The influence of emulsifier concentration on the rheological properties of an oil-in-water emulsion stabilized by an anionic soap

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The rheological properties of liquid paraffin emulsions stabilized by potassium laurate have been found to be markedly dependent on emulsifier concentration. Reversible aggregation of the emulsion began at $1 \cdot 0\%$ soap and the more highly aggregated systems demonstrated pseudoplastic flow. A maximum relative viscosity was found at $5 \cdot 0\%$ soap concentration. The viscosity was dependent on particle size but correction for particle size differences did not alter the viscosity concentration relation. The addition of electrolytes to the emulsion demonstrated the difference between surfactant aggregation and electrolyte aggregation. The latter was explained by the Derjaguin-Verwey-Overbeek theory of colloid stability, whilst the former was only satisfactorily explained by the theory advanced by Cockbain in 1952 involving polymolecular adsorption at the oil-water interface and hydrophobic bonding.

THE influence of the emulsifier concentration on the flow properties of emulsions has not been extensively examined. Earlier work by Wilson & Parkes (1936) and Toms (1941), who used Ostwald U-tube viscometers, showed that the relative viscosity increased with increased emulsifier concentration. Similar results were obtained by Lawrence & Rothwell (1957) who examined concentrated oil in water emulsions at low shear rates. In a series of papers, Sherman (1950, 1955, 1963) investigated the effect of emulsifier type and concentration on the viscosities of oil in water and water in oil emulsions for non-ionic agents. The emulsifying agent concentration influenced the volume fraction at which inversion of the emulsion occurred and the maximum viscosity before inversion. Sherman (1960, 1963) advocated that the precise influence exerted by the emulsifier concentration on viscosity could be assessed only when all the emulsions had the same globule size and size distribution.

Two empirical expressions relating emulsifier concentration and viscosity were derived by Sherman (1959). At constant high volume fraction of disperse phase the expression

$$\eta_{rel} = e^{ac+b}$$

was suitable. Where η_{rel} is the relative viscosity, c the emulsifier concentration as % w/w of the total emulsion and a and b are constants. A second expression in the form

$$\ln \eta_{rel} = ac\phi + b$$

was found to hold over a range of volume fractions (ϕ).

The absence of a detailed investigation on oil-in-water emulsions stabilized by anionic agents has lead to the present work.

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Experimental

MATERIALS

Liquid paraffin (B.P.). Lauric acid (99%) which was checked for purity by gas chromatography. Potassium hydroxide and potassium salts of Analar quality. Distilled water from an all glass still.

APPARATUS

Particle size measurement. A Coulter Counter, model A industrial, was used to size the emulsion systems employing a 30 μ aperture tube, calibrated with polystyrene lattices. The analysis of the results from the Coulter Counter measurements has been described by Shotton & Davis (1968).

Viscometry. A Couette viscometer was used which was basically that described by Perrin & Saunders (1966). Different bob and wire combinations allowed measurements to be made over the viscosity range of 0·8 to 80 centipoises. The apparatus was calibrated against suitable Newtonian liquids of known viscosity.

Microelectrophoresis. The charge on the oil globules was determined using a cylindrical microelectrophoresis cell based on the design of Bangham, Heard & others (1958). All measurements were made at 25·0° at the stationary level (zero electro-osmotic flow) at a field strength of 3·3 V cm^{-1}.

PROCEDURE

Formulation details are given in Table 1. Emulsions were prepared from weighed quantities of liquid paraffin and potassium laurate solution by initial dispersion with a dispersator and then passage through a hand homogenizer. Four days storage at 25° were allowed for interfacial equilibrium and the escape of air bubbles. The emulsion was then examined using microelectrophoresis, the Coulter Counter and the Couette viscometer.

Results

VISCOSITY

Table 1 summarizes the experimental results.

