

The control of oil-in-water emulsion consistency using mixed emulsifiers

B. W. BARRY

Department of Pharmaceutical Technology, School of Pharmacy, Portsmouth College of Technology, Portsmouth, England

Mixtures of emulsifiers of the surfactant-fatty alcohol type are widely used to stabilize oil-in-water emulsions and to alter their consistency from fluid to semi-solid. A mechanism, involving the formation of a viscoelastic network in the continuous phase, is proposed to explain this self-bodying action. Evidence has been adduced from published data on a variety of systems. Support for this concept is also provided by the results obtained from a concentric cylinder study of the rheology of liquid paraffin in water emulsions containing a fixed concentration of cetostearyl alcohol and varying amounts of polyoxyethylene sorbitan monooleate, cetomacrogol 1000, sodium dodecyl sulphate or cetrimide.

Formulation of oil-in-water emulsions having the mechanical properties of a semi-solid pose both theoretical and practical problems. Wide use is made of combinations of an anionic or cationic or non-ionic surfactant with a fatty alcohol, as in emulsifying wax B.P., cetrimide emulsifying wax B.P.C. and cetomacrogol emulsifying wax B.P.C. This control of rheological behaviour is effected by varying the amount of "mixed emulsifier" in the formulation according to its "self-bodying" action. In the present paper this is defined as the ability of a mixed emulsifier to produce a mobile emulsion when present at low concentrations and a semi-solid preparation when present in moderate amounts (about 10% or less of the total weight of the emulsion). This criterion is used because increasing the proportion of most emulsifiers in an emulsion formulation increases the apparent viscosity (see, for example, Sherman 1964, 1968). The essential feature of the self-bodying action is the introduction of a large elastic component into the rheological behaviour.

This paper attempts to present a coherent explanation of the mechanism of the self-bodying action of a variety of mixed emulsifiers using published data, and results from a re-examination of emulsion systems for which the proposed theory does not, at first, appear to apply. The data are derived from work using the surfactants sodium dodecyl sulphate, potassium laurate, cetrimide, cetomacrogol 1000, polyoxyethylene sorbitan monolaurate and monooleate, the alcohols oleyl, lauryl, cetyl and cetostearyl and the oils isopropyl myristate, liquid paraffin, light liquid paraffin, arachis and castor and thus the data cover a representative range of ingredients. The systems discussed range in consistency from fluid to solid, many showing both liquid and solid properties. Ideally, therefore, the data should be presented in the form of viscoelastic parameters, such as moduli of rigidity, compliances, coefficients of viscosity and retardation and relaxation times. These may be derived from, for example, creep or oscillatory testing. In general, however, continuous shear methods have been used and although having limitations (see Davis, Shotton & Warburton, 1968; Barry & Warburton, 1968) they often provide information from which useful conclusions may be drawn.

A SUGGESTED MECHANISM OF THE SELF-BODYING ACTION OF MIXED EMULSIFIERS

The proposed explanation of the mechanism by which the consistency of the emulsions to be discussed is controlled is based on the explanation offered by Barry (1968a) to account for the self-bodying action of the mixed emulsifier sodium dodecyl sulphate-cetyl alcohol in liquid paraffin emulsions. This mechanism is therefore considered in detail, using the above formulation as a model system.

