

Stabilization of oil-in-water emulsions by non-ionic detergents: electrical and entropic contributions to stability

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Calculations of the attractive and repulsive forces between globules of anisole and chlorobenzene in the presence of non-ionic detergents of varying polyoxyethylene chain length are presented. The equations of the Derjaguin-Landau-Verwey-Overbeek theory are used and the effect on the attractive potential of the adsorption of stabilizer onto the particle is taken into account. The adsorbed film was found to *increase* the attractive forces between the particles, V_A . In the previous paper (Elworthy & Florence, *J. Pharm. Pharmac.*, 1969, **21**, 70) it was shown that the electrical contribution to stability is a secondary stabilizing factor. More quantitative estimates of this contribution have been made. The entropic repulsion has been calculated using an equation of Ottewill & Walker. The energy-distance diagrams are discussed in the light of the experimental results presented in the previous paper.

Previous papers (Elworthy & Florence, 1967, 1969a, b) have dealt with experimental results on the stabilization of emulsions of anisole and chlorobenzene dispersed in water in the presence of non-ionic detergents of the polyoxyethylene ether class. In those papers the results were discussed qualitatively. The present paper attempts to correlate the experimental findings with the theoretical predictions for stability as given by the theory of stability of lyophobic colloids derived by Derjaguin, Landau, Verwey and Overbeek (D.L.V.O.); it includes a discussion of the contribution to stability from the interaction of the adsorbed polyoxyethylene chains on neighbouring particles, the so-called "entropic" contribution.

Modern theories of colloid stability agree that it is the balance between various attractive and repulsive forces operating between the dispersed particles that governs stability. The D.L.V.O. theory (Derjaguin & Landau, 1941; Verwey & Overbeek, 1948) has been reasonably successful in interpreting the flocculation of suspensions, but according to Vold & Vold (1965) the behaviour of emulsion systems deviates widely from its predictions.

Two main differences between emulsion droplets and solid dispersion particles can be listed: (i) the non-rigidity of the emulsion particles which can result in dispersal of energy and change in shape on the close approach of two particles, and (ii) the different criterion of stability which is coalescence and not flocculation. In emulsions, coalescence (i.e., the irreversible union of two or more globules to form one) may occur after flocculation but does not necessarily follow from it.

It was found (Elworthy & Florence, 1967) that electrical contributions to stability in emulsions of anisole and chlorobenzene stabilized with cetomacrogol 1000 are of secondary importance; reduction in the zeta-potential of the particles with increasing

concentration of cetomacrogol resulted in a slight increase in the rate of coalescence. However, salts at low concentration levels markedly affect the stability of non-ionic emulsions (Elworthy, Florence & Rogers, unpublished) and hence an electrical contribution to the repulsive forces must be included in any formulation of the forces between the particles. This, of course, does not preclude the possibility that salts dehydrate or alter the conformation of the polyoxyethylene chain, rendering in the first instance the particle more hydrophobic, or in the second the stabilizing layer less obtrusive.

Vold (1961) has calculated that the adsorbed detergent layer at the globule surface influences the value of the Hamaker constant, but Derjaguin (1966) has doubted whether attenuation of van der Waals' forces of attraction is the main reason for the stabilizing properties of solvated polymeric chains.

In this paper calculations have been made of the forces of attraction and repulsion operative in the present o/w emulsion systems in order to assess the role of the adsorbed layer in contributing to stability. Unfortunately, the entropic contribution to stability—the decrease of entropy caused by the intermingling of the polyoxyethylene chains on approaching particles and the consequent energy rise—has not been satisfactorily formulated. As a working basis, calculations have been made on the assumption that the particles were not deformed and that the detergent is not desorbed on close approach of the particles. The results of these calculations are presented in the first part of the paper. In the second part some possible reasons for deviation from behaviour as predicted by these calculations are given.

Attractive forces

Attractive forces between colloidal particles are due to van der Waals' forces. Between atoms, these forces are of short range, but when the London contribution (London, 1937) is summed over all the atoms on two colloidal particles, the attractive forces are long range. For two spherical particles, both of radius a , at a distance of separation between their surfaces, H , under the condition that $H/2a \ll 1$

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

where V_A is the mutual energy of attraction, and A is the Hamaker constant (Hamaker, 1937) defined by

$$A = \pi^2 q^2 \mu$$

where q is the number of molecules per cm^3 of material and

$$\mu = 3h\nu_0\alpha_0^2$$

in which h = Planck's constant, ν_0 is the characteristic frequency of the molecules, and α_0 their polarizability.

