284. *Studies in Emulsions. Part I.*

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In the examination of emulsions prepared by adding water to certain oil–soap mixtures, abrupt changes in viscosities were observed. These changes were so marked that they were studied in detail and comparisons made with other oil–soap mixtures.

The following systems have been compared: (*a*) Benzene–sodium oleate–water; (*b*) tetrahydronaphthalene–sodium oleate–water; (*c*) benzene–sulphonated fish oil–sodium hydroxide–water; (*d*) tetrahydronaphthalene–sulphonated fish oil–sodium hydroxide–water.

On the one hand, when sodium oleate was used as the emulsifier, regular changes in viscosities on dilution with water were observed; and on the other hand, with the fish-oil soap as the emulsifier, the changes were abrupt. The viscosities of the different series of emulsions have been determined, and these correlated with their type as determined by the electrical conductance method. Photomicrographs and microscopic examination of some members of the series have yielded information which supports the conclusions drawn as to the nature of the emulsions examined.

EXPERIMENTAL.

(a) *Benzene–Sodium Oleate–Water Emulsions.*—The emulsions were prepared by shaking 450 c.c. of A.R. benzene containing 4·6385 g. of oleic acid with 50 c.c. of an aqueous solution of 0·6573 g. of sodium hydroxide. The mixture was shaken intermittently (Briggs, *J. Physical Chem.*, 1920, **24**, 120) (1-minute intervals) until complete emulsification had taken place. The density of this emulsion containing 90% (by vol.) of benzene was then determined, and other concentrations were obtained by adding suitable quantities of water to weighed amounts of it. This procedure was rendered necessary by the high viscosity of the original emulsion. 50 C.c. of each concentration were prepared in 2-oz. glass-stoppered bottles, and after having been shaken for one hour, they were kept at rest for 4 days in a thermostat. Creaming took place upwards in all emulsions except those containing 80% and 90% of benzene, and this made accurate viscosity determinations somewhat difficult. Immediately before it was required, each bottle was removed from the thermostat and slowly turned end-over-end ten times. The viscometer, which had already been placed in the thermostat, was filled with emulsion by means of a long capillary tube with a wide end. The results are shown in the following table :

FIG. 1.

Benzene-sodium oleate-water.

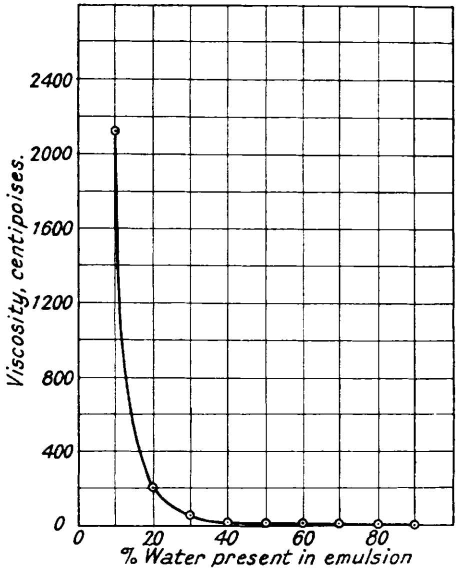
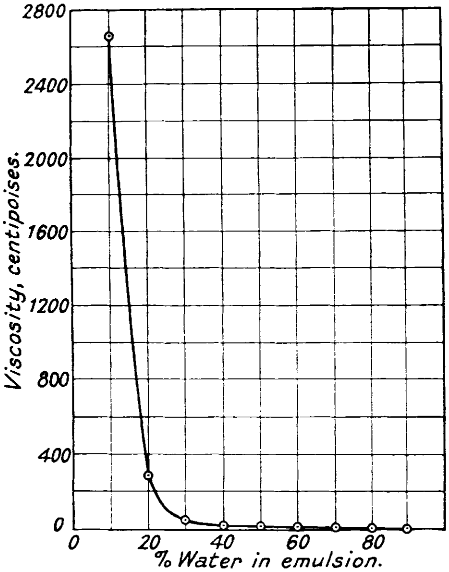


FIG. 2.

Tetrahydronaphthalene-sodium oleate-water.



Original + added water, %	10	20	30	40	50	60	70	80	90
η, centipoises	2130	200	47·8	15·2	6·8	3·76	2·40	1·38	1·13

The curve obtained by plotting these results (Fig. 1) showed no irregularities, and when the type of each emulsion of the series was investigated by the electrical-resistance and the drop-dilution method it was found that all were of the oil-in-water type. Similar series of emulsions stabilised by potassium and ammonium oleates and potassium and sodium stearates were investigated, and in each case a curve very similar to Fig. 1 was obtained.

