The transfer and penetration of fatty alcohols and fatty acids in relation to their self-bodying action in emulsions

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The transfer of fatty alcohols and acids from an oil phase to an aqueous solution of surfactant has been examined. Also, penetration of the solid amphiphile by these surface-active agents has been observed by optical microscopy. The findings have been correlated with the flow behaviour of emulsions and gels containing these materials. The results indicate that before a fatty alcohol or acid, in conjunction with a surfactant, will have any self-bodying action in an emulsion two conditions must be fulfilled. Firstly, a portion of the alcohol or acid must migrate from the oil to the aqueous phase and secondly, the surfactant molecules must be of such size or shape or present in sufficient concentration to permit penetration of the amphiphile crystal lattice and the formation of a ternary liquid crystalline phase.

Talman, Davies & Rowan (1967, 1968) have postulated that the flow properties of some of their emulsions were related to the migration of the oil-soluble component and the subsequent formation of a gel in the aqueous phase. Some microscopical evidence for the migration of cetostearyl alcohol has been presented (Talman & Rowan, 1968). This paper reports the results of further investigations into the transfer of the oil-soluble component to the aqueous phase and the role of the water-soluble surfactant.

EXPERIMENTAL

Materials. These were as previously described (Talman & others, 1967, 1968; Talman & Rowan, 1970).

Methods

Transfer experiments. An aqueous solution of the surfactant (0·5% w/w unless otherwise stated) and a liquid paraffin solution of the fatty alcohol or acid (usually 7% w/w) were separately heated to 60°. The aqueous phase was placed in a pear-shaped separating funnel and the oily solution immediately poured on top with minimal disturbance of the lower layer. A series of controls, omitting either the surfactant or the fatty amphiphile was also prepared. The systems were stored undisturbed at room temperature for 3 days. Transfer was reported to have occurred if a cloudiness or white amorphous mass appeared in the aqueous phase during this period.

Penetration experiments. A small amount of coarsely powdered fatty alcohol or acid was placed on a microscope slide and a few drops of the surfactant solution (0·5% w/w unless otherwise stated) was added. This system was observed as the

temperature was slowly raised by a Leitz hot stage attached to a Conference photo-microscope, Mark I (Gillet & Sibert Ltd, London). If penetration took place some of the crystals became striated and the edges indistinct and crenulate due to the formation of an envelope of liquid crystals. In some instances, where penetration was extensive, whole crystals disintegrated to form a mass of filamentous structures.

RESULTS AND DISCUSSION

Table 1 correlates the results of the transfer and penetration experiments with the flow behaviour of corresponding gels and emulsions. Detailed descriptions of the latter have appeared previously (Talman & others, 1967, 1968; Talman & Rowan, 1970).

Transfer of amphiphile

There was no evidence of transfer in any of the control systems. Where transfer occured in the test systems, sometimes it was not apparent until about 24 h had elapsed (cetostearyl alcohol–cetomacrogol 1000 systems). On other occasions a cloudiness became visible within minutes of the two layers being brought into contact (cetostearyl alcohol–cetrimide systems). Amorphous masses developed near the

Table 1. *Comparison of transfer, penetration, gel and emulsion data for preparations containing a range of fatty alcohols and fatty acids together with some surfactants*