Since ν_0 can be derived from refractive index data, the refractive indices of the four detergents were measured at the blue, green, and yellow lines of a mercury arc lamp using a Pulfrich refractometer. A temperature of 45° was used to ensure that all detergents were liquid; the difference in polarizabilities between 45° and 20° (the temperature of the stability work) was ignored. Refractive index data for anisole, chlorobenzene and water were obtained from Timmermans (1950) and Kaye & Laby (1957). Using a dispersion equation of the form (Bauer & Lewin, 1960)

$$\frac{1}{\psi} = \frac{v_0^2}{c} - \frac{v^2}{c} \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

where $\psi = (n^2 - 1)/(n^2 + 2)$, c is a constant, and v is the frequency of light at which the refractive index, n , is measured, v_0 was determined. As the value of ψ at zero frequency ($\psi)_{v^2=0} = 0$ can be obtained by a graphical treatment of equation (2),

$$\alpha_0 = \frac{3 V_m (\psi)_{v^2=0}}{4\pi N}$$

where V_m is the molar volume. The values of the relevant quantities are given in Table 1.

Table 1. Values of characteristic frequencies, polarizabilities and Hamaker constants of water, oils and detergents

	$v_0 \times 10^{-15}$ s ⁻¹	$\alpha_0 \times 10^{24}$ cm ³ mol ⁻¹	$\mu \times 10^{57}$ erg cm ⁶ mol ⁻²	$A \times 10^{13}$ erg
Water	3.27	1.45	0.0344	3.78
Anisole	2.54	12.52	1.98	6.05
Chlorobenzene	2.57	11.86	1.80	6.29
C ₁₆ N ₃	3.52	43.48	33.4	6.57
C ₁₆ N ₆	3.46	57.00	55.8	6.65
C ₁₆ N ₉	3.46	69.25	82.5	6.71
C ₁₆ N ₂₅	3.77	124.9	291.9	7.46

From Table 1 it is apparent that the Hamaker constants of the detergents are greater than those of the oils used; hence the effect of coating an oil particle with surfactant will be to increase the attractive force between particles.

Influence of medium and adsorbed films. The above Hamaker constants are for interactions between particles in a vacuum. If A_{11} is the constant for the oils *in vacuo* and A_{22} the constant for interaction between water molecules, then the Hamaker constant for oil particles in water is given by

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

For anisole-water $A = 2.6 \times 10^{-14}$ and for chlorobenzene-water $A = 3.1 \times 10^{-14}$ erg; the variation of the energy of attraction with distance can be calculated from equation (1).

A further modification is required when the particles are coated with a homogeneous adsorbed film (Vold, 1961). If the thickness of the film is δ and the surfaces of the coated particles are a distance Δ apart, Ottewill (1967) gives the equation

$$V_A = - \frac{1}{12} \left[(A_{22}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}})^2 \left(\frac{a + \delta}{\Delta} \right) + (A_{33}^{\frac{1}{2}} - A_{11}^{\frac{1}{2}})^2 \left(\frac{a}{\Delta + 2\delta} \right) \right. \\ \left. + \frac{4a (A_{22}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}}) (A_{33}^{\frac{1}{2}} - A_{11}^{\frac{1}{2}}) (a + \delta)}{(\Delta + \delta) (2a + \delta)} \quad \dots \quad \dots \quad \dots \right] \quad (3)$$

in which A_{33} is the Hamaker constant of the adsorbed film. Equation (3) permits evaluation of the attraction between particles with adsorbed layers of different thickness as a function of their distance apart. We assume in using equation (3) that the particles are monodisperse, that the adsorbed film is composed of detergent only, that it is homogeneous. Although none of these assumptions is entirely correct,

we are more concerned with the general picture emerging from the calculations than with details.

The values of V_A for anisole and chlorobenzene, calculated from equation (3), are very similar (1–2%) when coated particles are considered. In choosing a value for the film thickness, δ , two limits can be used. The first is the fully extended length of the surfactant monomers, measured from atomic models, which are 36, 50, 64 and 138 Å for $C_{16}n_3$, $C_{16}n_6$, $C_{16}n_9$ and $C_{16}n_{25}$ respectively. As the molecules are known to be contracted when present in a micelle, with total lengths of *ca* 32, 40, 46 and 48 Å respectively (Elworthy, 1960; Elworthy & Macfarlane, 1962, 1963; Elworthy & McDonald, 1964), these figures provide a more realistic set of values for film thickness than the fully extended lengths. In Fig. 1a, the effect on V_A of adsorbed films of

