and molecular models were constructed to investigate possible orientations.

From the volume of the micelle, its surface area and hence the surface area per monomer (a) were calculated. Like the area per molecule determined from the surface tension results at the air/water interface, the area per monomer at the surface of the micelle increased as the oxyethylene chain of the detergent increased. The latter areas were however considerably larger than those of the same detergent at the air/water interface. Two interpretations of these micellar areas were investigated:-

1) The spirals did not in any way overlap with adjacent spirals; the cross-sectional area per monomer at the micellar surface was taken as πr_1^2, where $r_1 = \frac{1}{2}a^{\frac{1}{2}}$



2) The cross-sectional area per monomer at the micellar surface was a circle of area = a i.e. $r_2 = (a/\pi)^{\frac{1}{2}}$.

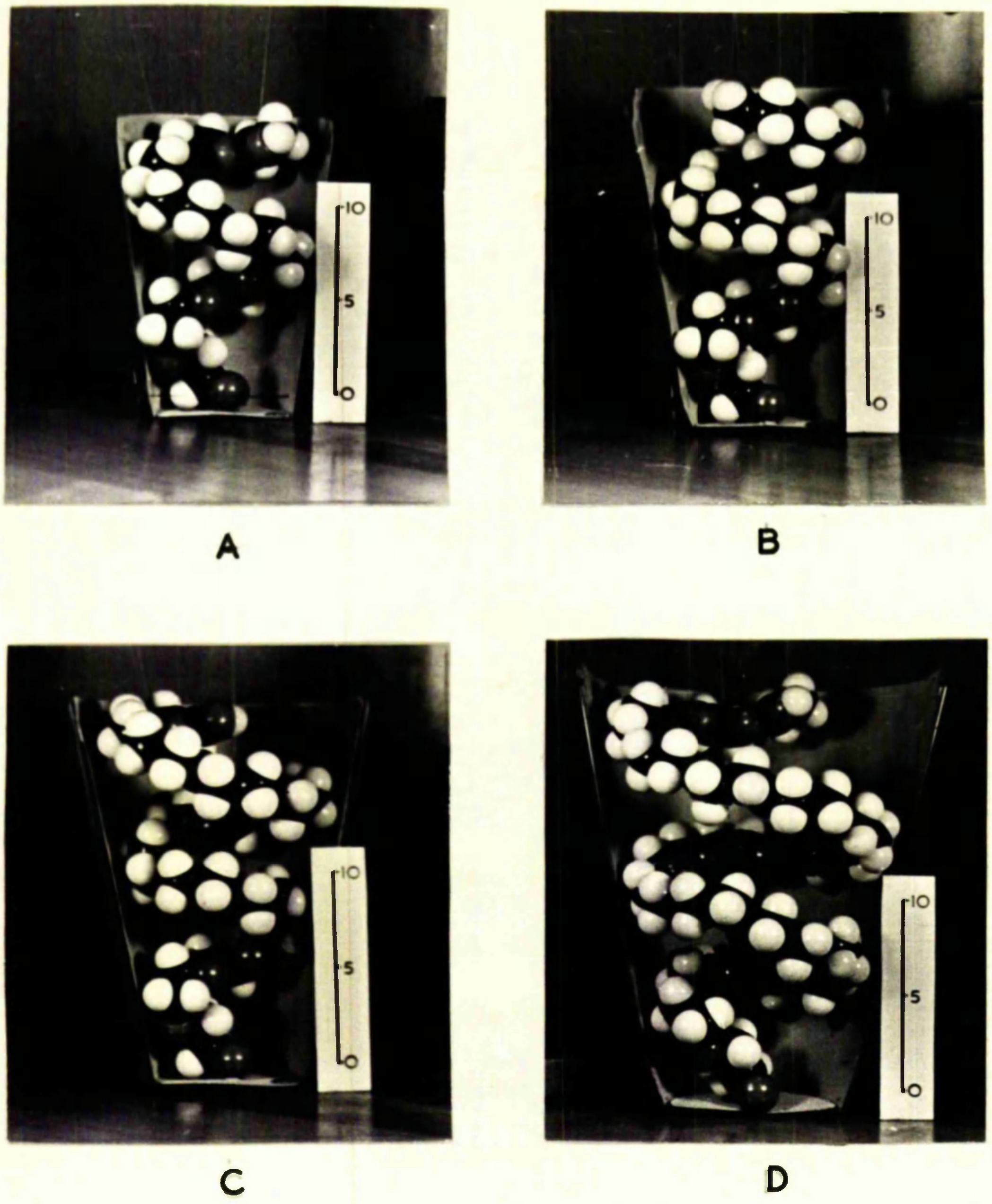


This allows for a certain degree of overlap between the adjacent spirals.

Although the area, a, was originally obtained from a curved surface, calculation of the other dimensions on the basis of a flat surface did not introduce any significant error to the values obtained.

Complementary values were calculated for the areas at the surface of the hydrocarbon core.

Experiments fitting Catalin molecular models into cones, manufactured to scale from the calculated



Catalin Models constructed to "r_1" dimensions.

