PETROL-WATER EMULSIONS.

By C. Varadhan and H. E. Watson.

The original object of the present investigation was the preparation of a number of high percentage petrol-water emulsions and their examination as regards suitability for use in internal combustion engines. China (*Proc. Chem. Eng. Group*, 1924, **6A**, 124) states that a 70 per cent. emulsion prepared in a Premier colloid mill with 2 per cent. of ammonium oleate as stabiliser was as efficient as petrol alone when used for a motor-car. After numerous attempts we have been unable to obtain emulsions sufficiently stable for such tests although many different stabilisers were tried; the results, however, have a certain interest in view of their bearing upon the theory of emulsions and consequently the more important of them have been recorded in the present paper.

With all the stabilisers tried it has been possible to obtain emulsions of two types, namely, water in petrol and petrol in water, varying in the time required for separation from a few seconds to years. Measurements have also been made of the interfacial tension between solutions of the stabilisers and petrol, from which it appears that solutions which have the highest interfacial tensions yield stable emulsions containing the highest proportion of petrol. Viscosity determinations show a rapid rise in viscosity with the quantity of petrol.

EXPERIMENTAL.

Experiments were made with the following stabilisers :—Sodium oleate, potassium oleate, ammonium oleate, potassium soap from olive oil fatty acids, ammonium soap from olive oil fatty acids, potassium linoleate, potassium palmitate, ammonium palmitate, potassium stearate, ammonium stearate, gelatin, gum arabic, agar-agar, tallow, dextrin, casein, glycerol, glucose, sucrose, alcohol and rosin. Of these, gelatin, gum arabic, agar-agar, casein and dextrin were found unsuitable as they formed with water thick jellies which could not be emulsified with petrol. Glycerol, glucose, sucrose, alcohol, and rosin were found to have little or no emulsifying power. Consequently, only the remaining substances, the soaps, were investigated in detail.

The petrol used was standard Shell motor-spirit having a density of 0·745. The sodium oleate and ammonium oleate were commercial specimens. The other soaps were prepared from the acids by neutralising with alkali.

The emulsions were prepared as follows :—The stabiliser was dissolved or brought into fine suspension in a measured volume of water, by heat if necessary. The solution or suspension was mixed with a measured volume of petrol and passed many times through a Premier colloid mill (for a description of the mill, see China, *loc. cit.*). The volume of liquid for each charge was usually about 500 c.c. and the gap in the mill between the rotating and the stationary members through which the liquid was passed 0·003 inch. One emulsion was prepared from another by adding to it the requisite quantities of stabiliser, petrol and water and again passing many times through the mill. Preliminary experiments showed that the width of the gap and the number of times of passing through the mill did not affect the properties of the emulsion after about six passages. It was also found that an emulsion had the same properties whether it was prepared directly from petrol and water, or by diluting or concentrating a previous emulsion. The emulsions were milk-white and viscous compared with petrol or water. In some cases they had the consistency of butter. Petrol in water emulsions were usually frothy.

The composition of an emulsion was found by shaking 25 c.c. in a measuring cylinder with an equal volume of 1 : 1 hydrochloric acid and reading the volumes of petrol and water after separation. The type of an emulsion was determined by the drop-dilution method first suggested by Pickering (*J.C.S.*, 1907, **91**, 2002). The indicator method (Robertson, *Kolloid-Z.*, 1910, **7**, 7) was found unsuitable, because in some cases the dye changed the type of the emulsions.

The emulsions were stored in bottles and the time noted at which the formation of a distinct clear layer could be observed. Separation took place in three ways, into (*a*) petrol and water, (*b*) petrol and emulsion, and (*c*) water and emulsion. The first occurred usually with the less stable emulsions of either type, the second with emulsions of water in petrol and the third with those of petrol in water. In the last two cases, separation proceeded slowly for days or even weeks, but after about one month it ceased, and the remaining emulsion was evidently of a very stable type.