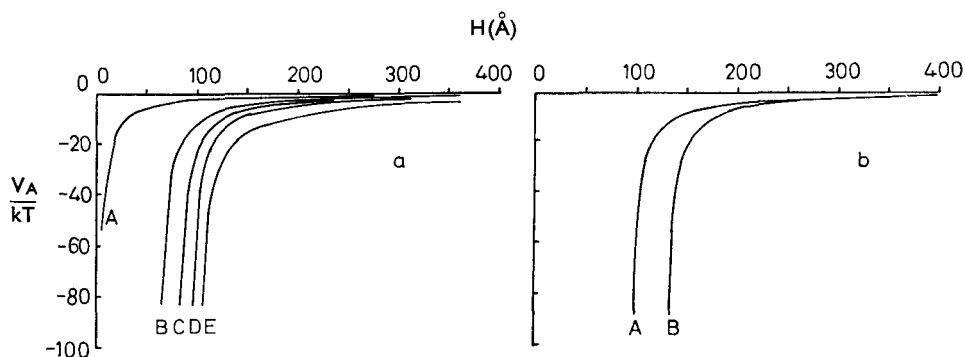


FIG. 1 a. The effect of an adsorbed layer of thickness δ Å on V_A , as a function of the distance between the surfaces of the particles, H . A. No adsorbed film, B. $C_{16}n_3$, $\delta = 32$ Å, C. $C_{16}n_6$, $\delta = 36$ Å, D. $C_{16}n_9$, $\delta = 40$ Å, E. $C_{16}n_{25}$, $\delta = 43$ Å. Values of A (Hamaker constant) as recorded in Table 1.

b. The effect of altering δ on V_A for the detergent $C_{16}n_9$. A. $\delta = 45.4$ Å, B. $\delta = 64$ Å. Value of A (Hamaker constant) as recorded in Table 1.

thickness equal to the micellar radius is given. The attraction between the particles is increased considerably when the film is present. Fig. 1b shows how increasing film thickness increases attraction between particles for a film of $C_{16}n_9$. In all subsequent calculations δ is taken as the length of the surfactant monomer in a micelle. This choice is made after consideration of the areas/molecule found at the relevant oil-water interfaces (Elworthy & Florence, 1969a) which are much greater than those which would be expected for fully extended molecules.

Repulsive forces

(i) *Entropic*. A number of workers have calculated the repulsive energy between two particles arising from the interaction of adsorbed polymer chains (Clayfield & Lumb, 1966; Meier, 1967; Fischer, 1958; Ottewill & Walker, 1968). Meier (1967) considers the loss of possible chain configurations on close approach of the particles and the change in free energy of mixing of polymer and solvent as the chains interact. Fischer (1958) obtained the following equation on consideration of interactions in the volume of overlap of the adsorbed layer, thickness δ on particles of radius a

$$V_{RS} = \frac{4\pi}{3} B'c^2 \left[\delta - \frac{H}{2} \right]^2 \left[3a + 2\delta + \frac{H}{2} \right] \dots \dots (4)$$

B' , the second virial coefficient, takes account of solvent-solute interactions, c is the concentration (g ml^{-1}) of the surfactant in the stabilizing layer, and H is the distance between the surfaces of the uncoated particle. A modified form of this equation has been used by Ottewill & Walker (1968) in which B' is replaced by the term $(\psi_1 - \chi_1)/V_1\rho_2^2$. ψ_1 is an entropy term equal to 0.5 and V_1 is the solvent molecular volume. χ_1 is a solvent-polymer interaction parameter which Ottewill & Walker take to be from 0.25 to 0.40 for $C_{12}n_6$, Malcolm & Rowlinson (1957) having obtained a value of ~ 0.35 for a polyoxyethylene glycol in water. The entropic repulsive force, V_{RS} , was calculated using the modified equation

$$V_{RS} = \frac{4\pi c^2}{3V_1\rho_2^2} \left[\psi_1 - \chi_1 \right] \left[\delta - \frac{H}{2} \right]^2 \left[3a + 2\delta + \frac{H}{2} \right] \quad \dots \quad (5)$$

c was calculated from the surface excess concentrations of the detergents obtained by Elworthy & Florence (1969a).

The choice of χ_1 , on which the magnitude of the calculated V_{RS} largely depends, is a more difficult problem. As χ_1 is a function of phase volume it is reasonable to expect that χ_1 will vary with Γ , that is, with c . Variation of χ_1 with c may be estimated in a very approximate manner by using values of χ_1 vs volume fraction obtained by Malcolm & Rowlinson (1957). In this the variation of χ_1 with c along a homologous series was obtained (Table 2).

The values of δ chosen from micellar radii gives values of c which appear to be reasonable if one calculates the hydration of the detergents in the film. For ceto-macrogol $c = 0.302 \text{ g ml}^{-1}$ gives approximately a hydration of 2.3 g water per g detergent, which agrees closely with the micellar hydration obtained by Elworthy (1960). If δ is chosen as the extended length of the molecule, i.e., 138Å, then $c = 0.088 \text{ g ml}^{-1}$ and the apparent hydration rises to 8.2 g g^{-1} which, although it might include the unbound water separating the detergent chains, does not agree with experimental values of hydration as does the former value.

