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SOME PROPERTIES OF OIL-IN-WATER EMULSIONS STABILIZED WITH MIXED NON-IONIC SURFACTANTS (BRIJ 92 AND BRIJ 96)

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SUMMARY

Mixture of Brij 92 (polyoxyethylene (2) oleyl ether) and Brij 96 (polyoxyethylene (10) oleyl ether) in the HLB range 4.9 to 12.4 were used to stabilize mineral oil-in-water emulsions. Particle size, stability to centrifugation and zeta potential were measured as a function of HLB and the effect of change in pH of the emulsions on zeta potential observed over the range of HLB values. Maximal stability occurs at an HLB at which particle size is at a minimum but there is no evidence for a maximum in the zeta potential at the critical HLB as has been suggested by Becher and co-workers. Photomicrography and measurements of viscosity of the emulsions at HLB 6 indicate flocculation at pH 4 reversed at pH 9.5. The rapid increase in electrical conductivity of the emulsions at low HLB is explained qualitatively on the basis of the formation of continuous networks of flocculated particles prior to phase inversion.

INTRODUCTION

Although steric stabilization undoubtedly plays an important role in preventing the aggregation and coalescence of droplets in emulsions stabilized by non-ionic surfactants and polymers, the presence of an electrical double layer on the globules gives rise to an electrical repulsive force. Vincent (1973) has suggested that the longer range electrical double-layer interaction forces will dominate inter-globular interactions which lead to aggregation, the final barrier to coalescence being provided by the layer of adsorbed non-ionic molecules at the interface. Elworthy and Florence (1967, 1969) in studying emulsions stabilized by non-ionic surfactants found that the concentration of the surfactant

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and the length of the polyoxyethylene chain influenced both electrophoretic mobility and stability. Stability decreased with decreasing zeta potential, but emulsions were stable even when the zeta potential of the globules was reduced to zero. Sulphation of the terminal hydroxyl of the polyoxyethylene chain of cetomacrogol 1000 (Attwood and Florence, 1971) increased the negative zeta potential of the disperse phase, but the sulphated cetomacrogol was a less efficient emulsifier than the parent compound. This finding led to the conclusion that the contribution of the electrostatic potential to stability was secondary to that of steric stabilization processes. The question of stabilization is far from being resolved, however.

Non-ionic stabilized systems are not immune to the effects of electrolytes. The superiority of mixed surfactants over single surfactants as emulsion stabilizers is acknowledged (Becher, 1976) yet has not been correlated with steric stabilization of DLVO theory. The use of the hydrophile–lipophile balance (HLB) of an emulsifier as an indicator of its potential to stabilize given systems has proved to be a powerful if empirical approach to emulsion formulation (Seiller et al., 1967, 1968, 1970). When mixtures of two non-ionic emulsifiers with different HLB numbers are used, at a certain HLB, here termed the critical HLB (Seiller, 1970) maximum stability will be observed. Recently, Becher and Tahara (1972) using mixtures of Tween 80 and Span 80 produced experimental evidence which suggested that at the critical HLB the zeta potential had its maximum value. Becher and coworkers (1976) have also found that systems with the optimal HLB showed the greatest resistance to the effects of added electrolyte: that is the concentration of electrolyte required to cause a marked fall in zeta potential was maximal at the critical HLB.

In the present paper we have examined the effect of change in pH of the aqueous phase on the stability of oil-in-water emulsions stabilized by mixtures of the non-ionic surfactants Brij 92 [1] and Brij 96 [1] in the HLB range 4.9–12.4. Recently, Kako and Kondo (1979) studied the stability of soya bean oil-in-water emulsion containing mono- and di-glyceride stabilizers, observing in particular the effect of pH on electrophoretic mobility. Apart from this one paper there appear to be few which report on the sensitivity of non-ionic o/w emulsions to pH, in spite of the importance of this aspect of their performance in respect to dilution of pharmaceutical emulsions in vitro and in vivo.

MATERIALS

The emulsion disperse phase was mineral oil whose specifications conformed to the requirements of the Pharmacopeé Française. The surfactants were polyoxyethylated oleyl alcohol ethers with 2 ethylene oxide units (Brij 92 [1], HLB 4.9) and with an average of 10 ethylene oxide units (Brij 96 [1], HLB 12.4) as used in previous work (Treguier, Lo et al., 1975; Lo, Florence et al., 1977). The continuous phase was water, distilled from neutral glass, equilibrated with ambient air and agitated mechanically for 30 min at 20°C; the final pH was 5.8. The pH of the continuous phase was adjusted with HCl or NaOH to a range of values between 4 and 9.5. Emulsions were prepared and the pH precisely adjusted to desired values by the addition of acid or base. Emulsions of 20% mineral oil

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[1] Brij 92 and Brij 96 are trademarks of ICI America Ltd. and are also used by Honeywill Atlas UK and by Atlas Chemical Industries NV in Europe.

contained 2.5 or 5% surfactant or surfactant mixture in the range of HLB values 4.9–12.4. The emulsions were prepared at 70°C by phase inversion and drop by drop addition of continuous phase, the system being agitated by a blade stirrer at 200 rpm for 30 min.