The emulsions were examined over the shear rate range of 0 to 120 sec^{-1}, the lowest shear rate measured being in the region of 2×10^{-1}sec^{-1}. Both Newtonian and non-Newtonian types of flow were exhibited but in all cases the flow curves passed through the origin. There was no evidence of time effects and the non-Newtonian flow curves were pseudoplastic in form. The analysis of the Newtonian flow curves was simple, as the gradient of the flow curve gave unique representation. Pseudoplastic flow was analysed by the following methods:

(i) The limiting viscosity calculated from the reciprocal of the slope of the straight line produced at higher shear rates (when all structure had been broken down) (η_{llm}).

(ii) The apparent viscosity at a given highest shear rate (120 sec^{-1}) calculated from the ratio of shear stress to shear rate (η_{app}).

(iii) The power law equation used originally by Farrow, Lowe & Neale (1928) and more recently by Scott Blair (1965)

TABLE 1. POTASSIUM LAURATE LIQUID PARAFFIN EMULSIONS FORMULATION DETAILS, VISCOSITY AND PARTICLE SIZE RESULTS

Laurate conc., % w/w	ϕ	Relative viscosity η_{rel}^{lim}	Relative viscosity η_{rel}^{app}	Cross equation η_0 centipoises	Cross equation α	n from power law eqn	Particle size Mean vol. diam., μ	Particle size s.d., σ
10.0	0.05	1.40	—	—	—	—	2.77	2.80
	0.11	1.92	2.03	—	—	—	2.56	2.57
	0.16	2.25	2.55	—	—	1.15	3.10	2.87
	0.22	3.14	3.88	24.3	—	1.30	2.20	2.28
	0.33	5.11	6.01	40.3	—	1.48	3.15	2.47
	0.43	7.86	12.5	170.2	0.0068	1.63	2.09	2.37
	0.53	13.2	21.9	291	0.0075	2.10	2.68	2.24
	0.63	23.5	44.5	653	0.0050	2.16	2.40	2.19
5.0	0.05	1.41	—	—	—	—	2.95	2.55
	0.11	1.86	1.96	—	—	—	3.62	2.54
	0.16	2.75	3.32	—	—	1.41	2.88	2.88
	0.22	3.31	4.11	28.3	—	1.51	3.06	2.31
	0.33	5.89	6.77	41.3	—	1.60	3.35	2.11
	0.43	10.9	14.7	184	0.0073	1.71	2.81	2.16
	0.53	23.8	31.3	330	0.0089	2.01	3.01	2.09
	0.63	44.0	72.3	840	0.0084	2.24	3.61	2.35
2.5	0.05	1.45	—	—	—	—	3.00	2.60
	0.11	1.80	2.10	—	—	—	3.98	2.45
	0.16	2.20	2.61	—	—	—	3.04	2.52
	0.22	2.75	3.24	5.82	—	1.08	4.07	2.31
	0.33	5.54	6.79	32.8	—	1.21	3.52	2.37
	0.43	8.15	15.1	72.5	0.0035	1.52	3.41	1.99
	0.53	15.0	22.3	219	0.0060	1.65	3.28	2.20
	0.63	23.3	45.8	360	0.0069	1.90	3.36	2.19
1.0	0.05	1.25		These systems exhibited Newtonian flow			3.50	2.52
	0.11	1.42					3.98	2.45
	0.16	1.72					3.34	2.49
	0.22	1.98					3.92	2.19
	0.33	2.75					3.97	2.24
	0.43	6.06					4.26	2.27
	0.53	12.5					3.39	2.02
	0.63	23.3					3.69	2.23
0.75	0.05	1.30					4.10	2.34
	0.11	1.45					4.00	2.34
	0.16	1.65					3.44	2.05
	0.22	2.02					4.17	2.23
	0.33	2.97					3.29	1.95
	0.43	5.32					3.92	2.16
	0.53	10.6					3.83	2.13
	0.63	22.0					3.78	2.21
0.5	0.11	1.49					5.12	2.43
	0.22	1.98					5.08	2.22
	0.33	3.03					4.45	2.10
	0.43	5.17					5.31	2.18
	0.53	9.53					4.49	2.19
	0.63	20.85					5.06	2.09

s.d. = standard deviation, log normal distribution.

$$\sigma^n = K\,\dot\gamma$$

where σ is the shear stress, $\dot\gamma$ the shear rate and K and n constants. The equation gives a simple mathematical representation of the pseudoplastic flow curves and provides a comparative constant n. The rheological significance of such double log plots is a matter of argument (Reiner, 1960, Scott Blair, 1965).

