

PETROL-WATER EMULSIONS.

PART II.—REPRODUCIBILITY AND VISCOSITY.

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In a previous communication (*this Journal*, 1930, 13A, 21) an account was given of some of the properties of petrol-water emulsions made in a colloid mill with soap solutions as stabilisers. It was pointed out that one of the main difficulties in measurements of this type was the fact that emulsions prepared under apparently identical conditions might differ widely in their properties, a fact well known to workers in this field. While making additional observations on the variation of viscosity with time similar to those described in Part I it was observed in several cases that freshly prepared emulsions gave the most irregular results. A possible explanation was the inclusion of air by the emulsion and this was confirmed experimentally. Shortly afterwards Sibree (*Trans. Faraday Soc.*, 1931, 27, 168) published similar observations for paraffin emulsions. By excluding air as far as possible and making the process of emulsification continuous, much more consistent values could be obtained. Emulsions so prepared still showed slow changes in viscosity and these have been examined in conjunction with the stability and particle size.

EXPERIMENTAL.

As hydrocarbon mixtures of different densities are known to give different results when emulsified, most of the experiments to be described were made with a fraction of Burmese petrol boiling between 100 and 150° and of density 0.7623 at 25°. In a few drop-number measurements a lower-boiling fraction was employed.

Sodium oleate used as a stabiliser was the purest obtainable. Ammonium oleate was made by passing dry ammonia into a petroleum ether solution of redistilled oleic acid; the white precipitate was washed with petroleum ether and preserved in a desiccator containing dry ammonia. Triethyl-ammonium oleate was prepared by mixing equivalent quantities of oleic acid and triethylamine in aqueous solution.

The emulsions were made in a Premier colloid mill modified as shown in Fig. 1 so as to give continuous circulation of the fluid and to prevent air being drawn into the gap between the rotor R and the stationary portion S. Using 500 c.c. of liquid and allowing it to circulate for about 5 minutes, equivalent to 20 passages through the mill, it was found that the resulting emulsions, when of the same composition and type, had very similar properties. This applied to emulsions made