Four series of emulsions were prepared. In the first series 9 emulsions were made with distilled water and had a final pH of 5.5. In the second series the emulsions were diluted with distilled water whose pH had been adjusted. In the third and fourth series N/10 HCl and NaOH was added directly to the initial emulsion to adjust the final pH to the desired value.

METHODS

Emulsions were studied 8 days after preparation by observation of macroscopic appearance, measurement of particle size by photomicrography and related techniques, electrical conductivity, stability to centrifugation, viscosity and measurement of electrophoretic mobility.

Particle size measurements were made using phase contrast microscopy and photomicrography. Confirmatory measurements were made in selected systems with a Coulter Counter Model TAII instrument (Coultronics France SA, Margency) and some measurements of systems with small average particle size in the region inaccessible to the microscope, using a Coulter Nano-Sizer. The range of this photon correlation spectrometer is 40–3000 nm and it produces an average particle diameter and not a particle size distribution. All methods which may be applied to emulsions suffer some disadvantages: microscopy from the lower cut-off point of 1 μm; Coulter counting by the need to dilute the emulsion into electrolyte and the resultant potential problem of flocculation and instability; the Nano-Sizer from its upper limit of 3 μm. For our purposes the combination of techniques gave adequate information on the change in mean particle size with change in surfactant HLB.

Electrical resistivity was measured using a resistivity meter comprising a Kohlrausch bridge fed with alternating current at 1000 Hz.

Stability to centrifugation was determined in 10 ml graduated tubes at 1500 *g* for 15 min, followed by 15 min at 3000 *g* and at 4500 *g* for 15 min. After this time (45 min) the volume of separated or creamed oil phase was recorded and the percentage or oil creamed or coalesced calculated.

Electrophoretic mobility was measured in a Rank Brothers (Cambridge, U.K.) Mark II microelectrophoresis apparatus, the cell being held in the vertical plane. As dilution of the emulsions is essential prior to measurement of particle velocities, the stability of the emulsions on dilution was determined by observing their physical features over 24 h. 100-fold dilution was considered optimal for the resulting measurements, and distilled water of the appropriate pH was used as diluent, as the surfactant mixtures all contain an insoluble component, Brij 92, which made the use of surfactant solutions as diluent impracticable.

The mobility of the globules was determined by timing the passage of globules over 50 μm under the influence of a potential of 9.6 V cm^{-1}. Thirty measurements were made in each system, the polarity of the electrodes being reversed between each measurement to avoid polarization. After each series of measurement the position of the stationary layer was checked. Four series of 30 measurements were made for each emulsion, the cell being filled with a fresh sample of diluted emulsion for each series. The standard deviation of the calculated zeta potential was ±10% of the mean.

A mobility of 2.58 ± 0.2 μm cm V^{-1} s^{-1} and a zeta potential of 33 ± 3 mV was obtained for a suspension of titanium dioxide using the formula (Smoluchowski, 1914):

$$\mu = \frac{\epsilon\zeta}{4\pi\eta} \qquad (1)$$

where μ is the mobility, ϵ is the dielectric constant of the continuous phase and η its viscosity. After conversion of μ to cm and e.s.u. to mV the zeta potential in mV is obtained from the relation,

$$\zeta = 14.08\,\mu \qquad (2)$$

Henry's (1931) equation which takes account of the retardation of particles as influenced by the ionic strength of the medium is

$$\mu = \left(\frac{\epsilon\zeta}{4\pi\eta}\right) f(\kappa a) \qquad (3)$$

The error in neglecting the variation in the term $f(\kappa a)$ (κa being the reciprocal Debye-Huckel thickness in m^{-1}) due to the differences in particle radius a is not significant in these experiments, the maximum error being estimated to be in the region of 10%.

The value of η can be obtained by measurement of the viscosity of the continuous phase obtained by centrifuging unstable emulsions. In the experiments following dilution with water the viscosity of the continuous phase differs little from that of water. Structured emulsions with high bulk viscosity lose this structure on dilution. Mineral oil was found to have a zeta potential of –60 mV in water, in good agreement with the value of –66 mV obtained by Tadros (1976).