Fig. 2a and b shows V_{RS} as a function of H for 1 μm globules stabilized with the non-ionic detergents and shows the effect of polyoxyethylene chain length using the values of δ and χ_1 listed in Table 2. When equal values of χ_1 are used for all detergents V_{RS} does not increase in the way shown for small values of H ($< 30\text{Å}$) but at greater distances the same trends apply.

Table 2. Surface excess concentrations (Γ), concentrations (c) and solvent interaction parameters (χ_1)

Detergent	Oil	Γ^* mol cm^{-2}	δ (Å)†	c g ml^{-1}	χ_1	$(\psi - \chi_1)$
$C_{16}n_3$	Anisole	3.69×10^{-10}	32	0.43	0.44	0.06
$C_{16}n_3$	Chlorobenzene	3.46×10^{-10}	32	0.41	0.41	0.09
$C_{16}n_6$	Anisole	2.97×10^{-10}	40	0.38	0.37	0.13
$C_{16}n_6$	Chlorobenzene	2.08×10^{-10}	40	0.26	0.24	0.26
$C_{16}n_9$	Anisole	2.19×10^{-10}	46	0.31	0.30	0.20
$C_{16}n_9$	Chlorobenzene	1.66×10^{-10}	46	0.23	0.22	0.28
$C_{16}n_{25}$	Anisole	1.08×10^{-10}	48	0.30	0.28	0.22
$C_{16}n_{25}$	Chlorobenzene	0.90×10^{-10}	48	0.25	0.23	0.27

* From interfacial tension data (Elworthy & Florence, 1969a).

† δ = micellar radius, i.e., non-extended length of molecule.

Note.—When the effect of alteration in δ is considered c is correspondingly altered; the values of c quoted have been adjusted in proportion, e.g., for $C_{16}n_{25}$ when $\delta = 138\text{Å}$, c for the chlorobenzene system is 0.088 g ml^{-1} .

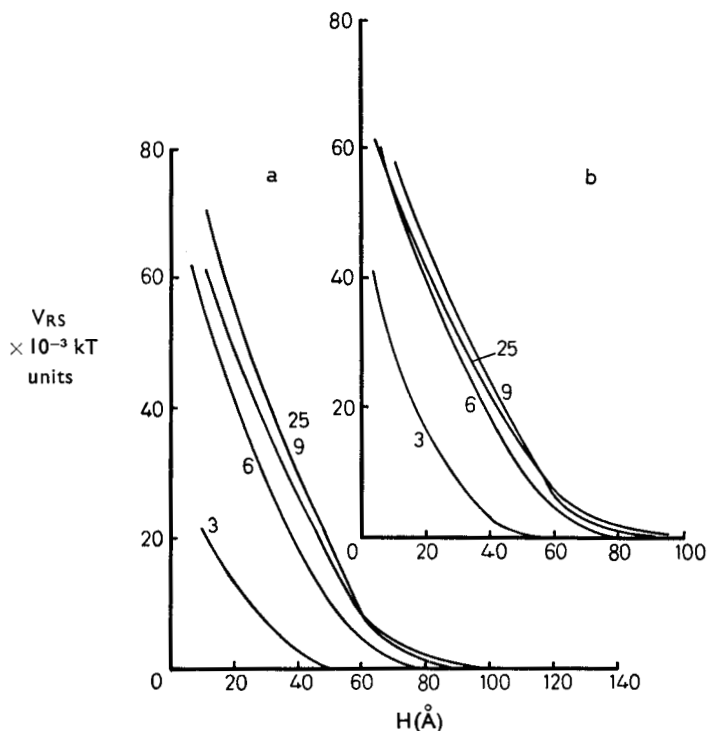


FIG. 2. The entropic stabilizing force V_{RS} as a function of distance of approach of the particles, H , (a) for anisole, (b) for chlorobenzene emulsions for four non-ionic detergents $C_{16}n_3$, $C_{16}n_6$, $C_{16}n_9$, $C_{16}n_{25}$. Ethylene oxide chain length marked. δ as in Fig. 1.