In the preparation of the emulsions, a mixture of cetyl alcohol in liquid paraffin at 65–70° is poured into an aqueous sodium dodecyl sulphate solution maintained at the same temperature, the resulting mixture being agitated until cold. An emulsion is formed and stabilized by complexing of the amphiphile and surfactant at the oil-water interface. Usually the concentrations of the emulsifiers are greater than those required to provide a complex condensed film at the interface, and excess material modifies the rheological properties of the emulsions. The excess surfactant remains in the aqueous phase, either monodispersed or as micelles, depending on its concentration and the temperature. Below the critical micelle concentration (CMC), mobile, somewhat unstable emulsions are formed. Above the CMC, a micellar pseudophase is present during the cooling process, and some of the amphiphile will diffuse from the oil into the aqueous phase. More will diffuse as the amphiphile concentration in the oil phase increases, due simply to a raised concentration gradient from oil to water. However, the amount of water-insoluble amphiphile which diffuses into a non-micellar aqueous environment is small. When the surfactant concentration is greater than the CMC, significant quantities of amphiphile may be solubilized within the micelles alongside the surfactant molecules. A small proportion of the oil phase may also be solubilized. The mixed micelle formed may have a typically spherical shape or alternatively it may exist as a lamellar smectic liquid crystal. This liquid crystal phase can form at low concentrations because of the closer molecular packing allowed when repulsion between the ionized head groups of the surfactant is reduced by interposition of the amphiphile, by the strong interaction of the alkyl chains and by the necessity of separating water away from these chains (Lawrence 1958, Boffey, Collison & Lawrence, 1959). Thus, as the temperature is decreased the amphiphile becomes progressively less soluble in the oil, diffuses from the disperse phase and is solubilized by the micellar phase. However, when the temperature falls below the melting point of the amphiphile (minus any depression caused by the other ingredients), solubilization is no longer possible (Hyde, Langbridge & Lawrence, 1954) and the amphiphile precipitates. This precipitate which may consist of finely divided amphiphile, or possibly an intimate mixture of amphiphile, surfactant and water, may maintain its structure for some time, forming metastable frozen micelles or frozen liquid crystals. This results in the formation of a viscoelastic gel which entraps oil globules and is responsible for the marked increase in consistency. I consider that this method of aggregation is more important than the theory of polymolecular adsorption of the surfactant (Cockbain, 1952; Riegelman, 1962) or the electrical theory (Higuchi, Okada & Lemberger, 1962) when dealing with the rheological properties of semi-solid emulsions of high alcohol content.

The water-soluble component of the mixed emulsifier

In considering the ability of a mixed emulsifier to form semi-solid emulsions, the part played by the surfactant needs examination. The surfactant should be capable of

combining with the amphiphile to form a complex, condensed film at the oil-water interface, to stabilize the emulsion. It should also be present in an amount sufficient to form micelles in the aqueous phase.

Using the mixed emulsifier sodium dodecyl sulphate-cetyl alcohol, Barry (1968a) has shown by continuous shear rheometry that when the surfactant is in excess of its CMC considerable structural order exists in the emulsion in the form of a gel-like network. During shearing in a Ferranti-Shirley viscometer, aggregates of globules were disrupted, releasing entrapped continuous phase, and thus the flow curves were in the form of hysteresis loops. The areas of these loops were a measure of the amount of breakdown which had taken place during the shearing cycle, and this in turn was related to the extent of gel formation in the continuous phase. Both of these increased rapidly with emulsifier concentration above the CMC. The fact that aggregates had been broken down during shearing was confirmed microscopically and by particle size analysis. Stronger evidence for the presence of a viscoelastic network was derived from creep experiments (Barry 1968a). The creep compliances fell rapidly as the surfactant concentration increased up to the CMC and there was a less rapid change upon further increase. Similarly, there was a steeply ascending portion to each viscosity curve, followed by a region where the slope decreased as emulsifier concentration increased. The initial fall in compliance and rise in viscosity with increase in emulsifier concentration were considered to reflect the build-up in structure in the continuous phase. Once the emulsion globules were well linked together by a gel structure of sufficient size, further addition to this network had a relatively minor effect on the viscoelastic parameters and the curves flattened out.

An increase of both the yield value and the plastic viscosity with surfactant concentration for autoclaved liquid paraffin emulsions containing sodium lauryl sulphate and a fixed concentration of cetyl alcohol were shown by Axon (1956). The findings of Talman, Davies & Rowan (1968) do not agree. These authors used a Ferranti-Shirley cone and plate viscometer in automatic mode to examine the effect of two ionic surfactants—cetrimide and sodium lauryl sulphate—and two non-ionic surfactants—Sorbester Q12 (polyoxyethylene sorbitan monolaurate) and cetomacrogol 1000—on the rheology of some liquid paraffin emulsions. At low shear rates the rheograms showed either a spur or an abrupt change of slope. The shear stress at this point was reported as a static yield value and their results are reproduced in Fig. 1 a, b, p. 539. The values from this type of experiment are probably dependent in part on the instrument and the mode of operation and, although they are not a measure of fundamental parameters, they may be used to show a trend when comparing members of a closely related series of materials. But the material must neither fracture in, nor be expelled from the cone-plate gap. Talman & others (1968) found that for a fixed concentration of cetostearyl alcohol the static yield value went through a maximum as the surfactant concentration increased. This finding does not support the suggested mechanism of self-bodying action. A re-examination of their systems using concentric cylinder geometry (Rotovisko) instead of a cone and plate (see experimental section) showed emulsion consistency to increase steadily with surfactant concentration to the extent that the torque reading went offscale at 5% concentration of the ionic surfactants. Only the maximum shear stress readings obtained at the lowest shear rate available were determined and they are plotted in Fig. 1 a and b. As with the Ferranti-Shirley viscometer results, the Rotovisko results as determined are only valid in as far as they establish a trend in a series of materials, as they will depend, amongst other