$A = Hn_9$ $B = Hn_{12}$ $C = Hn_{15}$ $D = Hn_{21}$

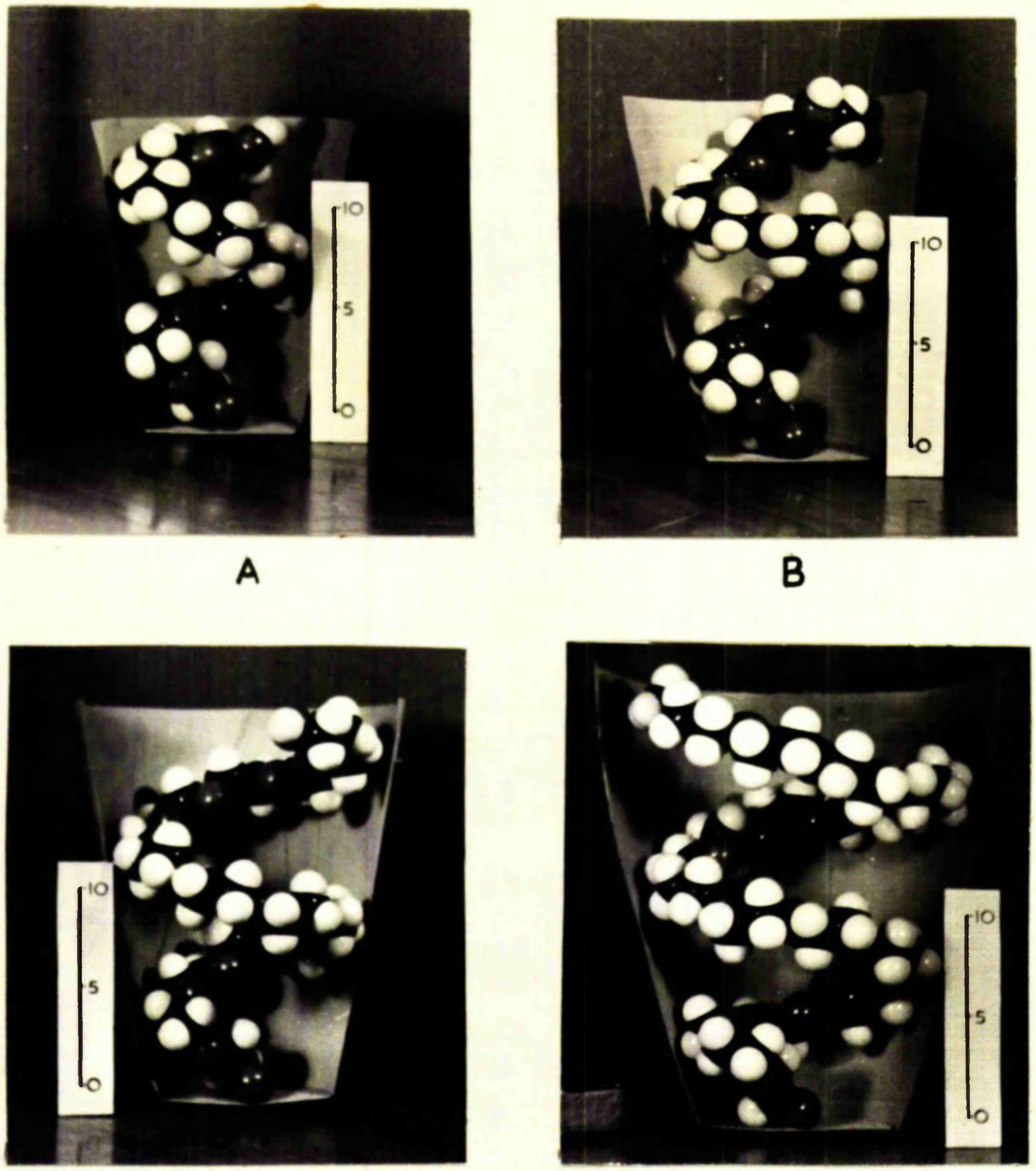
Table 14.

	a	r_1^{x}	$r_{1(H/C)}^{x}$	r_2^{x}	$r_{2(H/C)}^{x}$
Hn_9	116.5	5.4	3.5	6.1	4.0
Hn_{12}	165.5	6.4	3.7	7.2	4.2
Hn_{15}	219.5	7.4	3.9	8.3	4.4
Hn_{21}	357.5	9.5	4.3	10.6	4.8

$r_{1(H/C)}$ and $r_{2(H/C)}$ are the radii calculated at the hydrocarbon core surface corresponding to r_1 and r_2 respectively. (^{x}Å).

dimensions (tables 12 and 14) and assuming the spirals' axes came out vertically from the hydrocarbon surface, showed that the structures based on r_1, i.e. those allowing no overlap between adjacent spirals produced the more satisfactory steric arrangement and provided adequate space for trapping water molecules both inside and between the coils. (See photographs).

The actual arrangement of water molecules relative to the polyoxyethylene chains is still subject to speculation. Various types of orientation and bonding have been suggested[53,126,129,144-152], but a specific arrangement of water molecules around the ether oxygens is not in accord with the experimental results.



A B

C D

Catalin Models constructed to "r_2" dimensions.

A = Hn_9 B = Hn_{12} C = Hn_{15} D = Hn_{21}

Near the surface of the hydrocarbon core there is less space for the water molecules than further out in the micelle, thus the proportion of water molecules for each unit will increase as the chain lengthens. This is shown by the hydration values obtained (table 11). Kushner and Hubbard[90], found forty-three water molecules associated with a ten unit polyoxyethylene chain in Triton X 100 micelles, and proposed that twenty of these were hydrogen bonded to the ether oxygens, while the remainder were physically trapped by the polyoxyethylene chains. The endothermic $\Delta\bar{H}$ and the positive $\Delta\bar{S}$ values found, (p.152) suggest that the interaction of the water with the chains is rather similar to a mixing process, than to any specific arrangement of water molecules around the ether oxygens; or at any rate the mixing process predominates over any orientation effects.

The length of the short semi axis of the ellipsoid representing the micelle is greater for Hn_6 than for Hn_7 and the former compound gives less stable solutions than the latter.

