Stabilization of oil-in-water emulsions by non-ionic detergents: the effect of polyoxyethylene chain length

P. H. ELWORTHY AND A. T. FLORENCE

Department of Pharmaceutical Technology, University of Strathclyde, Glasgow, C.1, Scotland

The stability of emulsions of anisole and chlorobenzene in water has been estimated by following microscopically the size distribution of emulsions as a function of time. The effect of increasing the length of the polyoxyethylene glycol chain of the hexadecyl ether non-ionic stabilizers from three units to nine units was determined. Electrophoretic measurements indicated that the higher stability obtained on increasing the glycol chain length is not due to an increasing surface potential: it is ascribed to an entropic effect. Stability data are tabulated as rates of coalescence (s^{-1}) and results are presented relating these rates to zeta-potential, surface concentration and polyoxyethylene chain length. The results are discussed qualitatively and compared with the results obtained with cetomacrogol 1000 (Elworthy & Florence, *J. Pharm. Pharmac.*, 1967, **19**, 140S).

Non-ionic detergents are used widely in the pharmaceutical and food industries as emulsifiers and stabilizers because of their relatively low toxicity. The mechanism by which they exert their stabilizing action has not been elucidated, although some studies have made progress towards fuller understanding. Mathai & Ottewill (1966a, b) in investigations into the stability of some inorganic sols obtained evidence of steric stabilization resulting from the interaction of adsorbed polyoxyethylene glycol (PEG) chains on neighbouring particles.

Steric or entropic stabilization should be a function of polyoxyethylene chain length (Heller & Pugh, 1960). The present paper attempts to clarify some of the unknown factors concerning non-ionic-stabilized dispersions. It is concerned with the stability of emulsions of anisole and chlorobenzene emulsified with the cetyl ethers of tri-, hexa- and nona-oxyethylene glycol whose behaviour at the anisole–water and chlorobenzene–water interfaces we have already discussed (Elworthy & Florence, 1969a).

By varying the polyoxyethylene chain length we have altered the characteristics of the stabilizer molecules. With a knowledge of the effect of these changes on the interfacial film and on the charge on the particles, it should be possible to assess the mode of stabilization or at least to determine the contribution of electrostatic, entropic (steric) or solvational forces. A qualitative discussion of the results is included. A more rigorous scrutiny of the results in the light of current theories of colloid stability is made by Elworthy & Florence (1969b).

EXPERIMENTAL

The detergents used were synthetic cetyl polyoxyethylene glycol ethers, $C_{16}H_{33}[OCH_2CH_2]_xOH$ with x = 3, 6 and 9 (Elworthy & Florence, 1969a). The

oils used were anisole and chlorobenzene, whose characteristics have been described (Elworthy & Florence, 1967). They were chosen because their densities are close to unity.

The emulsions were generally prepared by ultrasonic dispersion. Measurement of particle size was made using a projection microscope immediately after their preparation. The emulsions were stored in sealed glass containers at room temperature ($23° \pm 1°$) and particle size was measured at intervals until oil-separation was noticeable.

Particle-size data were treated according to Elworthy & Florence (1967), rates of coalescence $k(^{-1})$ being calculated from the slope of log n *versus* time plots. Here, n is the number of particles in a certain arbitrary volume, taken as the volume of particles observed in the initial sizing, and proportional to $\Sigma n_i d_i^3$, d_i being the diameter of the particle.