Because of the danger of confusion of oil globules and air bubbles in the microelectrophoresis cell we sought to differentiate between them by measurement of the mobility of both. Usui and Sasaki (1978) have found the zeta potential of argon gas bubbles in water and in dilute solutions of non-ionic surfactants to remain constant over a range of surfactant concentrations at –40 mV. We have found air bubbles in water to have an electrophoretic mobility of -3×10^{-2} μm cm V^{-1} s^{-1} and a zeta potential of –43 mV, compared with –60 mV for oil in the absence of surfactant.

RESULTS

Emulsions without added electrolyte were used in the determination of the influence of surfactant mixtures on the stability of mineral oil emulsions. Fig. 1 shows the results of particle size determinations and coalescence under centrifugal stress at two levels of surfactant. At the 2.5% level stability to centrifugation is maximal at an HLB of 7.5, while at the higher surfactant concentration maximal stability occurs at an HLB of 8.5.

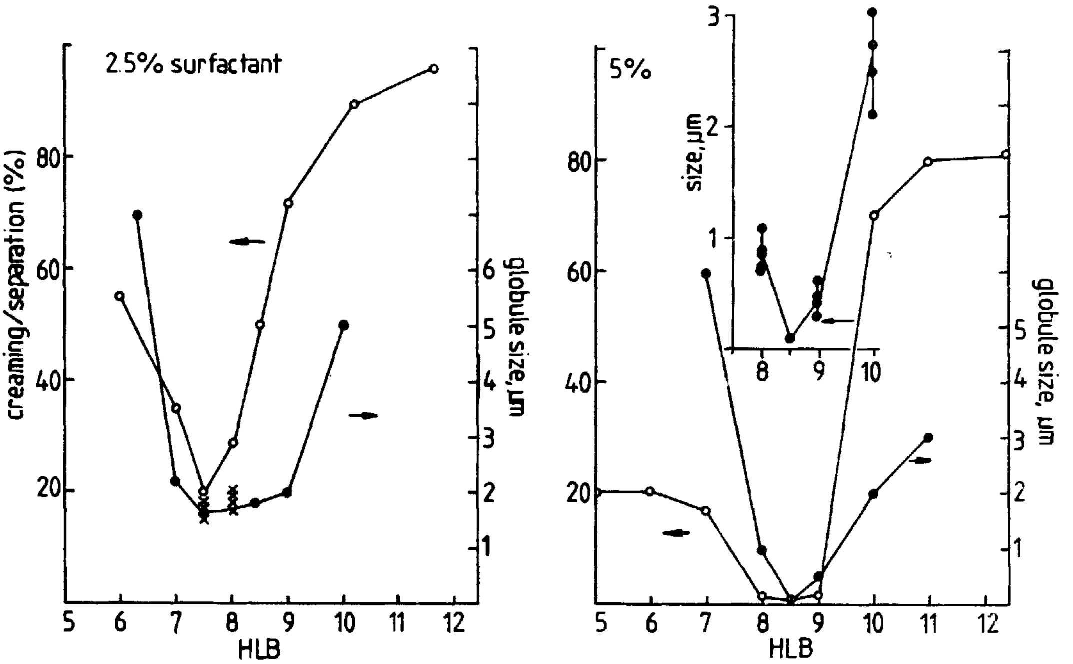


Fig. 1. A: plot of percentage creaming or coalescence (o) and mean globule size (µm) (•) as a function of the HLB of the emulsifier mixture at 2.5% surfactant level. Results from the Coulter Nano-Sizer shown thus (X). B: as above at 5% surfactant concentration. Inset shows details of particle size in the critical HLB region obtained by the Coulter Nano-Sizer.

Maximal stability coincides with minimum particle size. In most stable emulsion systems the particle size is of the order of 1 µm, at the limit of the microscopic techniques available for sizing. In order to verify the results other techniques were employed and the results from the Coulter Nano-Sizer are shown as an inset in Fig. 1B. Microscopy indicates that the minimum particle size with 5% surfactant occurs at an HLB of 8.5; the more precise results from the Nano-Sizer confirm that the minimum particle size of about 0.1 µm occurs at this HLB. At lower surfactant concentrations it appears that the minimum particle size has shifted to a lower HLB, a fact confirmed by the Nano-Sizer results and by other work in our laboratories (Depraétere, David et al., 1977). This shift in optimal HLB of the surfactant mixture with increasing surfactant concentration must reflect changes in the interfacial layer as the concentration increases, and is most likely a reflection of the changes in the ratio of the Brij 92 and Brij 96 in the interfacial layer. As the total bulk concentration increases the amount of the more hydrophobic surfactant in the interface should decrease as it becomes solubilized in the bulk in micelles of the hydrophilic surfactant (Mysels and Florence, 1969). If, however, multilayers are forming at the interface prediction of the resultant effects is not easy.