things, on the inertia of the torque sensing apparatus. But the increase in consistency agreed with the behaviour of the emulsions when they were loaded into the viscometer; the resistance to the insertion of the bob into the cup due to the presence of the sample in the gap increased steadily as the concentration of surfactant increased, which does *not* indicate a maximum in the relevant rheological properties. It would seem, therefore, that provided the surfactant concentration is not so high as to promote instability, the consistency of the systems increases as surfactant concentration increases.

In the official B.P. and B.P.C. oil-in-water creams, the surfactant concentrations are above the CMC values, and thus these preparations should show evidence of structure in the continuous phase. This has been confirmed by Davis (1969) who examined them by a continuous shear method and obtained rheograms of the hysteresis loop type with yield stress. On creep testing, viscoelastic curves were obtained, which also indicates a network structure linking globules of disperse phase.

The oil-soluble component of the mixed emulsifier

The oil-soluble component should be an amphiphilic compound which by itself promotes water-in-oil emulsions, and is capable of complexing with the hydrophilic component to form a complex film at the oil-water interface. It should be present at least in sufficient concentration to form this close-packed mixed monolayer, when a mobile emulsion will be formed; to form a semi-solid preparation at the test temperature it should be near or above its saturation concentration in the oil. In the systems examined by Barry (1968a) this was so. Similarly, Axon (1956) has shown that the plastic viscosity and the yield value of liquid paraffin emulsions containing sodium lauryl sulphate and cetyl alcohol increase exponentially with cetyl alcohol concentration. Talman, Davies & Rowan (1967) examined emulsions formulated with different oils, several surfactants and with the oil-soluble components oleyl, lauryl and cetostearyl alcohols. The concentration of oleyl alcohol was *below* its saturation point in the oil phase and all emulsions prepared with this alcohol were fluids of low apparent viscosity and zero static yield value. On increasing the concentration of this alcohol, but still remaining within the limits of its solubility, only a slight rise in apparent viscosity was recorded and this the authors attributed simply to an increase in disperse phase content. This is in agreement with the self-bodying postulate. Fluid emulsions were also produced by Talman & others using low concentrations of cetostearyl alcohol. On increasing the alcohol concentration, a position was reached at which the apparent viscosity versus concentration curve diverged markedly from that given by the oleyl alcohol emulsions. This divergence concentration was identical with the saturation concentration of the alcohol in the oil. Above the divergence concentration, static yield values were reported, which increased with further increase in the alcohol concentration. This is precisely what would be expected if the theory holds. The third alcohol tested by Talman & others was lauryl alcohol. It was miscible in all proportions with liquid paraffin and the rheological behaviour of emulsions containing it was found to be dependent on the type of water-soluble component. Fluid products of low apparent viscosity were obtained with non-ionic components, but cetrimide and sodium lauryl sulphate produced more viscous emulsions, some of which exhibited static yield values. Now a small amount of the alcohol would be expected to partition with the micellar phase, but this should not precipitate on cooling to 25°, as the penetration temperature

(see, e.g. Barry & Shotton, 1967b), and hence the minimum temperature for solubilization, should be less than the melting point of the alcohol. Thus the emulsions should not exhibit semi-solid properties such as significant static yield values. Samples of emulsions containing the largest proportion of lauryl alcohol (which exhibited the highest yield values in the series) have been prepared (see experimental) and they were viscous pourable preparations and not semi-solid. Their static yield values and apparent viscosities, as measured in the Rotovisko viscometer, were only about one tenth that of similar emulsions containing cetostearyl alcohol. Thus, overall, the data of Talman & others (1967) agree well with the requirement that the amphiphile should diffuse from the disperse phase and precipitate on cooling, and these authors explained their results on the basis of a diffusion process.

