

Gels in soap stabilized emulsions

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In some soap stabilized liquid paraffin emulsions a correlation has been found between emulsion type and the contact angle of the soap gel (the stabilizing agent) at the o/w interface. Two unrelated series of emulsions have been prepared, one series being stabilized by magnesium oleate gels and the other series by ammonium oleate gels. The soap gels were prepared by double decomposition and suppression of ionization respectively. Unlike the magnesium oleate system no inversion to w/o emulsions occurred with the ammonium oleate series. This dissimilarity is predicted from differences in the contact angles of the soap gels at the o/w interface.

Soaps were among the earliest materials used to stabilize emulsions and consequently most of the early theories of emulsion stability relate to soaps. These early theories suggested that monomolecular films were formed at the o/w interface (Harkins & Beeman, 1929) although the possibility of multi-molecular films for oil-soluble soaps was later realized (Alexander, 1947; Sherman, 1955). It also seems probable that water-soluble soaps form multi-molecular films (Martynov, 1949) and indeed the reversible aggregation of oil globules in soap stabilized emulsions has been explained on the basis of such films (Cockbain, 1952; Davis, 1971).

Soaps form gels under conditions often met during inversion of o/w emulsions suggesting that gel particles are the agents for stabilization of w/o emulsions. Pink (1941), for instance, has shown that stabilization of w/o emulsions by heavy metal soaps occurs by precipitation of the soap at the interface. With magnesium oleate this involves the formation of a hydrated soap insoluble in both benzene and water. Since heavy metal soaps give monolayers which easily collapse under conditions operating in emulsions it must be concluded that the soap is in the form of solid particles (Alexander & Johnson, 1950). This is a criticism of the theory of Schulman & Cockbain (1940) who suggested that w/o emulsions were stabilized by rigid monolayers.

If soap gels act as solid particles a prerequisite of this must be accumulation of the gel particles at the interface. In this position a state of minimum energy is achieved which represents a balance between the oil, water and solid interfacial energies. Contact angle measurements ought therefore to be a test of the extent to which emulsions are stabilized by particles of soap gel.

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Little work has been reported on the use of contact angle measurements in relation to emulsion technology. Schulman & Leja (1954) adsorbed various surfactants on to barium sulphate particles and measured the aqueous surfactant/benzene contact angles at the particle surface. Their data led them to conclude that formation of a w/o or o/w emulsion depended on the contact angle being slightly more or less than 90° respectively. Partial confirmation of this correlation was reported by Lucassen-Reynders & van den Tempel (1963) who produced emulsions stabilized with glyceryl tristearate crystals. These had a contact angle of 110° at the aqueous surfactant/paraffin oil interface.

As part of an extended investigation we have prepared magnesium oleate and ammonium oleate soap gels and measured their contact angles at the o/w interface. These gels have been used to prepare emulsions and the resulting emulsion type correlated with the measured contact angles.

MATERIALS AND METHODS

Materials

Magnesium chloride hexahydrate (101.8% MgCl₂·6H₂O) was Analar grade. Oleic acid (acid value 200), sodium hydroxide pellets and liquid paraffin were of B.P. quality. Ammonia solution and ammonium chloride (99.9% NH₄Cl) were S.L.R. grade. All materials were used as received. Water was distilled from a Quickfit all glass still.

Methods

Preparation of soap gels. Magnesium oleate gels were prepared from oleic acid, sodium hydroxide and water giving an acid soap mixture consisting of 0.5 molal sodium oleate and 0.5 molal oleic acid. MgCl₂·6H₂O solution was added to portions of this mixture containing 10 mmol soap giving a range of Mg²⁺ content as in Fig. 1. The final mixtures

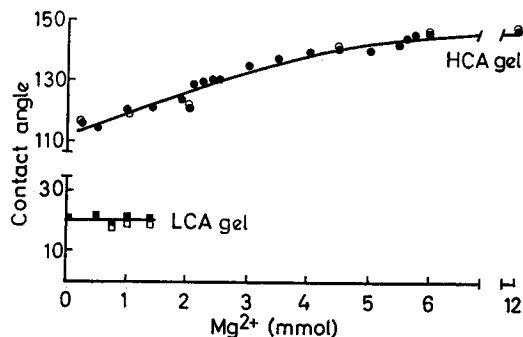


FIG. 1. Contact angles (measured through the aqueous phase) of the gels of the magnesium oleate system at the water/liquid paraffin interface. x axis—mmol Mg^{2+} reacting with 10 mmol soap. Open symbols indicate contact angles of the gels where water is replaced by the liquid in which the gels were formed.

were maintained at 60° for 1 h and the cooled gel phases separated by centrifuging at about 7500 g for 20 min. Generally, in order to simulate the conditions operating when making emulsions, the acid soap mixtures were dispersed in 450 g water (equivalent to the aqueous phase of an emulsion) before addition of Mg^{2+} . However, with small amounts of Mg^{2+} in the range 0–1.4 mmol no extra water was used since the gels would have been too fragile for easy contact angle measurements. It was shown that the presence of excess water had no significant effect on the contact angle at the o/w interface.

