

## REVIEW

# Emulsion stabilization by non-ionic surfactants: experiment and theory\*

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Two recent texts (Becher, 1965, Sherman, 1968) have dealt in some detail with emulsions, but little attention has been given to mechanisms of emulsion stabilization by non-ionic materials, in spite of the widespread industrial use of non-ionic surfactants. Emulsions stabilized by these non-ionic compounds present interesting problems not encountered in systems which contain ionic surfactants.

At first sight it would appear that stability cannot be explained by the electrostatic repulsive forces which operate in many dispersions, but it is known that pure hydrocarbon droplets dispersed in pure water possess a net negative charge. The problems which arise in the theory of non-ionic dispersions are these. To what extent do electrostatic forces contribute to stability? How is any charge on the dispersed particles affected by the presence of non-ionic detergents or polymer molecules at the interface? What is the nature of other stabilizing forces?

Lyklema (1968) recently discussed the principles of stability of colloidal dispersions in non-aqueous media. Much of what he has written is relevant here, although we will restrict our discussion mainly to oil-in-water emulsions. The outline of the theories of stability will thus be kept to a minimum.

It is the purpose of this review to consider relevant aspects of colloid stability theory and the relation of some recent experiments to this theory, and to discuss this with regard to the use of these emulsion systems. We will deal mainly with stabilizers which are derivatives of polyoxyethylene glycols.

### ASPECTS OF EMULSION STABILITY

Emulsions have been defined as heterogeneous systems of one liquid dispersed in another in the form of droplets usually exceeding  $0.1 \mu\text{m}$  (Becher, 1965) in diameter. The two liquids are immiscible, chemically unreactive, and form systems characterized by a minimal thermodynamic stability.

Unless the free energy of the oil-water interface is zero, an emulsion cannot be a thermodynamically stable system, since reduction of the area of oil in contact with the water will always result from coalescence of the droplets. "Stability" is therefore a relative term; but the degree of stability can be assessed by observing the rate of change of a parameter such as interfacial area or droplet diameter. Unstabilized emulsions, referred to as oil hydrosols by King (1941), coalesce rapidly, while stabilized emulsions can retain a highly dispersed internal phase for months or years. As the free energy of the interface is the driving force for coalescence, emulsions can be stabilized by the inclusion of a surface-active substance in the

\* The first of two articles, the second of which will appear on p. 233 *et seq.* and includes all the references.

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system which concentrates at the oil-water interface. The role played by the surface-active material may be threefold, depending on the chemical nature of the adsorbing material and the adsorbent. The adsorbed surfactant molecules:

(i) can decrease the free energy of the system. Although at one time this effect was considered to be largely responsible for the stability, emulsions having the same interfacial free energy may have widely differing stabilities. However, statements can still be found ascribing stability loosely to interfacial tension (e.g. Richardson, 1953);

(ii) can form a barrier delaying the coalescence of the globules. This barrier represents a combination of steric, viscous and elastic properties (Schulman & Cockbain, 1940a,b; King, 1941; Cockbain & McRoberts, 1953; and Cockbain, 1956) depending on the emulgent;

(iii) may affect the electrostatic charge of the dispersed particles.

### *Instability*

Emulsion instability is manifested in changes in the physical properties of the dispersion such as its droplet size distribution or its rheological properties (Richardson, 1953a) or other parameters which are a consequence of the coalescence of globules or their flocculation, that is, of the alteration in the real or effective mean globule diameter respectively. *Flocculation*, which is often the precursor of coalescence can affect the appearance of both liquid and solid emulsions. It accelerates the rate of *creaming* or *settling* which in itself is regarded as a form of instability.

*Inversion* of emulsion type is rare although localized inversion may occur through interaction of the components of the systems with packaging materials. This type of instability is dealt with later in relation to phase volume and emulsifier type.

The problem is to prevent instability, not only to maintain the appearance of the emulsion, but so that the characteristics of the emulsion and of medicaments dissolved in the emulsion are as little changed on ageing as possible. As an example, ageing might alter the absorption of heparin from o/w emulsions where absorption of heparin appears to be directly related to the particle size and total surface area of the oil droplets (Engel & Riggi, 1969). Fat emulsions are used extensively in intravenous feeding (Geyer, 1960), but the state of the art is exemplified by the statement (Today's Drugs, 1970) that "the emulsions must be stored in a refrigerator and no antibiotics, vitamins or potassium supplements added because they may break the emulsions". Lynn (1970) reports some experiments on the addition of disodium carbenicillin and sodium cloxacillin to intravenous lipid emulsions which verify this statement.

The preservation of emulsions by lyophilization and later reconstitution (Richter & Steiger-Trippi, 1960; Lladser, Medrano & Arancibia, 1968) is not yet a sufficiently advanced technique for widespread use, hence we must consider those factors which are responsible for stability and instability in the prepared emulsion.

### *Macromolecules as stabilizers*

The tough "skins" formed at the interface between oil and aqueous solutions of macromolecular substances have been known for many years. Qualitative experiments on emulsions stabilized by this class of emulsifier have been made by Serrallach & Jones (1931) and Serrallach, Jones & Owen (1933). These compounds, many of which are naturally-occurring, include cellulose derivatives, gums and proteins. Many synthetic polymers exhibit similar properties, including polyvinyl alcohols, ethers, pyrrolidones, salts of the alkyd resins and many others. Characterized by high molecular weights (50 000–500 000), they are frequently employed as viscosity builders

in emulsions, thereby decreasing the creaming rate and the number of collisions between the dispersed particles i.e. reducing orthokinetic flocculation). Few reports have been published on the nature of the interfacial film which presumably forms a mechanical barrier to coalescence in these emulsions (Mussellwhite, 1964; Hamill & Petersen, 1966; El-Shimi & Izmailova, 1967; Petersen & Hamill, 1968) although thorough studies in this respect have been made by Shotton & co-workers (e.g. Shotton, Wibberley & Vaziri, 1964). Films of alginates and gelatin on emulsified liquid paraffin droplets were estimated to be about  $0.25 \mu\text{m}$  thick.

In systems of light petroleum stabilized by bovine serum albumin, a direct correlation between emulsion stability and the viscoelastic properties of protein films was observed by Biswas & Haydon (1960, 1962). In a study of monolayers of bovine plasma albumin at the benzene-solution interface, Davies & Mayers (1960) were able to measure substantial interfacial viscosities. It should be pointed out, however, that in any consideration of interfacial viscosity, the magnitude of the surface rheological parameters is not a measure of the overall stability of the droplets but only an indication that some stability will be present (van der Waarden, 1958). The nature of the film is of more import than its high viscosity. For example, rigid films of hexadecanol do not produce stable emulsions of chlorobenzene (Elworthy, Florence & Rogers, 1971b). Sonntag, Netzel & Unterberger have recently confirmed this view in their statement (1970) that "in monomolecular adsorbed layers of surfactants agreement between coalescence stability on the one hand and the mechanical properties, measured parallel with the interface, on the other, would occur only in a few selected instances."