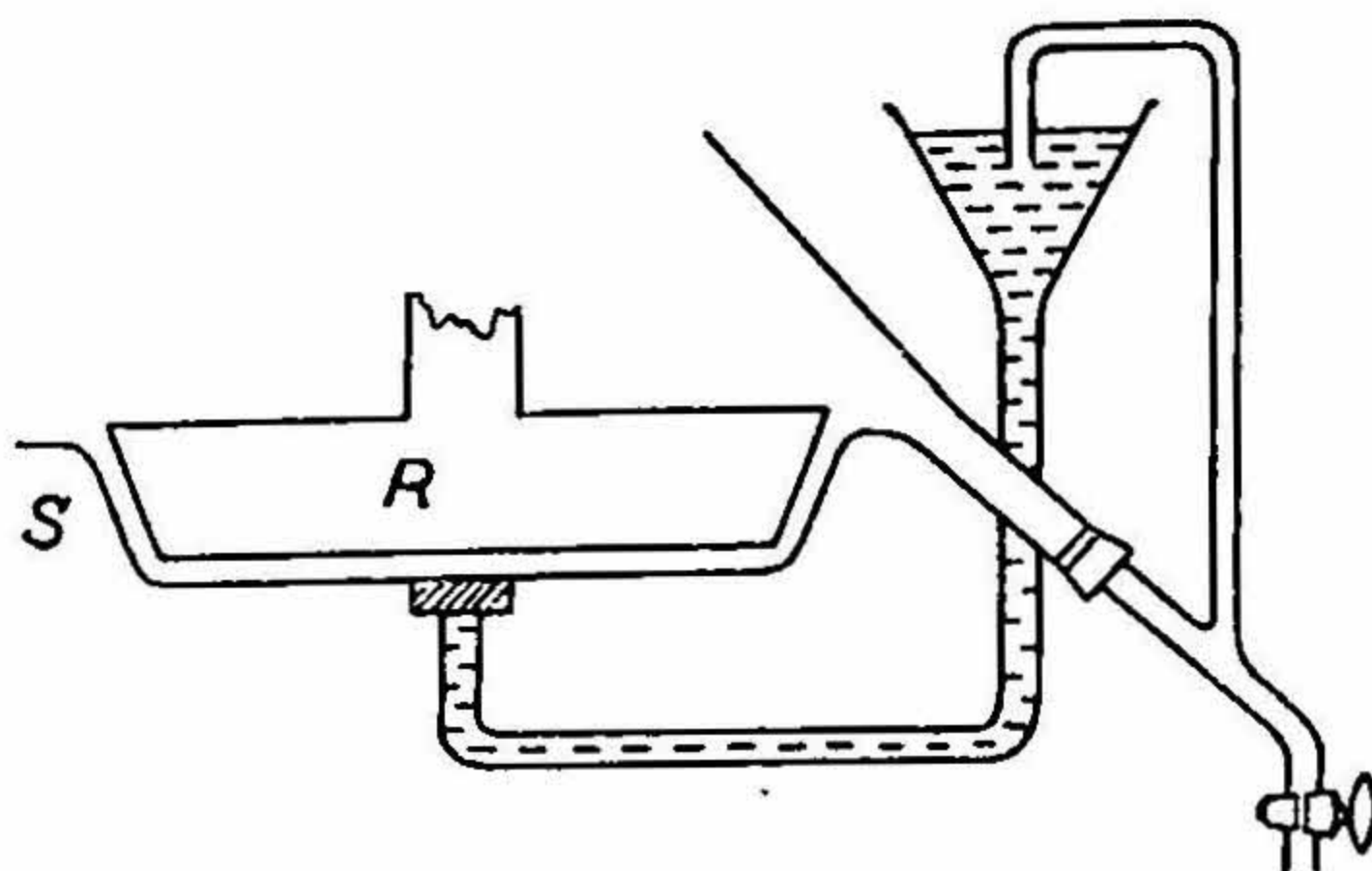


Fig. 1.

directly from the original constituents and to those made by adding one constituent to a previously prepared emulsion of different composition, the final products being indistinguishable.

The type of an emulsion was determined by the drop dilution method and the composition by adding hydrochloric acid to 25 c.c. contained in a burette and reading the volume of the petrol which separated. All percentage compositions given are in terms of volume.

Viscosities were measured at 25° in one of three Ostwald viscometers which were standardised at 20° with a glycerin-water mixture having a density 1.143 and viscosity 0.0794 c.g.s. units at that temperature, the times of flow being 390.4, 66.6 and 50.1 seconds. Objections have been raised to the use of this type of viscometer on the ground that passage through a capillary tends to break an emulsion. No error arising from this cause could be detected in the present experiments, successive readings giving identical values except for a few freshly prepared emulsions the viscosity of which was changing rapidly. Concordant results were also obtained for the same emulsion in different viscometers.

The effect of air.—When preparing emulsions with the colloid mill in its original form which necessitates the intermittent addition of the mixture, air is apt to be sucked in from time to time and this becomes dispersed in fine bubbles throughout the emulsion. The same result is obtained when emulsions are made by shaking in a bottle. It was found that the density of such emulsions was always less than the calculated value and that it increased rapidly at first and more slowly afterwards until the theoretical figure was reached. The initial drop in viscosity was also rapid, but this quantity continued to fall after the density had reached a constant value.

Emulsions from which air had been excluded as far as possible had also a slightly lower density than the calculated value indicating that they contained some air, but the variation of viscosity with time was far less marked.

Some typical figures are shown in Table I, the time t being in hours.

TABLE I.

Density and Viscosity of Emulsions. 1 per cent. Sodium oleate.