It has been suggested[158] that hydration decreased with increasing temperature; the results on Hn_7 show the opposite effect in the 20-30° temperature range but, despite this, the increasing ω is accompanied by an increasing micellar weight indicating that the extra water molecules trapped do not in any way enhance the solubility of the chain.

At 20° the polyoxyethylene chains form tighter spirals than at 25° (r_e, table 12) thus the decreased stability, as reflected by an increase in micellar weight, occurring with increase in temperature or decrease in the number of units per oxyethylene chain is accompanied by the assumption of a more extended configuration by the chain. On the spiral model, this would imply that the straightening of the chain causes a diminution of the protection afforded to the hydrocarbon core by the spiral structure and/or a decrease of the "hydrophilic powers" of the oxyethylene chain.

REFERENCES.

1. LAURENCO, Compt. rend., 1859, 49, 619.
   Ann. Chim. Phys., 1863, 69, 257.
2. WURTZ, Compt. rend., 1859, 49, 813.
   Ann. Chim. Phys., 1863, 69, 317.
3. ROITHNER, Monatsh., 1894, 15, 665.
4. SKEEN, Chem. Eng., 1950, 57, 331.
5. FINE, J. Amer. Oil Chemists' Soc., 1958, 35, 540.
6. COHEN, Compt. rend., 1948, 226, 1366.
7. KARABINOS, BARTELS, AND KAPELLO, J. Amer. Oil Chemists' Soc., 1954, 31, 419.
8. VAUGHN, JACKSON, AND LUNSTED, ibid., 1949, 26, 289.
9. VAUGHN, JACKSON, AND LUNSTED, ibid., 1952, 29, 240.
10. WRIGLEY, SMITH, AND STIRTON, ibid., 1957, 34, 39.
11. DREW, HOWARD, AND SCHAEFFER, Ind. Eng. Chem., 1958, 50, 1253.
12. SCHULMAN, MATALON, AND COHEN, Discuss. Faraday Soc., 1951, 11, 117.
13. STEVENS, J. Amer. Oil Chemists' Soc., 1957, 34, 181.
14. GEE, HIGGINSON, AND MERRAL, J. Chem. Soc., 1959, 1345.
15. FLORY, J. Amer. Chem. Soc., 1940, 62, 1561.
16. MOLINA, "Poisson's Exponential Limit," D. Van Nostrand Co., Inc., 1942.