The presence of rigid interfacial films can be demonstrated by withdrawing aged pendant drops of disperse phase into a syringe. Crinkled films appear because of the reduction of surface area in contact with solution (Shotton & White, 1963; Strassner, 1968).

The questions to be posed in relation to viscous surface layers are: to what extent is the viscosity of the film itself contributing to stability and is any increased stability due to the fact that molecules of stabilizer are prevented from escape from the surface layer? It can be calculated that the concentration of the surface active components used by Schulman & Cockbain (1940) to produce their emulsions was always more than that required to form a monolayer. The excess forms, in many cases, viscous gels in the aqueous phase, hence placing doubt about the major role played by the viscosity of the interfacial film (Talman, Davies & Rowan, 1967).

#### *Non-ionic surfactants as stabilizers*

Non-ionic surfactants have many advantages over ionic surfactants as emulsifiers. In general they are less toxic and less sensitive to electrolytes and pH variations. Emulsions prepared with Triton X-400 were stable over the pH range 2.5 to 11 and exhibited stability and compatibility with many substances used in dermatology (Casadio, 1951).

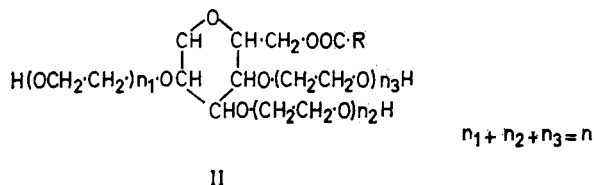
In recent years the use of commercial heterogeneous and pure synthetic non-ionic detergents in surface-chemical studies has been widespread. The compounds most widely studied have been polyoxyethylene adducts of alcohols and esters. The former may be represented by the general chemical formula I.



I

(Non-ionic surfactants having this general formula will be abbreviated to  $\text{C}_{m+1}\text{E}_n$  where  $n$  is the number of ethylene oxide units in the molecule.) Synthetic homogeneous detergents of different chain lengths of the hydrocarbon portion or polar

portion may be prepared (Mulley, 1968). One widely used commercial series of non-ionic esters (Tweens or polysorbates) is represented by the chemical formula II.

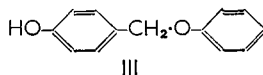


The great advantages of non-ionics are their lack of strong electrical charges and the ease by which their degree of hydrophilicity can be altered by increasing or decreasing the length of either the non-polar or polar chains of the molecule. The properties of non-ionic surfactants in solution have been reviewed (Shinoda, Nakagawa & others, 1963; Elworthy & Macfarlane, 1965; Schick, 1967) and their utility as emulsifying agents well documented (Becher, 1965; Sherman, 1968). However, the problem still remains of exactly how they function as emulsifying agents, and how far they are stable in the presence of electrolytes and other additives.

Polyoxyethylated non-ionics owe their solubility in water to hydrogen-bonding of solvent molecules to the ether oxygens of the hydrophilic chains. Thus, in micelles in aqueous solution and at the oil-water interface, the polyoxyethylene chains are extended outwards into the aqueous medium, while the hydrocarbon chains are orientated in the non-polar environment. It has been a matter for debate whether non-ionics make any contribution to the electrical atmosphere around dispersed emulsion globules (Becher, 1962). It was concluded from a study of the coalescence of mercury droplets stabilized with a series of non-ionic co-polymers of ethylene oxide and propylene oxide that electrostatic repulsion can be neglected in comparison with the stability imposed by the physical presence of the polymers (Watanabe, Matsumoto & Gotoh, 1965). Similar conclusions were reached from studies on water-in-benzene emulsions (Albers & Overbeek, 1959a,b). The character of the adsorbed surface film of emulsifier is regarded as being of primary importance in determining emulsion stability (Mardles & de Waele, 1951). It has been postulated that the viscosity of the interfacial film is the foremost stabilizing factor (Davies & Mayers, 1960; Gold, 1962; Sonntag & Klare, 1963; Isemura & Kimura, 1952). Some workers have suggested that film elasticity may play a role (Prins & van den Tempel, 1964; van den Tempel, Lucassen & Lucassen-Reynders, 1965). Both of these properties are dependent on the length of the polyoxyethylene chain and on the orientation of the surfactant molecule at the interface. In addition, the helical conformations of the hydrophilic chains probably function by hindering the close approach of emulsion droplets, thus preventing coalescence.

Although non-ionic surfactants are often chosen for emulsified systems because of their relatively low toxicity, several problems in formulation have arisen with their use. Most emulsions of edible fats and oils must be preserved against microbial attack. The most effective preservatives have often been the *p*-hydroxybenzoic acids. Unfortunately, these acids are inactivated by interaction with polyoxyethylene compounds in the system, and, in addition, changes in emulsion stability have occurred. The formation of complexes between phenolic compounds and ethylene oxide condensates has been frequently demonstrated (Higuchi & Lach, 1954; Guttmann & Higuchi, 1956). Complex formation reduces the solubility of the polyoxyethylene non-ionic surfactants and renders them less effective as emulsifiers. Nevertheless an example has been quoted (Casadio, 1951) where the increase in viscosity caused

by the addition of a phenol (III) to emulsions stabilized by a polyoxyethylene non-ionic increased the resistance of the emulsion to separation by centrifugation.



Over the years, liquid emulsions have been a useful dosage form in pharmaceutical practice, because of their ability to incorporate both oil- and water-soluble components, although the emulsion has not been a modern pharmaceutical favourite. However, there have been signs of renewed interest in the possibilities they offer as dosage forms. For example, a recent communication has described the use of a w/o/w multiple emulsion as a delayed release system for chlorpromazine (Collings & Schneider, 1970). The problems associated with stability have frequently imposed restrictions on the use of emulsions as vehicles for all types of drugs.

The special problems of stabilization of aerosol emulsions and foams has been reviewed by Sanders (1970).

#### ASPECTS OF THE PHYSICAL CHEMISTRY OF NON-IONIC SURFACTANTS RELEVANT TO DISPERSION STABILIZATION

Non-ionic surfactants adsorb at interfaces, and above certain concentrations form micelles in aqueous solutions and in some non-aqueous solvents. The physical chemistry is discussed here briefly, with special emphasis on those properties which are likely to be of importance in emulsion stability.

Micelles of non-ionic surfactants of the polyoxyethylene ether class have a structure which is diagrammatically represented in Fig. 1. It is possible that some of the

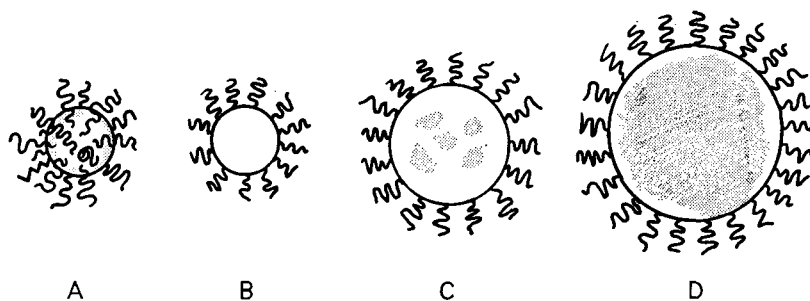


FIG. 1. A. Diagrammatic representation of a non-ionic micelle showing the inner hydrocarbon core and outer hydrated polyoxyethylated layer. B. Cross section of a micelle. C. A solubilizate laden micelle with solubilizate (stippled) in hydrocarbon region and D, a small emulsion globule

data reported on such structures can be used in the interpretation of the behaviour of non-ionics at emulsion interfaces. There is no obvious distinction between a micelle containing a large amount of solubilizate and a small globule of an emulsion (Fig. 1).