Measurements of globule mobility were made using a Zeta-Meter (Zeta Meter Inc.) by dilution of a quantity of emulsion (generally 0·1 ml) into water saturated with oil. As the partitition coefficients of the detergents always favoured the oil, dilution with water rather than detergent solution was valid. (Saturation of the water with the anisole or chlorobenzene had considerable effect on the electrophoretic mobility.) The electrophoretic mobility (u) was calculated from v/x, where v is the mean velocity of at least ten particles and x is the field strength. The calculation of zeta-potential, ξ, from mobility measurements is simple only when κa is very large ($\geqslant 100$) or very small ($\leqslant 0·1$). κ is the reciprocal Debye-Hückel length in cm^{-1} and a is the radius of the particle in cm. For intermediate values of κa a variable κ-dependent correction must be applied. The value of κa for the anisole–water and chlorobenzene–water systems being about 6·5 these corrections must be applied. Henry's (1931) equation was employed in the form:

$$u = f(\kappa a) \frac{\epsilon \xi}{4\pi\eta}$$

where $f(\kappa a)$ was obtained from Fig. 1, curve 1 of Henry's paper.

For log $\kappa a = 0·812$, $f(\kappa a) = 0·762$. Thus

$$u = \frac{0·762}{4\pi\eta} \epsilon \xi$$

where $\eta = 0·01005$ poise and $\epsilon = 80$. We have quoted the values of u in $\mu m\ s^{-1}\ V^{-1}\ cm^{-1}$. For conversion of these results into zeta-potentials (mV) the relation is

$$\xi = 18·66\ u$$

Consideration of the paper of Wiersema, Loeb & Overbeek (1966) shows there is only a small error, of 1 to 2·5 mV, in using Henry's equation in calculations of ξ for such values of κa.

RESULTS AND DISCUSSION

Some typical globule size distribution plots and how they change with time are shown in Fig. 1. The greater stability as the detergent series is ascended and the increased stability as the concentration of the $C_{16}n_3$ stabilizer is increased, is immediately apparent.
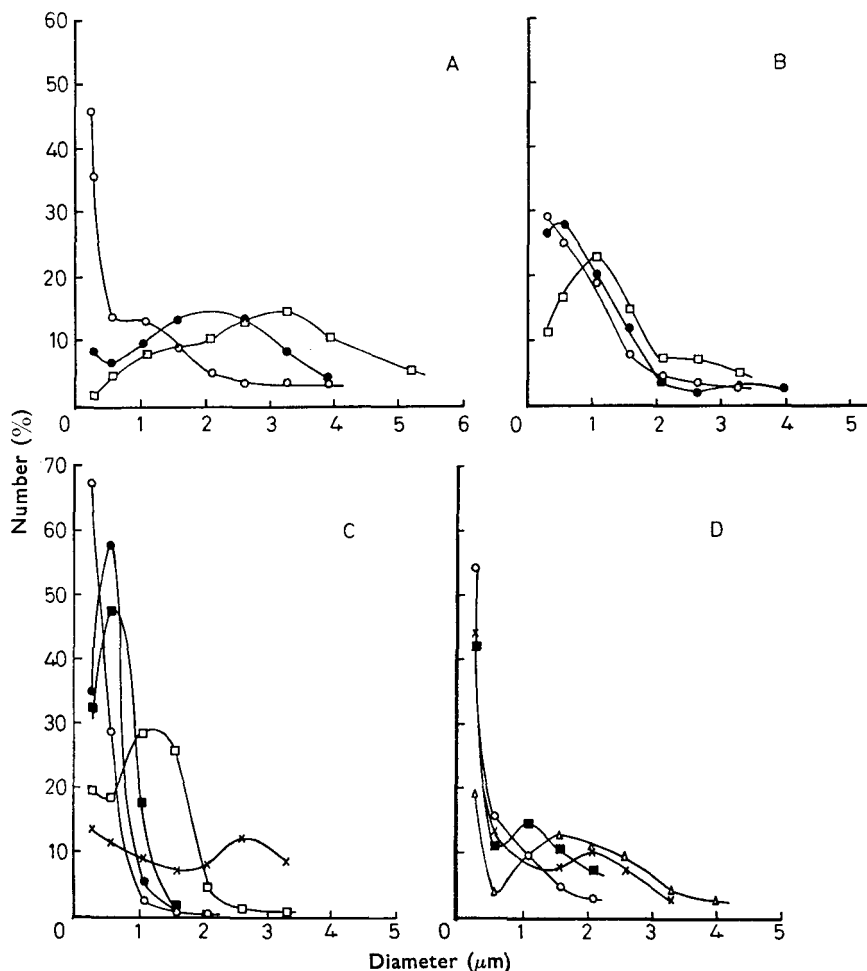
FIG. 1. Globule size distribution plots for typical emulsions of anisole and chlorobenzene showing ageing of the emulsions by changes in the number percentage–diameter distributions. A. Anisole emulsion, $\phi = 0.20$, 0.1% $C_{16}n_3$. B. Anisole emulsion, $\phi = 0.20$, 9.99% $C_{16}n_3$. C. Chlorobenzene emulsion, $\phi = 0.14$, 0.1% $C_{16}n_6$. D. Chlorobenzene emulsion, $\phi = 0.20$, 0.11% $C_{16}n_9$. A, O 0h, ● 1h, □ 4·5h. B, O 0h, ● 3·5h, □ 3 days. C, O 0h, ● 40 min, ■ 2·5h, □ 44h, × 234h. D, O 0h, ■ 3·5h; × 6h; △ 24 days.