17. WEIBULL AND NYCANDER, Acta Chem. Scand., 1954, 8, 847.

18. NATTA AND MANTICA, J. Amer. Chem. Soc., 1952, 74, 3152.

19. WRIGLEY, SMITH, AND STIRTON, J. Org. Chem., 1960, 25, 441.

20. MILLER, BANN, AND THROWER, J. Chem. Soc., 1950, 3623.

21. MAYHEW AND HYATT, J. Amer. Oil Chemists' Soc., 1952, 29, 351.

22. BIRKMEIER AND BRANDNER, Agric. and Food Chem., 1958, 6, 471.

23. SCHECHTER AND WYNSTRA, Ind. Eng. Chem., 1956, 48, 86.

24. RICHARDSON, KERN, MURRAY, AND SUDHOFF, P.B. 6684, C.I.O.S., No.22/1G, 1945.

25. CHITWOOD AND FREURE, J. Amer. Chem. Soc., 1946, 68, 680.

26. STAUDINGER AND SCHWEITZER, Ber., 1929, 62, 2395.

27. GINN, CHURCH, AND HARRIS, Analyt. Chem., 1961, 33, 143.

28. TISCHBIREK, 3rd Internat. Congress on Surface Activity, section A, p.126, Mainz Univ. Press, 1961.

29. RAPHAEL, Manuf. Chemist, 1958, 105.

30. KELLY AND GREENWALD, J. Phys. Chem., 1958, 62, 1096.

31. GALLO, Boll. chim. farm., 1953, 92, 332.

32. MOHR, Z. Chem., 1866, 495.

33. MOHR, Chem. Zentr., 1866, 865.

34. CAROTHERS, Chem. Rev., 1931, 8, 391.

35. FORDYCE, LOVELL, AND HIBBERT, J. Amer. Chem. Soc., 1939, 61, 1905.

36. PERRY AND HIBBERT, Canad. J. Chem., 1936, B 14, 77.

37. BARNES AND ROSS, J. Amer. Chem. Soc., 1936, 58, 1129.

38. KURIYAMA, Kolloid Z., 1962, 180, 55.

39. NAKAGAWA, KURIYAMA, AND INOUE, J.Colloid Sci., 1960, 15, 268.

40. BRANDNER, LOCKWOOD, NAGEL, AND RUSSEL, F.I.A.T. Report, No.1141, p.11.

41. GOTO, SUGANO, AND KOIZUMI, Bull. Inst. Chem. Res., Kyoto Univ., 1953, 31, 305.

42. CHAKHOVSKOY, MARTIN, AND VAN NECHEL, Bull. Soc. chim. belges, 1956, 65, 453.

43. GINGRAS AND BAYLEY, Canad. J. Chem., 1957, 35, 599.

44. GINGRAS AND BAYLEY, ibid., 1958, 36, 1320.

45. CORKHILL, GOODMAN, AND OTTEWILL, Trans. Faraday Soc., 1961, 57, 1627.

46. TURNER, SAUNDERS, AND WILLAMAN, Conn. Agr. Expt. Sta., 1951, Bull. No. 543, 6.

47. WRIGLEY, STIRTON, AND HOWARD, J. Org. Chem., 1960, 25, 439.

48. MULLEY, J.Chem. Soc., 1958, 2065.

49. MULLEY, as ref. 28, p. 31.

50. LANGE, Fette u. Seifen, 1962, 64, 457.

51. SHIRLEY, ZEITZ, AND REEDY, J. Org. Chem., 1953, 18, 378.

52. WEIBULL, as ref. 28, section C, p. 121.

53. WURZSCHMITT, Z. analyt. Chem., 1950, 130, 105.

54. SCHAEFFER AND CRITCHFIELD, Analyt. Chem., 1947, 19, 32.

55. SCHONFELDT, Kolloid Z., 1955, 142, 164.

56. OLIVER AND PRESTON, Nature, 1949, 164, 242.

57. STEVENSON, Analyst, 1954, 79, 504.

58. HAAKH, von CANDIE, AND MOBUS, Melliand Textilber, 1951, 32, 699.

59. BROWN AND HAYES, Analyst, 1955, 80, 755.

60. COPPINI AND CAMERON, Boll. chim. farm., 1953, 92, 363.

61. McALLISTER AND LISK, Analyt. Chem., 1951, 23, 609.

62. KHO AND STOLTEN, Antara Chemicals, 1958.

63. ELKINS, STORLAZZI, AND HAMMOND, J. Ind. Hyg., 1942, 24, 229.

64. WERNER AND MITCHELL, Ind. Eng. Chem., 1943, 15, 375.

65. MORGAN, ibid., 1946, 18, 500.

66. SIGGIA, STARKE, GARIS, STAHL, Analyt. Chem., 1958, 30, 115.

67. NAKAGAWA AND NAKATA, J. Chem. Soc. Japan, Ind. Chem. Sect., 1956, 59, 710, 1154.

68. ELWORTHY, J. Pharm. Pharmacol., 1963, 15, 216.

69. PETHICA, as ref. 28, p. 212, and refs. cited there.

70. McBAIN AND HUTCHINSON, "Solubilisation," Academic Press, New York, 1955.

71. DEBYE, J. Phys. Chem., 1949, 53, 1.

72. DEBYE, Ann. N.Y. Acad. Sci., 1949, 51, 575.