(iv) The method of Cross (1965) using the equation

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)/(1 - \alpha\dot\gamma^{2/3})$$

where η_0 is the limiting viscosity at zero shear, η_∞ the limiting viscosity at infinite shear and α a constant associated with the rupture of linkages.

At lower shear rates a plot of $1/\eta$ against $\dot{\gamma}^{2/3}$ gave a straight line from which the constants η_o and α could be evaluated.

Systems containing 1·0% or less of soap were Newtonian in their flow properties (1·0% showed slight aggregation) whereas those with a greater quantity of soap were highly aggregated and demonstrated pseudoplastic flow.

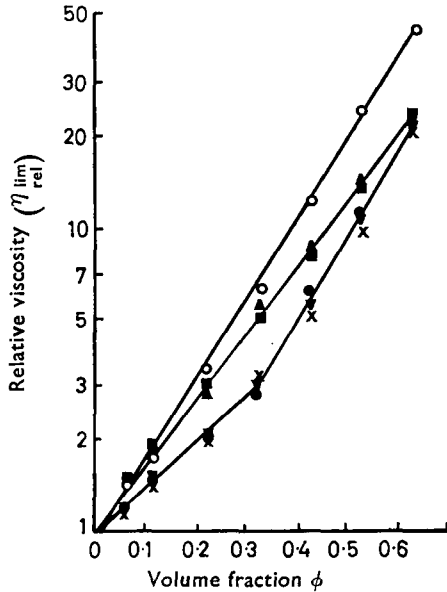For soap concentrations greater than 1·0% the relation between relative

FIG. 1. The change in relative limiting viscosity with volume fraction for liquid paraffin-potassium laurate emulsions of different soap concentrations (log plot). Concentration of soap % w/w ■ 10·0, ○ 5·0, ▲ 2·5, ● 1·0, ▼ 0·75, × 0·5.
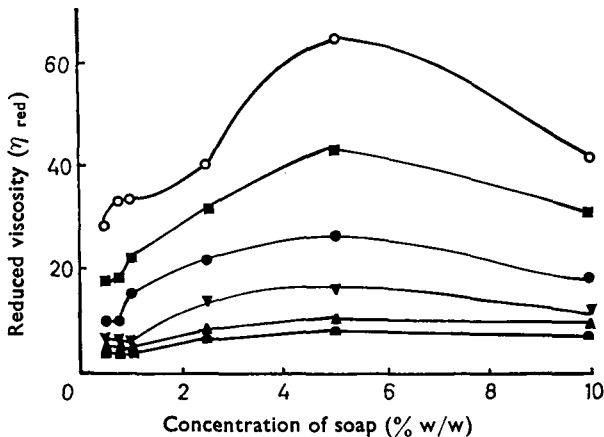

FIG. 2. The change in reduced viscosity with soap concentration for liquid paraffin-potassium laurate emulsions of different volume fraction. Volume fraction ○ 0·63, ■ 0·53, ● 0·43, ▼ 0·33, ▲ 0·22, ● 0·11.

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limiting viscosity and volume fraction (Fig. 1) could be represented by the Richardson (1933) equation

$$\eta_{rel}^{lim} = e^{k\phi}$$

The systems of lower soap concentration gave a linear relation that showed a change of gradient at a volume fraction of 0·34 to 0·37.

The exponent n from the power law relation shows an approximately linear relation with volume fraction, with n having a maximum value for those systems containing 5·0% of soap.

To compare the results at different volume fractions on the same scale, they are expressed in Fig. 2 as reduced viscosity against soap concentration where the reduced viscosity

$$\eta_{red} = (\eta_{rel}^{lim} - 1)/\phi$$

Different volume fractions all show the same type of curve. The viscosity increases from 1·0% to a maximum at 5·0% soap and then falls.