In this form the results are difficult to compare. The rates of coalescence (s^{-1}) calculated from the change in the logarithm of the number of globules n in a given volume with time (Van den Tempel, 1957) are useful for comparison and are collected in Table 1. As was evident with the cetomacrogol emulsions (Elworthy & Florence, 1967), an initial fast rate of coalescence is followed by a slower rate which continues for a longer period of time. The time over which each rate holds is obviously a factor determining the state of the emulsion at some point in time. If the faster rate is due to equilibration or distribution of the detergent, the more quickly this is achieved the better the emulsion will be when the second rate begins.

k_1 for chlorobenzene emulsions stabilized with 1·0, 5·0 and 7·8% $C_{16}n_3$ holds over 6, $5\frac{3}{4}$ and 2 h respectively while k_2 was followed up to 180 h. In the cetomacrogol emulsions k_1 held up to about 4 days and the particle sizes of many of these emulsions were measured for ~100 days. The general trend is that k_1 persists longer as the poly-

oxyethylene chain length is increased, and, for any one detergent, the duration of k_1 decreases as the concentration of detergent is increased.

Table 1. *Rates of coalescence* (k_2 s^{-1}) *of emulsions of anisole and chlorobenzene in water stabilized with polyoxyethylene glycol ethers*

Detergent	Anisole			Chlorobenzene		
	Detergent (%)	Phase volume (ϕ)	Rate (10^6 k_2)	Detergent (%)	Phase volume (ϕ)	Rate (10^6 k_2)
$C_{16}n_3$	0·1*	0·20	7·2	0·1*	0·20	27·4
	1·0*	0·20	17·2	1·0*	0·10	1·44
	5·0*	0·20	2·7	1·0*	0·20	1·11
	10·0*	0·20	0·31	1·0*	0·50	1·67
	10·0*	0·10	0·12	4·9*	0·10	0·52
	10·0*	0·20	0·42	4·9*	0·20	0·53
	—	—	—	7·8*	0·20	1·67
	—	—	—	10·0*	0·02	0·26
	—	—	—	10·0*	0·05	0·06
	—	—	—	10·0*	0·20	0·11
$C_{16}n_6$	0·11	0·20	4·72	0·1	0·14	3·61
	0·11*	0·05	2·81	0·5	0·20	2·67
	1·0*	0·20	0·29	1·0*	0·20	0·44
	1·0	0·02	6·21 (20°)	5·0*	0·20	0·14
	1·0	0·02	22·8 (30°)	10·0*	0·10	0·44
	1·0	0·05	32·5	—	—	—
	1·0	0·20	5·7	—	—	—
	5·0*	0·20	0·24	—	—	—
$C_{16}n_9$	—	—	—	0·11	0·20	2·7
	—	—	—	0·1*	0·10	1·04
	0·1	0·20	2·78	0·1*	0·02	0·24
	0·1*	0·20	0·46	1·0*	0·20	0·70
	1·0	0·20	0·21	1·0	0·20	0·27
	—	—	—	1·0	0·20	0·19
	5·0*	0·20	0·24	5·0	0·20	0·05
	—	—	—	5·0*	0·20	0·23
	—	—	—	10·0*	0·20	inverts

* Surfactant dissolved in oil.