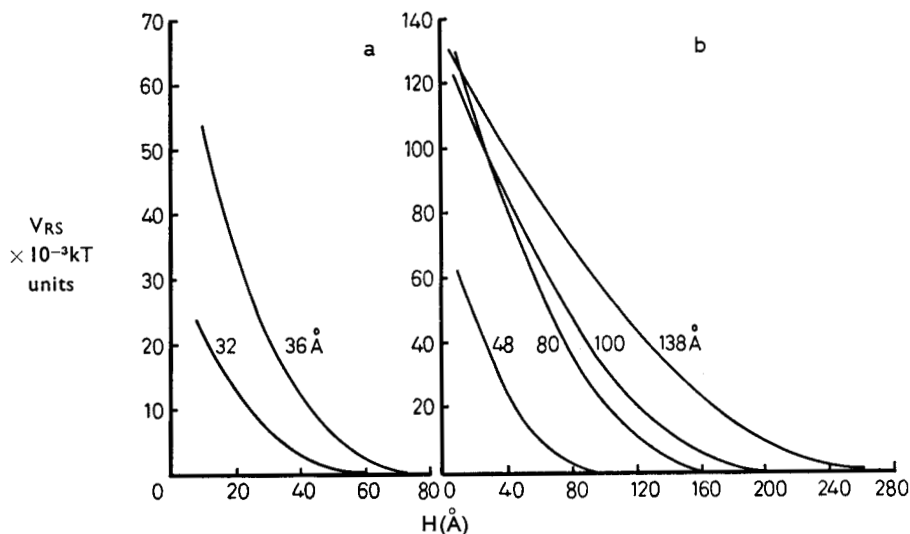


FIG. 3. The effect of V_{RS} vs H plots of altering δ for (a) $C_{16}n_3$ and (b) $C_{16}n_{25}$. δ (Å) as marked on diagram.

The effect of altering δ for $C_{16}n_3$ and cetomacrogol 1000 ($C_{16}n_{25}$) is illustrated in Fig. 3, giving the expected increase in V_{RS} with increasing δ . Obviously some choice has to be made in the absence of experimental data of a value of δ and for bulk of the calculations of total interaction curves the micellar radius δ has been chosen.

Whilst the equation of Ottewill & Walker refers to a homogeneous adsorbed layer, this is not the situation with the non-ionic detergent layer. This can be overcome to some extent by consideration of the polyoxyethylene glycol layer only. Some calculations of V_{RS} on this basis are summarized in Fig. 4. These show the same trend of an increasing entropic repulsion as the ethylene oxide chain length is increased, but there is a greater variation up the series and in two cases negative values of V_{RS} are obtained for anisole systems. The relative merits of considering the adsorbed layer to be detergent or glycol are discussed later.

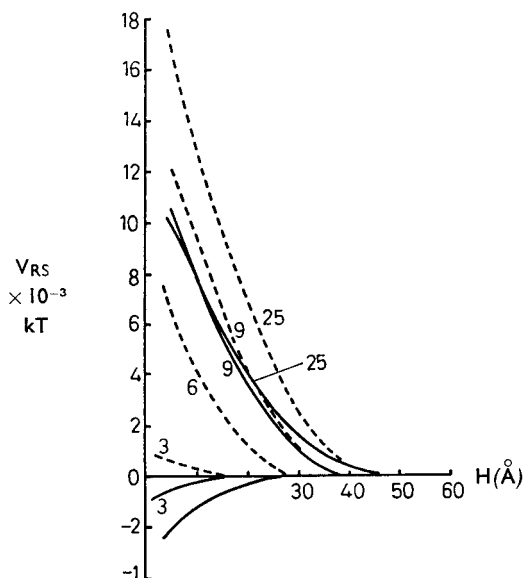


FIG. 4. Entropic stabilizing force, V_{RS} , as a function of distance of approach of particles, H , taking only the polyoxyethylene glycol region into account. Ethylene oxide chain length marked on plots. Solid lines anisole, broken lines chlorobenzene emulsions.

(ii) *Electrical forces.* The electrical contribution to stability V_R was calculated using the equation

$$V_R = \frac{1}{2} \epsilon a \psi_0^2 \ln [1 + \exp(-\kappa H)] \quad \dots \quad (6)$$

where ϵ = dielectric constant, a is the particle radius, κ the reciprocal Debye-Hückel length and H the distance between the surfaces of the particles. The zeta-potential, ξ , was substituted for ψ_0 , the values from Elworthy & Florence (1969; Table 2) being used. The equation is valid for systems in which $\kappa a \geq 1$ and for separations, H , large compared with $1/\kappa$. We have used equation (5) for smaller values of H , and when V_R is compared with the energy of repulsion taken from the tables* of Verwey & Overbeek (1948), the error is not large when the other uncertainties are taken into account, namely the substitution of zeta-potential for ψ_0 . In the present system, where the ionic concentration is extremely low, the error in equating ξ and ψ_0 is a small one because of the slow decay of the double layer potential. In any case, the error will be uniform throughout the series.

* Tables XV-XX, on pp. 152-155 extended by extrapolation to the value of κa used in the present system.

At close distances of approach the distortion of the globules or the formation of a flat lamella between them will increase the repulsive forces as the area of contact will be increased. This refinement has been neglected.

The effect of detergent concentration above the CMC is not reflected by the calculated values of V_{RS} or V_A . It appears only in V_R , due to the lowering of ψ_0 with increasing detergent concentration (Fig. 5), but according to this the total repulsive energy decreases. The experimental results indicate increasing stability with increasing concentration. If the surface concentration c increases above the CMC, V_{RS} will also increase and this could explain the increased stability. Closer packing at the interface could conceivably increase the depth of the adsorbed layer through the extension of the polyethyleneglycol (PEG) chain.