TABLE 2. THE EFFECT OF PARTICLE SIZE ON THE VISCOSITY OF LIQUID PARAFFIN EMULSIONS

Laurate conc., % w/w	ϕ	H*	Relative viscosity η_{rel}^{lim}	η_{rel}^{app}	Mean vol. diam. μ	s.d., σ	Laurate conc., % w/w	ϕ	H*	Relative viscosity η_{rel}	Mean vol. diam. μ	s.d., σ
10·0	0·22	1	2·68	2·80	5·51	2·71	1·0	0·22	1	2·52	6·01	2·23
		2	2·75	2·92	4·75	2·62			2	2·45	5·35	2·25
		3	2·83	3·10	4·20	2·76			3	2·25	4·50	2·15
		4	2·95	3·40	3·41	2·66			4	2·23	4·10	2·16
	0·43	1	6·46	8·47	5·52	2·45		0·43	1	6·25	5·95	2·15
		2	7·08	9·32	4·52	2·22			2	6·00	5·35	2·15
		3	7·30	9·95	4·06	2·43			3	5·95	4·80	2·24
		4	7·61	11·05	3·42	2·52			4	5·75	4·45	2·02
	0·63	1	17·4	20·9	6·75	2·42		0·63	1	24·0	6·11	2·02
		2	19·6	24·2	5·49	2·52			2	24·6	5·60	2·06
		3	20·4	26·3	4·51	2·41			3	24·9	4·73	2·04
		4	22·5	30·4	4·02	2·44			4	24·8	4·20	2·00
5·0	0·22	1	2·70	2·85	5·58	2·27	0·75	0·22	1	2·40	6·25	2·16
		2	2·81	2·90	5·30	2·24			2	2·45	5·50	2·21
		3	2·95	3·15	4·55	2·26			3	2·21	4·61	2·16
		4	3·20	3·61	3·65	2·30			4	2·15	3·72	2·19
	0·43	1	6·52	8·05	6·00	2·29		0·43	1	6·98	7·03	2·01
		2	7·20	8·95	5·56	2·26			2	5·99	5·51	1·99
		3	7·51	10·1	4·35	2·35			3	5·60	4·80	2·12
		4	7·83	11·0	4·02	2·32			4	5·38	4·10	2·12
	0·63	1	20·4	22·2	6·12	2·14		0·63	1	20·2	8·13	2·06
		2	22·1	29·3	5·34	2·21			2	20·9	5·98	2·12
		3	28·0	40·2	4·49	2·14			3	21·4	5·51	2·00
		4	31·2	48·1	3·99	2·17			4	21·8	5·50	2·08
2·5	0·22	1	2·53	2·96	5·50	2·51	0·5	0·22	1	—	6·78	2·28
		2	2·58	2·95	4·83	2·41			2	1·95	5·15	2·22
		3	2·62	3·05	4·45	2·43			3	1·75	4·85	2·16
		4	2·65	3·15	4·00	2·50			4	1·78	4·79	2·26
	0·44	1	6·10	7·68	6·02	2·12						
		2	6·22	7·75	5·11	2·14						
		3	6·38	8·33	4·53	2·20						
		4	6·52	8·81	4·01	2·12						
	0·63	1	21·1	26·2	5·61	2·12						
		2	24·2	30·5	4·80	2·04						
		3	25·8	34·2	4·35	2·00						
		4	28·8	38·4	3·80	2·00						

*H = No. of times homogenized.
s.d. = standard deviation, log normal distribution.

The results calculated from the equation of Cross (1965) show that the greatest η_0 and α are also to be found at 5·0% (Table 1). The α values derived are much lower than those obtained by Cross (1965). However, the systems that he examined were polymer solutions and dispersions of solids of high viscosity that showed non-linear behaviour even at high shear rates ($1·5 \times 10^4 sec^{-1}$). An attempt to represent the results in Fig. 2 by the equations of Sherman (1959) was not successful.

THE EFFECT OF PARTICLE SIZE ON EMULSION VISCOSITY

The precise influence of concentration cannot be assessed quantitatively unless all the emulsions have the same particle size (Sherman, 1963). A series of experiments was therefore made to ascertain the effect of variation of globule size on emulsion viscosity. The results are given in Table 2.