(a) 48 per cent. P. in W. air.			(b) 42 per cent. P. in W. air.			(c) 58 per cent. P. in W. no air.			(d) 38 per cent. P. in W. no air.		
t	d	$\eta \times 10^4$	t	d	$\eta \times 10^4$	t	d	$\eta \times 10^4$	t	d	$\eta \times 10^4$
0	0.8749	824	0	0.8870	404	0	0.8570	1632	0	0.9062	318
0.5	0.8798	751	2	0.8921	386	5	0.8584	1632	5	0.9077	314
1	0.8832	711	3	0.8942	376	24	0.8600	1632	24	0.9089	306
44	0.8845	645	4	0.8963	370				27	0.9096	296
116	0.8854	642	24	0.8989	365				48	0.9097	289
140	0.8856	642									
144	do.	641									
164	0.8859	618									
260	do.	608									
284	do.	560									
308	do.	563									
332	do.	517									

It will be observed that in the case of emulsions (a) and (b) containing air, the rise in density was 11–12 units in the third place corresponding with the presence of 1.2–1.3 per cent. of air by volume. For (c) and (d) equilibrium was not attained, but taking into account the density values calculated from the composition, the initial quantity of air was about 0.5 and 0.2 per cent. respectively and with this amount the viscosity changes were far less, emulsion (c) which was very viscous exhibiting a constant viscosity for 24 hours. If the viscosity values for (a) are plotted against time it will be seen that the initial fall is very rapid, subsequently up to about 250 hours the rate of change is slow but it then increases. The first stage is probably due to elimination of the larger bubbles of air, the second is a normal change exhibited by all but the most stable emulsions and the third corresponds with incipient breaking of the emulsion. Similar changes have been observed with many emulsions an interesting case being that of a 44 per cent. petrol in 1 per cent. sodium oleate emulsion the viscosity of which fell slowly from 0.0389 to 0.0346 in 12 days and then dropped to 0.0126 the next day and to 0.0092 two days later. In this case the emulsion showed signs of separation after two days and was gently shaken daily to render it homogeneous.

The part played by air in emulsions is important especially when proteins are used as stabilisers (*cf.* Clayton, *Proc. Chem. Eng. Group*, 1932, 14, 158) but the above-mentioned experiments indicate that by reducing the quantity of air as far as practicable, emulsions showing small initial viscosity changes can be prepared.

To test the reproducibility of such emulsions four mixtures of petrol and 1 per cent. sodium oleate solution were prepared with the proportion of petrol varying from 28 to 58 per cent. Each was divided into two portions which were emulsified separately until the viscosity became constant. The viscosities of the duplicate emulsions corrected for slight changes in composition during emulsification and measured at equal times after the end of this operation were found to be identical within the limit of experimental error the maximum difference being 0.7 per cent.

Drop-numbers.—Drop-numbers for petrol in several soap solutions were given in Part I. Additional measurements have now been made for the stabilisers used in the present experiments and two petrol fractions boiling at 60–100° and 100–150° respectively. The temperature was 23° and the aqueous solution was allowed to drop into the petrol whereas the reverse procedure was adopted previously. The actual drop-numbers were consequently different, but on multiplying by the arbitrary factor 4.5 they yielded results of the same as before as may be seen from Table II.

TABLE II.

Drop-numbers of 1 per cent. Stabiliser Solutions in Petrol.

Stabiliser.	60–100°.	100–150°.	Former value.
Sodium oleate	.. 262	257	226
Triethylammonium oleate	.. 117	112	..
Ammonium oleate	.. 68	68	70
Water	34	38

Stability and Viscosity.—Numerous emulsions have been prepared and their stability and viscosity examined. In all cases emulsification was conducted until the viscosity became constant and air was excluded as far as possible. Some emulsions were prepared directly, others by diluting an emulsion with one of the components and re-emulsifying. The latter process was more convenient when it was desired to prevent a change of type. When the type was the same, emulsions prepared by both methods had identical properties. Table III gives the time which elapsed before initial separation was visible. The disperse phase (petrol or water) is noted in column 3. The letter M denotes emulsions of mixed type which will be referred to later.

TABLE III.

Stability and Composition of Emulsions.