Table 1 shows that the values of k_2 (the second rate) of some of the emulsions prepared with high concentrations of short chain detergents approach the earlier reported values obtained for emulsions stabilized with cetomacrogol (Elworthy & Florence, 1967), but the second rate of coalescence of the latter holds over longer periods.

The results will be discussed under two main headings.

Effect of detergent concentration. The critical micelle concentration determined in simple aqueous solution bears no relation to the apparent critical micelle concentration (CMC) obtained in the presence of polar oil phase (Elworthy & Florence, 1969a). Increasing the surfactant concentration above that apparent CMC in emulsions stabilized by $C_{16}n_3$, $C_{16}n_6$ and $C_{16}n_9$ resulted, in general, in increased stability. This is in contrast to the behaviour of $C_{16}n_{25}$ (cetomacrogol 1000) which when present in high concentrations caused a slight increase in the rate of breakdown.

Fig. 2 shows the slower rate of growth in the presence of increasing concentrations of $C_{16}n_3$. Here the mean number diameter (dn_m) is plotted against time, where

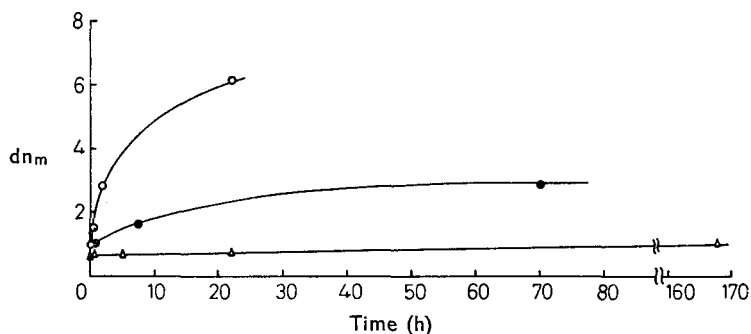$$dn_m = \left(\frac{\Sigma n_i d_i^2}{\Sigma n_i} \right)^{\frac{1}{2}}$$

FIG. 2. Plot of dn_m vs time (h) showing the rate of growth of anisole emulsions, $\phi = 0.20$ as a function of detergent concentration. ○ 1·0% $C_{16}n_3$. ● 5·0% $C_{16}n_3$. △ 9·99% $C_{16}n_3$.

In emulsions stabilized by cetomacrogol 1000 the interfacial tension is virtually constant above the CMC; in the present series, however, there is a fall in interfacial tension above the CMC.

Fig. 3 indicates that there is an empirical relation between interfacial tension (σ_i) and log k_2 at 0·1% surfactant levels for both anisole and chlorobenzene emulsions, but at higher concentrations results for anisole and chlorobenzene do not fall on the same line. Hence other factors influencing stability are coming into play at higher concentrations.
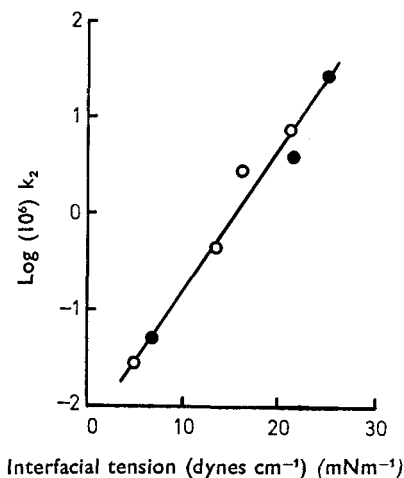

FIG. 3. Plot of log k_2 vs interfacial tension indicating an empirical relation between the stability of emulsions stabilized with 0·1% $C_{16}n_3$, $C_{16}n_6$, $C_{16}n_9$ and cetomacrogol 1000. ○ Anisole emulsions. ● Chlorobenzene emulsions.

