A note on the stability of emulsions at high dilution

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The behaviour of liquid paraffin–potassium laurate emulsions has been investigated at high dilution using the Coulter Counter, microelectrophoresis, and centrifugation. The results show that the state of the oil–water interface is dependent on emulsifier concentration below and above the critical micelle concentration.

A N investigation has recently been made to examine the effect of emulsifier concentration on the rheology and physical properties of emulsions of liquid paraffin stabilized by potassium laurate (Shotton & Davis, 1967, 1968a). Further experiments are now described in which the emulsions have been subjected to high dilution. The behaviour of the diluted droplets was found to depend on the emulsifier concentration in the original emulsion.

Experimental and results

Materials and formulation details have been given elsewhere (Shotton & Davis, 1968a). In addition to the emulsions described therein, emulsions containing 0, and 0·25% of potassium laurate as emulsifier at volume fractions of 0·11 and 0·43 were also prepared and the more stable fraction that remained after 6 hr creaming was used in the experiments. The effect of diluting the emulsions was examined by the three methods below.

(1) *The Coulter Counter.* Emulsions, of volume fraction 0·11 at potassium laurate concentrations of 0, 0·25, 0·5, 1·0, 5 and 10% w/w were diluted $1:5 \times 10^5$ by a two-step dilution using normal saline and examined using a Coulter Counter model A (industrial) with a 30 μ orifice tube (Shotton & Davis, 1968b). The change in the total number of particles greater than 0·9 μ with time was then followed (Fig. 1). Those systems originally containing soap concentrations above the critical micelle concentration (CMC) in the region of 0·5% (Cockbain & McRoberts, 1953) show a small drop in cumulative count in 45 min whilst for concentrations below the CMC the fall in count is great. At all soap concentrations the fall in count depended on the soap concentration in the original emulsion. Counting the particles at 7 μ demonstrated a slight gain in particle number. Microscopic examination of the diluted emulsion showed the absence of aggregates and it is concluded that the count loss at $> 0·9 \mu$ level is due to coalescence, rather than to the aggregation phenomenon described by Groves (1966) for emulsions stabilized by a soap-amphiphile complex. The particles had a mean volume diameter in the region of 4 μ which from Stoke's Law gives a creaming distance of about 0·25 cm in 45 min. Any effects due to creaming were minimized by stirring the counting dilution; the same arbitrary stirring speed was used throughout so that the effect of stirring on coalescence was kept constant. The slight increase in

particle count (Fig. 1) for 10% soap may be accounted for by coalescence of particles below the sizing limits of the apparatus.
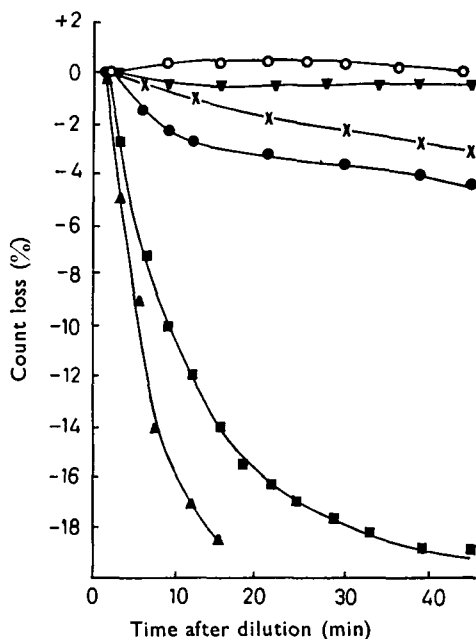

FIG. 1. The loss of count with time on the Coulter Counter for particles greater than 0·9 μ and its dependence on the soap concentration in the original emulsion. Concentration of soap % w/w. ▲ 0·0; ■ 0·25; ● 0·5; ✕ 1·0; ▼ 5·0; ○ 10·0.

It is concluded that coalescence and hence the strength of the interfacial film depends on the concentration of emulsifier in the original emulsion.