The falling-sphere viscometer was used in the determination of the viscosity of the emulsion containing 90% of benzene. Since the passage of the sphere through the emulsion could not be observed in the usual way, it was necessary to use a modification of the special electrical viscometer devised by Symmes and Lantz (*Ind. Eng. Chem., Anal.*, **1929**, **1**, 35). The viscosities of all other members of the series were investigated by means of a set of four Ostwald U-tube viscometers, constructed in accordance with the specification of the British Engineering Standards Association (Pub. No. 188, 1929). All viscosity measurements were carried out at 20°.

(b) *Tetrahydronaphthalene–Sodium Oleate–Water Emulsions.*—These emulsions were prepared in exactly the same manner as those in series (a), purified tetrahydronaphthalene being used instead of benzene. Owing to the similarity in the densities of tetrahydronaphthalene and water, creaming took place very slowly in these emulsions, and they were thus very suitable for viscosity determinations. The results are shown below and also graphically in Fig. 2.

Original + added water, %	10	20	30	40	50	60	70	80	90
η. centipoises	2650	280·0	41·9	15·8	7·05	3·75	2·50	1·65	1·26

The emulsions were all of the oil-in-water type. Microscopic investigation, by means of a dark-ground illuminator, revealed that each member of the series contained globules of many different diameters, but in no case was an emulsion of a multiple nature observed. Plate I shows a photomicrograph of the emulsion containing 90% of water. This emulsion, which is typical of the series, was chosen because it was found that, as the concentration of disperse phase was increased, it became increasingly difficult to obtain a satisfactory photograph owing to the scattering of light by the globules. The viscosity of the emulsions containing 10% of water was, as in series (a), obtained by means of the falling-sphere method.

(c) *Benzene–Liquid Soap–Alkali–Water Emulsions.*—500 C.c. of A.R. benzene were shaken with 100 c.c. of fish-oil soap and 12·5 c.c. of a 30% solution of sodium hydroxide were run in. After it had been thoroughly shaken, separate portions of this mixture were measured into glass-stoppered bottles of 2-oz. capacity, by means of a burette. Various amounts of water were then added to each bottle, a range of emulsions containing 0, 10, etc., % of added water being obtained. The bottles were shaken for 1 hour, and then kept at rest for 7 days in a thermostat at 20°. The viscosity of each member of the series was then determined after homogeneity had been obtained as in series (a). The concentrations of the various members of the series, together with their viscosities, are shown in the following table:

Added water, %	0	10	20	25	27·5	30	35	40
η, centipoises	2·90	5·16	7·88	24·8	733	323	138	78·6
Added water, %	45	50	55	60	70	80	90	
η, centipoises	52·5	30·0	14·6	8·73	3·97	2·33	1·24	

The curve obtained by graphing the % of added water against the viscosity is shown in Fig. 3.

The type of each member of the series was investigated by the electrical-conductance and the drop-dilution method. The results obtained from both methods indicated a change of type after 25% of water had been added.

Microscopic examination revealed that the emulsions containing 20 and 25% of added water were of a multiple type. The globules of the disperse phase (water) contained smaller globules of the continuous phase (oil). The emulsions containing from 27·5 to 55% of added water were also of a dual type. Multiple emulsions had previously been observed by Seifriz (*J. Physical Chem.*, 1925, **29**, 738), who investigated the effects of various electrolytes on emulsion stability. Plate II shows a photomicrograph of the emulsion containing 25% of added water.

(d) *Tetrahydronaphthalene–Liquid Soap–Alkali–Water Emulsions.*—This series of emulsions was prepared as in the last case, purified tetrahydronaphthalene being substituted for benzene. The viscosity of each member of the series is given below:

Added water, %	0	10	20	25	27·5	30	35	40
η, centipoises	9·70	13·2	21·9	34·6	28·0	49·8	363	212
Added water, %	45	50	55	60	70	80	90	
η, centipoises	54·1	31·4	22·8	18·5	5·22	2·64	1·38	

Each member of the series was examined under the microscope, and it was found that the emulsions containing from 20 to 60% of added water were of a multiple type. The globules

Plate I.