It is likely that the hydration of the surfactant at the oil-water interface is at least as high as that of the dispersed molecules because the area/molecule at the oil-water interface is greater than at the air-water interface. With regard to charge effects in dispersed systems, the presence of a net positive charge on non-ionic micelles due to oxonium ion formation has been argued by Becher (1962). Schick (1963) also

concluded from studies on surface films that the ether oxygens in the ethylene oxide adducts form oxonium ions, and Hsiao, Dunning & Lorenz (1956) also attribute the weak positive charges associated with the micelles of polyoxyethylated detergents to possible oxonium ion formation.

While adsorption of non-ionic polyethers on negatively charged particles reduces the negative charge on the particles (Glazman, 1966; Elworthy & Florence, 1967), adsorption on positively charged silver iodide sols results in charge reversal (Glazman & Kabysch, 1969). It is unlikely that positively charged chains could accomplish this sign change. However, as all oil droplets in aqueous media initially possess a *negative* charge it is reasonable to assume that the former behaviour is typical of emulsion systems.

The addition of electrolytes to non-ionic stabilized emulsions can, perhaps surprisingly, cause pronounced effects on stability (Elworthy, Florence & Rogers, 1971a). In solutions of non-ionic surfactants, generally the addition of electrolytes causes a dehydration of the ethylene oxide chains (Doscher, Myers & Atkins, 1951; Greenwald & Brown, 1954; Bailey & Callard, 1959) by disruption of hydrogen bonds (Stewart, 1943; Schick, 1962). Selected salts have been shown to exhibit interaction with polyethylene oxide ethers, reducing their solvation and producing more compact molecular conformations (Lundberg, Bailey & Callard, 1966; Hammes & Swann, 1967). The interaction appears to be more pronounced in non-aqueous solvents. The mechanism involved is unknown but has been suggested to arise from an ion-dipole interaction (Lundberg, Bailey & Callard, 1966).

The effect of salts on the interfacial tension of solutions of cetomacrogol 1000 and other detergents has been studied by Wan & Poon (1969).

#### *Conformation of the polyoxyethylene chain*

The conformation of lower molecular weight polyoxyethylene polymers has been termed "zig-zag" by Standinger (1932) and Ellis (1935), whereas higher polymers exist in the "meandering" form (synonymous with the fully extended "*trans*" form and the more condensed "*gauche*" form of Rosch (1956, 1957). Viscosity measurements led Lovell & Hibbert (1940) to the conclusion that the long polyoxyethylene chain is highly convoluted in aqueous solution. Dipole moment measurements of polyethylene glycols (PEG) in dioxan indicated a progressive increase in convolution with increase in the degree of polymerization. Since this would not infer a helical chain structure, a free rotation model of a random coil was considered (Uchida, Kurita & others, 1956), leading to the suggestion of the existence of mixtures of both the "*trans*" and "*gauche*" conformations. In aqueous solution, the "*gauche*" form probably predominates. Electrolytes reduce the configurational entropy of the ethylene oxide chains and increase the aggregation number in micelles of polyoxyethylene surfactants (Schick, Atlas & Eirich, 1962). That is, the "salting out" effect of the electrolyte causes a collapse of the chains. Such changes in conformation might have relevance in the effectiveness of non-ionics in stabilized dispersions in the presence of salts.

The conformation of polyoxyethylene chains of non-ionic detergents has been postulated from their areas per molecule calculated from surface tension measurements by application of Gibbs' equation. A series of polyoxyethylene derivatives of hexadecyl alcohol at the solution-air interface occupied areas which were much larger than the cross-sectional area of a hydrocarbon chain (0.21 nm<sup>2</sup>) (Elworthy & Macfarlane, 1962) and the areas were less than the corresponding areas at the oil-water interface (Elworthy & Florence, 1969a). Examples of areas per molecule and micellar radii of some members of this series are listed in Table 1, the latter to show the non-extended nature of the molecules. The areas per molecule increase

Table 1. Areas per molecule and micellar radii of polyoxyethylene glycol hexadecyl ethers.

Oil phase	Detergent	Area/molecule (nm <sup>2</sup> ) at oil-water interface	Area/molecule (nm <sup>2</sup> ) at air-water interface	Micelle radius (nm)
Anisole .. ..	C <sub>16</sub> E <sub>3</sub>	0.45	0.31	3.2
	C <sub>16</sub> E <sub>6</sub>	0.56	0.38	4.0
	C <sub>16</sub> E <sub>9</sub>	0.76	0.53	4.6
	C <sub>16</sub> E <sub>25</sub> *	1.54	1.20	4.8
Chlorobenzene ..	C <sub>16</sub> E <sub>3</sub>	0.48	0.31	3.2
	C <sub>16</sub> E <sub>6</sub>	0.80	0.38	4.0
	C <sub>16</sub> E <sub>9</sub>	1.00	0.53	4.6
	C <sub>16</sub> E <sub>25</sub> *	1.84	1.20	4.8

\* Cetomacrogol 1000. Data from Elworthy & Florence (1967, 1969a,b).

with increase in length of the hydrophilic chain, but the areas per ethylene oxide unit decrease, indicating a curled chain lying almost perpendicular to the interface. A similar conclusion was reached by Schick (1963). Thus the cross-sectional area of the solvated polyoxyethylene chain is the controlling factor in the packing of the molecules in the interface. Conditions which lead to a reduction in the cross-sectional area should lead to tighter packing of the molecules, resulting eventually in a very coherent, impervious film. However, a very close packed film with hindered hydrophilic chains would be unable to confer entropic stabilization to the system as interpenetration of the chains on neighbouring particles would then be impossible. This might partially explain the greater effect of long chain PEG compounds in stabilizing dispersions (see later).