The difference in the mean particle size of the emulsions makes a direct comparison of their behaviour difficult. During formation of the emulsion the optimum surfactant mixtures, possibly because of the low interfacial tension, produce the best dispersion, which then, almost regardless of subsequent stabilizing power of the adsorbed layer, will be more stable, because of the decreased attractive forces and the increased ratio of adsorbed stabilizing layer to bulk hydrocarbon in the smaller droplets. Measurement of emulsion viscosity and conductivity indicate that changes occur in the properties of the emulsions at HLB values around the critical values (Fig. 2). Below HLB 8 in 5% emulsions there is an increase in viscosity and resistivity. Some changes in viscosity will be dependant on the average globule size of the emulsions, the decreasing particle size as the HLB falls towards the critical value would account qualitatively for the observed increase in viscosity (Sherman, 1970). Electrical resistivity of dispersed systems should be independent of particle size if the particles are spherical (Dukhin, 1971). Asymmetry of the disperse phase leads to an increase in resistivity over dispersions of spherical particles, but the shape effect according to Fricke (see Meredith and Tobias, 1962) cannot account for the extent of the increase noted in the emulsions prepared with 5% surfactant (Fig. 2). Cross-linking of networks of particles in a flocculated state is the most likely cause of significant increases in resistivity; Mackie and Meares (1955) obtained an equation for the obstruction effect in a system with an infinite network of obstructions of volume fraction, ϕ, which gives the ratio of the diffusion coefficient (D) of a small molecule in the system compared to its diffusion coefficient in water (D_0):

$$\frac{D}{D_0} = \left[\frac{1-\phi}{1+\phi}\right]^2 \qquad (4)$$

Conductivity can be substituted directly for D, or the equation may be rewritten in terms

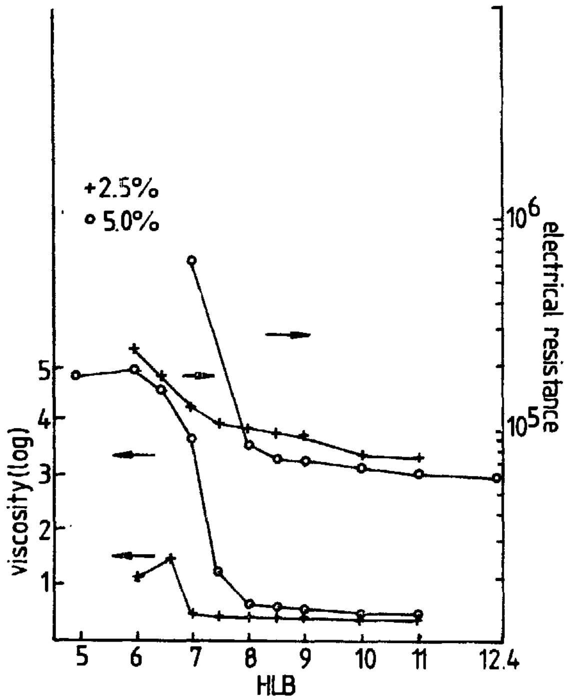


Fig. 2. The viscosity and electrical resistance of emulsions at 2.5% (+) and 5% (○) surfactant levels as a function of surfactant HLB.

of resistivity R as

$$\frac{R}{R_0} = \left[\frac{1+\phi}{1-\phi}\right]^2 \tag{5}$$

The volume fraction of the emulsions is 0.2 and thus R/R_0 is 2.25 when the globules are forming a network. The resistivity of the system at HLB 7 (5% surfactant) is 11 times that of the emulsion prepared with Brij 96 alone. This suggests that the water bound up in the aggregates increases the effective volume of the aggregates. A volume fraction of 0.54 is required in Eqn. 5 to give a resistivity ratio of 11. Klugman (1974) has discussed the increase in the dielectric constant of emulsions resultant on flocculation. The cross-linking of particles is a prelude to inversion; at the lowest HLB at higher surfactant levels. inversion does in fact occur.

Zeta potentials calculated from electrophoretic mobilities in the second series of emulsions are shown in Table 1. The zeta potential of droplets decreases as the hydrophilicity of the surfactant mixtures increases, following the trends observed with single surfactants (Elworthy and Florence, 1969). This confirms the expectation that the more hydrophilic surfactants with longer polyoxyethylene groups move the plane of shear further out into the bulk phase. The effect of increasing surfactant concentration is to decrease electrophoretic mobilities; as this occurs with single surfactant species also (Elworthy and Florence, 1967, 1969) this cannot be due to a change in the composition of the interfacial film. More likely it is due to the formation of multilayers. According to Tadros (1976) it should be possible to calculate from the decrease in zeta potential the thickness (Δ) of an adsorbed non-ionic layer using the equation,