Fatty amphiphile	Surfactant	Transfer	Penetration	Gels	Emulsions*
Oleyl alcohol	Cetomacrogol 1000	0		0	Thin fluids
	Sorbester Q 12	0		0	Thin fluids
	Sodium lauryl sulphate	+		0	Thin fluids
	Cetrimide	+		only at 5% w/w sur-factant	Thin fluids except at 5% w/w surfact-ant
	Solumin FX170SD	0		0	Thin fluids
	Texofor FX170	0		0	Thin fluids
Lauryl alcohol	Cetomacrogol 1000	0		+	Thin fluids
	Sorbester Q 12	0		+	Thin fluids
	Sodium lauryl sulphate	++		++	Semi-solids
	Cetrimide	++		++	Semi-solids
	Solumin FX170SD	0		0	Thin fluids
	Texofor FX170	0		0	Thin fluids
Cetostearyl alcohol	Cetomacrogol 1000	++	++	++	Semi-solids
	Sorbester Q 12	++	++	++	Semi-solids
	Sodium lauryl sulphate	+++	+++	+++	Semi-solids
	Cetrimide	++++	++++	++++	Semi-solids
	Solumin FX170SD	0	0	0	No emulsion
	Texofor FX170	0	0	0	No emulsion
Myristyl alcohol	Cetomacrogol 1000	++	++	++	Semi-solids
	Cetrimide	+++	+++	+++	Semi-solids
Cetyl alcohol	Cetomacrogol 1000	++	++	++	Semi-solids
	Cetrimide	++++	++++	++++	Semi-solids
Stearyl alcohol	Cetomacrogol 1000	0	0	0	Contained waxy particles
	Cetrimide	+	+	+	Contained waxy particles
Lauric acid	Cetomacrogol 1000	0		lumpy	Thin fluids
	Cetrimide	+		lumpy	Thin fluids except at 5% w/w sur-factant

Fatty amphiphile	Surfactant	Transfer	Penetration	Gels	Emulsions*
Myristic acid	Cetomacrogol 1000	0	0	0	Unstable, waxy particles
	Cetrimide	+	0·5% w/w 0	+	0·5% w/w unstable, waxy particles
			5% w/w +		5% w/w semi-solids
Palmitic acid	Cetomacrogol 1000	0	0	0	0·5% w/w unstable, waxy particles 5% w/w some pseudo plastic and some as above
	Cetrimide	+	0·5% w/w 0	0	0·5% w/w unstable, waxy particles
			5% w/w +		5% w/w semi-solids
Stearic acid	Cetomacrogol 1000	0	0	0	Unstable, waxy particles
	Cetrimide	+	0·5% w/w 0	0	0·5% w/w unstable, waxy particles
			5% w/w +		5% w/w semi-solids
Behenic acid	Cetomacrogol 1000	0	0	0	Unstable, waxy particles
	Cetrimide	0	0	0	Unstable, waxy particles
Erucic acid	Cetomacrogol 1000	0		0	Thin fluids
	Cetrimide	+		0	Thin fluids

All experiments were made with 0·5% w/w surfactant unless otherwise stated.
* Emulsions refer to those containing high concentrations of fatty amphiphile.