There is a marked difference in the behaviour of non-ionic surfactants at polar and at non-polar oil-water interfaces. This can be demonstrated by the interfacial tension results obtained by Becher and shown in Fig. 2. The positions of non-ionic

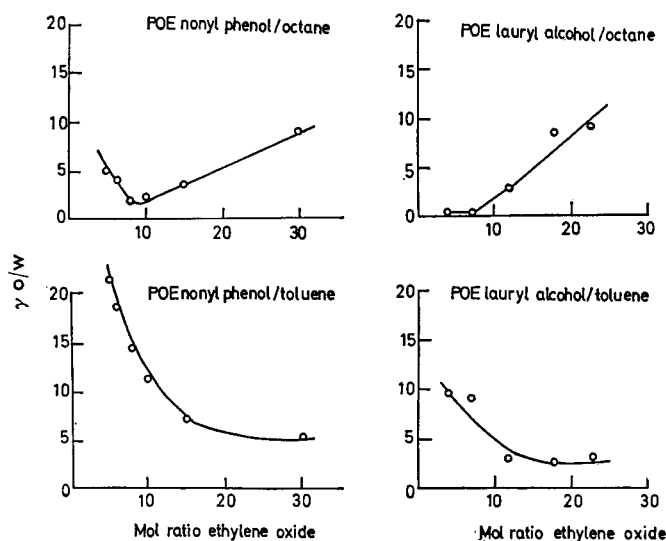


FIG. 2. Interfacial tension of lauryl alcohol ethers and nonyl phenol ethers at 0.1% concentrations against a non-polar oil (octane) and polar oil (toluene) showing the differences in behaviour as a function of ethylene oxide chain length. Reproduced from Becher (1963) by permission of Academic Press.

surface-active agents at oil-water interfaces have been estimated by Becher (1963) on consideration of the hydrogen-bonding contribution of these molecules to the net interfacial free energy. Knowledge of the effect of ethylene oxide chain length on the interfacial tension at aromatic hydrocarbon-water interfaces led to the assumption that a portion of the polyoxyethylene chain was immersed in the oil phase with the hydrocarbon chain. Fig. 3 illustrates the relative positions of the molecules. Thus,

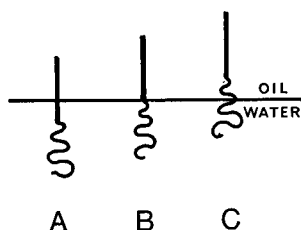


FIG. 3. Possible orientations of a non-ionic surfactant at an oil-water interface, after Becher (1963). For explanations of A, B and C see text.

a degree of hydrogen-bonding with aromatic hydrocarbons diminishes the dispersion force contribution of the oil to the interfacial free energy, resulting in higher interfacial tensions. This occurs with short ethylene oxide chains (model C in Fig. 3). With increasing ethylene oxide chain lengths, hydrogen-bonding with the aqueous phase becomes more pronounced and the molecule shifts in its direction (model B or A). With aliphatic hydrocarbons, only positions A or B would be expected. Presumably, the solvation layer surrounding emulsified oil globules would increase as the polyoxyethylene chains protrude further into the aqueous medium, and the consequences of this could explain the increase in stability of these systems with non-ionics of increasing hydrophilic chain length from  $E_3$  to  $E_{25}$  (Elworthy & Florence, 1969a).

The importance of the hydrate layer in maintaining stability is indicated by Levi & Smirnov (1959) who showed that monoglycerides became efficient emulsifiers only when they possessed sufficient hydroxyl groups. These authors also noted that the introduction of ionizable carboxylic acid groups into the non-ionic stabilizer molecule containing many hydroxyl groups greatly increased its emulsifying properties. The introduction of ionic groups is not always beneficial, nor the explanation of their action simple, as work in this laboratory (Attwood & Florence, 1971) has shown. The addition of a sulphate group into cetomacrogol gives



an emulsifier with decreased emulsifying power in chlorobenzene-in-water emulsions compared with the non-ionic parent compound, in spite of higher zeta potentials. The explanation of this behaviour is still being sought.

The differences in interfacial tension at polar and non-polar interfaces will partly explain the difference in stability of chlorobenzene and hexadecane emulsions stabilized by  $C_{16}E_3$ . Hexadecane in water emulsions are much more stable than chlorobenzene or anisole emulsions stabilized by the same detergent (Florence, unpublished) as shown by the results presented in Fig. 4.

#### *Interaction forces between dispersed particles*

The theory of stability of lyophobic colloids published by Derjaguin & Landau (1941) and by Verwey & Overbeek (1948) (the "DLVO theory") is still the most successful treatment of stability. The theory was developed primarily to deal with



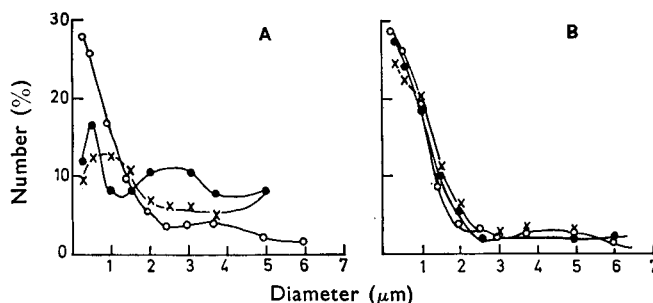


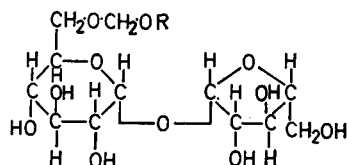
FIG. 4. Globule size distribution plots showing the greater stability of hexadecane emulsions (B) (phase volume 0.2) stabilized with 1%  $C_{16}E_8$ , compared with an anisole emulsion (A) of identical phase volume with the same concentration of the same surfactant. Values at  $\circ$ , 0 h;  $\bullet$ , 2 days;  $\times$ , 15 days in both cases.

the stability of inorganic sols, which possess intrinsic electrostatic charges, but over the years, the theory and modifications of it, have been applied to suspensions of clays and to emulsions. In general, the theory predicts the energy requirements of the system which will lead to stability against flocculation or coagulation of the particles—this step being the final one for solid dispersions in a liquid medium but the initial stage of instability in emulsions, as flocculation can occur without coalescence. However, as the average proximity of the particles will be governed by the forces discussed by the theory, the barrier to flocculation should give an indication of the need for the barrier to coalescence to be an effective one.

Particles of all types possess a net electrostatic charge when suspended in a simple aqueous medium. The origin and magnitude of this charge is dependent on the nature of the medium, the nature of the particle surfaces and the presence or absence of other components in the system.

The DLVO theory of stability takes into account the interaction of two kinds of long-range forces which determine the closeness of contact of two particles approaching as a result of Brownian movement. The forces concerned are (1) the London-van der Waals' forces of attraction, and (2) the electrostatic repulsion between electrical double layers.

Since the origin of the one force is completely independent of the other, each force may be evaluated separately and the net result of their interaction obtained by summation. However, in addition to these forces of interaction, a free energy of interaction force arising from a third source: steric hindrance, involving the free energy of mixing solvated adsorbed layers, becomes of importance in systems containing non-ionic surfactants. This is particularly true for the polyoxyethylene type of non-ionic surfactants; to a lesser extent true for alkoxymethyl ethers of sucrose (IV) in which the hydrophilic chain is neither long nor very flexible.



