141. *Studies in Water-in-oil Emulsions. Part II. The Interfacial and Surface Activities of Magnesium and Calcium Oleates and the Rôle played by these Soaps in the Stabilisation of Water-in-oil Emulsions.*

By Richard C. Pink.

The effect of magnesium and calcium oleates on the interfacial tension between benzene and water has been measured by the drop-weight method. The marked lowering observed is an important factor in the stabilisation of water-in-oil emulsions. The effect of these soaps on the surface tensions of benzene and water has also been examined.

It has been established that those oil-soluble soaps which are capable of acting as efficient stabilisers for oil-continuous emulsions are precipitated from their solutions in oils when a sufficient quantity of water has been added (Wellman and Tartar, *J. Physical Chem.*, 1930, **34**, 379; Pink, J., 1938, 1252; this vol., p. 53). It is this precipitated soap which, by virtue of its ability to prevent coalescence of the water globules, acts as a stabiliser for water-in-oil emulsions. There is, however, a second factor of importance in the stabilisation of oil-continuous emulsions with oil-soluble soaps. It is generally accepted that lowering of interfacial tension and emulsifying power are very closely related (Hillyer, *J. Amer. Chem. Soc.*, 1903, **25**, 513; White and Marden, *J. Physical Chem.*, 1920, **34**, 617), and it has been assumed that these soaps lower the oil–water interfacial tension in the same manner as the water-soluble soaps. This has not so far been shown experimentally. Mead and McCoy (" Colloid Symposium Monograph," 1926, **4**, 44) attempted to do so, but found it impracticable, as they were unable to obtain satisfactory solutions of their soaps in the oils which they used.

Magnesium oleate has already been prepared in the anhydrous form by the author (*loc. cit.*), and the preparation of anhydrous *calcium oleate* is now described. The effect of these soaps on the benzene–water interfacial tension has been measured, and a study has also been made of their effect on the surface tensions of benzene and water.

EXPERIMENTAL.

Materials.—The oleic acid was obtained from Kahlbaum, and the other chemicals used were of " AnalaR " standard. Benzene (thiophen-free) was rendered anhydrous by standing over sodium, and was redistilled immediately before use. All the water used was freshly distilled.

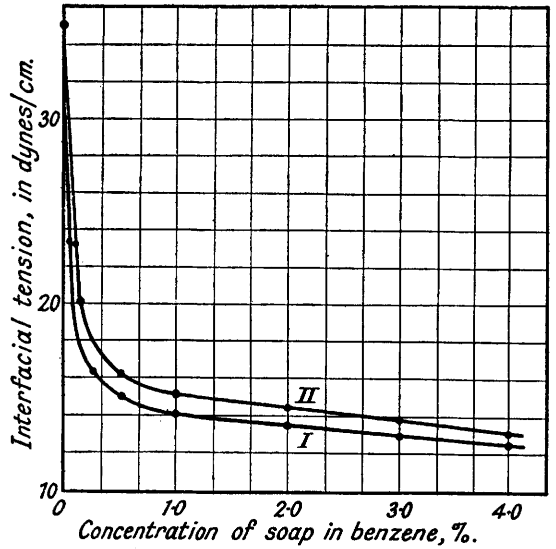
The anhydrous magnesium oleate was prepared from the hydrated soap obtained by metathesis of sodium oleate with magnesium chloride by the method already described (*loc. cit.*). It was recrystallised twice from dry benzene before use. No difficulty was found in preparing 20% solutions in benzene, and the soap showed no tendency to form gels even at this high concentration. According to Mead and McCoy (*loc. cit.*), the magnesium oleate prepared by them solvated in oil at 100° to give a clear solution, but later attempts to dissolve it were unsuccessful.

Preparation of calcium oleate. A solution of 50 g. of sodium oleate in 2 l. of water, prepared by neutralisation of 46·4 g. of oleic acid with the calculated amount of N-sodium hydroxide, was heated to 90°, and a solution of 25 g. of calcium chloride in 200 c.c. of water added drop-wise. The white precipitate obtained was filtered off, washed free from chloride, and dried in a desiccator over calcium chloride. On being heated at 105° in the air-oven for 45 mins., it was converted into a pale yellow, transparent solid [Found : loss, 2·90, 2·93, 2·89. $Ca(C_{18}H_{33}O_2)_2,H_2O$ requires loss, 2·90%]. As with magnesium oleate, the *calcium oleate* obtained by metathesis is hydrated. Confirmation of this was obtained by ignition of the hydrated soap at a bright red heat for 30 mins. [Found : CaO, 8·95, 8·98. $Ca(C_{18}H_{33}O_2)_2,H_2O$ requires CaO, 9·03%]. The anhydrous soap was ignited under the same conditions [Found : CaO, 9·24, 9·28. $Ca(C_{18}H_{33}O_2)_2$ requires CaO, 9·30%]. It was subsequently found that a more satisfactory product was obtained if the hydrated soap was dried at 105° under reduced pressure. The anhydrous soap was recrystallised from dry benzene and stored in a vacuum desiccator. In contact with the air it was slowly converted into the hydrated form.