interfaces and were extremely difficult to separate from their respective aqueous phases. They could not be removed by centrifugation at 35 000 g or by filtration. Isolation was finally achieved by discarding most of the lower part of the aqueous phase and drying the remainder, which contained the bulk of the transferred material, in a vacuum desiccator for 10 days over concentrated sulphuric acid. Although the infrared spectra of the dried materials were not identical with those of the alcohols or surfactants, a number of features which could be attributed to the alcohols were identified, e.g., a vestigial peak at 3·55 μm in the spectrum of material from ceto-stearyl alcohol–cetomacrogol 1000 systems and a prominent peak at 6·85 μm for material from cetyl alcohol–sodium lauryl sulphate systems. Optical microscopy showed the amorphous masses to consist of thin laminae or filaments (Fig. 1a). These were somewhat similar in appearance to the fatty alcohols (Fig. 1b, c) or fatty acids after penetration by a surfactant. There was also a distinct resemblance to the filaments which were seen in coarse emulsions prepared with cetostearyl alcohol and cetomacrogol 1000 or cetrimide which were reported earlier (Talman & Rowan, 1968). When the strength of the surfactant solution in systems containing ceto-stearyl alcohol was increased from 0·5 to 5·0% w/w, visual examination suggested that the amount of alcohol that migrated to the aqueous phase also increased. The difficulty of isolation, mentioned above, precluded quantitative estimation of the amount of transferred material. Varying the quantities of cetostearyl alcohol to correspond with those used in the emulsion (viz. 0·25, 0·5, 0·75, 1·5, 2·5, 4·0 and
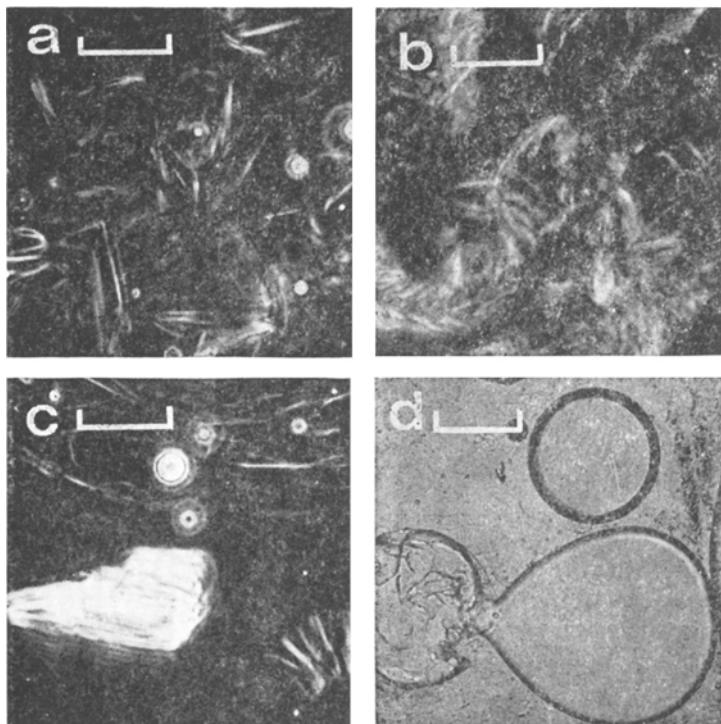
FIG. 1. Photomicrographs of: (a) amorphous mass in aqueous phase of cetostearyl alcohol–cetomacrogol 1000 transfer experiment; (b) penetration of cetostearyl alcohol by cetrimide; (c) penetration of cetostearyl alcohol by cetomacrogol 1000; (d) mechanical separation of cetostearyl alcohol from a liquid paraffin droplet.   One division = 30 μm.

7·0% w/w), showed that transfer occurred at all levels of concentration, even those at which the alcohol was completely soluble in the liquid paraffin.

Penetration of amphiphile

Penetration of an amphiphile by a surfactant in aqueous solution to form a ternary liquid crystalline phase has been studied by Lawrence (1958, 1961a, b).   In 1959 he postulated that penetration took place, not on the flat surface of the amphiphilic crystal, but on the edges, in those positions where the polar heads lie adjacent to one another.   He pointed out that this was not due to simple thermal opening of the crystal lattice, although both he and Barry & Shotton (1967) reported that there was a critical temperature below which interaction would not occur.   The latter workers quoted 46° as the temperature of penetration for cetyl alcohol by 1% w/w sodium dodecyl sulphate.   A small quantity of coarsely powdered cetostearyl alcohol was mixed with 0·5% w/w cetrimide solution at room temperature.   After approximately 30 min a weak but definite "set" or structure had developed.   This effect was much enhanced by a reduction in particle size; micronized cetostearyl alcohol gave a gel in 10 min when dispersed in the 0·5% w/w cetrimide solution.   The occurrence of interaction without the aid of heat strongly indicated that interaction was not due to simple thermal opening in the crystal lattice which is in agreement with Lawrence (1959).   If this is so, it would be reasonable to suppose that the size and shape of the surfactant molecule should affect penetration.

Both cetomacrogol 1000 and Sorbester Q 12 penetrated the cetostearyl alcohol lattice much more slowly and less extensively than either sodium lauryl sulphate or cetrimide. Of the two latter surfactants, attack with cetrimide was the more vigorous. The relative ease with which sodium lauryl sulphate and cetrimide penetrated the alcohol may be due to the fact that their molecular size is about one-third that of either cetomacrogol 1000 or Sorbester Q 12. Differences in the vigour of penetration with the ionic surfactants, in spite of their similar molecular size, may be ascribed to the nature of their polar heads (Lawrence, 1958). It is significant that the ease with which emulsions containing surfactants and cetostearyl alcohol could be prepared was paralleled by the ease with which the surfactants penetrated the crystal lattice. Neither Solumin FX170SD nor Texofor FX170 penetrated cetostearyl alcohol even after prolonged heating; emulsions made with these surfactants and high concentrations of the alcohol, contained waxy particles. Solumin FX170SD and Texofor FX170 are cresol derivatives comparable in molecular size to cetomacrogol 1000 and Sorbester Q 12. The lack of penetration may be accounted for by the presence of a substituted aromatic ring. It should be noted that Solumin FX170SD and Texofor FX170 permitted the preparation of stable emulsions with oleyl, lauryl or low concentrations of cetostearyl alcohol. This shows that they are capable of forming a condensed complex film in spite of their molecular size and shape.