73. DEBYE AND ANACKER, J.Phys. Chem., 1951, 55, 644.

74. PHILIPS AND MYSELS, ibid., 1955, 59, 325.

75. MYSELS AND PRINCEN, ibid., 1959, 63, 1696.

76. MYSELS, J.Colloid Sci., 1955, 10, 507.

77. PRINCEN AND MYSELS, ibid., 1957, 12, 594.

78. KUSHNER AND HUBBARD, ibid., 1955, 10, 428.

79. TARTAR, ibid., 1959, 14, 115.

80. McBAIN, Trans. Faraday Soc., 1913, 9, 99.

81. McBAIN AND SALMOND, J. Amer. Chem. Soc., 1920, 42, 426.

82. BUNBURY AND MARTIN, J. Chem. Soc., 1914, 105, 424.

83. REYCHER, Kolloid Z., 1913, 12, 183.

84. SCATCHARD, J. Amer. Chem. Soc., 1932, 54, 2676.

85. GONICK AND McBAIN, ibid., 1947, 69, 334.

86. GONICK, J. Colloid Sci., 1946, 1, 393.

87. McBAIN AND MARSDEN, J.Chem. Phys., 1947, 15, 211.

88. GOTO, SUGANO, AND KOIZUMI, J.Chem. Soc. Japan, Pure Chem. Sect., 1954, 75, 73.

89. KUROIWA, ibid., Ind. Chem. Sect., 1956, 59, 65.

90. KUSHNER AND HUBBARD, J. Phys. Chem., 1954, 58, 1163.

91. McBAIN AND MARSDEN, J. Phys. Colloid Chem., 1948, 52, 110.

92. GREENWALD AND BROWN, J.Phys. Chem., 1954, 58, 825.

93. REICH, ibid., 1956, 60, 257.

94. OOSIKA, J. Colloid Sci., 1954, 9, 254.

95. PHILIPS, Trans. Faraday Soc., 1955, 52, 561.

96. MATIJEVIC AND PETHICA, ibid., 1958, 54, 587.

97. FLOCKHART, J.Colloid Sci., 1961, 16, 484.

98. OVERBEEK AND STIGTER, Rec. Trav. chim., 1956, 75, 263.

99. MYSELS, J. Phys. Chem., 1954, 58, 303.

100. HUTCHINSON, Z. phys. Chem., 1959, N.F. 21, 38.

101. OVERBEEK, Chem. Weekblad, 1958, 54, 687.

102. HUTCHINSON AND BAILEY, Z. phys. Chem., 1959, N.F. 21, 30.

103. HOEVE AND BENSON, J. Phys. Chem., 1957, 61, 1149.

104. WHITE AND BENSON, J. Colloid Sci., 1958, 13, 584.

105. HUTCHINSON AND WINSLOW, J. Phys. Chem., 1956, 60, 122.

106. VOEIS AND HOERR, J. Colloid Sci., 1960, 15, 489.

107. ARANOW, J. Phys. Chem., 1963, 67, 556.

108. MUKERGEE, ibid., 1962, 66, 1375.

109. KUSHNER, HUBBARD, AND DOAN, ibid., 1957, 61, 372.

110. SCHICK, J. Colloid Sci., 1962, 17, 801.

111. SCHICK, ATLAS, AND EIRICH, J. Phys. Chem., 1962, 66, 1326.

112. DEBYE AND PRINS, J. Colloid Sci., 1958, 13, 86.

113. NAKAGAWA AND KURIYAMA, J.Chem. Soc., Japan, 1957, 78, 1568.

114. FOWLER AND GUGGENHEIM, "Statistical Thermodynamics" Cambridge, 1956, Chapter 8, p. 372.

115. HILL, J. Chem. Phys., 1955, 23, 617.

116. GRINDLEY AND BURY, J. Chem. Soc., 1929, 679.

117. BURY AND BROWNING, Trans. Faraday Soc., 1953, 49, 209.

118. COHEN, Mem. Services chim. Etat, 1952, 37, 85.

119. NAKAGAWA, KURIYAMA, INABA, AND TORI, J. Chem. Soc. Japan, 1956, 77, 1563.

120. WEIL AND STIRTON, J. Phys. Chem., 1956, 60, 899.

121. ROSS AND OLIVIER, ibid., 1959, 63, 1671.

122. BECHER, ibid., 1959, 63, 1675.

123. ELWORTHY, J. Pharm. Pharmacol., 1960, 12, 293.

124. NAKAGAWA, KURIYAMA, AND TORI, J. Chem. Soc. Japan, 1956, 77, 1684.

125. NAKAGAWA AND KURIYAMA, J. Chem. Soc. Japan, 1957, 78, 1573.

126. SCHICK, J. Colloid Sci., 1963, 18, 378.

127. NAKAGAWA AND MUNEYUKI, Ann. Rept. Shionogi Res. Lab., 1957, 7, 509.

128. LANGE, as ref. 28, p. 279.

129. HSAIO, DUNNING, AND LORENZ, J. Phys. Chem., 1956, 60, 657.

130. HILDEBRAND, ibid., 1947, 15, 225.

131. SHINODA, TAMAKA, AND KINOSHITA, J. Phys. Chem., 1959, 63, 648.

132. OSIPOW, SNELL, AND HICKSON, Proc. 2nd Internat. Congress on Surface Activity, p. 50, Academic Press, New York, 1958.