The composition of several such stable emulsions was examined when ammonium oleate was used as a stabiliser, and although no exact relation could be deduced, it appeared that there was a tendency for the emulsion to assume a definite composition depending upon the amount of stabiliser present. Thus the 1 per cent. ammonium oleate emulsions mentioned in Table II gave, on separation, emulsions with 28 to 32 per cent. of petrol containing 2·2 per cent. of stabiliser. Two figures for an initial concentration of 2 per cent. stabiliser were 46 and 39 per cent. of petrol with 3·5 and 3·7 per cent. of stabiliser; and one value for the 5 per cent. of stabiliser was 56 per cent. of petrol. Similar results were obtained by Pickering (*loc. cit.*) working with emulsions of a mineral oil in 1 per cent. soap solution. For this concentration he found that the final residual stable emulsion which he calls 'cream' contained about 80 per cent. of oil, irrespective of the amount of oil in the original emulsion.

The approximate hydrogen-ion concentration of each emulsion was found by adding a few drops of B.D.H. universal indicator and noting the colour. P_H for all the emulsions was found to lie between 10·5 and 8·0, but there was no definite relation between its value and the other properties of the emulsion.

Drop-Number Measurements.—As one of the most important factors in the emulsifying action of soaps is the lowering of the interfacial tension between the two liquids to be emulsified, it was considered desirable to make measurements of the interfacial tension between petrol and the soap solutions used for emulsification. For this purpose the 'drop-number' method was employed, absolute values of the interfacial tension not being required, and the values given being sufficiently accurate, particularly as the solutions were all similar.

The drop-pipette (Donnan, *Z. physikal. Chem.*, 1899, **31**, 42; Lewis, *Phil. Mag.*, 1908, **15**, 499) used for the measurements had a capacity of about 5 c.c. and its curved up tip was ground flat. The drops were allowed to rise through the soap solution at intervals of about 5 seconds. The maximum variation recorded between duplicate experiments was 4 per cent. Each determination was repeated several times and the mean value taken as the drop-number. The temperature of the solutions varied from 26° to 29° and was not regulated more closely, as small variations of temperature have only very slight influence on the drop-number (Clayton, *Trans. Faraday Soc.*, 1921, **16**, appendix, 24; *Emulsions and their Technical Treatment*, 36). Three strengths of solution were used in each case, 2, 1 and 0·5 per cent. The drop-numbers could not be found for ammonium palmitate, potassium stearate and ammonium stearate as the solutions formed a thick jelly on cooling. The results are shown in Table I.

TABLE I.

Drop-Numbers of Petrol in Soap Solutions.

Stabiliser	Mean Drop-Number		
	2 per cent.	1 per cent.	0·5 per cent.
Potassium palmitate	390	365	332
Potassium linoleate	342	296	241
Sodium oleate	249	226	201
Potassium oleate	251	215	176
Potassium soap from olive oil ...	210	192	156
Ammonium soap from olive oil ...	90	77	67
Ammonium oleate	Not found	70	60

Drop-Number of Petrol and Water. 38.

The results of some emulsification experiments are shown in Table II. The time for separation is the period which elapsed (in minutes, hours or days) before two distinct layers could be observed. The time for equilibrium to be established was much longer.

TABLE II.

Composition, Type and Stability of Petrol-water Emulsions.