When the particle size was decreased, the viscosity of emulsions containing a soap concentration of 1·0% and below changed little whereas those of higher soap content showed an increased viscosity, as expected from the work of Richardson (1950), Lawrence & Rothwell (1957) and Sherman (1960).

The particle sizes (Table 1) ranged from 2 to 5 μ giving a mean particle size in the region of 3·5 μ. For this particle size the relative limiting viscosity for each laurate concentration was found from a plot of relative viscosity against mean volume diameter at each volume fraction. The change in relative viscosity with soap concentration at constant particle size (Fig. 3) shows the same maximum at 5% soap as in Fig. 2.

THE ADDITION OF ELECTROLYTES

It has been shown from the above work and by Shotton & Davis (1967) that increased soap concentration causes aggregation in the region of 1·0% with a maximum state of aggregation and aggregate size at 5·0% of soap. A possible explanation of the increase in aggregation with soap concentration is the Derjaguin-Verwey-Overbeek (D–V–O) theory (Derjaguin, 1940; Verwey & Overbeek, 1948) of colloidal stability. The thickness of the double layer and hence the forces of interparticulate repulsion are reduced as the counter ion content rises because of the increased soap concentration. The theory does not, however, provide an explanation of the aggregation maximum.

The mechanism of aggregation was investigated by the addition of various potassium salts (laurate, acetate, sulphate, chloride) to a standard liquid paraffin emulsion of 20% oil and 1·0% soap (a system beginning to show aggregation). After each addition the flow curve was measured and η_{rel}^{app} calculated. The effect of added sulphate, chloride and acetate was similar, with the relative viscosity being slightly increased. Potassium laurate shows a great increase in viscosity with increase in salt concentration (Fig. 4). The effect of adding additional laurate to a laurate emulsion, up to a given concentration, is the same as using laurate solutions of the given concentration initially.

From double layer considerations the results should be examined on the basis of added counter ion concentration. This has been done in Fig. 5
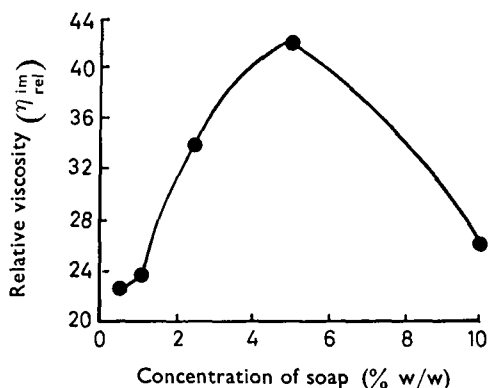
FIG. 3. The change in relative viscosity with potassium laurate concentration for liquid paraffin-potassium laurate emulsions at constant mean particle diameter (3·5 μ). Volume fraction = 0·63.
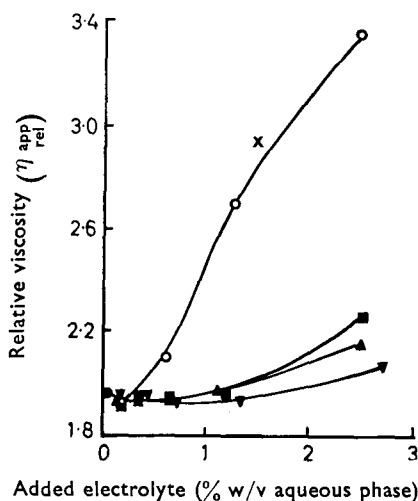

FIG. 4. The effect of added electrolyte on the relative apparent viscosity of a standard liquid paraffin-potassium laurate emulsion. Soap concentration = 1·0%. Volume fraction = 0·22. ● original system, ▲ chloride, ■ sulphate, ▼ acetate, ○ laurate, × equivalent laurate system from Table 1.

where the counter ion concentration is expressed in terms of the emulsion conductivity. The difference between laurate and the other electrolytes is further emphasized.

MICROELECTROPHORESIS

The mobility of liquid paraffin droplets increased up to a maximum at the critical micelle concentration (CMC) of the soap (0·6% w/v) and then fell slightly (Fig. 6). The zeta potential at the maximum, calculated from the Helmoltz-Smoluchowski equation, gives a value of −120 mV.

