## 236. *The Phase Volume Theory and the Homogenisation of Concentrated Emulsions. Part II.*

By JOSEPH B. PARKE.

IN a previous paper (J., 1933, 1458) the more important conclusions in regard to the " phase volume " theory of emulsions were briefly summarised, and a series of experiments was described which showed that in all the emulsions investigated a partial breakdown occurred on homogenisation provided the disperse phase was present in a concentration sufficient to exceed that necessary for the globules to be in closest packing. In all the experiments described, either sodium or potassium oleate was used as the emulsifier, and experience has shown that these soaps, as a rule, are capable of stabilising only the oil-in-water type of emulsion. Since there was no substance present in the emulsion capable of stabilising the reverse (water-in-oil) type of emulsion, a partial breakdown, rather than the change of type suggested by Wa. Ostwald (*Kolloid-Z.*, 1910, **6**, 103; **7**, 46) might have been expected to take place when the globules of disperse phase were forced into closest packing during homogenisation.

The present investigation concerns the examination of emulsions containing two emulsifying agents, each of which normally stabilises a different type of emulsion. The emulsifier employed throughout was a mixture of sodium and magnesium oleates. Experiment showed that the latter was the most satisfactory simple emulsifier of known composition for the emulsification of water in oil.

### EXPERIMENTAL.

*Preparation of Materials.—Sodium oleate.* This was prepared by neutralisation of a weighed amount of purified oleic acid with *N*-sodium hydroxide solution. *Magnesium oleate.* Pure magnesium oleate could not be obtained from the commercial product on account of the free oleic acid present, and attempts to synthesise it from magnesium oxide and oleic acid also proved unsatisfactory; it was finally obtained as follows. A solution of 50 g. of sodium oleate in 2 l. of water, prepared by neutralising 46·38 g. of oleic acid with 164·31 c.c. of *N*-sodium hydroxide, was heated to 90°, and a solution of 20 g. of magnesium chloride in 100 c.c. of water was slowly added with constant stirring. Magnesium oleate was immediately precipitated; it was filtered off after 24 hours, and extracted for 10 minutes with boiling benzene, which was then decanted, while still hot, from the residue. On evaporation of the solution to dryness, a horny, pale brown solid was obtained [Found, by calcination at bright red heat for $\frac{1}{2}$ hour: Mg, 4·13, 4·13, 4·15. Calc. for $Mg(C_{18}H_{33}O_2)_2$: Mg, 4·14%].

*Determination of Type.*—The type of each member of the various series investigated was determined by a modification of Clayton's electrical conductance method (*Brit. Assoc. Colloid Reports*, 1918, **2**, 114), which enabled alternating instead of the usual direct current to be used.

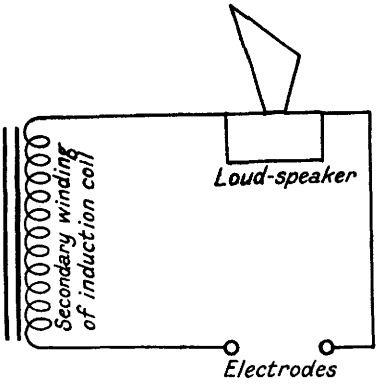
The secondary winding of a small induction coil was wired in series with a pair of electrodes and a loud speaker as shown in Fig. 1.

Normally only a very faint note is heard from the loud speaker, and this is not altered in intensity when the electrodes are immersed in an emulsion of the oil-continuous type.* If, however, the emulsion is of the water-continuous type, there is a very pronounced increase in the intensity of the note when the electrodes are immersed in it. When direct current is used in emulsion-type determinations, as in the usual method, rapid polarisation takes place, and frequently only a very small kick can be observed in the milliammeter needle. With alternating current, no polarisation occurs, and the electrodes can be left in the emulsion for any desired length of time. The gradual change over from one type of emulsion to the other, which in some cases occupied as much as 10 seconds, could thus be followed with ease, being indicated by a gradual increase or diminution in the volume of sound emitted by the loud speaker.

The homogeniser used throughout this work was a Pentecrême hand-operated model (*Pharm. J.*, 1934, 337). No advantage was derived by passing an emulsion through the instrument more than 5 times, and accordingly this was adopted as the standard treatment for the emulsions described in the present paper.