(2) *Microelectrophoresis.* Emulsions, of volume fraction 0·11, were diluted 1 : 1 × 10⁴ with distilled water and examined in a cylindrical micro-electrophoresis cell similar to that described by Bangham, Heard & others (1958). Mobility measurements were made at different depths in the cell and the mobility at the stationary level (zero electro-osmotic flow) determined. The charge on the particles (zeta potential) depended on the emulsifier concentration in the original emulsion (Fig. 2). The quantity of surfactant that reached the final dilution, although small, may have had some effect. Measurements were therefore repeated using different dilutions, i.e. different quantitites of surfactant in the final dilution, but the mobilities were unaffected.

(3) *Washing of emulsions.* The method used was that of repeated centrifugation and removal of the aqueous phase (Shotton & Wibberley, 1960). A convenient volume of emulsion was diluted to twice its volume with water and centrifuged in an M.S.E. refrigerated centrifuge at 6000 rev/min for 30 min. The separated aqueous phase was carefully removed and replaced by a similar volume of water and the emulsion remixed. The process was repeated three times. The volume of separated oil was then
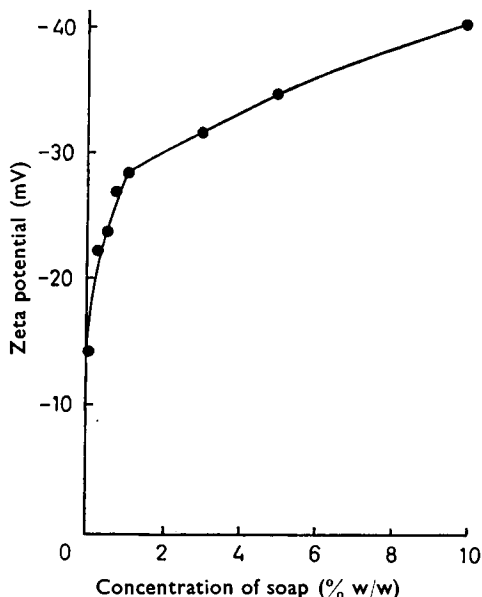
FIG. 2. The change in zeta potential of liquid paraffin–potassium laurate emulsions dispersed in distilled water with the soap concentration in the original emulsion.

measured and was found to depend on the soap concentration in the original emulsion (Fig 3). The amount of oil separating with decrease in emulsifier concentration above the CMC was much less than that separating below it.

Finally, the original emulsions were sized using the Coulter Counter and stored for 6 months when they were sized again. Table 1 shows that the emulsion coalesced to a small extent when the emulsifier concentration was above the CMC. Below the CMC the emulsion was unstable.

TABLE 1. THE EFFECT OF STORAGE ON THE PARTICLE SIZE DISTRIBUTION AND SPECIFIC SURFACE AREA OF POTASSIUM LAURATE/LIQUID PARAFFIN EMULSIONS. (LOG NORMAL DISTRIBUTION) Volume fraction = 0·43.

Soap concentration % w/w	Mean volume diameter μ	Standard deviation σ	Specific surface area cm² g⁻¹
	4 days		
10·0	2·09	2·07	$2·02 \times 10^4$
5·0	2·62	2·16	$1·62 \times 10^4$
2·5	3·41	2·00	$1·28 \times 10^4$
1·0	4·26	2·27	$8·83 \times 10^3$
0·75	4·17	2·23	$8·89 \times 10^3$
0·50	5·31	2·18	$7·16 \times 10^3$
0·25	≃10	≃2·2	$≃3·6 \times 10^3$
	6 months		
10·0	2·30	2·20	$1·61 \times 10^4$
5·0	2·76	2·26	$1·37 \times 10^4$
2·5	3·23	2·20	$1·19 \times 10^4$
1·0	4·26	2·21	$9·27 \times 10^3$
0·75	4·24	2·11	$8·75 \times 10^3$
0·50	5·67	2·19	$6·67 \times 10^3$
0·25	∞	—	—

Discussion

The results from the Coulter Counter and centrifugation show that the emulsion droplets retain some or all of their original interfacial film on dilution. The strength of the film (resistance to coalescence) depends on the potassium laurate concentration in the original emulsion for concentrations above and below the CMC. In both cases a discontinuity is found at the CMC. The decrease in stability with concentration below the CMC is greater than that above it. The microelectrophoresis results show that the charge on the droplet, and hence the amount of surfactant that remains adsorbed on dilution, depends on the emulsifier concentration in the undiluted emulsion. In this case a discontinuity was found at 1·0% soap.