IV

The repulsion between two particles originating in this manner has been termed entropic repulsion because of the loss of configurational entropy of the adsorbed molecules on mixing. This entropy loss is manifested as a repulsive force. This force has far greater importance in emulsion systems than in conventional lyophobic

colloids because of its short range nature, which means it is usually operative in already flocculated or coagulated systems. However, conclusions about the stability of disperse systems may be reached only if the short and the long range forces affecting the interaction of the particles are assessed. The DLVO theory can be applied without difficulty only to monodisperse particles and therefore, its application to systems having wide particle size distributions is limited. Attempts have been made by Hogg, Healy & Fuerstenau (1966) and Ho & Higuchi (1968) to assess the effect of heterodispersity.

*The London-van der Waals' force of attraction*

The attractive forces which exist between like molecules in a vacuum have been quantitatively identified by London (1930). The relation for a pair of equal spheres of finite particles was derived by Hamaker (1937). For values of  $H/a \ll 1$  the relation for two spherical particles of radius "a" can be reduced to

$$V_A = - \frac{Aa}{12H} \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

Where the distance of separation is H. A is the Hamaker constant in ergs ( $10^{-7}$  J).

When the particles "1" are not in a vacuum but are embedded in a medium of substance "2", the total interaction of two particles is dependent on the net interactions of all molecules. Hamaker deduced this interaction to be

$$A = A_{11} + A_{22} - 2A_{12} \quad \dots \quad \dots \quad \dots \quad (2)$$

where  $A_{22} = \pi^2 q_2^2 \beta_2$  for material "2" and  $A_{12} = \pi^2 q_1 q_2 \beta_{12}$  (q is the number of molecules per  $\text{cm}^3$  of material and  $\beta$  is related to the square of the polarizability) for the corresponding interaction between materials "1" and "2". If it is assumed that  $A_{12}$  can be taken as the geometric mean of  $A_{11}$  and  $A_{22}$ , then

$$A = (A_{11}^{\frac{1}{2}} - A_{22}^{\frac{1}{2}})^2 \quad \dots \quad \dots \quad \dots \quad (3)$$

Thus, A is always positive. Consequently, emulsion droplets are always subject to an attraction, which has the same value for droplets in a particular emulsion whether the dispersion is o/w or w/o. Values of the Hamaker constant differ for different pairs of liquids, ranging from  $1 \times 10^{-20}$  J for paraffin-in-water to  $2 \times 10^{-19}$  J for carbon tetrachloride-water. The accuracy of estimating A is low, being often of an order of magnitude (Kitchener & Musselwhite, 1968; Gregory, 1970).

In systems of dispersed particles containing adsorbed layers of surface-active substances, the effective Hamaker constant between the particle and the medium may be radically altered. If the Hamaker constant of the solvation sheath is close to that of the dispersion medium, the sheath simply acts as a mechanical barrier preventing the close approach of the dispersed particles in the range where attractive forces become strong. This layer would then contribute to stability.

Vold (1961) has analysed the effect of adsorption on the attraction of spherical colloidal particles of radius a. In the case of a *homogeneous* adsorbed layer of thickness  $\delta$ , having a Hamaker constant,  $A_{33}$ , the potential energy of attraction is given by (Ottewill, 1967, pp. 646-648):

$$V_A = - \frac{1}{12} \left[ (A_{22}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}})^2 \left( \frac{a + \delta}{\Delta} \right) + (A_{33}^{\frac{1}{2}} - A_{11}^{\frac{1}{2}})^2 \left( \frac{a}{\Delta + 2\delta} \right) + \frac{4a (A_{22}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}}) (A_{33}^{\frac{1}{2}} - A_{11}^{\frac{1}{2}}) (a + \delta)}{(\Delta + \delta) (2a + \delta)} \right] \quad (4)$$

where  $\Delta$  is the distance between the surfaces of the adsorbed layers.

Using Vold's equation and estimating  $A_{33}$  from refractive index measurements, Elworthy & Florence (1969c) obtained a result which is surprising in the light of Ottewill's calculations: the adsorbed layer *increased* the attraction between chlorobenzene particles dispersed in water. Both equation and experimental derivation of  $A_{33}$  assumed that the surfactant layer is homogeneous. This is an over simplification. However, even if the magnitude of the effect is not correct, the *trend* is.

Sonntag (1968) has given equations for  $V_A$  for oil-in-water and water-in-oil emulsions based on Vold's equation, as  $V_A$  is not the same in the presence of an adsorbed layer in the two types of emulsion.

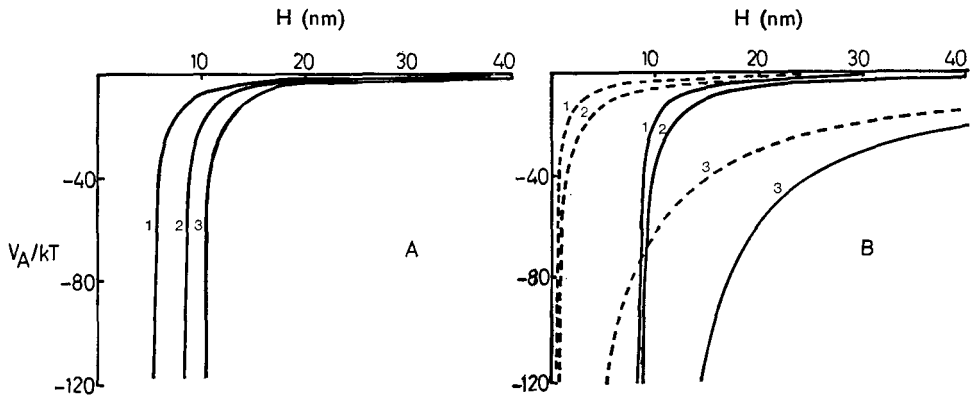


FIG. 5A. The influence of the thickness ( $\delta$ ) of an adsorbed layer of  $C_{16}E_6$  and the attraction between two chlorobenzene droplets for a particle of size  $a = 0.5 \times 10^{-4}$  cm. 1.  $\delta = 2.5$  nm. 2.  $\delta = 4.0$  nm. 3.  $\delta = 5.0$  nm.

B. Influence of particles size "a" on the attraction between two chlorobenzene droplets: --- uncoated; — coated with a layer of  $C_{16}E_6$  with  $\delta = 4.0$  nm. 1.  $a = 0.5 \times 10^{-4}$  cm. 2.  $a = 1 \times 10^{-4}$  cm. 3.  $a = 10 \times 10^{-4}$  cm.