133. KLEVENS, J. Amer. Oil Chemists' Soc., 1953, 30, 74.

134. MULLEY AND METCALF, J.Colloid Sci., 1962, 17, 527.

135. BECHER AND CLIFTON, ibid., 1959, 14, 519.

136. BALMBRA, CLUNIE, CORKILL, AND GOODMAN, Trans. Faraday Soc., 1962, 58, 1661.

137. DWIGGENS AND BOLEN, J. Phys. Chem., 1961, 65, 1787.

138. DWIGGENS, BOLEN, AND DUNNING, ibid., 1960, 64, 1175.

139. ELWORTHY, J. Pharm. Pharmacol., 1960, 12, 260T.

140. TOKIWA AND ISEMURA, Bull. Chem. Soc. Japan, 1962, 35, 1737.

141. OKUYAMA AND CHUJO, ibid., 1954, 27, 259.

142. NAKAGAWA AND INOUE, J.Chem. Soc. Japan, 1958, 79, 345.

143. FERGUSON, J.Amer. Chem. Soc., 1955, 77, 5288.

144. CHWALA AND MARTIN, Melliand Textilber., 1937, 18, 998.

145. CHWALA AND MARTIN, Textil. Rundschau, 1947, 147.

146. TRINCHIERI, Amer. Dyestuff Reporter, 1952, 41, 729.

147. ROSCH, Kolloid Z., 1956, 147, 78.

148. KEHREN AND ROSCH, Melliand Textilber., 1956, 37, 434.

149. BAILEY AND CALLARD, J. Appl. Polymer Sci., 1959,156.

150. KARABINOS, HAZDRA, AND BALLUN, Euclides, 1955, 15, 145.

151. KARABINOS AND METZIGER, Trans. Ill. Stat. Acad. Sci., 1955, 48, 118.

152. BOEHMKE AND HEUSCH, Fette u. Seifen, 1960, 62, 87.

153. BOON, COLES, AND TAIT, J. Pharm. Pharmacol., 1961, 13, 200T.

154. DUNNING, Chem. Eng. Data, Series 2, 1957, No. 1, 88.

155. BECHER, J. Colloid Sci., 1961, 16, 51.

156. STAUF AND RASPER, Kolloid Z., 1957, 151, 148.

157. NAKAGAWA AND KURIYAMA, J. Chem. Soc. Japan, 1957, 78, 1568.

158. KURIYAMA, Kolloid Z., 1962, 181, 144.

159. RAPHAEL, Proc. 1st Internat. Congress of Surface Activity, Vol. 1, p. 56, Paris, 1954.

160. CURME AND JOHNSTON, "Glycols," p. 180, Reinhold Publ. Corpn., New York, 1952.

161. HIBBERT AND LOVELL, J. Amer. Chem. Soc., 1940, 62, 330.

162. SAUTER, Z. phys. Chem., 1933, 21, 161.

163. ELLIS, Chemistry of Synthetic Resins, Vol. 1, p. 74, Reinhold Publ. Corpn., New York, 1935.

164. ROSCH, Kolloid Z., 1957, 150, 153.

165. BECHER, J. Colloid Sci., 1962, 17, 325.

166. UCHIDA, KURITA, KOIZUMI, AND KUBO, J. Polymer Sci., 1956, 21, 313.

167. KURODA AND KUBO, ibid., 1957, 26, 323.

168. KURODA AND KUBO, ibid., 1959, 36, 453.

169. FINEMAN, BROWN, AND MYERS, J. Phys. Chem., 1953, 56, 963.

170. NAKAGAWA AND TORI, Kolloid Z., 1960, 168, 132.

171. MACLAY, J. Colloid. Sci., 1956, 11, 272.

172. KAWAMURA AND MINAMI, J. Oil Chem. Soc. Japan, 1952, 1, 26.

173. STEELE AND BERGER, Soap and Sanit. Chem., 1956, 32, 48.

174. KURIYAMA, Kolloid Z., 1962, 183, 68.

175. NAKAGAWA, KURIYAMA, AND INOUE, Symposium on Colloid Chem. (Chem. Soc. Japan), 12th Symposium, p. 29, 1959.

176. NAKAGAWA, INOUE, TORI, AND KURIYAMA, J. Chem. Soc. Japan, 1958, 79, 1194.

177. STAINSBY AND ALEXANDER, Trans. Faraday Soc., 1950, 46, 587.

178. FLOCKHART AND UBBELHOLDE, J. Colloid Sci., 1959, 8, 428.

179. BOLLE, as ref. 28, p. 294.

180. DOSCHER, MYERS, AND ATKINS, J. Colloid Sci., 1951, 6, 223.

181. MANKOWICH, Ind. Eng. Chem., 1956, 47, 2175.

182. BECHER, J.Colloid Sci., 1963, 18, 196.

183. STEWART, J.Chem. Phys., 1943, 11, 72.

184. ALEXANDER AND JOHNSON, "Colloid Science," p. 628, Oxford, 1950.

185. HARKINS, MITTELMAN, AND CORRIN, J. Phys. Colloid Chem., 1949, 53, 1350.

186. WEIDEN AND NORTON, J. Colloid Sci., 1953, 8, 606.

187. LIVINGSTONE, ibid., 1954, 9, 365.

188. KARABINOS, Soap Chem. Spec., 1955, 31, 50.

189. DAVIS, WATTMAN, SPEEL, Soap and Sanit. Chem., 1955, 31, 73.

190. MULLEY AND METCALF, J. Pharm. Pharmacol., 1956, 8, 774.

191. PATEL AND KOSTENBAUDER, J. Amer. Pharmaceut. Assoc. (Sci. Edn.), 1958, 47, 289.

192. HIGUCHI AND LACH, J. Amer. Pharmaceut. Assoc. (Sci. Edn.), 1954, 43, 465.

193. HIGUCHI AND GUTTMAN, ibid., 1956, 45, 659.

194. NAKAGAWA, J. Pharm. Soc. Japan, 1954, 74, 1116.

195. NAKAGAWA, ibid., 1956, 76, 1113.

196. ALLAWALA AND RIEGELMAN, ibid., 1953, 42, 267.

197. ALLAWALA AND RIEGELMAN, ibid., 1953, 42, 396.

198. OSOL AND PINES, ibid., 1952, 41, 289.

199. BROST AND KRUPEN, Soap Chem. Spec., 1957, 33, 93.

200. BARTLETT AND SCHMIDT, Appl. Microbiol., 1957, 5, 355.

201. RIEGELMAN, ALLAWALA, HRENOFF, AND STRAIT, J. Colloid Sci., 1958, 13, 208.

202. RIGG AND LIN, J. Amer. Oil Chemitsts' Soc., 1953, 30, 14.

203. SHEPHERD AND GEDDES, J. Chem. Phys., 1945, 13, 63.

204. NAKAGAWA, Ann. Rept. Shionogi, Res. Lab., 1958, 8, 886.

205. NIMOTA, J. Chem. Soc. Japan, Ind. Chem. Sect., 1959, 62, 592.

206. HEILBRON AND BUNBURY, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1953.

207. NAKAGAWA AND SHINODA, "Colloidal Surfactants," p. 135, Academic Press, London, 1963.

208. MULLEY, J. Pharm. Pharmacol., 1961, 13

209. WINSOR, Chem. and Ind., 1960,