Myristic, palmitic and stearic acids were penetrated by 5·0% w/w cetrimide solution but, contrary to Lawrence's (1959) report that penetration occurred with 0·1% surfactant solutions, we were unable to demonstrate the penetration of the foregoing acids by 0·5% w/w cetrimide solution. It is possible that attack by the weaker surfactant solution was so slow that it was not detected by our experimental procedure which involved a period of time similar to that required for the preparation of emulsions. Emulsions containing these acids and 5·0% w/w cetrimide were semi-solid preparations, whereas waxy particles were present in products containing large quantities of the acids and the lower concentration of surface-active agent. Fatty acids were generally less readily penetrated than the alcohols. Both acids and alcohols associate to form dimers by hydrogen bonding. Such association is much stronger in the case of the acids where dimers persist even in the liquid state. This accounts for their unexpectedly high melting and boiling points (Allen & Caldin, 1953). The strong bonding between carboxyl groups, at the point in the crystal lattice of the solid acids where Lawrence (1959) has suggested that penetration occurs, may explain their less ready penetration by surfactants.

Requirements for self-bodying action

Caution must be exercised in using the results of static transfer and penetration experiments to predict the likely behaviour of amphiphiles under the more dynamic conditions which are obtained during the preparation of emulsions. Nevertheless, from the result as a whole it may be concluded that two requirements must be fulfilled before a fatty acid or a fatty alcohol, in conjunction with a surfactant, can produce bodied gels or emulsions. Firstly, a portion of the alcohol or acid must be transferred across the oil–water interface into the aqueous phase. Secondly, the surfactant must penetrate the amphiphile crystal lattice and form a ternary liquid crystal phase. Lauryl alcohol, for example, produced weak gels with cetomacrogol 1000 or Sorbester Q 12 but transfer could not be detected under static conditions. In

emulsions containing these surfactants there would be no opportunity for gel formation in the aqueous phase and this explains why these emulsions were thin fluids. For products which had been prepared with high concentrations of the C_{14}–C_{22} acids and 0·5% w/w surfactant it was clear that the first condition had been fulfilled since the aqueous phase contained oil-soluble component in the form of hard waxy particles. The C_{14}–C_{22} acids were either not penetrated or only slightly penetrated by this concentration of surfactant. It was, therefore, the second condition which had not been met and which was apparently responsible for the lack of bodying action.

With the acid–0·5% w/w surfactant systems, transfer of the amphiphile was not detected *under static conditions* and may be contrasted with the ready migration of cetostearyl alcohol when treated in the same way. Since this alcohol transferred at concentrations lower than its solubility in liquid paraffin, migration was probably taking place in these circumstances by a partitioning process as postulated previously for lauryl alcohol (Talman, Davies & Rowan, 1967). Whilst we consider such a process to be an essential feature of self-bodying action—see also Barry (1969)—it should be noted that we have shown the location of cetostearyl alcohol in an emulsion to be influenced by the method of preparation (Talman & Rowan, 1968). Hand stirring gave poor emulsions with large globules containing crystals of alcohol. Fig. 1d shows the effect of shearing such emulsions between a slide and coverslip and demonstrates that these crystals may be mechanically separated from the oil phase. When preparations were homogenized the alcohol was probably transferred by the combined action of partitioning and mechanical separation. It was not possible to determine the relative contribution of these mechanisms to the overall transfer process in the case of cetostearyl alcohol, but mechanical separation alone would satisfactorily explain the presence of waxy particles of amphiphile in emulsions made with C_{14}–C_{22} acids.

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