Stabiliser.	Petrol per cent.	Disperse phase.	Time for separation.
1 % sodium oleate ..	90	W	<1 m.
	80	W	4 ms.
	73.3	P	...
	52	P	1 day
	50	P	1 day
	44	P	2 days
	40	P	2 days
	20	P	4 days
	10	P	10 days
8	P	10 days	
1 % triethylammonium oleate	90	..	<1 m.
	76.5	P	2 ms.
	51	P	1 day
	46	P	1 day
	32.8	P	1 day
	24.4	P	1½ days
1 % ammonium oleate	80	..	<1 m.
	74	P	30 ms.
	60	P	40 ms.
	52	P	1 hr.
	38	P	4.5 hrs.
	36.8	P	5 hrs.
	8	P	5 hrs.
5 % triethylammonium oleate	90	..	<1 m.
	80	W	3 ms.
	68.6	P	1 day
	61.2	P	2 days
5 % ammonium oleate	62.6	W	10 ms.
	53.6	W	30 ms.
	41.2	W	10 days
	40	W	Stable
	35.6	W	do.
	31.2	W	do.
	27	W	do.
	15	W	do.
	31.2	P	Stable
	29.6	P	do.
	23.6	P	do.
	20.0	P	do.
	12	P	do.
	8.4	P	do.
	48.8	M	Stable
36	M	do.	
32	M	do.	
30.2	M	do.	

The results in general resemble those given in Part I but they are much more uniform owing to the improved method of preparation. The former figures were mostly for higher concentrations of stabiliser than were used in the present experiments and so a close comparison is not possible. A striking difference, however, is to be found in the results for one per cent. sodium oleate solutions with less than 40% of petrol. These were previously obtained by direct mixing and were very unstable; the present series was obtained by dilution and also by direct mixing, and the emulsions were stable for several days. The reason may be the difference in the petrol used or effect of air since it has been pointed out by Clayton (*loc. cit.*), a gas may have a very marked effect upon the stability. As before, water in petrol emulsions could be obtained with sodium oleate when the proportion of petrol was large and the same effect was observed with triethylammonium oleate but only with 5 per cent. solutions and in all cases these emulsions were very unstable. With 5 per cent ammonium oleate the proportion of petrol could be reduced to 15 per cent. without producing a change in type, and these emulsions were very stable. This may indicate that the strength of the base is a more important factor than the drop-number in determining the type and stability. In this case concentration has a marked influence, water in petrol emulsions not being obtained with 1 per cent. of stabiliser. With sodium oleate on the other hand a 5 per cent. solution gave results differing very slightly from those with the smaller quantity.

The viscosities of the more stable emulsions referred to in the Table III as well as those of several others were measured and the results plotted on a logarithmic scale are shown in figs. 2 and 3. It will be noticed that the experimental points lie much closer to the curves than those given in Part I. The curves for 1 per cent. sodium oleate and triethylammonium oleate are nearly straight for proportions of petrol below 45 per cent. but it is remarkable that emulsions made with the latter emulsifier have approximately 6 times the viscosity of those made with the former. With ammonium oleate the curvature is in the opposite direction and much more pronounced, while at higher petrol concentrations there is an abrupt bend indicating perhaps an incipient change in type. With these stabilisers no water in petrol emulsions sufficiently stable for measurement could be obtained. Fig. 3 shows the results for 5 per cent. ammonium oleate. In this case stable water in petrol emulsions were obtained over a wide range, two of which with 27 and 15 per cent. of petrol were semi-solid so that their viscosity could not be measured. These were made by emulsifying a mixture of 55 parts of petrol and 45 of water, adding water to the product and again emulsifying. This process was repeated until the emulsion became too viscous to put through the mill. It is remarkable that although the disperse phase was added there was no change in