210. NAKAGAWA AND INOUE, J. Chem. Soc. Japan, 1957, 78, 636.

211. MATOON, STEARNS, AND HARKINS, J. Chem. Phys., 1948, 16, 644.

212. BRADY AND HUFF, J. Phys. Chem., 1958, 62, 644.

213. RALSTON AND EGGENBERGER, J. Amer. Chem. Soc., 1948, 70, 983.

214. HERZFIELD, CORRIN, AND HARKINS, J. Phys. Chem., 1950, 54, 271.

215. CRIEGEN, Ann. N.Y. Acad. Sci., 1949, 51, 828.

216. ROSSI AND BALDACCI, Ann. Chim. (Italy), 1951, 41, 534.

217. BALDACCI, ibid., 1950, 40, 358.

218. COHEN, Mem. Services chim. État, 1951, 36, 207.

219. BURY, Phil. Mag., 1927, 4, 980.

220. HSAIO AND DUNNING, J. Phys. Chem., 1955, 59, 362.

221. WARD AND TORDAI, J. Chem. Phys., 1946, 14, 453.

222. WARD, "Surface Chemistry", p. 55, Butterworths, London, 1949.

223. KUNO AND ABE, Kolloid Z., 1961, 177, 40.

224. KUNO AND ABE, Kolloid Z., 1962, 181,

225. RAYLEIGH, Phil. Mag., 1871, 41, 107, 447.

226. FRANK, "Introduction to Electricity and Optics", McGraw-Hill, New York, 1950.

227. MOELWYN HUGHES, "Physical Chemistry", p. 389, Pergamon, London, 1961.

228. SMOLUCHOWSKI, Ann. Physik, 1908, 25, 205.

229. SMOLUCHOWSKI, Phil. Mag., 1912, 23, 165.

230. OSTER, Chem. Rev., 1948, 43, 319.

231. EINSTEIN, Ann. Physik, 1910, 33, 1275.

232. DEBYE, J. Appl. Phys., 1944, 15, 338.

233. DEBYE, J. Phys. Colloid Chem., 1947, 51, 18.

234. TANFORD, Physical Chemistry of Macromolecules, p. 283, Wiley, London, 1961.

235. FIXMAN, J. Chem. Phys., 1955, 23, 2074.

236. GANS, Z. Physik, 1923, 17, 353.

237. CABANNES AND ROCARD, "La Diffusion Moleculaire de la Lumiere", University Press, Paris, 1929.

238. GEIDUSCHEK, J. Polymer Sci., 1954, 13, 408.

239. DEBYE, Ann. Physik, 1915, 46, 809.

240. GUINIER, Ann. Physique, 1939, 12, 161.

241. ZIMM AND STOCKMAYER, J. Chem. Phys., 1949, 17, 1301.

242. DEBYE, ibid., 1946, 14, 636.

243. ZIMM, ibid., 1948, 16, 1099.

244. RAYLEIGH, Proc. Roy. Soc., 1911, A84, 25.

245. GANS, Ann. Phys. Lpz., 1925, 76, 29.

246. NEUGEBAUER, Ann. Physik, 1943, 42, 509.

247. STACEY, "Light-Scattering in Physical Chemistry", p. 62, Butterworths, London, 1956.

248. GEIDUSCHEK AND HOLTZER, Adv. Biol. Med. Phys., 1958, 6, 431.

249. BENOIT AND DOTY, J. Phys. Chem., 1954, 59, 624.

250. HOLTZER, J. Polymer Sci., 1955, 17, 432.

251. EINSTEIN, Ann. Physik, 1906, 19, 289.

252. EINSTEIN, ibid., 1911, 34, 591.

253. SIMHA, J. Phys. Chem., 1940, 44, 25.

254. MEHL, ONCLEY, AND SIMHA, Science, 1940, 92, 132.

255. ONCLEY, Ann. N.Y. Acad. Sci., 1940, 41, 121.

256. TIMMERMANS, "Physico-chemical Constants of Pure Organic Compounds," Elsevier, London, 1950.

257. HARKINS AND ANDERSON, J. Amer. Chem. Soc., 1937, 59, 2189.

258. HARKINS, in Weissberger, "Physical Methods of Organic Chemistry, 3rd ed., Vol. 1, part 1, p. 772, Interscience, New York, 1959.

259. PETHICA, Trans. Faraday Soc., 1958, 54, 1382.

260. HUGO AND NEWTON, J. Pharm. Pharmacol., 1960, 12, 447.

261. ALEXANDER AND JOHNSON, as ref. 184, p. 519.

262. PARRIERA AND OTTEWILL, J. Phys. Chem., 1958, 62, 912.

263. ROBINSON, Ph.D. Thesis, London, 1959.

264. ELWORTHY AND McINTOSH, J. Pharm. Pharmacol., 1961, 13, 663.

265. SCHULZ, CANTOW, AND MEYERHOFF, J. Polymer Sci., 1952, 10, 79.

266. ALEXANDER AND STACEY, Proc. Roy. Soc., 1952, A212, 274.

267. DEBYE AND NEUMANN, J. Phys. Chem., 1951, 55, 1.

268. LOCHET, Compt. rend., 1950, 230, 437.

269. GORING AND NAPIER, J. Chem. Phys., 1954, 22, 147.

270. FESSENDEN AND STEIN, ibid., 1954, 22, 1, 778.

271. McINTOSH, PhD. Submission, Glasgow, 1963.

272. MARON AND LOU, J. Polymer Sci., 1954, 14, 29.

273. HERMAN AND TRAPP, Rec. Trav. chim., 1954, 73, 167.

274. CARR AND ZIMM, J. Chem. Phys., 1950, 18, 1, 616.

275. BRICE, HALWER AND SPEISER, J. Opt. Soc. Amer., 1950, 4, 768,

276. BRICE, HALWER, AND SPEISER, J. Opt. Soc. Amer., 1954, 44, 340,

277. TANFORD, as ref. 234, p. 391.

278. FRISCH AND SIMHA, "The Viscosity of Colloidal Suspensions and Macromolecules" in "Rheology", Vol. 1, Ch. 14, Acad. Press., New York, 1956.

279. ROBINSON AND SAUNDERS, J. Pharm. Pharmacol., 1959, 11, 304.

280. DAVIES, Statistical Methods in Research and Production, pp. 175-205, Oliver and Boyd, London, 1961.

281. OGSTON AND STANIER, Biochem. J., 1953, 53, 4.

282. GEORGE, M.Sc. Submission, Glasgow, 1963.

283. GIBSON AND ADAMS, J. Amer. Chem. Soc., 1933, 55, 2679.

284. STOKES AND ROBINSON, "Electrolyte Solutions", 2nd Edition, p. 457, Butterworths, London, 1959.

285. BARRER AND KELSEY, Trans. Faraday Soc.,
1961, 57, 452.

286. FLETCHER, unpublished results.

287. MANKOWICH, J. Phys. Chem., 1954, 58, 1027.

288. TANFORD, as ref. 234, p. 196.

Appendix 1.

Estimation of the Limits of Error in the c/τ Intercept.