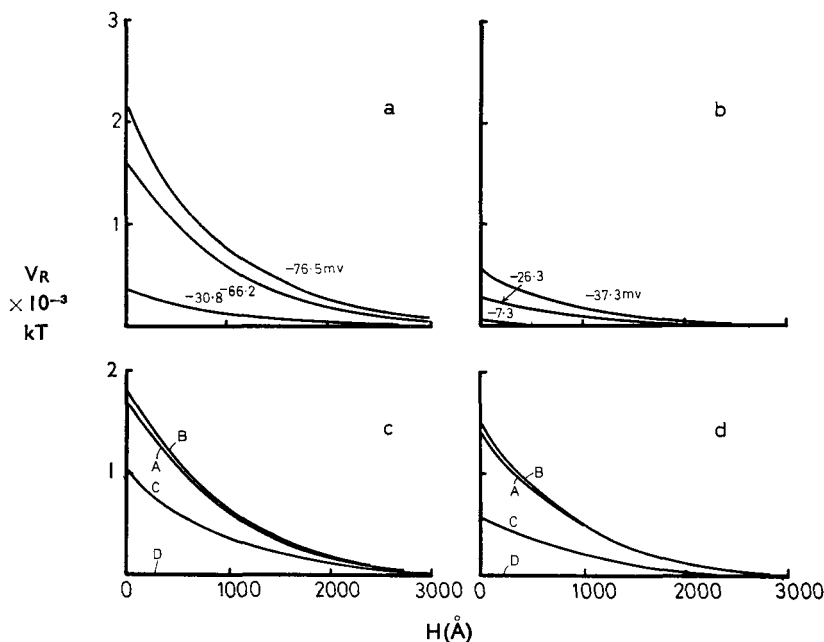


FIG. 5. V_R as function of H at three detergent concentrations of (a) $C_{16}n_3$ -anisole and (b) $C_{16}n_{25}$ -anisole. Concentration dependence of V_R is reflected by a change in ψ_0 . Values in mV shown on graph are experimental values from electrophoresis at 0.1, 1.0 and 10% levels for $C_{16}n_3$ and 0.1, 1.0 and 5% levels for $C_{16}n_{25}$. (c) V_R as a function of detergent at 5% concentration levels. PEG chain length A:3, B:6, C:9, D:25; (d) same but 10% surfactant. Oil in (c) and (d) is chlorobenzene.

CORRELATION OF EXPERIMENT AND THEORY

Electrical factors. Experimental facts are that as the series is ascended the emulsions become more stable. At the same time the electrical contribution to stability becomes smaller, so it must be concluded that there is some movement of charge on approach of the particles stabilized by the short chain detergents, that is, those with the highest apparent V_R .

The conclusion drawn, therefore, is that the primary stabilizing force must be the entropic one but the inability of reasonably high zeta-potentials (~ 70 mV) to stabilize the particles must be explained.

The origin of the charge on these particles is not, as in the case of ionic detergents, due to the presence of large charged molecules but to the presence on the globule

surface of adsorbed hydroxyl ions. These ions have a high mobility and the movement of the ions may or may not be directly related to the mobility of the detergent films. Fig. 6 shows the effect of neglecting the electrical contribution to stability on the energy/distance relation of $C_{16}n_3$ and $C_{16}n_{25}$ emulsions. The minimum is deeper in the more stable ($C_{16}n_{25}$) system hence one might conclude that some charge remains effective in this system—which has a more coherent surface film.

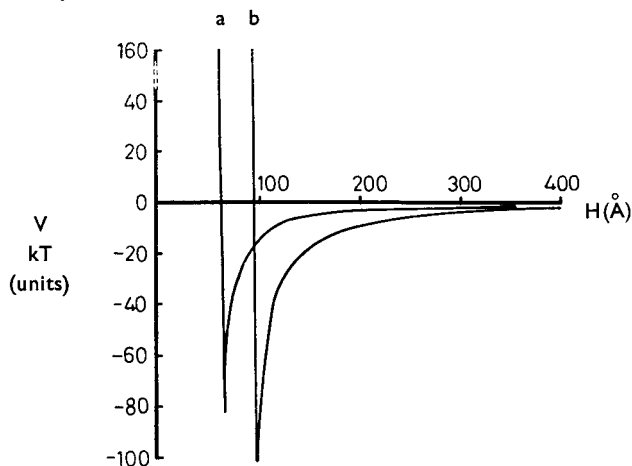


FIG. 6. Plot of $V_{RS} + V_A$ vs H for $C_{16}n_3$ (a) and $C_{16}n_{25}$ (b), neglecting V_R the electrical repulsive force. The two plots are not sufficiently different to explain the totally different behaviour of $C_{16}n_3$ and $C_{16}n_{25}$ stabilized emulsions.