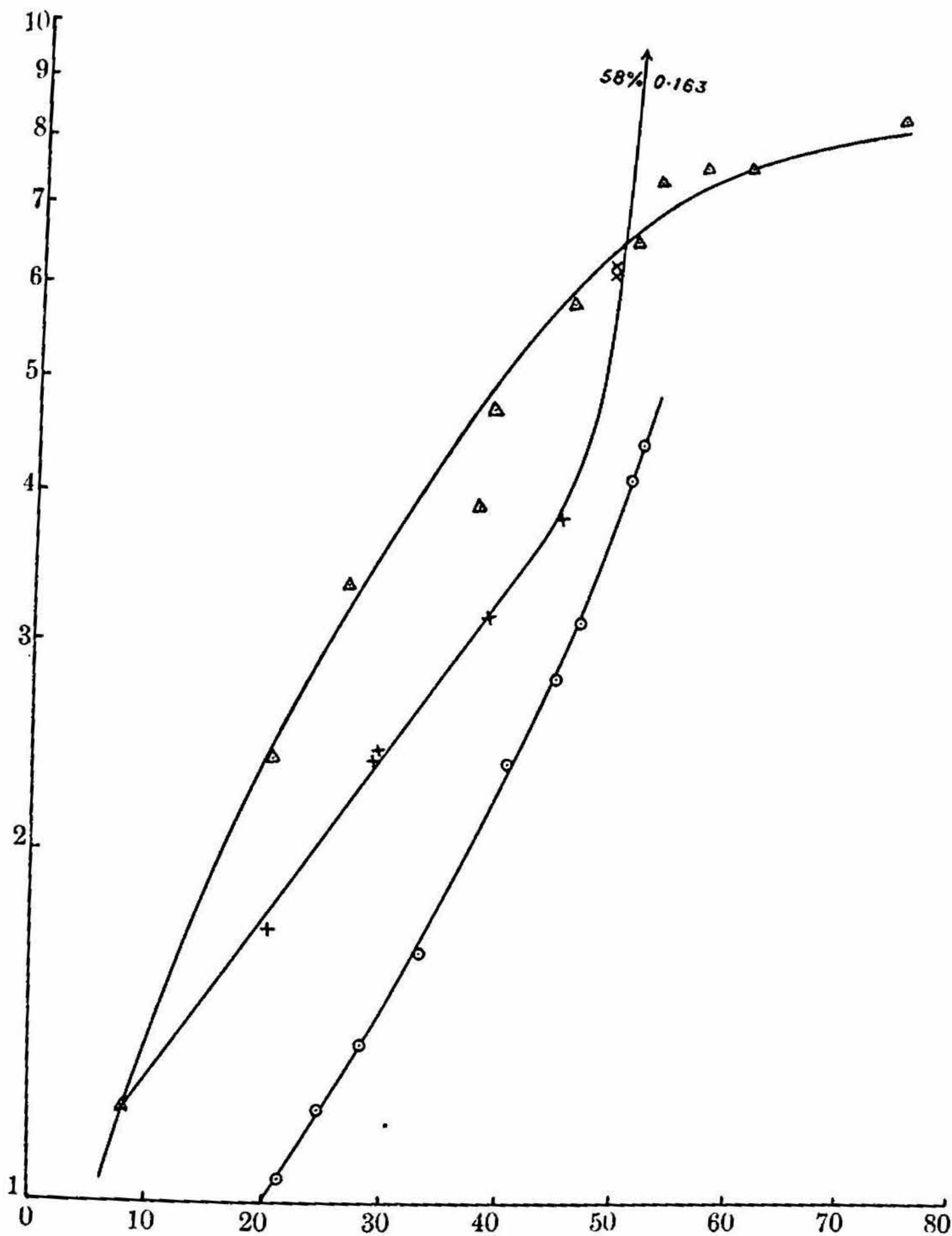


Fig. 2.