An emulsion can never be thermodynamically stable. Stability is therefore relative and whatever the barriers to coalescence these can be overcome. Interfacial energy must be the driving force for coalescence, hence a decreased interfacial tension will inevitably result in increased stability, but at a particular interfacial tension other stabilizing factors can alter the lifetime, i.e., "stability" of the emulsion.

Table 2 lists the electrophoretic mobilities (u) and zeta potentials (ζ) of globules of anisole and chlorobenzene with varying concentrations of detergents. It is apparent that the increasing detergent concentration lowers the zeta potential of the

Table 2. *Electrophoretic mobilities and zeta-potentials*

Detergent	Anisole			Chlorobenzene		
	Detergent (%)	u (μm s^{-1} V^{-1} cm^{-1})	ξ (mV)	Detergent (%)	u (μm s^{-1} V^{-1} cm^{-1})	ξ (mV)
$C_{16}n_3$	0·1	−4·1	−76·5	0·1	−4·2	−78·4
	1·0	−3·55	−66·2	1·0	−4·05	−75·6
	5·0	−2·35	−43·9	5·0	−3·65	−68·1
	10·0	−1·65	−30·8	7·8	−3·5	−65·3
	—	—	—	10·0	−3·3	−61·6
$C_{16}n_6$	0·11	−3·7	−69·0	0·1	−4·0	−74·6
	1·0	−3·45	−64·4	1·0	−3·95	−73·7
	5·0	−3·30	−61·6	5·0	−3·75	−69·9
	—	—	—	10·0	−3·35	−62·5
$C_{16}n_9$	0·1	−3·95	−73·7	0·1	−3·4	−63·4
	1·0	−3·7	−69·0	1·0	−4·0	−74·6
	5·0	−2·88	−53·7	5·0	−2·8	−52·2
	—	—	—	10·0	−2·1	−39·2
$C_{16}n_{25}$*	0·1	−2·0	−37·3	0·1	−1·7	−31·7
	1·0	−1·40	−26·1	1·0	−1·3	−24·3
	5·0	−0·40	−7·5	5·0	−0·35	−6·5
	10·0	0	0	10·0	0	0

* Values for cetomacrogol mobilities are those published previously (Elworthy & Florence, 1967); the zeta-potentials are larger than the previously quoted values because of the use of the more exact Henry's equation.

globules and hence the increasing stability must be due to some source other than the interaction of double layers, although the electrical contribution is not unimportant.

Effect of polyoxyethylene glycol chain length. As was seen from Fig. 1, increasing PEG chain length increased stability at a given detergent concentration. Fig. 4 shows for one representative detergent concentration the variation of stability (as log $10^6 k_2$) and electrophoretic mobility as a function of polyoxyethylene chain length; results for cetomacrogol are also included. The experimental quantity of electrophoretic
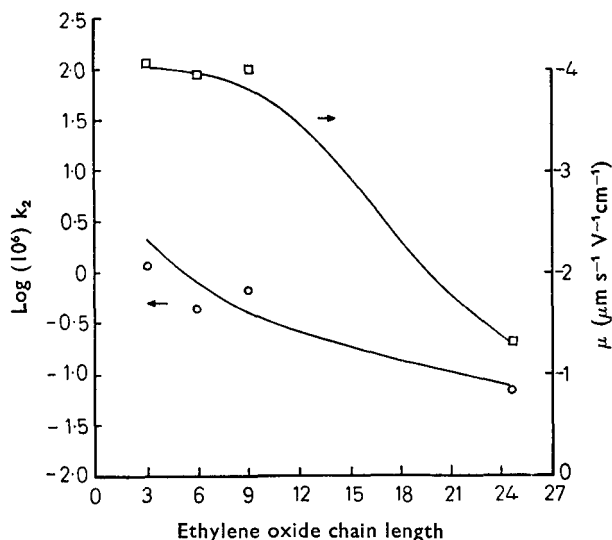