*The Series : Benzene–Magnesium Oleate–Sodium Oleate–Water.*—A 10% solution of sodium oleate in water and a 19·28% solution of magnesium oleate in A.R. benzene were prepared immediately before they were required. 10 C.c. of the former were run into each of a number of 4-oz. glass-stoppered bottles. A calculated volume of water was then added to each bottle. After the bottles had been shaken, 10 c.c. of the magnesium oleate solution were added to each. After further shaking, a calculated volume of A.R. benzene was added in separate 10 c.c. portions interspersed by vigorous shaking of the emulsions. If in any particular case the volume of benzene to be added was not an even multiple of 10 c.c., the balance was added last. In this way a series of emulsions, containing a constant mass of sodium and magnesium oleates and a varying proportion of water to benzene, was prepared. The total volume of liquids in each emulsion was 100 c.c.

FIG. 1.



The type of each member of the series was investigated, and it was found that a change from the water-continuous to the oil-continuous type took place between the emulsions containing 60 and 65% of benzene. Microscopic examination, by means of a dark-ground illuminator, revealed that all the emulsions were very complex. The water-continuous emulsions contained clots of the reverse type and *vice versa*.

Each emulsion was homogenised, and in no case was a change of type brought about by this treatment. The viscosity of each member of the series was then measured by means of a set of 4 Ostwald U-tube viscometers constructed and calibrated in accordance with standard recommendations (B.E.S.A. Pub. No. 188, 1929). All viscosity measurements were carried out at 20°, and are given in Table I, $\eta$ being the viscosity in centipoises.

TABLE I.

| $C_6H_6$, % ........... | 20 | 25 | 30 | 35 | 40 | 50 | 60 | 65 | 70 | 75 | 80 | 90 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\eta$ .................... | 2·56 | 3·12 | 4·08 | 5·54 | 8·86 | 16·9 | 66·9 | 1470 | 27·7 | 15·4 | 6·77 | 3·03 |

Change of type.

The viscosity–concentration graph (Fig. 2) was quite regular apart from the break due to a change of type, and in this respect differed from the curves given by Parke and Graham (J.,

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* Since many of the emulsions examined were of a multiple type, it has been found convenient to adopt the following nomenclature. When stating the type of an emulsion, the continuous phase is given, *i.e.*, water-continuous or oil-continuous. The usual expressions, oil-in-water and water-in-oil, only give an incomplete and to some extent misleading description of a multiple emulsion, since the globules of dispersed oil or water contain further drops of water or oil. The term " primary disperse phase " has been used to designate that liquid or emulsion in contact with the continuous phase, the secondary disperse phase is that dispersed through and in contact with the primary disperse phase, and so on.

**1933**, 1214) for a series of emulsions stabilised by sulphonated fish-oil soaps. In the latter case, a break in the curve at one point indicated a change from the simple to the multiple type of emulsion. This is in agreement with the results obtained from microscopic examination, which showed that none of the emulsions was of a simple oil-in-water or water-in-oil type. The multiple nature of the emulsions also accounts for their relatively high viscosity.

A second series of emulsions which contained equal weights instead of equimolecular proportions of the two soaps was prepared, 1 g. of each soap being present in 100 c.c. of emulsion. As before, the benzene was added in 10 c.c. portions. The emulsions changed from water-continuous to oil-continuous after 80% of benzene had been added. When the emulsions were passed through the homogeniser the point at which the type changed altered. That containing 65% of benzene was of the water-continuous type, and that containing 70% of benzene was of the other type. Microscopic examination again revealed that all the emulsions were of a multiple nature. The viscosity–concentration graph of the series (Fig. 3) is very similar in character to that of the first series except that the individual viscosities are, on the whole, smaller. The data for the viscosities of these emulsions are given in Table II.

FIG. 2.

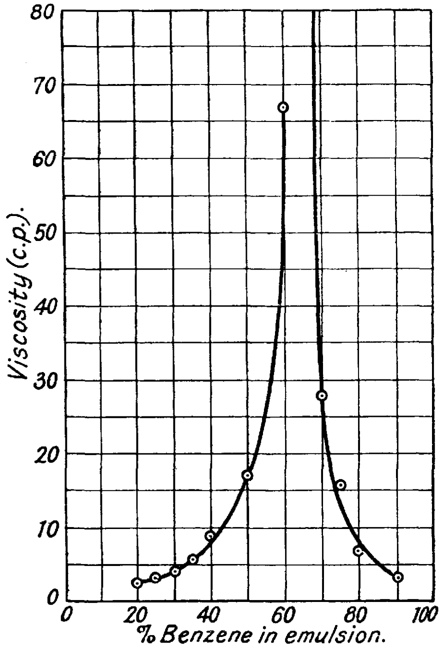

FIG. 3.