Stabiliser	Stabiliser per cent	Petrol per cent.	Disperse phase	Time for separation	Stabiliser	Stabiliser per cent.	Petrol per cent.	Disperse phase	Time for separation
Sodium oleate	5	73	w.	5 m.	Potassium oleate	1	70	w.	10 m.
		69	w.	...			70	p.	10 m.
		54	p.	2 d.			50	p.	1 d.
	2	65	p.	2 d.			48	p.	1 h.
		62	p.	3 d.			44	p.	30 m.
		53	p.	3 d.			39	p.	1 h.
		47	p.	3 h.			33	p.	15 m.
		43	p.	2 d.					
		42	p.	12 h.					
		33	p.	15 m.					
Ammonium oleate	5	79	w.	30 m.	Potassium linoleate	2	68	w.	0
		67	w.	6 h.			64	p.	1 d.
		60	w.	3 d.			60	w.	5 m.
	2	90	w.	5 m.			59	p.	1 d.
		69	w.	2 d.			50	p.	1 d.
		67	w.	1 d.			38	p.	1 h.
		44	w.	25 d.			29	p.	1 h.
		27	p.	stable			20	p	30 m.
		26	w.	stable		1	68	w.	0
		15	p.	stable			58	p.	1 d.
	1	90	w.	0			48	p.	1 d.
		72	w.	1 h.			41	p.	1 d.
		69	w.	1 h.			30	p.	1 d.
		67	w.	1 d.			21	p.	1 d.
		67	w.	5 h.			13	p.	1 d.
		44	w.	4 h.					
		22	p.	1 d.					
Ammonium soap from olive oil fatty acids	4	70	w.	1 h.	Potassium soap from olive oil fatty acids	1·8	79	w.	30 m.
		58	w.	stable			75	w.	5 m.
		48	w.	stable			74	w.	5 m.
		40	w.	stable			68	w.	15 m.
		33	p.	stable			67	w.	15 m.
		27	p.	stable			64	p.	25 d.
		20	p.	stable			52	p.	4 d.
	2	70	w.	2 h.			50	p.	1 d.
		60	w.	1 d.			41	p.	4 d.
		54	w.	2 h.			39	p.	1 h.
		40	w.	2 d.			35	p.	3 d.
		30	p.	4 d.			29	p.	1 d.
							18	p.	1 d.
							11	p.	1 d.

TABLE II.

(*Composition, Type and Stability of Petrol-water Emulsions.*—contd.)

Stabiliser	Stabiliser per cent.	Petrol per cent.	Disperse phase	Time for separation	Stabiliser	Stabiliser per cent.	Petrol per cent.	Disperse phase	Time for separation
Ammonium palmitate	2	65	w.	30 m.	Potassium palmitate	2	72	w.	10 m.
		62	w.	1 d.			49	w.	2 h.
		49	w.	3 h.			39	w.	2 h.
		40	w.	stable			32	w.	2 h.
		39	w.	1 d.			25	p.	1 d.
		9	p.	0			18	p.	5 m.
	1	67	w.	30 m.		1	69	w.	15 m.
		61	w.	1 h.			61	w.	15 m.
		50	w.	1 h.			53	w.	1 h.
		38	w.	1 d.			52	p.	1 d.
		30	w	stable			48	p.	1 d.
		18	p.	3 d.			40	w.	1·5 h.
		9	p.	3 d.			30	w.	5 m.
Ammonium stearate	2	68	w.	15 m.	Potassium stearate	2	53	w.	1 h.
		60	w.	stable			38	p.	30 m.
		60	w.	1 d.			30	p.	30 m.
		48	w.	1 d.					
		33	p.	stable		1	70	w.	1 d.
							65	w	30 m.
	1	67	w.	30 m.			64	w.	2 h.
		59	w.	2 d.			52	w.	1 h.
		49	w.	2 h.			50	p.	1 d.
		40	w.	3 d.			30	p.	stable
		30	p.	5 d.					
		28	p.	stable		0·5	33	w.	1 d.
		16	p.	stable					

All the emulsions mentioned in Table II were so made that the proportion of stabiliser was calculated for the whole emulsion ; thus in a series of emulsions containing say, 2 per cent. of stabiliser, owing to the insolubility of the stabiliser in petrol, the amount dissolved in a given volume of the aqueous phase increased as the proportion of petrol in the emulsion increased. For the sake of comparison, a second series of emulsions was made with petrol and a 5 per cent. solution of sodium oleate so that the proportion of stabiliser in the aqueous phase was constant. The nature of these emulsions is shown in Table III. The symbol W⟶P indicates that the emulsions were originally of the water in petrol type and changed type on shaking or standing. The figures for stability and viscosity were obtained subsequently to the change.