$$\tanh e\zeta/kT = \tanh e\psi/4kT(\exp[-\kappa(\Delta - \delta)]) \tag{6}$$

where ψ is the Stern potential, δ the thickness of the Stern plane, taken to be about 0.4 nm. Using this equation the thickness of the adsorbed layer has been calculated and found to be approximately 50 nm at HLB 12 (pH 5.5) and 20 nm at HLB 4.9 at 5% surfactant levels, while the length of the polyoxyethylene chain of Brij 92 is only 1 nm and that of Brij 96, 4.5 nm. Tadros (1976) estimates the thickness of adsorbed poly (vinyl alcohol) at the paraffin water interface to increase with increasing bulk concentration from 3.5 nm at 1 ppm to 67.7 nm at 20 ppm. Casein forms films approximately 9 nm thick and bovine serum albumin films 19 nm thick at the air–water interface (Graham and Phillips, 1976) but it is not possible solely on the evidence of results from application of Eqn. 6 to implicate multilayer formation. Kayes (1976) has, however, found adsorbed layer thicknesses using this equation for alkyl polyoxyethylene monoethers to be 3.2 and 9.2 nm for derivatives with 30 and 60 ethylene oxide residues, which approximates to monolayer coverage on solid particles.

The effect of pH on zeta potential is shown in Table 1. The zeta potential is decreased to zero at pH values below 4.5 or above 12. At pH 9.5 the zeta potential reaches a maximum (negative) value in all the systems studied (Fig. 3). Specific conductivity measurements on the same systems clearly show that the zeta potential is not a simple function of the electrolyte concentration (Fig. 4). At low and high pH values, Fig. 3 shows the zeta

TABLE 1

ZETA POTENTIAL (mV) OF MINERAL OIL DROPLETS AS A FUNCTION OF pH_i EMULSIONS STABILIZED WITH SURFACTANT MIXTURES OF DIFFERENT HLB, DILUTED 1 IN 100 FOR STUDY. SURFACTANTS BRIJ 92 AND BRIJ 96

pH	4	4.5	5	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	10.5	11	11.5	12
HLB 4.9	0	0	−19	−24	−26	−32	−44	−48	−54	−58	−60	−63	−56	−48	−40	−22	0
HLB 6	0	0	−15	−19	−23	−27	−30	−34	−39	−40	−52	−56	−50	−40	−31	−20	0
HLB 7	0	0	−14	−18	−21	−24	−27	−31	−36	−42	−49	−55	−49	−38	−29	−19	0
HLB 8	0	0	−12	−15	−15	−17	−20	−21	−23	−28	−35	−37	−30	−25	−20	−14	0
HLB 8.5	0	0	−12	−14	−16	−16	−19	−20	−21	−27	−34	−35	−29	−22	−19	−12	0
HLB 9	0	0	−10	−14	−15	−13	−16	−17	−18	−25	−29	−34	−26	−22	−16	−10	0
HLB 10	0	0	−13	−13	−16	−15	−16	−16	−18	−21	−30	−35	−28	−21	−15	−10	0
HLB 11	0	0	−10	−14	−14	−16	−16	−17	−18	−19	−31	−33	−26	−20	−14	−11	0
HLB 12.4	0	0	−11	−13	−16	−15	−16	−17	−18	−20	−30	−34	−27	−22	−16	− 9	0

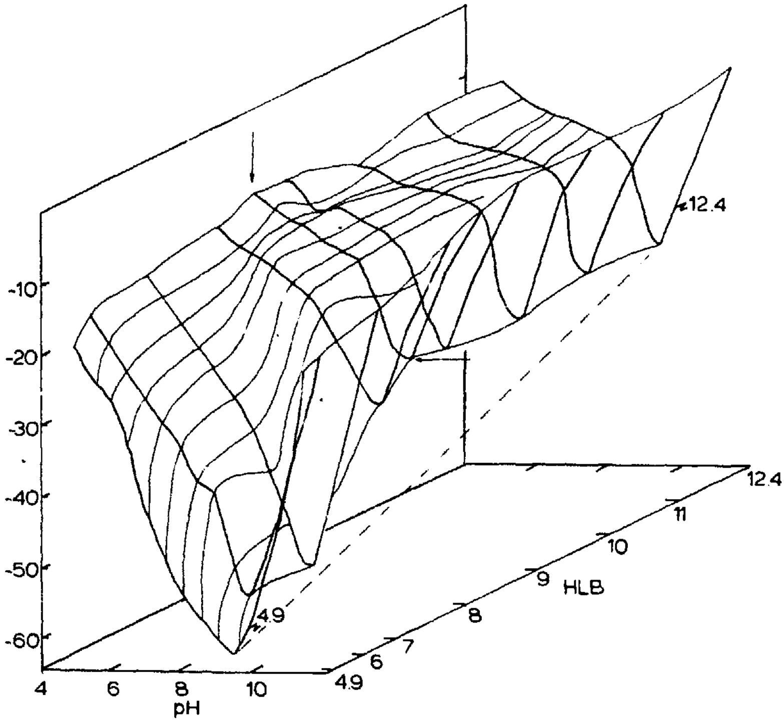


Fig. 3. A plot of zeta potential of emulsions (ordinate, mV) as a function of pH of the aqueous phase and surfactant HLB. The arrows mark the critical HLB of the system in the absence of added electrolyte.