Fig. 5 illustrates the effect of different thicknesses of adsorbed layers of a polyoxyethylene ether  $C_{16}H_{33}[O\cdot CH_2\cdot CH_2\cdot]_6OH$  ( $C_{16}E_6$ ) on the calculated attraction energy between two chlorobenzene droplets  $1 \mu\text{m}$  in diameter. As the thickness of the homogeneous layer of  $C_{16}E_6$  increases, the attraction between the droplets increases. At a separation of  $12.5$  nm, the attraction energy is approximately doubled by increasing the layer thickness from  $2.5$ – $4.0$  nm. A thickness of  $5$  nm results in a four-fold increase in the attractive forces. In this particular system, the Hamaker constant of the adsorbed layer was greater than that of the dispersed oil. ( $A_{33} = 6.7 \times 10^{-20}$  J,  $A_{22} = 6.3 \times 10^{-20}$  J,  $A_{11} = 3.78 \times 10^{-20}$  J.) Likewise, the attraction increases with increasing particle size for a given adsorbed layer thickness (Fig. 5) and a significant change is observed on the introduction of an adsorbed layer onto uncoated particles. It appears, therefore, that large particles will be more difficult to stabilize by adsorbed layers than small ones if only the effect on  $V_A$  is considered. In the development of the theory, Vold (1961) explains that a reduction in the interparticle attraction occurs when the density of the particle is greater than that of the medium, and the particle is coated with a weakly interacting adsorbed layer. Furthermore, it is pointed out that adsorbed layers on dispersed particles can never change the interparticle attraction into a repulsion. Derjaguin (1966) has doubted whether attenuation of attractive forces could contribute significantly to stability: this has been the conclusion of other work also (Elworthy & Florence, 1969c).

*Repulsive forces arising from interaction of electrical double layers*

In the DLVO theory, the distribution of counter-ions in the immediate vicinity of the charged colloidal particle is assumed to obey the Poisson-Boltzmann distribution.

The work required to bring together identical spherical particles from infinity to a distance of separation  $H$  in a liquid medium is given in an approximate form by (Derjaguin, 1939).

$$V_R = \frac{\epsilon a \psi_0^2}{2} \ln(1 + e^{-\kappa H}) \quad \dots \quad (5)$$

This formula is valid only for low potentials ( $< 25$  mV), for spheres that are large in radius compared to the thickness of the double layer (i.e.  $\kappa a \geq 1$ ), and for a large separation between the spheres compared with double layer thickness (i.e.  $H > 1/\kappa$ ). However, it can be used as an approximation for most practical systems, particularly emulsions.

In equation (5), the surface potential,  $\psi_0$ , is usually equated to  $\zeta$ , the zeta potential as determined from measurements of electrophoretic mobility. The two quantities are by no means always identical, but in view of the experimental difficulties of assessing  $\psi_0$ , zeta potential may be used as a close approximation.  $\zeta$  is the experimentally accessible potential difference between the bulk solution and the electrokinetic "slipping plane" or "plane of shear" which is situated in the diffuse layer close to the immobile Stern layer. (The meaning of these planes in molecular terms when a long chain hydrophilic non-ionic surfactant is adsorbed at the globule surface is not clear.)

In emulsions, as opposed to solid dispersions, the potential energy barrier to contact of two globules can increase if distortion of the globules occurs as a result of their mutual repulsion. The significance of this effect is not estimable in unstabilized emulsions. When adsorbed layers of surface-active material are present, it is less likely that distortion occurs on collision. Minute amounts of surfactant retard circulation in droplets because adsorption increases the interface viscosity. Trace amounts of surfactant cause the motion of small bubbles and drops through a liquid to resemble that of rigid bodies (Newitt, Dombrowski & Krelman, 1954).

Diffuse double layers extending into the disperse phase from the interface have been considered by Verwey (1939) but they do not appear to influence the external electrical layers to any significant extent. If the disperse phase is polar (e.g. water), then the concentration of counter-ions in the disperse phase would serve to reduce the net electrokinetic potential attributed to the particle.

The degree of stability of many dispersions cannot be explained solely on the basis of  $V_A$  and  $V_R$ . Elworthy & Florence (1969c) have treated the stability of emulsions of chlorobenzene and anisole stabilized with a series of synthetic polyoxyethylene ethers in light of colloid theory and have shown that electrical stabilization alone cannot explain the stability observed. The nature of this "other force" which is invoked to explain discrepancies between theory and experiment is not fully worked out. Nevertheless much interest has been shown in this alternative mechanism of the stabilization, which for "non-ionic" emulsions appears to play the major role (Elworthy & Florence, 1967). Results have indicated that the thickness and degree of solvation of adsorbed layers is critical (van der Waarden, 1950). Thus, the particular conformation and length of the polyoxyethylene chains of non-ionic surfactants at interfaces is likely to be an important factor in the stabilization of emulsified droplets.

The overall free energy change when the adsorbed layers on identical spherical particles mix on contact is assumed to arise from the additive contributions of several

energy changes. This free energy, being positive, results in repulsion between the particles because work is required to overcome these energy barriers.

If  $\Delta G$  is the net free energy change, then

$$\Delta G = \Delta G_m + \Delta G_v + \Delta G_s + \Delta G_e^* \quad \dots \quad (6)$$

$\Delta G_m$  is the free energy change of mixing of the adsorbed layers which results in an increased concentration and density of chains in the overlap region. The increase of the chemical potential for a given polyoxyethylene chain in this region increases the polymer-solvent interactions. When the coated particles are separated by a distance less than  $2\delta$ , restrictions are imposed on the volume occupied per chain, governed by the particular conformations of the chains. This excluded volume effect is manifested as a free energy change,  $\Delta G_v$ . Considerations of interacting adsorbed layers on emulsion globules must include the tendency towards desorption of the molecules at the interface as the compression due to overlapping increases. This tendency will cause an increase in the local interfacial tension which constitutes an increase of the surface free energy,  $\Delta G_s$ . Collisions between emulsion particles do not always result in the formation of an aggregate or in coalescence. In fact, the dispersed droplets have been observed to exhibit a certain degree of elasticity on collision. This phenomenon may be considered as an elastic energy of repulsion,  $\Delta G_e$ .

In order to assess the magnitude of each of these energy barriers to coagulation, calculations have frequently been made on models for which certain assumptions and simplifications have been introduced.

As Lyklema (1968) points out, the term "entropic" has been applied somewhat indiscriminately to the forces of repulsion arising from interaction of the adsorbed surfactant layers. This term arises because the long chains of the surfactant being restricted on contact suffer a loss of entropy and contribute to the positive free energy change, in addition to changes in solute-solvent interactions in the overlap region.

#### *Steric or entropic repulsion*

Mackor (1951), Mackor & van der Waals (1952), Clayfield & Lumb's (1966) and Meier's (1967) approaches have been discussed in some detail by Lyklema (1968). For this reason they are not treated here. Instead we concentrate on the theory of Fischer (1958) whose final equation contains parameters more amenable to substitution with experimental data than the others.