FIG. 4. Log k_2 and electrophoretic mobility of chlorobenzene emulsions with 1·0% detergent as a function of ethylene oxide chain length. The lower k_2 the greater the stability.

mobility (u) rather than calculated zeta-potential has been used because of doubt about the exact relation between the two (Elworthy & Florence, 1969b). It is again obvious that the electrical contribution to stability decreases as the series is ascended and hence other factors must come increasingly into play.

At 0·1% detergent levels there is a noticeable difference in stability between the $C_{16}n_3$-stabilized emulsions and those stabilized with higher members of the series, but at higher concentrations the differences are small. For example, 10% $C_{16}n_3$ and 10% $C_{16}n_{25}$ give similar rates of coalescence in emulsions of anisole of phase volume (ϕ) 0·2.

Stryker, Helin & Mantell (1966) observed little difference in the stability of poly-ethylene latexes in the presence of 9·5 and 16 unit octyl phenyl polyoxyethylene condensates and at longer chain lengths a decrease in stability was observed.

The particle size distribution plots in Fig. 1 show that for $C_{16}n_3$ emulsions, the peak of the distribution moves rapidly to higher diameters; with $C_{16}n_6$ the increase is not so rapid and the decrease in the number percent of particles below 0·5 μm is slower. Emulsions stabilized with $C_{16}n_9$ sometimes showed a bimodal distribution (see Fig. 1D) in which the smallest particles which could be observed microscopically ($\sim$0·5 μm) appear to be more stable than those of the 0·5 μm–1·5 μm range. The result is that the numbers of particles in the 0·5 μm–1·0 μm range decrease more rapidly than those in the smallest range, and two maxima appear.

Kinetics of breakdown

Emulsions stabilized with cetomacrogol exhibited two phase breakdown, a rapid initial change in particle number (n) followed by a slower rate during which log n varied linearly with time (Elworthy & Florence, 1967); in addition, a function of globule surface area Σ^{-1} defined previously (see Hill & Knight, 1965) was linear with time and the Smoluchowski equation, which is essentially $\Sigma^{-3} = ct + d$, was found not to hold. The same applies to the present series, in spite of these emulsions being less stable. They must still be regarded as "slowly coagulating systems" in terms of the kinetics of breakdown. For the more common examples of rapid coagulation, the time for coagulation is of the order of seconds (Verwey & Overbeek, 1948). In Fig. 5 plots of log n and Σ^{-1} and Σ^{-3} versus time are given, showing the non-linear variation of Σ^{-3} for an emulsion of chlorobenzene ($\phi = 0\cdot14$) stabilized by 0·1% $C_{16}n_6$.
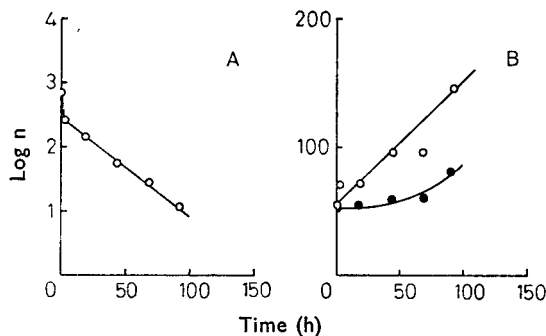

FIG. 5. A. Plot of log n *vs* time (h) for a chlorobenzene emulsion, $\phi = 0\cdot14$, stabilized with 0·1% $C_{16}n_6$ from which k_1 and k_2 can be calculated. Ordinate: log n. B. Hill & Knight plot for the same emulsions of Σ^{-1} (○) and Σ^{-3} (●) *vs* time indicating the linearity of the former within experimental error. Ordinate in arbitrary units. ○ = 104 (interfacial area, cm²)/π and ● = $\Sigma^{-3} \times 10^4 + 50$.