As V_A increases with increasing polyoxyethylene chain length, consideration of $V_A + V_R$ alone results in a decreasing barrier to coalescence as the series is ascended. This leads to the conclusion of the primary importance of V_{RS} or some other physical property of the surfactant film.

Properties of the surface film and entropic stabilization. The barrier to coalescence must be a final barrier at close approach. The only force which we have calculated which has a direct relation to stability as assessed by rates of coalescence (K_2) is V_{RS} . Fig. 7 shows this relation for the $C_{16}n_3$, $C_{16}n_6$ and $C_{16}n_9$ compounds. The

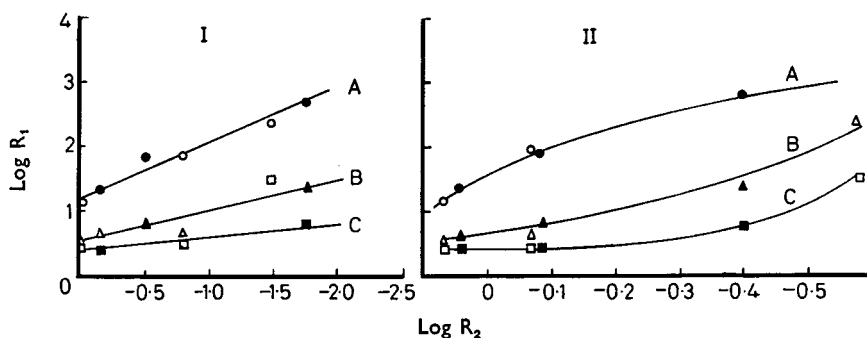


FIG. 7. Relation between stability and V_{RS} expressed as ratios. I showing entropic repulsion taking into account PEG layer only (V_{RS} values chosen at $H = 10\text{\AA}$), II takes whole molecule into account (V_{RS} being taken as $H = 20\text{\AA}$). In both, results for three different concentrations of detergent are shown: A 0.1, B 1 and C 5%. $R_1 = (K_2)_{n-x}/(K_2)_{n-25}$, $R_2 = (V_{RS})_{n-x}/(V_{RS})_{n-25}$ where $(K_2)_{n-x}$ and $(V_{RS})_{n-x}$ refer to experimental rates of coalescence and entropic stabilization for emulsions stabilized with $C_{16}n_x$. Open symbols, anisole, solid symbols, chlorobenzene emulsions.

fact that the theory predicts large entropic barriers for all the emulsions studied suggests that when the emulsions are found experimentally to be less stable, the entropic force calculated is an over-estimate. One possible reason for this is the movement of the stabilizing molecules away from the point of contact. This was the explanation given by Albers & Overbeek (1959a) for the anticorrelation which existed between the zeta-potential of water-in-oil emulsions stabilized by oleates and stability.

It is possible, therefore, that the experimental stability values can be correlated with the compressibility of the film or its surface viscosity, η_s . Results published earlier (Elworthy & Florence, 1969a) indicate that the ease of compression varies in the order

$$C_{16}n_3 > C_{16}n_6 > C_{16}n_9 > C_{16}n_{25}$$

which is the order in which rates of coalescence vary with chain length. The quantity, π_R , calculated previously (Elworthy & Florence, 1969a) bears an empirical relation to V_{RS} (Fig. 8).

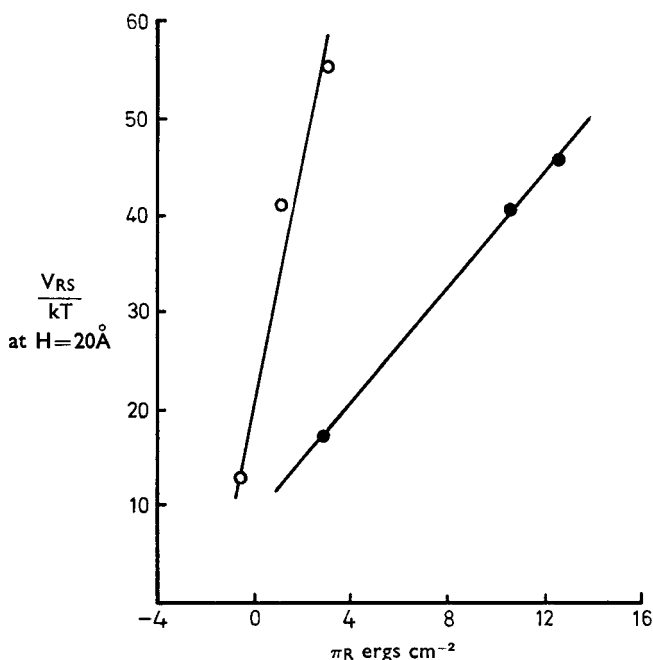


Fig. 8. Plot of V_{RS}/kT vs π_R showing the linear relation between them for detergents with $x = 3, 6$ and 9 units. ○ Anisole, ● Chlorobenzene.

