298. *Reversal of Emulsion Type.*

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In general, the use of a " simple " emulsifier with a pure oil and water will under all conditions give the same type of emulsion; *e.g.*, sodium oleate with benzene–water always gives oil-in-water emulsions, no matter in what proportions the benzene and water are present, and similarly magnesium oleate gives emulsions of the reverse type. Further, it has always been held that in order to reverse the type of an emulsion it is necessary to add an appreciable amount of a new substance which either has in itself, or will produce by its action on the emulsifier, an opposite emulsifying effect; *e.g.*, addition of magnesium chloride to the former emulsion will eventually change the type when there is a greater equivalent of magnesium than of sodium present.

In this investigation a reversal of type has been observed under conditions which approach more nearly to those obtaining with the use of a simple emulsifier. If an emulsion is formed with sodium oleate as emulsifier in water and benzene, the salt is hydrolysed just as it is in aqueous solution, and it is therefore present as a mixture of sodium hydroxide, oleic acid, and sodium oleate, rather than as a simple substance. In consideration of this, an investigation has been made of the effect of varying the amounts of alkali and oleic acid present.

Experimental.

The emulsifier was in all cases prepared by the addition of the required amounts of sodium hydroxide and oleic acid to the benzene–water. In Series I, each emulsion contained 70 c.c. of benzene, 1·4118 g. of oleic acid, and 30 c.c. of aqueous solution containing the following volumes of *N*-sodium hydroxide :

No.	1	2	3	4	5	6	7	8	9	10
N-NaOH, c.c.	1	2	3	4	5	6	7	8	9	10

The 70 : 30 ratio of benzene to water was used because of the relation between phase volume and homogenisation (Parke, J., 1933, 1458). No. 5 contained equivalent amounts of alkali and acid. Nos. 2—10 were apparently normal oil-in-water emulsions, and all gave an alkaline reaction with phenolphthalein. From No. 5, with increasing alkali, there was an increase in the amount of free aqueous phase, and further increase in the excess of alkali decreased the stability of the emulsion, finally breaking it.

No. 1 was a water-in-oil emulsion. In order to investigate this unexpected phenomenon, an attempt was made to find the exact point of reversal; Series II, therefore, covered the region in question, the conditions being exactly as in Series I, but with $N/10$-alkali :

No.	1	2	3	4	5	6	7	8	9	10
$N/10$-NaOH, c.c.	2	4	6	8	10	12	14	16	18	20

Nos. 1, 8, 9, and 10 gave fairly stable oil-in-water emulsions on shaking; the others would not give definite or stable emulsions. On homogenisation by means of a small homogeniser similar to that used by Parke (*loc. cit.*), the types were as follows : 1, Oil-in-water, fairly stable; 2, oil-in-water, with a large amount of free benzene; 3, 4, 5, 6, 7, water-in-oil; 8, 9, 10, oil-in-water, stable.

The comparative conductivities of the emulsions of this series were measured by means of the kick on a milliammeter when a current was passed through them. These confirmed the type of 1, 2, 8, 9, and 10, and showed that 3 and 4 are probably dual emulsions, and 5, 6, and 7 are almost entirely water-in-oil emulsions.

That the reversal of type is of a very complex nature is shown by this double reversal in Series II, as well as by other investigations on the phenomenon. These show that, in general, a large excess of oleic acid gives with small amounts of sodium oleate, on homogenisation, a water-in-oil emulsion when there is an excess of benzene over water; but when there is 50% benzene, no emulsion of this type can be obtained, the lowest percentage of benzene giving such an emulsion being 62%. It was also found that the type was more influenced by variation in the amount of sodium hydroxide than in that of oleic acid.

Gentle continuous shaking tends to give water-in-oil emulsions, whereas vigorous intermittent shaking gives the opposite type, which are reversed on homogenisation if the necessary amount of oleic acid is present. Also, if the benzene is added in 5 c.c. portions with shaking after each addition, the type is still oil-in-water when the 70% benzene has been added, and again the type is changed on homogenisation. This would seem to show the necessity for homogenisation in all cases in order to standardise the resulting emulsion.

DISCUSSION.

In considering the causes of these phenomena, it would seem that there are two agents to be taken into account. The first is the marked lowering of surface tension of the water, and hence of the interfacial tension, by the addition of the soap, as observed by Reynolds (J., 1921, **119**, 460). The second is the presence of the large excess of oleic acid in the benzene. It is thought that the action of the latter may be somewhat similar to that taking place in a magnesium oleate–benzene–water emulsion, in which, since the solubility of magnesium oleate in water is 0·23 g./l., the greater part of the emulsifier is contained in the benzene phase, a water-in-oil emulsion being formed.

The action of such an emulsifier as sodium oleate + oleic acid may be taken to have two separate and definite functions; (1) to lower the interfacial tension, and (2) to render the globules, once formed, stable, presumably by some form of coating by adsorption to the interface.

It is significant that phenol–water and aniline–water, on addition of oleic acid alone, give emulsions which are stable after some weeks. In both cases the interfacial tension is very low, and the lowering action of the soap is not necessary. Difficulties arise in the investigation of the result of the addition of substances other than oleic acid, owing to their effect on the interfacial tension and the possibility of compounds being formed.

The reversing action of oleic acid can in no way be considered to be an electrolytic reversal of the type cited by Clayton (" Emulsions," 1923, p. 74 *et seq.*) on account of the low solubility of this acid in water; also, since oleic acid does not itself emulsify benzene–water, it cannot be considered as an emulsifier of opposite type. The second reversal (see above) still remains unexplained.

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