Phase volume (ϕ)

In the less stable emulsions the effect of varying the phase volume of the disperse phase is pronounced. Fig. 6 illustrates the effect of phase volume on the rate of breakdown of an anisole emulsion.
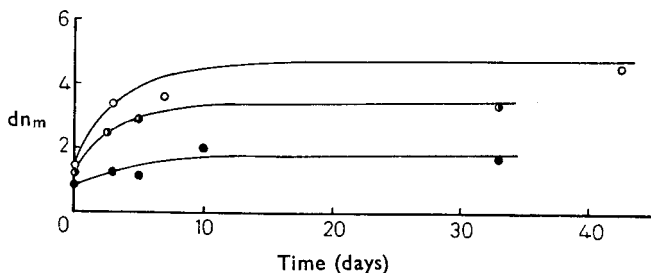

FIG. 6. Plot of dn_m (mean number diameter) *vs* age of emulsion (days) for an anisole emulsion stabilized with 9·99% $C_{16}n_3$ showing the effect of phase volume. ● $\phi = 0·02$, ◑ $\phi = 0·10$ ○ $\phi = 0·20$.

The ratio of the rate of coalescence of the 0·20 and 0·02 phase volume anisole emulsions (9·99% $C_{16}n_3$, interfacial tension $\sim$5 mNm^{-1}) is 1·4, while for the 0·1% $C_{16}n_9$ chlorobenzene emulsions (interfacial tension $\sim$13 mNm^{-1}) the ratio is about 4. The increase in interfacial energy in the latter case is greater and even if the stabilizing forces remained the same at both $\phi = 0·02$ and 0·20, the driving force for coalescence would be much greater in the latter emulsion.

Zeta-potentials

The reduction in effective electrical repulsion on increasing phase volume due to the overlap of broad double layers, is discussed by Albers & Overbeek (1959). This might be a factor which should be taken into account with the present systems. For practical reasons, zeta-potentials are determined in extremely dilute emulsions and the extrapolation to real systems is not always straighforward. However, the percentage reduction in the repulsive energy which results from the initial overlap of double layers may be calculated, using Albers & Overbeek's (1959) derivation, and this indicates a 6·7% correction to be applicable. This is deemed unimportant in view of the other approximations used.

When the detergent is dissolved in the oil phase initially, slower rates of coalescence are observed. As an example, when a chlorobenzene emulsion was stabilized with 0·1% detergent $C_{16}n_9$ in the *oil* $\phi = 0·2$, k_2 had a value of 10·4 $\times$ 10^{-7} s^{-1}. With 0·11% detergent in the *water*, a value of 26·9 $\times$ 10^{-7} s^{-1} was observed. For the equivalent anisole emulsion with detergent in the aqueous phase, k_2 was 27·8 $\times$ 10^{-7} s^{-1}. Prigorodov, Nikitina & Taubman (1965) noted a similar effect in emulsions of xylene in water with the emulsifier octyl phenyl nonaoxyethylene glycol ether (OPn$_{10}$). With 0·25% OPn$_{10}$ in the xylene there resulted a more rapid and more effective stabilization than the same concentration in the aqueous phase. This is perhaps due to re-equilibration in the system. As K_w^o for the aqueous $C_{16}n_9$-anisole and chlorobenzene system is high,* at equilibrium most of the detergent will be in the oil. It can be envisaged that the higher interfacial tension of the

* Rough K_w^o values have been determined for chlorobenzene. These are: $C_{16}n_6$ 100 (0·1%), 300 (1%), $C_{16}n_9$ 50 (0·1%), 120 (1·0%), cetomacrogol, 8·8 (0·2%), 4·9 (1%). These are expected to be approximate because of the lack of sensitivity of existing assay procedures at low concentrations of non-ionics.

non-equilibrated system will lead to a more rapid breakdown, hence when the second rate of coalescence comes into play the mean particle size is already greater and the particles exhibit a faster rate of coalescence. The effect of initial particle size has been noted in anisole emulsions stabilized with 1.0% $C_{16}n_9$ (in the oil phase), that emulsion having the larger initial mean number diameter grew more rapidly than a finer emulsion.