Neither π_R or V_{RS} appear to be significantly concentration-dependent so the increase in stability with increase in surfactant concentration above the CMC is still not completely explained. One experimental quantity which is known to vary with concentration is η_s . If we write

$$\Delta G_{\text{coalescence}} \propto A' \eta_s$$

where η_s is in surface poises (sP) and A' in cm² then for two $1 \mu\text{m}$ particles with $\eta_s = 1 \times 10^{-4}$ sP, ΔG is of the order of 1 or 2 kT for a contact area, A' , of 4×10^{-10}

cm². For a high surface areal viscosity of 1×10^{-2} sP, ΔG is 100–200 kT. These are crude estimates but would seem to show that the magnitudes of η_s found by Carless & Hallworth (1967) for non-ionic detergents, i.e., around 10^{-4} sP are not sufficient in themselves to account for stability.

If the film is mobile on close approach of the globules, the adsorbed molecules may move to the far side of the globule leaving an exposed surface ($V_{RS} = 0$). If $V_{RS} = 0$ the resultant energy-distance diagrams still show a decreasing barrier to coalescence and flocculation with increasing detergent concentration. It might be concluded, therefore, that as the concentration of detergent is increased above 0.1% the surface viscosity increases to prevent movement of the molecules. The surface viscosity does increase with increasing concentration of cetomacrogol 1000 (Elworthy, Florence & Rogers, unpublished). Hence this might explain the increase in stability with increase in detergent concentration.

If the film cannot be compressed it is possible that the detergent can diffuse into the disperse phase and again produce the situation where $V_{RS} = 0$ (MacRitchie, 1967). The more water-soluble the detergent, in the series considered here, the more likely this is to happen. This may further explain the trend of increasing stability as the non-ionic chain length is increased. Whether the time of encounter of two globules undergoing a collision due to Brownian motion is long enough to allow the surfactant molecules to desorb is a factor in this argument. If two particles, radius a , are separated by a distance $2x$ the time, t , for collision as a result of normal Brownian motion is

$$t = \frac{x^2}{2D} \text{ where } D = \frac{kT}{6\pi\eta a}$$

For a particle of radius $0.5 \mu\text{m}$, and $D = 5.0 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, t is of the order of 10^{-6} s. It is doubtful whether the molecule can desorb in this time. Studies of the behaviour of detergent films during rupture are likely to provide answers to this question to some extent (Mysels, Florence & Frens, 1969).

The effect of concentration of surfactant is not satisfactorily formulated in any of the equations discussed. Neither is the effect of emulsion phase volume (ϕ). Albers & Overbeek (1959b) calculated the percentage reduction in V_R from the simple equation due to the overlap of extended double layers in concentrated emulsions. In the present systems with $\kappa = 1.42 \times 10^5 \text{ cm}^{-1}$, $a = 5 \times 10^{-5} \text{ cm}$ and $\phi = 0.20$ the lowering of V_R based on the two particle equation is 6.7%, which is not deemed significant. Decrease in stability with increasing phase volume is partly due to the increased probability of two particles colliding. In addition, the greater the value of ϕ , the greater the surface free energy of the system.

HLB and stabilizing forces. The concept of HLB (hydrophile-lipophile balance) is often used practically in determining the detergent to employ for optimum stability of a given oil-in-water emulsion. It was therefore of interest to determine whether any of the calculated stabilizing forces could be correlated with HLB. Chlorobenzene has been stated to require for optimum stability a surfactant with HLB of 13 ± 1 (Atlas Chemical Industries, 1967). This corresponds to $C_{16}n_9$, whereas $C_{16}n_{25}$ emulsions are more stable. The HLB of $C_{16}n_{25}$ is 16.9. It must be considered that HLB is not an entirely satisfactory parameter. It neglects the concentration-dependence of stability. The optimum HLB is said to hold whatever the non-ionic detergent type used, but this probably neglects subtle differences in rates of breakdown.

CONCLUSIONS

The application of theories of colloid stability to the present systems has enabled the contributions of the entropic and electrical barriers to be assessed, and has led to the following conclusions:

1. Electrical forces appear to be not significant due to the possibility of charge movement from the point of contact of the globules.
2. Entropic stabilization is of major importance with the longer PEG chain compounds.
3. Attractive forces can be increased by the presence of an adsorbed film which means that the term "protective colloid" can have an ambiguous meaning.
4. Where the surface film is not desorbed or mobile, electrical repulsive forces will contribute to stability and the reduction in zeta-potential will result in a slight decrease in stability. Where the mobility of the film is high the potential will bear no relation to stability and stability will increase with an increase in the compact nature of the film.

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