King (1941) was one of the first to suggest that the emulsifier concentration was a quantitative source of interfacial film strength, and Osipow, Birsan & Snell (1957) derived an equation relating the logarithm of emulsion stability to the root of the ratio of the emulsifier concentration to the CMC.

Vold & Groot (1962) and Rehfeld (1962) found that the stability of sodium dodecyl sulphate emulsions to ultracentrifugation (without dilution) increased with increasing soap concentration up to the CMC. The latter author further found that the amount of oil separating was linearly related to the log of the soap concentration with a discontinuity at the CMC. A similar relation has been found in the present work (Fig. 3).
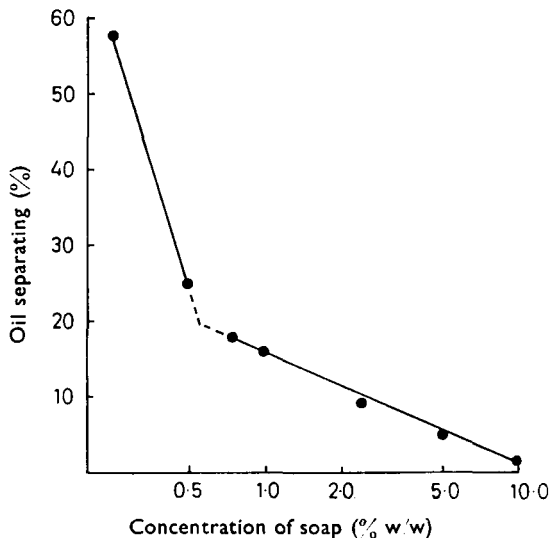

FIG. 3. The effect of the soap concentration in the original emulsion on the stability to dilution and centrifugation of potassium laurate–liquid paraffin emulsions.

However, both Vold & Groot and Rehfeld stated that the stability of the emulsions above the CMC was independent of emulsifier concentration through it is interesting to note that in a later paper, Vold & Groot (1964), when commenting on their earlier publication, have changed "independent" to "only slightly affected".

In comparison, Cockbain & McRoberts (1953) found that the stability to coalescence of soap stabilized droplets was at a maximum at concentrations above the CMC. These concentrations were close to those where aggregation of the emulsions occurred due to polymolecular adsorption of soap molecules (Cockbain, 1952). Aggregation of potassium laurate-liquid paraffin emulsions is known to commence in the region of 1.0% soap (Cockbain, 1952; Shotton & Davis, 1967, 1968a). We found that a discontinuity in the zeta potential concentration plot (Fig. 2) also occurred in this region.

Both Rehfeld (1962) and Vold & Groot (1962) concluded that the packing of surfactant molecules at the oil-water interface reached a maximum at the CMC. The results from the present work show that the state of the interface is markedly dependent on emulsifier concentration below the CMC and that emulsions containing less than 0.5% potassium laurate break down completely on storage. The state of the interface above the CMC is influenced by soap concentration but to a lesser extent. This may be due either to closer packing of the molecules and/or the adsorption of polymolecular layers although it is doubtful that such layers would be retained on dilution.

Closer packing may result from the reduction of charge on adjoining molecules due to an increased counter ion concentration (Powell & Alexander, 1952). Vold & Groot (1964) have found that the adsorption of soap at the o/w interface increases directly with the log of the total concentration of counter ion.

The nature of both the emulsifier and disperse phase may well be important. The chemical nature of the disperse phase is known to have an influence on the stability of an emulsion (Davis, 1967) and Rehfeld (1967) has found that layers of sodium dodecyl sulphate adsorbed at the unsaturated hydrocarbon interface were much more expanded than at the saturated hydrocarbon interface. Further work may show whether the retention of surfactant at the interface is restricted to systems where the disperse phase and lipophilic groups of the surfactant are similar structurally, as is the case in the present work.

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