42. *Studies in Water-in-Oil Emulsions. Part III. The Effect of the Relative Phase Volumes on the Type of Emulsions stabilised by Magnesium Oleate.*

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The effect of the relative phase volumes on the type of emulsions stabilised by magnesium oleate has been investigated. The type of emulsion produced depends to a certain extent on its method of preparation, but with a suitable method and with a sufficient concentration of soap, emulsions containing 90% of water dispersed in benzene can readily be obtained. A number of the water-continuous emulsions underwent a reversal of type on standing.

NEWMAN (*J. Physical Chem.*, 1914, **18**, 34), studying the emulsifying powers of magnesium oleate, found that more than 80% of water (by vol.) could be emulsified in a " concentrated " solution of the soap; with a mixture of magnesium and sodium oleates an emulsion of water in benzene, containing 96% of water, could be prepared. Similar results were obtained by Briggs and Schmidt (*ibid.*, 1915, **19**, 478). Wellman and Tartar (*ibid.*, 1930, **34**, 371), however, state that, when benzene solutions of magnesium oleate were shaken with water, emulsions containing more than 50% of water by volume usually had water as the continuous phase. When equal volumes of the soap solution and water were used, the type of the resulting emulsion depended on the method of shaking employed. Gentle or moderate shaking invariably produced emulsions of the water-in-oil type, whereas violent shaking produced emulsions in which water was the continuous phase. Wellman and Tartar were unable to extend the scope of these investigations. In an attempt to explain this discrepancy in the above results, a detailed investigation of the effect of the ratio of the phase volumes on the type of the resulting emulsions has been carried out over a wide range of soap concentration.

EXPERIMENTAL.

The magnesium oleate was prepared by the method already described (J., 1938, 1252). The emulsions were prepared in test-tubes stoppered with good-quality corks, which were carefully freed from grease and washed before use. The electrical conductivity method (Clayton, *Brit. Assoc. Colloid Reports*, 1918, **2**, 114) was adopted for the determination of the type of the emulsions, an apparatus similar to that described by Parke (J., 1934, 1112) being used.

In Series I the emulsions were prepared as follows. The benzene and a sufficient volume of a 20% soap solution were run into the test-tubes and thoroughly mixed; the water was then added from a burette, and the tubes were given 100 shakes by hand, according to Cheesman and King's method (*Trans. Faraday Soc.*, 1938, **34**, 594) for the production of water-in-oil emulsions. The soap concentration varied from 0·25 to 2·0 g./100 c.c. of emulsion. Immediately after preparation, the emulsions were examined and their type determined. All the emulsions with more than 50% of water were water-continuous. After standing for 24 hours in the thermostat at 20°, they were re-shaken and their type re-determined. In a number of the emulsions with higher concentrations of soap a reversal of type had taken place; of the emulsions with 2 g. of soap/100 c.c. of emulsion, only those with more than 70% of water were water-continuous.

It is believed that this reversal of type with magnesium oleate emulsions on standing has not previously been observed. The emulsions were stored in the thermostat for a further period of a week and again shaken and examined. No further changes of type had occurred, but all the emulsions were much less stable. This decrease in stability may be due to the fact that, on standing, the precipitated soap (see Pink, J., 1938, 1252) becomes hard and brittle and hence much less suitable as a stabilising film. For instance, freshly prepared hydrated magnesium oleate, suspended in benzene, gives stable water-in-oil emulsions, whereas several days after preparation when the soap has become granular it will give only very unstable emulsions under the same conditions.

In Series I all the water was added to the oil at once. It is well known that a more satisfactory method of making emulsions is to add the liquid which is to become the disperse phase in small amounts accompanied by shaking after each addition. This principle was adopted in Series II. The soap concentrations and the final phase-ratios were the same as in Series I, but the water was added to the soap solution 1 c.c. at a time. After each addition the emulsions received 10 shakes by hand and were then allowed to stand for one minute. All the emulsions in Series II were oil-continuous. On standing for 24 hours the emulsions with 90% of water containing 0·25 and 0·50 g. of soap/100 c.c. of emulsion broke completely and could not be re-emulsified on shaking. With these exceptions all the emulsions were very much more stable than those in Series I, but the same decrease in stability was observed on standing for a week.

The reversal of type observed in Series I is readily explained on the basis of the theory outlined in previous papers (Pink, *loc. cit.*; J., 1939, 619). It will be true of any emulsion that, once a particular phase is established as the continuous one, there will be a strong tendency for it to remain in that condition, notwithstanding the fact that it might be more stable when reversed. In the case of these particular systems there are two factors producing emulsification: (1) the reduced interfacial tension between water and benzene produced by the soap, and (2) the film of hydrated soap precipitated at the interface. At the moment of mixing only the first factor is operative, but as the precipitation of the soap proceeds, the second factor becomes of greater importance and is eventually sufficient to overcome the tendency of the water-continuous emulsions to remain in that condition. This effect is more marked in Series II, for the water is added slowly and sufficient time is therefore given for a more complete precipitation of the soap.

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