10^3c (10^3x)	$\frac{c - c_1}{\tau - \tau_1}$ (y)
0.923	3.94
1.101	3.90
1.790	3.98
1.809	4.07
1.905	4.21
2.187	4.26
2.351	4.20
2.492	4.32
2.617	4.51
2.777	4.59
2.995	4.66
3.172	4.36
3.283	4.44
3.820	4.71
3.860	4.83
3.895	4.71
4.595	5.11
4.790	5.00
6.384	5.79

$\Sigma x = 0.056746$

$\bar{x} = 0.0029866315$

$\Sigma x^2 = 0.202536692 \times 10^{-3}$

$(\Sigma x)^2 = 0.3220108516 \times 10^{-2}$

$(\Sigma x)^2/n = 0.00016947939$

$\Sigma xy = 0.26668116$

$\Sigma y = 85.59$

$\bar{y} = 4.5047368$

$\Sigma y^2 = 389.4933$

$(\Sigma y)^2 = 7325.6481$

$(\Sigma y)^2/n = 385.56042$

$\Sigma x \Sigma y/n = 0.25562579$

$$b = \frac{0.01105537}{0.33057302 \times 10^{-4}}$$

$$= 334.43$$

$$\frac{c}{\tau}(c=0) = \bar{y} - b\bar{x}$$

$$= 3.5059$$

Sum of squares due to the regression = 3.6972

Sum of squares about the regression = 0.2357

This is based on 17 degrees of freedom;

Variance about the regression = 0.01386

Variance of the regression coefficient = 419.27

Variance of the regression estimate =

$$0.0073 + 419.27(x_k - \bar{\bar{x}})^2$$

Variance of an estimate = Variance of regression estimate

+ Variance about the regression

$$= 0.0146 + 419.27(x_k - \bar{\bar{x}})^2$$

$\therefore$ for $x_k = 0$ = 0.01834

Standard Error = 0.1354

$\therefore$ The 95% confidence limits for the intercept on the y axis

$$= 3.5059 \pm 2.1 \times 0.1354$$

$$= 3.5059 \pm 0.2843$$

$$= 3.5059 \pm 8\%$$

Appendix 2.

$10\log.10^4C$ (y)	100τ (x)
4.54	3.41
4.66	3.30
4.74	3.31
4.72	3.18
4.79	3.90
4.83	3.28
4.94	5.43
4.97	5.46
5.00	6.03
5.11	5.59
5.16	6.12
5.32	8.86
5.39	8.95
5.46	9.94
5.47	9.84
5.48	9.69
5.82	13.03
5.94	15.44
6.02	14.59
6.03	13.19

$$\Sigma xy = 831.7599$$

$$\Sigma(y^2) = 548.8739$$

$$(\Sigma y)^2 = 10893.0969$$

$$(\Sigma y)^2/N = 544.65485$$

$$\Sigma(y - \bar{y})^2 = \Sigma(y^2) - (\Sigma y)^2/N$$

$$= 4.2191$$

$$\Sigma(x^2) = 1477.0610$$

$$(\Sigma x)^2 = 23268.4516$$

$$(\Sigma x)^2/N = 1163.42258$$

$$\Sigma(x - \bar{x})^2 = \Sigma(x^2) - (\Sigma x)^2/N$$

$$= 313.6384$$

$$\Sigma x\Sigma y = 15920.5998$$

$$\Sigma x\Sigma y/N = 796.02999$$

$$\Sigma(x - \bar{x})(y - \bar{y}) = \Sigma xy - \Sigma x\Sigma y/N$$

$$= 35.7300$$

$$\Sigma x = 152.54$$

$$\bar{x} = 7.627$$

$$\Sigma y = 104.37$$

$$\bar{y} = 5.2185$$

$$\Sigma y_1 = 33.20 \qquad \Sigma x_1 = 25.81$$

$$\bar{y}_1 = 4.742857 \qquad \bar{x}_1 = 3.687142$$

$$\Sigma y_3 = 40.22 \qquad \Sigma x_3 = 85.72$$

$$\bar{y}_3 = 5.745714 \qquad \bar{y}_3 = 12.245714$$

$$b = \frac{\bar{y}_3 - \bar{y}_1}{\bar{x}_3 - \bar{x}_1} = \frac{5.745714 - 4.742857}{12.24571 - 3.687142}$$

$$= 0.117175$$

$$Y = \bar{y} + b(x - \bar{x})$$

$$= 5.2185 + 0.11718x - 0.8937$$

$$= 4.3248 - 0.11718x$$

$$\sigma_y^2 = k^2\sigma_x^2 = \frac{\Sigma(y - \bar{y})^2 - b\Sigma(x - \bar{x})(y - \bar{y})}{N - 2}$$

$$= \frac{0.0324}{18}$$

$$y = 0.001800$$

$$\sigma_x^2 = \frac{\Sigma(x - \bar{x})^2}{N - 2} - \frac{\Sigma(x - \bar{x})(y - \bar{y})}{(N - 2)b}$$

$$= \frac{313.6384}{18} - \frac{35.7300}{2.10915}$$

$$= 0.483882$$

$$k^2 = \frac{\sigma_y^2}{\sigma_x^2} = \frac{0.001800}{0.483882}$$

$$= 0.003719915$$

Variance of b.

$$V(b) = \frac{\sigma_x^2 (k^2 + b^2)^2}{k^2\ (x - \bar{x})^2 + b\ (x - \bar{x})(y - \bar{y})}$$

$$= \frac{0.000147341}{5.353365}$$

$$= 0.000027523$$

The Variance of a predicted value of y for a given value of x, (x_0), is

$$V(y_0) = k^2\sigma_x^2/N + (x_0 - \bar{x})^2 V(b) + b^2\sigma_x^2(1 + 1/N)$$

Thus for the intercept of the y axis (where $x_0 = 0$)

$$V(y_0) = 0.008667$$

and the standard error $= 0.9310 \times 10^{-1}$

The 95% confidence limits for the intercept on the

$$\text{y axis} = 4.325 \pm 0.0931 \times 1.74$$

$$= 4.325 \pm 0.162$$

$$\text{But } 4.325 = 10 \log.\ 10^4 C$$

$$C = 2.707 \times 10^{-4}$$

$$\text{Limits of error of C} = 2.71 \pm 0.10$$

$$= 2.71 \pm 3.8\%$$