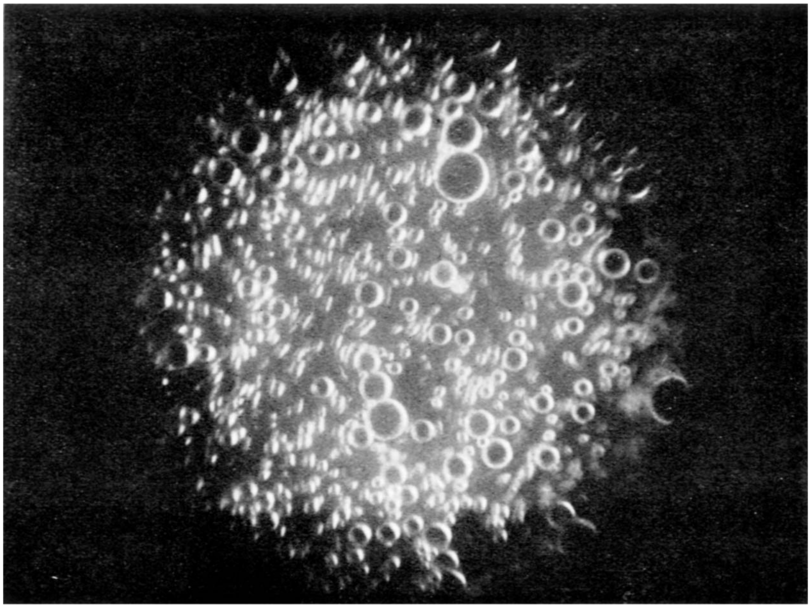
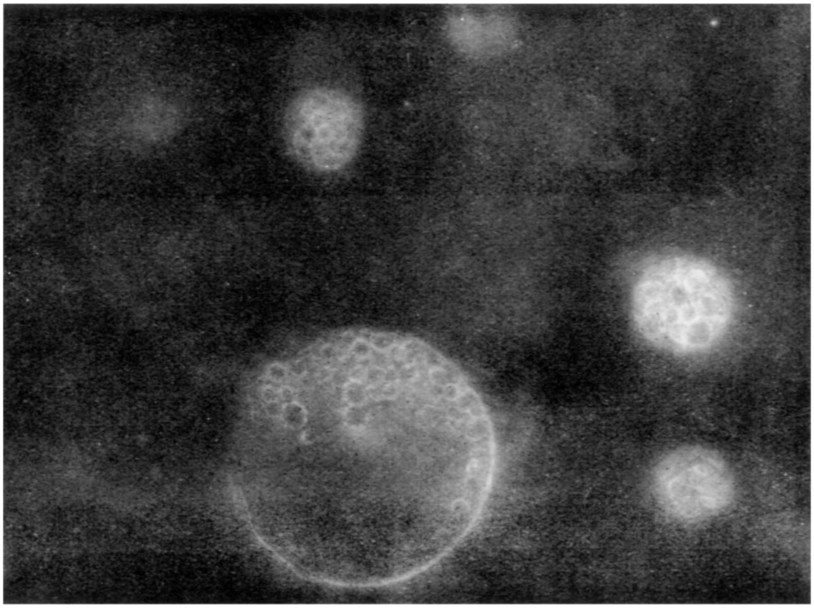


Plate II.



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in the emulsion containing 90% of added water were relatively large, but as the percentage of water decreased the globules became smaller until the emulsion containing 35% of added water was reached, and this contained a tightly packed mass of small multiple globules of practically uniform diameter.

FIG. 3.

Benzene–liquid soap–alkali–water.

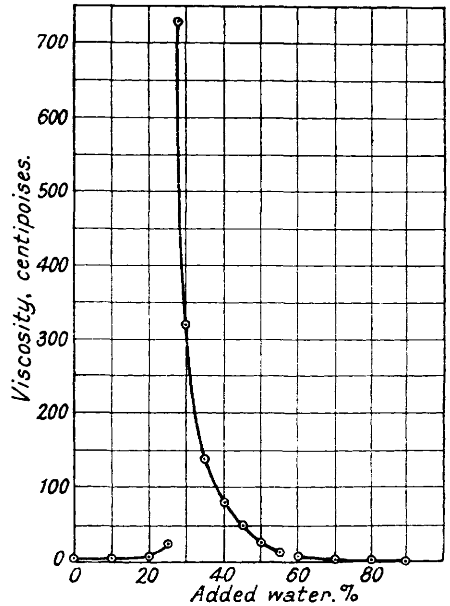
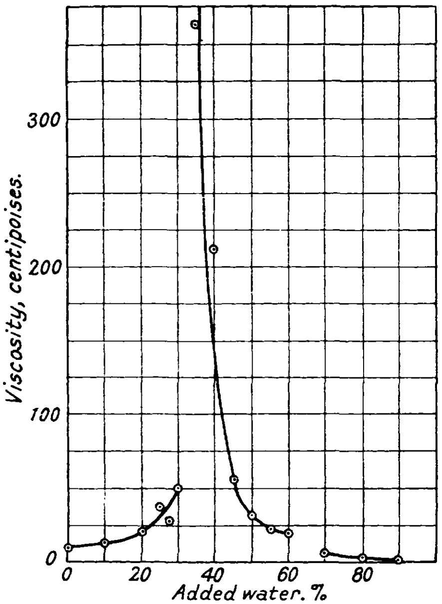


FIG. 4.

Tetrahydronaphthalene–liquid soap–alkali–water.



Discussion of Results.—The abrupt changes in viscosity observed when emulsions stabilised by certain fish-oil soaps are mixed with increasing amounts of water have been proved to be due to a change of type. The break after 60% of water had been added in the viscosity–concentration graph in the case of the tetrahydronaphthalene–liquid soap–alkali–water emulsions is obviously due to the formation of multiple emulsions at this point. The inclusion of globules of continuous phase within those of the disperse phase has the effect of increasing the volume of the latter phase present and hence the viscosity of the emulsion.

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