- 1% Triethyl-oleate.
 × „ Sodium-oleate.
 △ „ Ammonium-oleate.

type. Petrol in water emulsions containing 8.2 to 31.2 per cent. of petrol were prepared in a similar way by adding successive quantities of petrol to the 8.4 per cent. emulsion and again emulsifying. In this case when the proportion of petrol exceeded 31 per cent. a change in

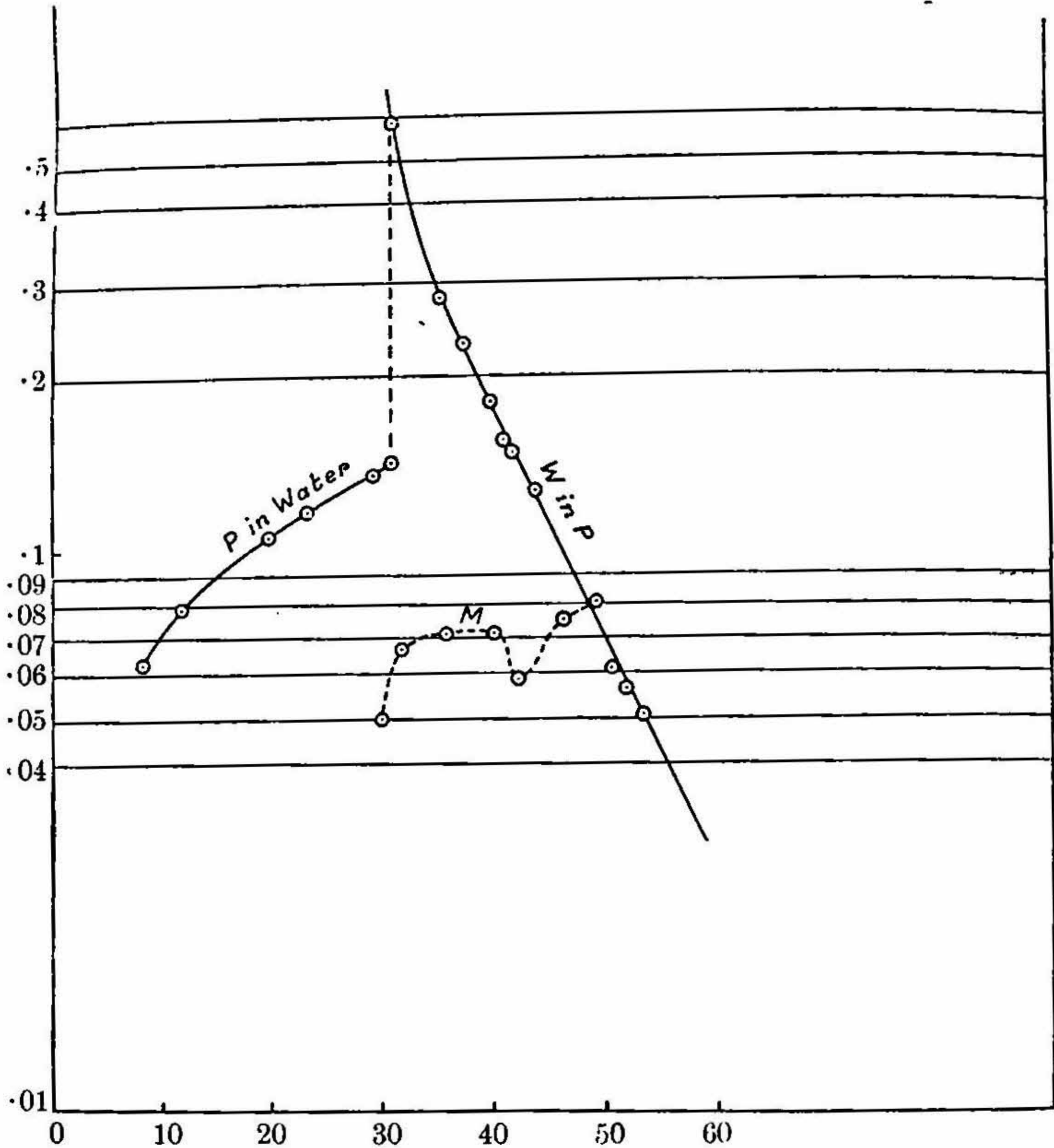


Fig. 3.