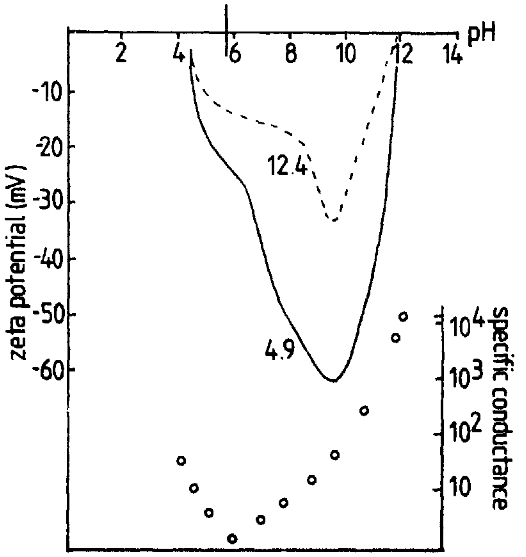
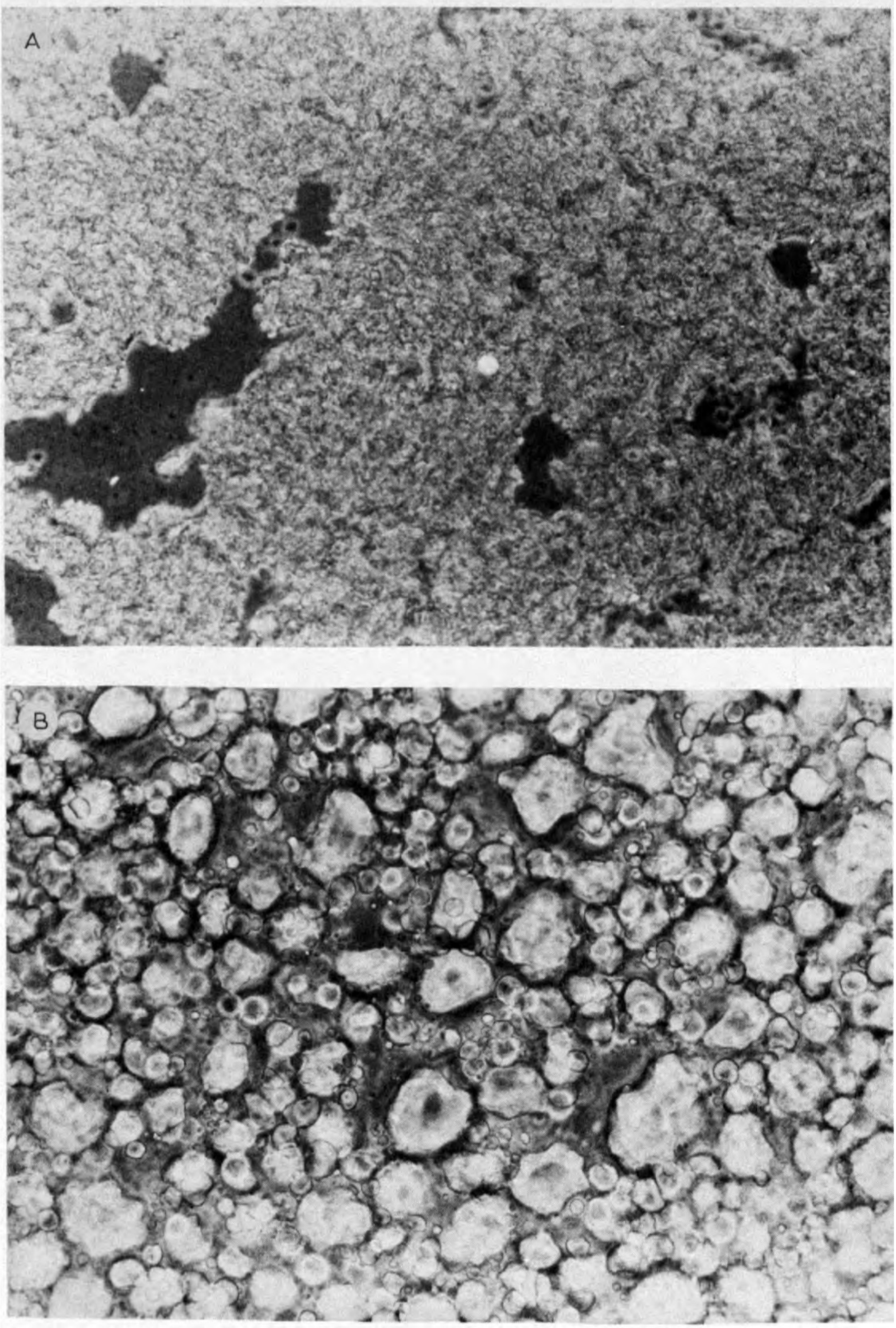