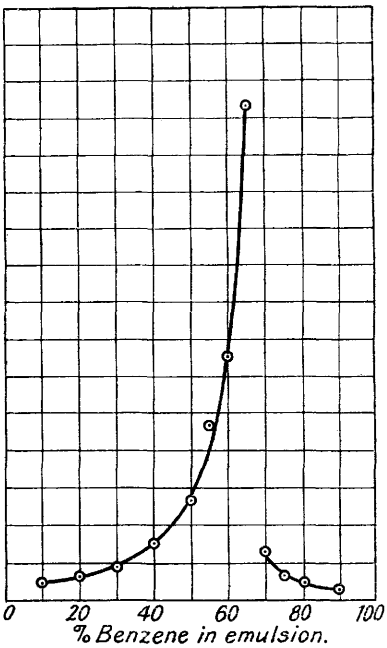

TABLE II.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_6H_6$, % | 10 | 20 | 30 | 40 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 90 |
| $\eta$ | 2·04 | 2·90 | 4·32 | 7·61 | 13·2 | 23·5 | 32·7 | 66·6 | 6·32 | 3·16 | 2·40 | 1·44 |

Change of type.

The magnesium oleate solution, being less concentrated in this case, would have a lower viscosity, and hence the emulsions of oil-continuous type should not be so viscous. No information is available as to the effect of the viscosity of the disperse phase on the viscosity of the emulsion as a whole.

The formula deduced by Hatschek (*Kolloid-Z.*, 1910, **7**, 301; 1911, **8**, 34; *Trans. Faraday Soc.*, 1913, **9**, 80) for the calculation of the viscosity of an emulsion does not involve any factor which depends on the viscosity of the disperse phase, and if this is strictly true it is probable that in some of the emulsions investigated the lower viscosity in the present series indicates a less complex type.

In the first series after homogenisation the change of type occurred between 60 and 65% of benzene, and in the second series after similar treatment between 65 and 70% of benzene,

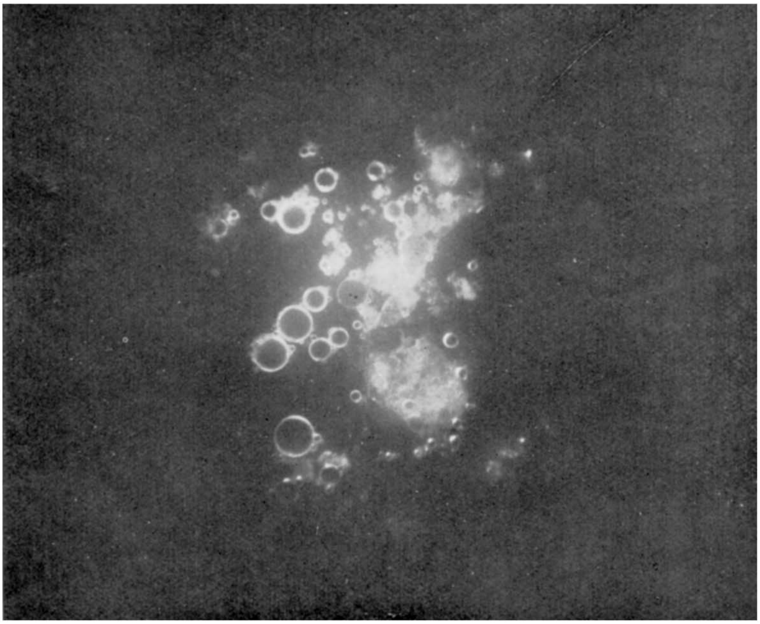

PLATE II.