A sample of the emulsion used for the electrolyte–viscosity studies was diluted with continuous phase containing different concentrations of
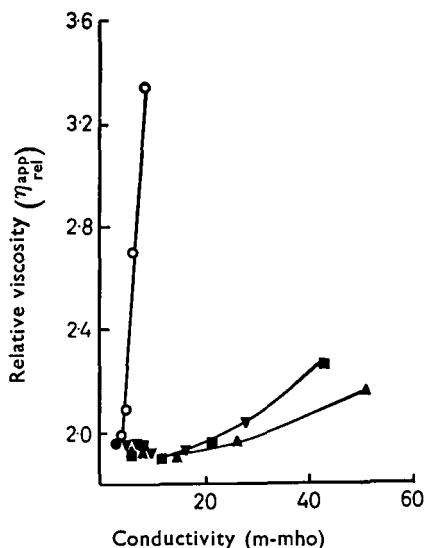
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FIG. 5. The effect of counter ion concentration of the relative apparent viscosity of a standard liquid paraffin emulsion (counter ion concentration expressed in terms of conductivity). ● original emulsion, ▲ chloride, ■ sulphate, ▼ acetate, ○ laurate.
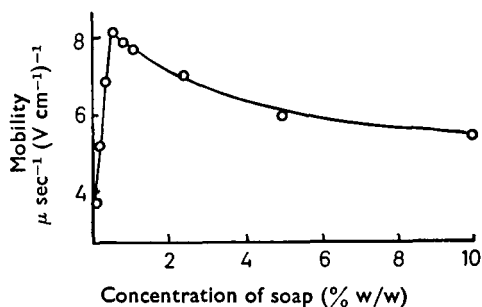

FIG. 6. The mobility of dispersed liquid paraffin in potassium laurate solutions of different concentrations.

chloride and laurate. The results (Fig. 7) show that chloride produces the expected reduction in zeta potential (D–V–O theory) whilst laurate has little effect.

Discussion

THE NATURE OF THE AGGREGATION

Two theories have been advanced to explain the increase in viscosity of a particulate system on aggregation. Goodeve (1939) and others considered link formation between particles and the work done in breaking them, whilst Mooney (1946) dealt with the entrapping of continuous phase and the subsequent increase in volume fraction. In previous work (Shotton & Davis, 1967), the volume of entrapped continuous phase
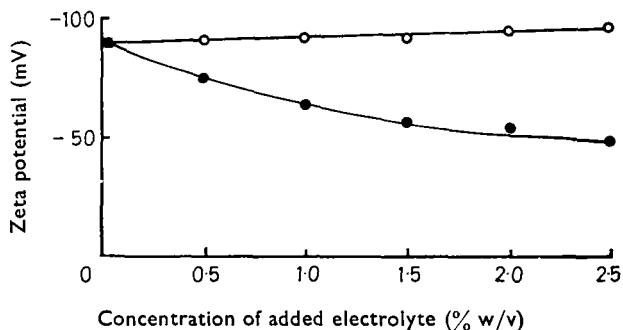
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FIG. 7. The change of zeta potential of a liquid paraffin-potassium laurate emulsion in 1·0% potassium laurate solution containing added electrolyte. ○ laurate, ● chloride.

increased with soap concentration at all concentrations and therefore does not provide an explanation of the viscosity maximum. An estimate of interparticulate forces, obtained from the α value of the Cross (1965) equation, gives a maximum at 5·0% soap concentration. We conclude that the shape of the viscosity-concentration curve is due to particle-particle interaction (link formation) of the Goodeve type. Although continuous phase will be entrapped in the aggregates the contribution to viscosity appears to be small.

Many workers have explained the aggregation of particulate systems by the D–V–O theory of colloidal stability with aggregation caused by a reduction in the zeta potential. The present results are contrary to this theory, for at 1·0%, where aggregation commences, the zeta potential is only slightly lower than the maximum at the CMC, and above a 5·0% soap concentration disaggregation occurs. The electrolyte addition experiments show that the action of laurate is different from that of strong electrolytes. The latter give the classical counter ion effect of increased aggregation with increasing concentration, whilst laurate produces a far greater aggregative effect. It appears that laurate causes aggregation through the anion and not the cation (counter ion).