Fig. 4. The zeta potential of the emulsion globules as a function of the pH of the system at two HLB numbers, 4.9 and 12.4, showing the maximum negative zeta potential to occur at an HLB of approximately 9. Also shown are the specific conductance results (o) for the systems under consideration.


A
B

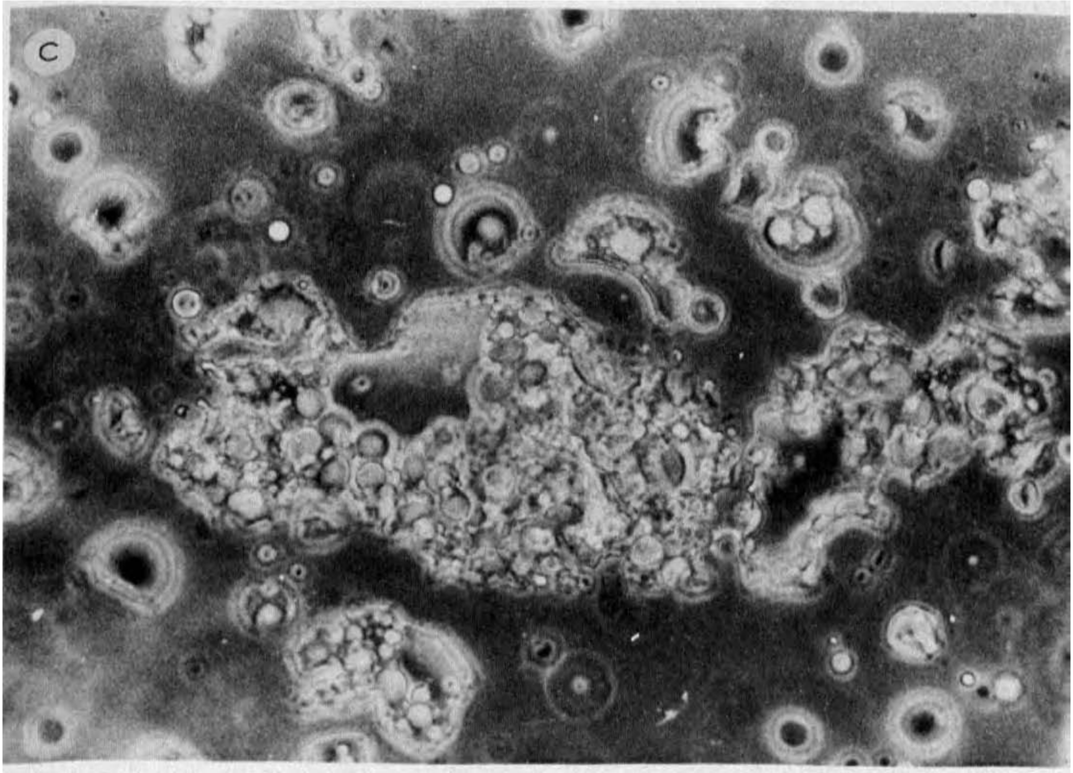


Fig. 5. Photomicrographs of emulsions (×1000), HLB 6. A: an emulsion prepared with mixed surfactants of HLB 6 at a pH of 4 showing aggregation of particles. B: as in A but at pH 9.5 showing separate particles. C: the emulsion as in B prepared at pH 9.5 but adjusted to pH 4 showing the aggregates which form.

potentials of the emulsions to be virtually independent of surfactant HLB; the most pronounced effects occur at a pH of 9 where it is seen that the electrophoretic mobility decreases with increasing HLB showing relatively little change at HLB values above the critical HLB.