An attempt was made to prepare anhydrous zinc oleate. The material obtained by metathesis of sodium oleate with zinc sulphate was a white powdery substance with a greasy feel. On being heated in the air-oven at 110° for 2 hours, it darkened and apparently suffered decomposition. It was then heated in a vacuum over phosphoric oxide for 2 hours at 170°, but on cooling it melted unchanged at 65—67°, and was found to have undergone no appreciable loss in weight. Ignition at a red heat for 30 mins., however, indicated that the *salt* obtained may have contained water of hydration [Found: ZnO, 12·63, 12·65. $Zn(C_{18}H_{33}O_2)_2,H_2O$ requires ZnO, 12·60%. $Zn(C_{18}H_{33}O_2)_2$ requires ZnO, 12·93%]. It should be noted, however, that analysis of the soap dried as far as possible is not by itself a satisfactory method for determining the residual water (Lawrence, *Trans. Faraday Soc.*, 1938, **34**, 660).

As zinc oleate was found to be an indifferent emulsifier for benzene–water systems, no interfacial measurements were made with it.

Interfacial-tension Measurements.—The interfacial tensions between the benzene solutions and water were measured by the drop-weight method, a modified form of stalagmometer being used. This consisted essentially of a small pipette, the lower extremity of which was sealed to a capillary tube having a ground and polished end. Previous workers on interfacial tension with this apparatus have shown that the size of the drop depends largely on its time of formation. Tate (*Phil. Mag.*, 1864, **27**, 176) suggested 40 secs. for each drop-release as the minimum time necessary for equilibrium. Lewis (*ibid.*, 1908, **15**, 499; 1909, **17**, 466) found this unnecessary and suggested 12—15 secs. as the necessary minimum time (see Powney and Addison, *Trans. Faraday Soc.*, 1937, **33**, 1243). With the apparatus used in these experiments it was found that reproducible results were obtained when the time of drop formation exceeded 1 minute. A set of fine capillaries which could be joined to the upper end of the pipette was therefore used, and by choice of appropriate capillaries a time of 1 minute was maintained throughout the experimental work. Precautions were taken to ensure that the polished tip of the lower capillary was completely wetted by water before each determination of the drop number, as it was found in preliminary experiments that errors in measurement were frequently due to a lack of such precautions. Strict control of temperature was maintained by immersing the apparatus in a thermostat at 20°. Interfacial tensions were calculated from the drop numbers by the use of Harkins and Brown's correction factors (*J. Amer. Chem. Soc.*, 1919, **41**, 499). In many cases the measurements made by the method described were checked by using a Du Nouy tensiometer adapted for interfacial measurements. The results obtained with magnesium and calcium oleates are shown in the figure.



I. *Magnesium Oleate.* II. *Calcium Oleate.*

The curves show a rapid fall in interfacial tension with a very small concentration of soap, indicating marked adsorption at the interface. Of the two soaps, magnesium oleate gives a slightly lower tension at all concentrations, a fact which is paralleled by its more efficient emulsifying power.

Surface-tension Measurements.—The surface tensions were measured with a Du Nouy tensiometer. The design of this instrument did not permit of accurate control of the temperature of the test solution. All measurements, however, were made in a room in which the temperature remained within the range 19—21°. The variations in the readings under these conditions were not greater than 0·2 dyne/cm. except with the very dilute solutions of calcium oleate in water, where variations of 0·5 dyne/cm. were recorded. At least 30 readings were made with each solution, and the average value taken. The results with benzene solutions of magnesium and calcium oleates are shown below :

% Magnesium oleate in benzene	0·00	0·50	1·00	2·00	3·00	4·00	5·00
Dynes/cm.	28·90	28·90	29·00	29·10	29·10	29·10	29·10
% Calcium oleate in benzene	0·00	0·50	1·00	2·00	3·00	4·00	5·00
Dynes/cm.	28·90	28·90	28·90	29·00	29·00	29·00	29·00

The very slight increase in surface tension observed is to be expected from theoretical considerations, since in such solutions negative adsorption will probably take place.

The surface tensions of saturated aqueous solutions of magnesium and calcium oleates were also determined and found to be 32·3 and 47·8 dynes/cm. These solutions contained 0·231 g./l. and 0·045 g./l. respectively.

Discussion.—In the formation of water-in-oil emulsions with soaps of multivalent metals, two factors are of importance. The reduced interfacial tension permits easy subdivision of the water in the oil and assists in rendering such a subdivision stable, and the film of hydrated soap, precipitated at the interface, effectively prevents coalescence of the globules. There is no doubt that globules of water are also simply entangled in the precipitated soap. This is particularly true of emulsions stabilised with aluminium palmitate, where the precipitate is highly gelatinous (Briggs and Schmidt, *J. Physical Chem.*, 1915, **19**, 478). The precipitated soap is much more readily wetted by oil than by water (Wellman and Tartar, *loc. cit.*), and it is this fact which is apparently the type-determining factor.

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