Formation of two gels together with a sodium oleate rich liquid phase occurred at low magnesium contents. One of these gels was a hydrous loosely packed gel while the other was a more solid and compact gel. The latter gel being less dense than the former gel made separation by centrifugation possible. The final traces of loosely packed gel were removed from the compact gel by repeated washing with water.

Ammonium oleate gels were made as follows: 45.0 g dilute ammonia solution (10% w/w NH_3) in 30.0 g water was added to 8.33 g oleic acid giving an oleic acid: NH_3 mol ratio of 1:9. The system was shaken and various amounts of ammonium chloride (0.625, 1.25, 2.50, 5.00 or 12.5 g) in 32.5 g water was added to this ammonium oleate mixture, again with shaking. The gels were separated by centrifuging at about 4500 g for 10 min.

Contact angle measurements of the soap gels at the o/w interface

The soap gel was spread evenly on a circular Perspex rod to a uniform thickness of about 1 mm.

This was placed vertically in an optical cell half filled with the aqueous phase. The latter was water for the magnesium oleate gels but in order to maintain the integrity of the ammonium oleate gels an ammonia–ammonium chloride solution was used which was of identical strength to that used to prepare the gel. Liquid paraffin was then carefully layered on this and the contact angle observed by projection. No change in contact angle was noted over a 5 min period at the end of which it became necessary to raise the rod so bringing fresh gel to the interface. The rod was raised 10 times and the angle remeasured each time with a precision generally better than $\pm 3^\circ$ of the mean. All experiments were repeated and the replication was within this variation. The accuracy of this method has been demonstrated using hard paraffin at the air/water interface. A contact angle of 105° was measured (International Critical Tables, 1928 give 106°).

Preparation of emulsions. Magnesium oleate emulsions were prepared by mixing 5 g gel with 50 g liquid paraffin at 60° followed by the addition of 45 g water also at 60° . The resulting emulsion was homogenized hot using an Ormerod plate valve homogenizer, model URF/1 (Ormerod Engineers Ltd., Rochdale, Lancs.).

Although ammonium oleate emulsions can be prepared using separated gels, identical results were obtained by forming the soap gels *in situ*. The latter technique was adopted in order to resemble the usual preparation of White Liniment. This involved mixing 8.33 g oleic acid with 25 g liquid paraffin and shaking with 45 g dilute ammonia solution diluted with 30 g water to give 43 mmol soap in 115 cm^3 o/w emulsion. Then the appropriate amount of ammonium chloride dissolved in the remaining 32.5 g water was added and the emulsion shaken. The ammonium chloride used was in the range 0.625 to 12.5 g equivalent to 11.7 to 234.0 mmol. This formulation basically resembled that for White Liniment B.P.C. (1968) except that liquid paraffin replaced turpentine oil and the mol ratio of oleic acid to ammonia was 1:9, instead of 1:0.9. Separate experiments had shown that with the smaller ratio, the method of preparation of emulsions with less than 0.625 g NH_4Cl is type determining. This is not so with the amount of ammonia employed here.

Emulsion type was determined both by dilution with water and oil and by microscopic examination for mixed emulsions.

RESULTS AND DISCUSSION

An acid soap mixture consisting of a 1:1 molal ratio of sodium oleate and oleic acid forms a gel when heated and cooled. At an o/w interface this gel is better wetted by water than by oil and when used as an emulsifier gives rise to an o/w emulsion. A soap gel is also formed when magnesium chloride is added either directly to the acid soap mixture or to the acid soap mixture dispersed in a large volume of water followed by heating and cooling. Contact angle measurements of the soap gels for the magnesium oleate system are shown in Fig. 1.

Below 2 mmol Mg^{2+} two gels are formed, one having a high contact angle (HCA) and the other a low contact angle (LCA) at the o/w interface. The proportion of HCA to LCA gel increases with increasing Mg^{2+} content but above 1.4 mmol Mg^{2+} the LCA gel is represented only by a fluid aqueous phase which was less than 14% of the total gel present (Fig. 2).

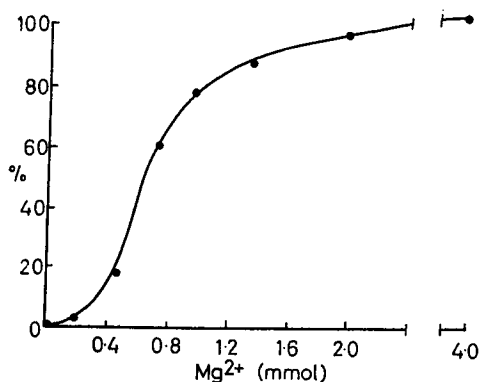


FIG. 2. Effect of magnesium content on the proportion of HCA and LCA gels. x axis—mmol Mg^{2+} reacting with 10 mmol soap; y axis—% HCA gel.