There is a limit to the amount of, for example, cetyl alcohol which can diffuse out of the oil phase to be solubilized in the hot aqueous micellar phase. In many formulations, the concentration of the alcohol remaining in the oil phase may exceed its maximum solubility in the oil when the emulsion is cooled, and this should lead to precipitation within the disperse phase. Although such precipitation within disperse phase globules would have no direct significant effect on the bulk rheology of the emulsion, it is important as it indicates that the solubility of the alcohol in the oil has been exceeded. Barry (1968a) has published photomicrographs of such crystals which were sufficiently well formed to distort the emulsion globules and similar crystals have been detected by Talman & Rowan (1968).

Viscoelastic structure

The presence of a viscoelastic structure entrapping disperse phase globules is crucial to the suggested mechanism of the self-bodying action of mixed emulsifiers as defined. For preparations in which the elastic properties (both instantaneous and retarded) predominate i.e. semi-solid creams, the disperse phase in the *cooled* emulsion may be considered to approximate simply to a geometric diluent which serves as loci for the establishment of a gel network. Barry & Shotton (1967a, c) have photographed gels prepared from mixtures of cetyl alcohol, sodium dodecyl sulphate and water, in which solid alcohol provided loci and frozen liquid crystal the gel matrix. Both continuous shear data and creep analysis supported the hypothesis of a network, and the apparent relative viscosity versus temperature curve went through a maximum as the frozen smectic phase melted to liquid crystal. This result has been confirmed by Davis (1969), using the identical system, when he found that the compliance in a creep test (which is qualitatively equivalent to the reciprocal of the apparent viscosity) went through a minimum at the same temperature. When oil is introduced into the ternary system so as to form semi-solid creams, the rheological behaviour still strongly suggests a viscoelastic network (Barry 1968a). Davis (1969) has investigated aqueous cream B.P. by creep analysis at different temperatures and has found that the compliance had a minimum value at a similar temperature as the ternary system dealt with above, which again suggests melting of a gel network. However, it is difficult to demonstrate unequivocally the presence of a gel matrix existing in the bulk of an emulsion. It is not readily apparent microscopically in an undiluted emulsion, as fine resolution is difficult, and on diluting the system the labile gel structure readily breaks down. In such a diluted preparation, remnants of the network can be detected, but to photograph them clearly it is easier to increase the proportion of the alcohol. Barry (1968b) has published photomicrographs of diluted emulsions in which this has been done, and in

ordinary light a network enclosing disperse phase droplets was visible. Both precipitated cetyl alcohol and any frozen pseudomorphic mixture of surfactant, amphiphile and water will be optically anisotropic and show up between crossed polarizers. As this was the situation in these photomicrographs, further evidence of the nature of the gel network was provided. Photomicrographs under phase contrast of a filamentous structure enveloping globules or dispersed in the continuous phase have also been published by Talman & Rowan (1968).

The viscoelastic network is also important as an aid to emulsion stability as it hinders close approach of disperse phase droplets and thus retards coalescence and ultimate cracking of the emulsion.

CONCLUSION

It would appear that the suggested mechanism of the self-bodying action of mixed emulsifiers discussed is sufficient to explain the ability of a number of mixed emulsifiers to produce semi-solid emulsions, particularly when the surfactant is ionic. When this is non-ionic, the surfactant-alcohol complex is probably weaker than that formed by ionic surfactants as the non-ionic molecule is bulky (Rowe 1965). This explains the results of Talman & others (1968) and my own findings which show that emulsions formulated with ionic surfactants and cetostearyl alcohol have a greater consistency than those containing non-ionic surfactants. Davies (1969) considers that this difference also explains why chlorhexidine cream B.P.C. contains more surfactant (cetomacrogol) and cetostearyl alcohol than do those official oil-in-water creams based on ionic surfactants combined with cetostearyl alcohol. However, I consider that part of the increased quantity of mixed emulsifier in this cream is probably required so as to form a more extensive network as the liquid paraffin concentration is low (10 w/w) and thus the globules are more widely separated.