Cockbain (1952) suggested that states of disaggregation occurring sometimes between well-defined states of aggregation could be accounted for if adsorption of soap took place as a secondary layer at concentrations above the CMC. At concentrations just above the CMC single soap molecules would be adsorbed with their hydrocarbon chains orientated towards *the aqueous phase*. Such particles in an aqueous medium would be hydrophobic and aggregation would occur by hydrophobic bonding. At higher concentrations competitive adsorption of micelles would leave the outer surfaces of the particles hydrophilic and result in disaggregation. Cockbain's theory provides a far better explanation of the results of the present work than the D–V–O theory although the mechanism does appear at first sight to be rather improbable. Doubts have been expressed by Higuchi, Okada & Lemberger (1962) and by Becher (1965) who considered that the theory was improbable on stereometric grounds and put

forward his own explanation, based on the limited coalescence theory of Wiley (1954). It was considered that the "bleeding off" of surfactant molecules from the interface to the micelles, at the CMC, would lead to aggregation. It would seem, however, that too much attention has been paid to Cockbain's statement that aggregation occurs at concentrations at or a little greater than the CMC of the soap. In some cases Cockbain's results show, as do those of the present work, that a "little greater than the CMC" is almost twice the CMC.

The main assumption of Cockbain's theory is that multi-layer adsorption can occur in emulsion systems and the evidence for this will be discussed.

(a) The air-water interface: Although much of the work on the adsorption of surfactants at the air-water interface has indicated that using single pure agents the film is monomolecular, Adam (1941), Dixon, Judson & Salley (1954) and Ross (1945) consider multilayer formation to be possible, and Molliet, Collie & Black (1961) point out that multilayers may develop when two or more agents react to form a complex film.

(b) The solid-water interface: The adsorption of surfactants onto silver halide sols has been studied by Matijevic & Ottewill (1958) and Ottewill & Watambe (1958) and maxima and minima turbidities explained by multilayer formation and hydrophobic bonding. Powder suspensions were investigated by Griener & Vold (1949) and Vold & Konecny (1949) who attributed the maximal suspending power of the surfactant to a sharp drop in zeta potential. Doscher (1950), however, found and we have confirmed that the zeta potential was little affected by soap concentration, and he postulated a mechanism similar to that of Cockbain (1952). Moore & Lemberger (1963) and Somasundarin, Healy & Fuerstenau (1966) have suggested a film-film bridging mechanism for the maximum suspendibility of powders by surfactants.

The limitation of the D-V-O theory in explaining the aggregation of latex particles was demonstrated by Higuchi, Rhee & Flanagan (1965). It was considered that the surfactant (Aerosol O.T.) formed a weakly adsorbed, thick, hydrophilic layer, although they admitted that this was difficult to envisage.

(c) The oil-water interface: Recently, Cockbain's suggestion of multi-layer formation and film-film interaction has been used by Lemberger & Mourad (1965) to explain why Aerosol O.T. was more effective than electrolyte in the aggregation of hexadecane emulsions. Riegelman (1962) considered that micellar adsorption would occur when a co-emulsifier such as a long chain alcohol was present, a similar idea to that of Molliet & others (1961) for the formation of multilayers at the air-water interface.

The evidence suggests that multilayer formation will occur if a mixed emulsifier film is present. Davis & Bartell (1941) and Martin & Hermann (1941) have concluded that the stability of soap emulsions is due to the formation of acid soap by hydrolysis at the interface, and resulting in a complex film of the Schulman & Cockbain (1940) type. Interfacial

hydrolysis will in fact occur even at high pH where the bulk hydrolysis is negligible (Eagland & Franks, 1960).

It may be postulated that in emulsions stabilized by emulsifiers that can be hydrolysed at the interface to produce a complex film, multilayer formation will take place at certain emulsifier concentrations, with the resultant formation of interparticulate bonds of the Cockbain type.

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