Emulsions stabilized with $C_{16}n_3$, $C_{16}n_6$ and $C_{16}n_9$ are sensitive to increased temperature. An emulsion stabilized with 1% $C_{16}n_9$ broke after 2 days at $30°$ and after 1 day at $37°$. At $20°$ the rate of coalescence of 1% $C_{16}n_6$-anisole emulsion was 6.2×10^{-6} s^{-1} and at $30°$, 22.8×10^{-6} s^{-1}. Using standard equations the enthalpy of coalescence was found to be 20 Kcal, which might suggest that desolvation is involved in the process of coalescence.

Summary of results

Broad trends have been illustrated in this paper: the effect of detergent concentration, the effect of surfactant chain length, of phase volume and temperature. The electrophoretic properties of the emulsion globules indicate the magnitude of the surface charge of the particles and give some indication of the contribution of electrical double-layer repulsion to the stabilizing forces. But it is apparent that a reduction in zeta-potential with increasing detergent concentration and chain length is accompanied by an increase in stability. Therefore, as with cetomacrogol, an electrical component must be taken into account, but it is a secondary stabilizing factor; the "entropic" mechanism must then be involved.

In qualitative terms, an increase in polyoxyethylene chain length will increase the closest distance of approach of two particles and, other things being equal, minimize the attractive forces between them. But the magnitude of the entropic stabilizing force is not known and the effect of the adsorbed layer on the attraction between two globules is not known.

Acknowledgements

REFERENCES

ALBERS, W. & OVERBEEK, J. TH. G. (1959). *J. Colloid Sci.*, **14**, 510–518.
ELWORTHY, P. H. & FLORENCE, A. T. (1967). *J. Pharm. Pharmac.*, **19**, Suppl. 140S–154S.
ELWORTHY, P. H. & FLORENCE, A. T. (1969a). *Ibid.*, **21**, 72–78.
ELWORTHY, P. H. & FLORENCE, A. T. (1969b). *Ibid.* **21**, Suppl., 79S–90S.
HELLER, W. & PUGH, T. L. (1960). *J. Polym. Sci.*, **47**, 203–217.
HENRY, D. C. (1931). *Proc. Roy. Soc.*, A133, p. 125.
HILL, R. A. & KNIGHT, J. T. (1965). *Trans. Faraday Soc.*, **61**, 170–181.
MATHAI, K. G. & OTTEWILL, R. H. (1966a). *Ibid.*, **62**, 750–758.
MATHAI, K. G. & OTTEWILL, R. H. (1966b) *Ibid.*, **62**, 759–769.
PRIGORODOV, V. N., NIKITINA, S. A. & TAUBMAN, A. B. (1965). *Colloid J., U.S.S.R.*, **27**, 734–737.
STRYKER, H. K., HELIN, A. F. & MANTELL, G. J. (1966). *J. appl. Polym. Sci.*, **10**, 81–96.
VAN DEN TEMPEL, M. (1957). *Proc. Second Int. Congress on Surface Activity*, **1**, 439–446. London: Butterworths.
VERWEY, E. J. W. & OVERBEEK, J. TH. G. (1948). *Theory of the Stability of Lyophobic Colloids.* Amsterdam: Elsevier.
WIERSEMA, P. H., LOEB, A. L. & OVERBEEK, J. TH. G. (1966). *J. Colloid Inter. Sci.*, **22**, 78–99.