When adsorbed layers form on dispersed spherical particles, a region of high concentration of macromolecule extends outward from the particle surface into a region of lower concentration of macromolecule. The layer forms a gradient of polymer concentration which is a function of the length of the adsorbed chains, the degree of surface coverage and the conformation of the polymer chains in the environment. Consider two identical spherical particles (Fig. 6) having identical adsorbed layers of polymer chains colliding in the common medium and forming, between the particles, an overlap volume of their adsorbed layers,  $dV$ . The concentration of polymer chains is increased and one can express the excess chemical potential change of the chains in the overlap volume as the difference between the observed chemical potential change and the change expected under ideal conditions: (eqn 7). Using this approach, the stabilization lent to disperse systems by adsorbed

$$(\Delta\mu_i)_E = \Delta\mu - (\Delta\mu_i)_{ideal} \quad \dots \quad (7)$$

\* Whether these are independent quantities, and therefore additive is a debatable point.

layers was analysed by Fischer (1958). The increase in chemical potential as a result of this process generates an excess osmotic pressure arising from solvent flow to the region of high concentration. This pressure,  $\pi_E$ , is manifested as an energy of repulsion to mixing and its magnitude is determined by the partial molar volume of the solute,  $\bar{V}_1$ , the initial concentration of chains in the adsorbed layer,  $C$ , and the degree of polymer-solvent interaction, related to  $B$ , the second virial coefficient. Equation (7) may then be written

$$(\Delta\mu_1)_E = -RTB\bar{V}_1C^2 = -\pi_E\bar{V}_1 \quad \dots \quad (8)$$

whence

$$\pi_E = RTBC^2 \quad \dots \quad (9)$$

The free energy of mixing in the volume element  $dV$  is related to  $C^2$  by

$$dG_m = \frac{2dV}{\bar{V}_1} \cdot RTB\bar{V}_1C^2 = 2d\bar{V}RTBC^2 \quad \dots \quad (10)$$

for the volumes of each adsorbed layer such that  $dV_1 = dV_2 = dV$ , where  $dV_1$  and  $dV_2$  are the volume elements in the adsorbed layers of the first and second particles, respectively. Therefore,

$$\Delta G_m = \int_0^{dV} 2d\bar{V}RTBC^2 = 2 \int_0^{dV} \pi_E dV = 2\pi_E dV \quad \dots \quad (11)$$

The total energy of repulsion over the whole overlap region between the spheres may be calculated by integrating the volume elements,  $dV$ .

The volume of a segment of a sphere is given by

$$V_s = \frac{\pi h^2}{3} 3(r_1 - h) \quad \dots \quad (12)$$

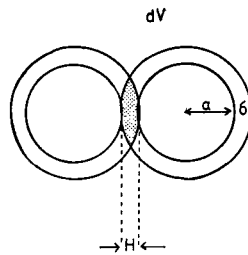


FIG. 6. The overlap of adsorbed layers on the approach of identical spherical particles: the model used to derive Fischer's equation.

In Fig. 6,  $h = \delta - \frac{H}{2}$  and  $r_1 = a + \delta$ , hence

$$V_s = \frac{2\pi}{3} \left[ \delta - \frac{H}{2} \right]^2 \left[ 3a + 2\delta + \frac{H}{2} \right] \quad \dots \quad (13)$$

If  $V_s = V$ , then from equation (11)

$$\Delta G_m = \frac{4\pi \cdot \pi_E}{3} \left[ \delta - \frac{H}{2} \right]^2 \left[ 3a + 2\delta + \frac{H}{2} \right] \quad \dots \quad (14)$$

Combining equations (9) and (14) gives

$$\frac{\Delta G_m}{kT} = \frac{B\mathcal{N}C^2 4\pi}{3} \left[ \delta - \frac{H}{2} \right]^2 \left[ 3a + 2\delta + \frac{H}{2} \right] \quad \dots \quad (15)$$

If the dispersion medium is water, the greater the hydrophilicity of the adsorbed layer, the larger is  $B$ , and the higher the free energy of mixing.  $\Delta G_m$  may be readily estimated from equation (15) providing a suitable value for  $B$  can be obtained. This parameter has been evaluated for solutions of non-ionic detergents (Elworthy & McDonald, 1964) and glycols (Malcolm & Rowlinson, 1957), but discrepancies exist, depending on the method of measurement. Furthermore, data are only available for micellar solutions and the behaviour of detergents at oil-water interfaces may, or may not, be identical to that in the micelles. However, Napper (1968) found that incipient flocculation of polymer latexes occurred in dispersion media which were  $\theta$  solvents for the stabilizing molecules in *free* solution as predicted by theory, viz.

$$B \propto \left(1 - \frac{\theta}{T}\right) \quad \dots \quad \dots \quad \dots \quad \dots \quad (16)$$

where  $\theta = \text{Theta temperature}$ . Thus when  $T = \theta$  deviations from ideality vanish. Using the critical flocculation temperature as a criterion of stability Napper (1969) observed that aqueous dispersions stabilized by two non-ionic polymers differing by a factor of 3 in molecular weight possessed similar stability, suggesting an insensitivity of the steric stabilization to molecular size. However, with amphipathic compounds such as the  $C_{16}E_x$  series of non-ionic detergents changes in molecular weight result in different adsorption properties and, hence, differing steric stabilizing powers (Elworthy & Florence, 1969b,c).

Fischer (1958) has evaluated  $\Delta G_m$  for molecular overlap when the stabilizer segment density in the overlap volume is constant. However, an equation of the form given by Meier (1967) should be employed for polymeric stabilizers. Thus, for  $L < H < 2L$  where  $L$  represents the contour length of the longest stabilizing moiety,

$$\Delta G_m = 2kT (\psi_1 - \chi_1) \frac{V^2}{V_1} (\rho_j \rho_k)_H dV \quad \dots \quad \dots \quad \dots \quad (17)$$

and for  $H < L$

$$\Delta G_m = 2kT (\psi_1 - \chi_1) \frac{V^2}{V_1} \left[ \int (\rho_j)_H^2 dV - \int (\rho_j)^2 dV + \int (\rho_j \rho_k)_H dV \right] \quad \dots \quad (18)$$

The relation between  $B$ , the second virial coefficient, and  $\chi$ , is

$$B = RT \frac{(\psi_1 - \chi_1)}{V_1 \rho_2^2} \quad \dots \quad \dots \quad \dots \quad \dots \quad (19)$$

where  $\rho_2$  is the density of the adsorbed layer.  $\psi_1$  is an entropy parameter which is given the ideal value of 0.5. Equation (18) represents the total change in Gibbs' free energy on bringing the particles from infinite separation to a distance,  $H$ , apart, where  $\rho_j$  and  $\rho_k$  are the segment density contributions in the volume element  $dV$  of the adsorbed chains on each particle surface.

Ottewill & Walker (1966, 1968) have used Fischer's equation (15) but substituted equation (19) for  $B$  giving

$$\frac{\Delta G_m}{kT} = \frac{4\pi \mathcal{N} C^2}{3V_1 \rho_2^2} \left[ 0.5 - \chi_1 \right] \left[ \delta - \frac{H^2}{2} \right]^2 \left[ 3a + 2\delta + \frac{H}{2} \right] \quad \dots \quad (20)$$

The calculated stabilizing contribution of adsorbed layers is represented by curves of  $\Delta G_m$  in  $kT$  units versus  $H$  in Fig. 7.