On the basis of the self-bodying mechanism, the requirements for the mixed emulsifiers may be listed:

Lipophilic component

1. This should be an amphiphilic compound which by itself promotes water-in-oil emulsions and is capable of complexing with the hydrophilic component at the oil-water interface.
2. Its concentration should at least be sufficient to form a close-packed mixed monolayer with the hydrophilic component. To promote semi-solid emulsions at room temperature it should be near or above the saturation concentration in the oil.
3. Excess material should diffuse readily from the warm oil phase into the warm aqueous micellar phase, and there be solubilized.
4. The melting point should be sufficiently high to precipitate solubilized material at moderate temperatures.

Hydrophilic component

1. This should be a surface-active agent which by itself promotes oil-in-water emulsions and is capable of complexing with the lipophilic component at the oil-water interface.
2. Its concentration should at least be sufficient to form a close-packed mixed

monolayer with the lipophilic component. To promote semi-solid emulsions it should be in excess of its critical micelle concentration in the aqueous phase.

3. It should be capable of solubilizing the lipophilic component whilst warm.

EXPERIMENTAL AND RESULTS

Materials. Water and sodium dodecyl sulphate were as used by Barry & Shotton (1967a), liquid paraffin as used by Barry (1968a), polyoxyethylene sorbitan mono-laurate (Sorbester Q12, from Howards Ltd., Ilford, Essex) and cetrimide, cetostearyl alcohol and cetomacrogol 1000 were commercial grades used without further purification.

Preparation of emulsions. Emulsions were prepared according to the general formula liquid paraffin, 50.0, cetostearyl alcohol, 7.0, water-soluble component, 0.125 to 5.0, distilled water to 100.0 g. The alcohol, dissolved in liquid paraffin at 65–70°, was added to an aqueous solution of the water-soluble component at the same temperature and mixed with a Silverson Multi-Purpose High Speed Laboratory Mixer fitted with an axial flow head and emulsor mesh. The resulting emulsions were cooled rapidly and each was distributed into several separate ointment jars, which were then stored for not less than 10 days at $25 \pm 1^\circ$ before testing. The contents of a separate jar were used for each test.

Rheological examination. Emulsions were examined with a Haake Rotovisko viscometer using measuring cup MV and rotary bob MVI (concentric cylinders) at $25 \pm 0.1^\circ$, and all measurements were made at least twice and results averaged. In general, systems showed complex rheological behaviour, including shear thinning and hysteresis. At high shear rates, the high consistency creams tended to be ejected