Chemical analysis of the LCA gel prepared by addition of 1.0 mmol Mg^{2+} directly to the acid soap mixture indicated magnesium dioleate, sodium oleate and free oleic acid in a mol ratio of 1:4:2. In contrast that of the HCA gel at 6.0 mmol Mg^{2+} indicated magnesium dioleate and free oleic acid in a mol ratio of 1:2. The marked difference in contact angles between these two gels is clearly associated with the sodium oleate content.

Within the range 0.2 to 1.4 mmol Mg^{2+} emulsions were prepared both with separated HCA and LCA gels and with these gels mixed in the ratio 1:2, 1:1 and 2:1. Gels HCA and LCA alone gave w/o and o/w emulsions respectively whereas gel mixtures produced mixed o/w emulsions. Only HCA gel

could be separated in the range 2 mmol Mg^{2+} and above. Up to 5 mmol Mg^{2+} this produced mixed w/o emulsions due to entrapment of some of the sodium oleate-rich equilibrium liquid but above 5 mmol Mg^{2+} the equivalent content of Mg^{2+} exceeded that of oleate and resulted in completely inverted w/o emulsions. This confirmed the observations of Parsons & Wilson (1921) that w/o emulsions are formed only when the equivalent concentration of Mg^{2+} is greater than that of the monovalent soap.

Contact angles of the magnesium oleate gels at the liquid paraffin/water interface (Fig. 1) are not modified when water is replaced by the aqueous phase formed from addition of the magnesium chloride solution directly to the acid soap mixture. These contact angles are therefore presumably those occurring when a sodium oleate/oleic acid stabilized emulsion is inverted by addition of magnesium chloride solution. The observation that mixed w/o emulsions occur in the region 2–5 mmol Mg^{2+} before complete inversion ensues is not unusual (Corran, 1946) and can be explained by the presence of residual amounts of o/w promoting materials.

Unlike the magnesium oleate system no w/o emulsions were formed with the ammonium oleate/ammonium chloride series. Ammonium oleate gels at the liquid paraffin/ammonia–ammonium chloride interface gave individual contact angles between only 20 and 26° (s.d. = 1.45) for an ammonium chloride content in the range 0.625–12.5 g. This variation was entirely within experimental error thus showing that the ammonium chloride had no significant effect on the contact angle. This system therefore like the magnesium oleate series is consistent with a correlation of the contact angle with emulsion type.

It can therefore be concluded that measurement of contact angles of these soap gels at the o/w interface can predict emulsion type in a way similar to that shown by Schulman & Leja (1954) for solid particles. However these authors stated that stable o/w and w/o emulsions were only formed when the contact angle is slightly removed from 90° whereas our results indicate that stable o/w and w/o emulsions can be produced with contact angles greatly different from 90°. This is reasonable since solid particles must be regarded as largely residing in one phase in order to minimize interfacial energies (Thomas, 1927). It is obvious, nevertheless, that solids cannot be completely wetted by one phase otherwise they would not remain at the interface and their stabilizing power would be lost.

The correlation established between contact angle

and emulsion type does not necessarily indicate a causal relationship between emulsion type and contact angle. We have shown that variables such as method of preparation, nature of the soap and the type of oil are important emulsion type determining properties.

REFERENCES

- ALEXANDER, A. E. (1947). *J. chem. Soc.*, 1422-1425.
ALEXANDER, A. E. & JOHNSON, P. (1950). *Colloid Science*, p. 654, 659. Oxford: University Press.
British Pharmaceutical Codex (1968). London: The Pharmaceutical Press.
COCKBAIN, E. G. (1952). *Trans. Faraday Soc.*, **48**, 185-196.
CORRAN, J. W. (1946). *Emulsion Technology*, 2nd edn., pp. 176-192. Brooklyn: Chemical Publishing Co.
DAVIS, S. S. (1971). *J. Pharm. Pharmac.*, **23**, Suppl., 161S-169S.
HARKINS, W. D. & BEEMAN, N. (1929). *J. Am. chem. Soc.*, **51**, 1674-1694.
LUCASSEN-REYNDERS, E. H. & TEMPEL, M. VAN DEN (1963). *J. phys. Chem.*, **67**, 731-734.
MARTYNOV, V. M. (1949). *Kolloidzeitschrift*, **11**, 255-259.
PARSONS, L. W. & WILSON, O. G. (1921). *Ind. Engng Chem.*, **13**, 1116-1122.
PINK, R. C. (1941). *Trans. Faraday Soc.*, **37**, 180-184.
SCHULMAN, J. H. & COCKBAIN, E. G. (1940). *Ibid.*, **36**, 661-668.
SCHULMAN, J. H. & LEJA, J. (1954). *Ibid.*, **50**, 598-605.
SHERMAN, P. (1955). *Research*, Lond., **8**, 396-401.
THOMAS, A. W. (1927). *J. Am. Leath. chem. Ass.*, **22**, 171-211.