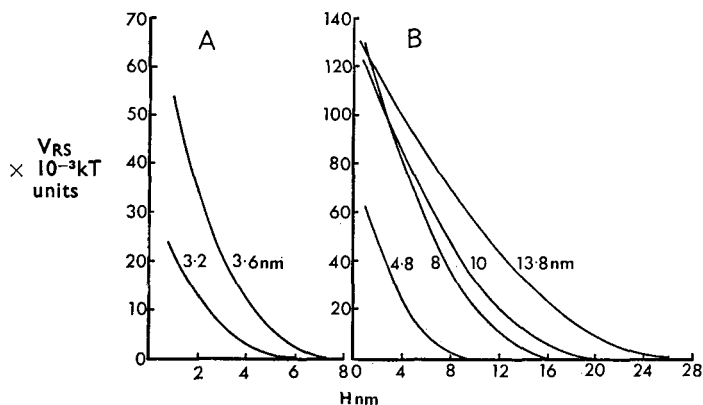


FIG. 7. The effect on  $V_{RS}$  of altering  $\delta$  for (A)  $C_{16}E_3$  and (B)  $C_{16}E_{25}$ .  $\delta$ (nm) as marked on diagram.

In equations (18) and (20) it is assumed that no desorption of stabilizer can occur, which is unlikely for some non-ionics (especially in the chlorobenzene and anisole-water systems). The loss of entropy resulting from the interaction of the chains should cause some of the molecules to desorb and to gain entropy by returning to the bulk solution (Verwey, 1966). In these cases the free energy change corresponding to this process will be largely determined by the free energy of desorption. Therefore a surfactant should have a high free energy of adsorption if it is to give rise to high stability. This is a function of its solubility in the disperse and continuous phases. When the surfactant is soluble in the disperse phase (for example like  $C_{16}E_3$  in chlorobenzene) it should be free to desorb at the point of collision and diffuse away into the globule. A more water-soluble detergent (e.g.  $C_{16}E_{25}$ ) will be prevented from doing so and must remain in the interface (MacRitchie, 1967), and hence should contribute more to the stability.

Because the entropic force, however it is formulated, is a short-range force it will be more directly related to coalescence behaviour than  $V_A$  or  $V_R$ .

The interaction parameter,  $\chi_1$ , may be determined in a number of ways, of which vapour pressure measurements provide the best method for concentrated solutions whereas osmotic pressure measurements are more accurate for dilute solutions. The osmotic pressure,  $\pi$ , is related to the concentration of a polymer of given molecular weight,

$$\frac{\pi}{C} = \frac{RT}{M} + \frac{RTC}{V_1\rho_2^2} \left( \frac{1}{2} - \chi_1 \right) \quad \dots \quad (21)$$

$\chi$  can be evaluated from plots of  $\pi/c$  versus  $c$ . Table 2 lists values of  $\chi_1$  from second virial coefficients on aqueous solutions of polyoxyethylene detergents and for glycols.

Since the calculated free energy of interaction is largely dependent on the value chosen for  $\chi_1$ , then evidence of the effect of salts on  $\chi_1$  could lead to significant conclusions on the stability of emulsions in the presence of salts. Several reports (Schick, 1962; Hammes & Swann, 1967; Gluzman & Fridman, 1968) on solutions of non-ionic surfactants and polyethylene glycols bear out the contention that electrolytes dehydrate the ethylene oxide chains and promote their "salting out". Kuriyama (1962) has calculated  $\chi_1$  values for solutions of methoxy polyoxyethylene-(12)-dodecyl ether (MP 1-12) in the presence of sodium and calcium chloride from light-scattering results.  $\chi_1$  was observed to increase slightly with salt concentration, as expected.



Table 2. *Second virial coefficients (B) and  $\chi_1$  values for aqueous solutions of polyoxyethylene compounds.*

Compound	$B \times 10^4$ (ml mol g <sup>-2</sup> )	$\chi_1$	Method	Reference
C <sub>16</sub> E <sub>7</sub> (20°)	0.84	0.499	l.s.	Macfarlane (1963)
C <sub>16</sub> E <sub>8</sub>	2.43	0.496	l.s.	Idem
C <sub>16</sub> E <sub>9</sub>	3.28	0.494	l.s.	Idem
C <sub>16</sub> E <sub>21</sub>	1.40	0.497	l.s.	Idem
Methoxy-C <sub>12</sub> E <sub>12</sub>	1.90	0.497	l.s.	Kuriyama (1962)
Ethylene glycol	196.2	0.060	v.p.	Elias & Lys (1966)
Dioxyethylene glycol	151.2	0.160	v.p.	Idem
Trioxyethylene glycol	126.7	0.216	v.p.	Idem
Hexaoxyethylene glycol	102.2	0.271	v.p.	Idem
Nonaoxyethylene glycol	85.8	0.303	v.p.	Idem
Polyoxyethylene glycol 300 (30°)	—	0.35	v.p.	Malcom & Rowlinson (1957)

\* All measurements at 25° unless otherwise specified.

v.p. = Vapour pressure. l.s. = Light scattering.

The same trend is observed when the temperature of the solutions was raised. This means that the interaction between solute and solvent decreases as temperature rises, as in the presence of salt. Calcium chloride exerted a small effect on the micellar weight and cloud point of MP 1-12 when compared with sodium chloride at the same ionic strength. But, if compared at the same molar concentration, calcium chloride is an equally (or a more) effective salt, increasing the micellar weight and decreasing the cloud point.

The second virial coefficient obtained from light-scattering measurements on micellar systems contains a term for interactions peculiar to micelles and hence of no relevance to dispersion stabilization. Negative second virial coefficients (suggesting  $\chi_1 > 0.5$ ) are found for a number of non-ionic systems. The change from positive to negative values with increasing temperature is coupled with decreasing stability with increasing temperature, but the negative values of B obtained for a number of glucosyl alkyl benzenes (Hutchinson, Sheaffer & Tokiwa, 1964) is probably not an indicator of stabilizing power.

A paper by Sata & Harisaki (1960) points out an interesting difference in the stabilizing power of an emulsifier of the general formula II (p. 156) in o/w and w/o emulsions. The compound stabilized drops of oil in water, but not drops of water in oil. The reason for this is that on the water side the stabilizing layer consists of three polyoxyethylene chains for every surfactant molecule, whereas on the oil side of the interface only one hydrocarbon chain protrudes and the drops of water in oil are insufficiently protected. This effect would be less marked in polyoxyethylene mono n-alkyl ethers, which might be expected to stabilize w/o emulsions equally as well as o/w emulsions given sufficient interfacial activity.

#### *Other entropic stabilizing mechanisms*

Another possible source of energy of repulsion between two dispersed particles is that arising from the elasticity of a collision, designated as  $\Delta G_e$ . This aspect of the potential energy of repulsion has been dealt with by Jäckell (1964).

The importance of short-range repulsive forces in certain disperse systems cannot be entirely overlooked. After the main entropic repulsive forces have been overcome during a collision between two coated particles, surface forces in liquid lamellae between the particles may play a significant role in stabilization. A discussion of these forces is given by Kitchener & Mussellwhite (1968) in light of recent experimental findings. The role of the liquid film between globules in maintaining stability is discussed in the second part of this review (p. 233 *et seq.*).