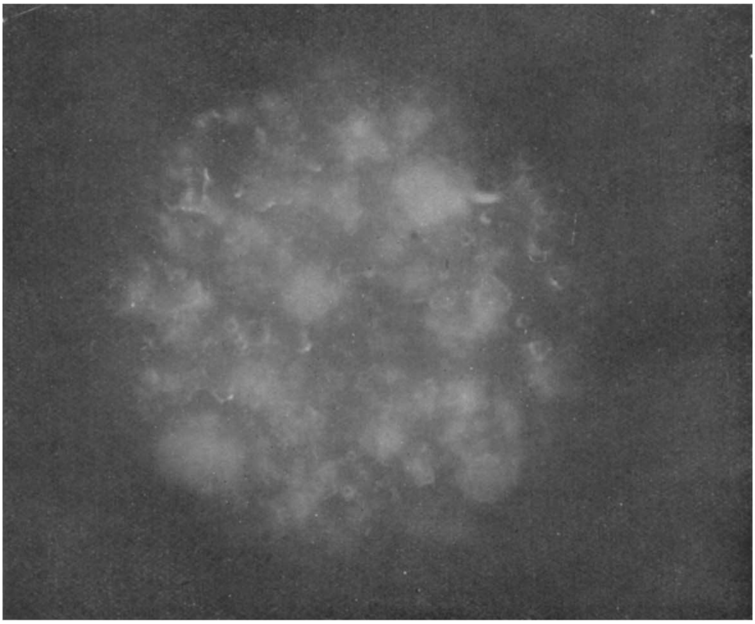

PLATE I.

[*To face p.* 1115.

the oil being in each case the primary disperse phase until a change of type occurred. This is to be expected if it is assumed that the emulsions of the first series were more complex than those of the second, the volume of primary disperse phase being greater owing to the larger amount of secondary disperse phase present.

In the preparation of the two series already described, the benzene was added last in small portions. Two further series, in which the water was added last in a similar way, were prepared, the sequence being : 10 c.c. magnesium oleate solution, benzene, 10 c.c. sodium oleate solution, water in 10 c c. quantities. In the first series the mass of sodium oleate present was 1 g. per 100 c.c. of emulsion. Magnesium oleate was present in molecularly equivalent proportion. The emulsions were all oil-continuous except that containing 90% of water. Microscopic examination again showed them to be of a multiple nature. On homogenisation, the point at which the change of type occurred altered to between 70 and 75% of water; below this concentration oil was the continuous phase. After homogenisation, the viscosities of the emulsions containing 50—70% of water were so great that they could not be determined with any degree of accuracy even by means of the falling-sphere viscometer : that having 70% of water would not pour out of a wide-necked bottle and was practically solid. Plate I is a photomicrograph of the unhomogenised emulsion containing 80% of water, and Plate II shows that containing 90% of water, now the continuous phase.

A series of emulsions containing equal amounts, 1 g. of each soap per 100 c.c. of emulsion, was examined. The change of type took place between 75 and 80% of water. At lower concentrations of water, oil was the continuous phase. On homogenisation this point changed to between 55 and 60% of water. These emulsions were also very complex in structure.

## Discussion.

The attainment in practice of a complete range of ideal simple emulsions, such as those pictured by Ostwald in his phase volume theory of emulsions, would be very difficult. If a reversal of type takes place in an emulsion when its concentration is altered, then obviously the emulsifier, or emulsifiers, present would have to be capable of stabilising both the oil-in-water and the water-in-oil type of emulsion. Suppose that, *e.g.*, benzene and water were shaken together in the presence of such a dual emulsifier, and assume that water were to become the continuous phase of the resulting emulsion. Since the emulsifier can also stabilise the water-in-oil type of emulsion it is to be expected that a greater or less amount of water should become emulsified in the benzene before the latter finally becomes dispersed in the remaining water. There is nothing to prevent this reasoning being carried one step, or in fact an infinite number of steps, further. It is only necessary to assume that the multiple emulsion is again dispersed in further benzene which becomes the new continuous phase. Very complicated multiple emulsions, therefore, should be the rule rather than the exception when a dual emulsifier is present, and this conclusion is supported by the experimental evidence described above.

It would be impossible to calculate when the globules of primary disperse phase in such an emulsion should be in closest packing, and accordingly no comparison can be made between the theoretical values and the results obtained in the four series of experiments. It is obvious that the liquid which is added in small portions tends to remain the disperse phase as long as possible, and that, in coalescence of the globules, the emulsion changes its type. Since the amount of primary disperse phase actually present is larger than the volume originally added, owing to the formation of a secondary disperse phase, this change of type should take place before 74% by volume is present (see J., 1933, 1458). In all the homogenised emulsions this was found to be so.

I wish to acknowledge my continued indebtedness to Professor A. W. Stewart and Dr. Hugh Graham for the interest which they have taken in this work.

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[*Received, May* 18*th*, 1934.]