5% Ammonium-oleate.

type occurred yielding a product with very low viscosity. Examination under the microscope and the behaviour on addition of a drop of one of the constituents indicated that this emulsion was of the mixed type (*cf.* Clayton, *loc. cit.*). On addition of more petrol, other mixed emulsions were obtained the viscosity of which did not change appreciably with composition. If the proportion of petrol exceeded 50 per cent. a change to the water in petrol type took place. Mixed emulsions with similar viscosity could also be obtained by direct emulsification of mixtures containing between 32 and 45 per cent. of petrol although in some cases the product was of the water in petrol type.

Particle size.—The 5 per cent. ammonium oleate emulsions were examined under the microscope and the approximate size of the particles determined. The results are shown in Table IV.

TABLE IV.

Petrol per cent.	Disperse phase.	Average size, μ .
52	W	4
40	W	8
37.6	W	20
32	W	80
27	W	200
15	W	do.
31	P	90
40.2	M	60-200
46.4	M	do.

In the case of the water in petrol emulsions the particle size decreased in a marked manner as the amount of petrol increased, that is to say, as the viscosity decreased. It is difficult to say whether this relation is accidental owing to the fact that water is more easily dispersed in solutions of low viscosity or whether there is a definite tendency for the particle size to depend on the composition of the emulsion. In view of the fact that emulsification was continued in all cases until the viscosity became constant and that although the petrol in water and mixed emulsions had a low viscosity, the particle size was large, it would appear that the second explanation is the more probable. Support is lent to this view by the fairly homogeneous nature of the water in petrol emulsions. The emulsions of mixed type contained particles of very different sizes although not many were small. It is somewhat remarkable that these indefinite mixtures all had a viscosity of the same order.

The relation between composition and viscosity.—As already mentioned the composition-viscosity curves shown in figs. 2 and 3 tend to be of a linear type within certain ranges of composition, showing that the relation is a logarithmic one.

To a first approximation the following equations hold good :—

Stabiliser.	Equation.	Observed η_0 .	Range of ϕ .
1 per cent. sodium oleate	$\text{Log } (\eta/0.0093)=1.42\phi$	0.0107	0.08-0.45
1 per cent. triethylammonium oleate	$\text{Log } (\eta/0.046)=1.94\phi$	0.0113	0.13-0.45
5 per cent. ammonium oleate P in W.	$\text{Log } (\eta/0.061)=1.17\phi$	0.0213	0.20-0.30
5 per cent. ammonium W in P.	$\text{Log } (\eta/0.00051)=4.26\phi$		0.45-0.65

where ϕ is the ratio of the volume of the disperse phase to that of the continuous phase. The curve for 1 per cent. ammonium oleate

could not be represented by an equation of this type. These equations do not correspond exactly with that of Arrhenius $\log (\eta/\eta_0) = K\phi$ where η_0 is the viscosity of the continuous phase. The values of this quantity are given above and although the divisor of η in the case of sodium oleate is not far from η_0 , for the other stabilisers the difference is much larger. It is remarkable that the curves of both 1 and 5 per cent. ammonium oleate petrol in water emulsions are concave towards the axis of X, whereas in the other cases there is a sharp upward trend as the limit is approached at which a change in type takes place.

It is evident therefore that although the relative volume of the phases is of importance in determining the viscosity, several other factors must be taken into consideration and before definite conclusions can be reached it will be necessary to make an extensive study of particle size, adsorptions of the continuous phase and the effect of stabilisers with different degrees of dissociation, to mention only the main items which affect the problem.

SUMMARY.

1. It has been found that many of the irregularities previously observed in the physical properties of apparently identical petrol-water emulsions were due to the presence of air. By excluding air and continuing the emulsification until the viscosity became constant, reproducible values have been obtained.

2. Emulsions have been prepared with sodium, triethylammonium and ammonium oleates as stabilisers and their viscosities measured. The first two stabilisers yield mainly petrol-in-water emulsions, the water-in-petrol type obtained with high proportions of petrol being very unstable. 5 per cent. ammonium oleate gives stable emulsions of both types and also a series of mixed type characterised by large particle size and low viscosity.

3. The relation between viscosity and composition is in most cases of logarithmic type over a considerable proportion of the stable range, but the equation connecting the two quantities is not that of Arrhenius.

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