Photomicrography was used to follow gross changes in the emulsions on change of pH over the range 4–9.5 pH units. In emulsions with surfactant HLB from 8 to 12.4 there was no significant change in appearance on changing the pH. In systems of lower HLB (4.9, 6 and 7) the globules are aggregated at pH 4 and are separated at pH 9.5, reflecting the influence of surface charge. When the pH of the latter emulsion is decreased from 9.5 to 4 aggregation of the globules is seen to occur (Fig. 5). Viscosity measurements on undiluted emulsions in the range HLB 7–12.4 at pH 4 and pH 9.5 (Table 2) indicate that at HLBs greater than or equal to 8 the viscosity of the emulsions is higher at higher pH values, although the situation is dramatically reversed at HLB 7. The very high viscosity of the emulsions at pH 4 at lower pH values is attributable to the formation of floccules. The maximum viscosity in non-flocculated systems occurs at HLB 8.5 where the particles are smallest.

There is no evidence from our results that the zeta potential is maximal at the critical HLB, as Becher (1972, 1976) found. Even if Eqn. 6 applies only approximately, this im-

TABLE 2

VISCOSITIES OF EMULSIONS BEFORE DILUTION AT pH 4 AND pH 9.5

HLB of surfactant mixture	Viscosity (cP)	
	pH 4	pH 9.5
7	4000	1.84
8	2.96	3.4
8.5	2.96	3.52
9	2.64	2.96
10	2.40	2.52
11	2.40	2.40
12.4	2.37	2.37

plies that there is no drastic change in the adsorbed layer at the critical HLB. Kako and Kondo (1979) observe an inflexion in zeta potential at a certain ratio of their mixed non-ionic surfactant at the oil–water interface and imply some special orientation of the surfactants occurs at that mixture. The results in Fig. 3 suggest merely that the zeta potential does not change as rapidly with change in HLB at HLB numbers above the critical value. Indeed the only parameter that changes significantly to reflect the marked change in stability at the critical HLB is the particle size. Unlike the situation with suspensions, the differences in the initial conditions of emulsions prepared with different surfactants may be over-riding in determining subsequent behaviour. As all emulsions in this series were prepared in the same way with the same input of energy, the differences in particle size must reflect differences in interfacial tension. If at the critical HLB the interfacial tension is at a minimum, the subsequent driving force for coalescencing will be at a minimum. The higher zeta potential of the emulsions with 2.5% emulsifier which are nonetheless less stable than those with 5% surfactant, quite clearly demonstrates the relative unimportance of this parameter in determining the stability of non-ionic emulsions; however, the influence of pH which affects properties such as viscosity, flocculation probably by affecting surface charge shows that electrolyte concentration and pH cannot be neglected. The ultimate stability of these emulsions, i.e. their ability to resist coalescence, resides in the nature of the interfacial barrier formed by the adsorbed non-ionic surfactants. As yet unexplained are the shifts in critical HLB that occur with increasing concentration of emulsifier. A fuller understanding requires studies of the interfacial characteristics of mixtures of the two surfactants used in this work, although Okamoto and Oishi (1977) have concluded that the optimal HLB is closely related to particle size but has little or no relation to the properties of the interfacial film as adduced by interfacial tension measurements. Without detailed knowledge of the nature of the interfacial film, calculation of the interactions between the globules in these emulsion systems is impossible. In calculating the entropic repulsive force using the equation; (Ottewill and Walker, 1966)

$$\frac{\Delta Gm}{kT} = \frac{4\pi Nc^2}{3\bar{v}_1\rho_2^2}[0.5 - \chi_1]\left[\delta - \frac{H}{2}\right]^2\left[3a + 2\,\delta + \frac{H}{2}\right] \qquad (7)$$

one requires knowledge of c, the interfacial concentration of stabilizer. When two surfactants are present with different chain lengths, δ_a and δ_b, with possibly different solvent interaction parameters, χ_1^a and χ_1^b, it is almost impossible to obtain a reasonable value of V_{RS}. Previous work on phase diagrams of ternary systems containing Brij 92–Brij 96 mixtures (Lo, Florence et al., 1977) suggested that geometric factors related to surfactant shape influenced the behaviour of mixtures, optimal properties being achieved when certain ratios of the two surfactants were reached, which allowed the molecules to form condensed films. One can surmise that low interfacial tension occurs at the critical HLB values, and hence one can assume that packing of the two molecules is optimal. In terms of repulsive forces, apart from the possibility of a film with high surface viscosity (Elworthy, Florence and Rogers, 1971) the spacing out of the longer Brij 96 molecules on the surface by the more compact Brij 92 molecules will give the Brij 96 chains more freedom than they would possess in a homogeneous film. The resultant possibility of a greater reduction in entropy on interaction with the interfacial layer of neighbouring droplets must be balanced by the change in c, which cannot be estimated at this juncture.

This work indicates that changes in surface potential can give some indication of the ability of the systems to aggregate and deaggregate, but say little about the ultimate stability of the systems, which is dependant on the nature of the interfacial film.

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