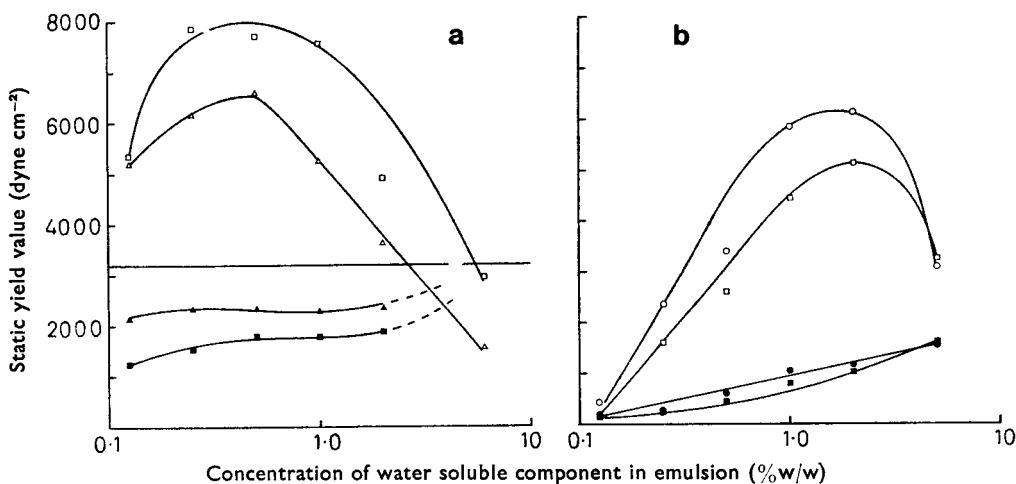


FIG. 1. Effect of water soluble component concentration (% w/w) on the static yield value of emulsions containing 7% w/w cetostearyl alcohol. (a), \triangle , sodium dodecyl sulphate, \square , cetrimide (static yield values determined by Talman & others (1968), using a Ferranti-Shirley cone and plate viscometer). \blacktriangle , sodium dodecyl sulphate, \blacksquare , cetrimide (static yield values determined with a Rotovisko concentric cylinder viscometer at 7.05 s^{-1}). Horizontal line represents shear stress scale limit of Rotovisko viscometer. (b), \circ , cetomacrogol 1000, \square , Sorbester Q12 (static yield values determined by Talman & others (1968), using a Ferranti-Shirley cone and plate viscometer). \bullet , cetomacrogol 1000, \blacksquare , Sorbester Q12 (static yield values determined with a Rotovisko concentric cylinder viscometer at 7.05 s^{-1}).

from the cylinder gap. When smaller diameter inner cylinders were used (so as to extend the range of measurable shear stress) these creams fractured in the gap. As the work was performed to compare results with the static yield values derived from a Ferranti-Shirley cone and plate viscometer (Talman, Davies & Rowan, 1968) reported results are limited to the maximum shear stress reading obtained at the lowest available shear rate (7.05 s^{-1}) starting from rest. These are plotted in Fig. 1 a and b, together with the results of Talman & others (1968).

Acknowledgement

The author wishes to thank Mrs. A. Friend and Miss S. Moth for technical assistance.

REFERENCES

- AXON, A. (1956). *J. Pharm. Pharmac.*, **8**, 762-773.
BARRY, B. W. (1968a). *J. Colloid Inter. Sci.*, **28**, 82-91.
BARRY, B. W. (1968b). *J. Pharm. Pharmac.*, **20**, 483-484.
BARRY, B. W. & SHOTTON, E. (1967a). *Ibid.*, **19**, *Suppl.*, 110S-120S.
BARRY, B. W. & SHOTTON, E. (1967b). *Ibid.*, **20**, 242-243.
BARRY, B. W. & SHOTTON, E. (1967c). *Ibid.*, **19**, *Suppl.*, 121S-129S.
BARRY, B. W. & WARBURTON, B. (1968). *J. Soc. cosmet. Chem.*, **19**, 725-744.
BOFFEY, B. J., COLLISON, R., & LAWRENCE, A. S. C. (1959). *Trans. Faraday Soc.*, **55**, 654-661.
COCKBAIN, E. G. (1952). *Ibid.*, **47**, 185-196.
DAVIS, S. S. (1969). *J. pharm. Sci.*, **58**, 418-421.
DAVIS, S. S., SHOTTON, E. & WARBURTON, B. (1968). *J. Pharm. Pharmac.*, **20**, *Suppl.*, 157S-167S.
HIGUCHI, W. I., OKADA, R., & LEMBERGER, A. P. (1962). *J. pharm. Sci.*, **51**, 683-687.
HYDE, A. J., LANGBRIDGE, D. H. & LAWRENCE, A. S. C. (1954). *Discuss. Faraday Soc.*, **18**, 239-258.
LAWRENCE, A. S. C. (1958). *Ibid.*, **25**, 51-58.
RIEGELMAN, S. (1962). *Am. Perfumer Cosmet.*, **77**, 59-62.
ROWE, E. L. (1965). *J. pharm. Sci.*, **54**, 260-264.
SHERMAN, P. (1964). *J. Pharm. Pharmac.*, **16**, 1-25.
SHERMAN, P. (1968). *Emulsion Science*, pp. 127-347, London: Academic Press.
TALMAN, F. A. J., DAVIES, P. J. & ROWAN, E. M. (1967). *J. Pharm. Pharmac.*, **19**, 417-425.
TALMAN, F. A. J., DAVIES, P. J. & ROWAN, E. M. (1968). *Ibid.*, **20**, 513-320.
TALMAN, F. A. J., & ROWAN, E. M. (1968). *Ibid.*, **20**, 810-811.