Viscosity Measurements.—Determinations of viscosity were made for these sodium oleate emulsions both immediately on formation and after various intervals, to determine if possible the changes which took place on standing and to examine the relation between the composition of the emulsions and their viscosity. The results, as might be expected, were irregular, particularly in the case of the less stable emulsions. Measurements were made at 30° in an Ostwald viscometer and it was possible in most cases to obtain concordant values for consecutive readings. On standing, however, many of the emulsions showed signs of separation and had to be shaken before another series of measurements could be made; the viscosity in these circumstances depended to some extent upon the amount of shaking. In spite of this it was possible to obtain average results which showed that, in general, all the emulsions decreased in viscosity on standing, presumably owing to gradual aggregation of the dispersed particles.

Table III gives the viscosities of the different emulsions measured as soon as possible after preparation. Fig. I shows the same values plotted against concentration of petrol and also the figures obtained after the emulsions had stood until the viscosity became approximately constant, usually after about 8 days. Fig. II gives a few of the more regular results obtained for the fall in viscosity. The 52 and 53 per cent. emulsions showed signs of separation after 0·5 and 1·5 hours respectively; consequently all measurements subsequent to the first had to be made after shaking. The two most concentrated petrol in water emulsions containing 69 and 70 per cent. of petrol were fairly stable and extremely viscous. The time of flow for the former was 1,234 seconds falling to 654 seconds in 2 days, during which period no separation had taken place. After 8 days there was separation, and the time of flow after shaking was 352 seconds. The initial time for the second sample was 600 seconds, separation started in 1·5 hours and the time after 26 days was only 218 seconds. The proportional fall was consequently much greater in these cases than it was for less concentrated solutions.

One of the 65 per cent. emulsions gave interesting results being initially of the water in petrol type. The effect of running through the viscometer was to change its type and during the process the viscosity rose to a high value and then fell as shown in the curve marked 65 p.c. in Fig. II. The time of flow then remained approximately constant at 230 seconds for several hours. Next day some separation had taken place and on shaking, the time of flow rose to 480 seconds and remained of this order of magnitude. The portion of the sample not used for viscosity measurements did not change its type until shaken. Two other emulsions were initially of the water in petrol type and exhibited reversal on shaking, but the original emulsions were too unstable to allow their viscosity to be measured.

TABLE III.

Emulsions of Petrol with 5 per cent. Sodium Oleate Solution.

Percentage of petrol	Type	Time for separation	Viscosity (5 p. c. Na—Oleate - 1)
78	W	0	...
72	W	5 m.	(2·30)
70	W	0	...
70	W—>P	30 m.	21·0
69	P	2 d.	43·0
67	W	10 m.	(1 58)
65	W	0	...
65	W—>P	30 m.	17·9
65	W	10 m.	(1·78)
62	P	2 h.	13·0
60	P	1 d	15·2
60	W	5 m.	...
59	P	1 d.	13·05
55	P	1 d.	19·25
53	W—>P	...	5·22
53	P	1 5 h.	5·41
53	P	1·5 h.	7·32
52	P	30 m.	6·08
52	P	1·5 h.	5·86
50	P	5 m.	...
48	P	1·5 h.	5·35
48	P	1 h.	5·20
45	P	2 h.	5·65
45	P	15 m.	4 32
40	P	5 m.	...
40	P	15 m.	2·04
33	P	0	...
20	P	0	...

DISCUSSION OF RESULTS.

A brief reference to Tables II and III will show that consistent results for the stability of an emulsion are most difficult to obtain, but nevertheless it is possible to form some idea of the relation between composition and stability by examining the general trend of the figures. The emulsions themselves varied from a thin fluid which separated into its constituents in a few seconds to a butter-like mass which was apparently indefinitely stable. In some cases the stability appeared to be accidental, emulsions of the same composition prepared in the same way exhibiting widely different properties. A striking instance of this was observed in the case of two emulsions containing 60 per cent. of petrol with 2 per cent. of ammonium stearate ; one of these separated within 24 hours and the other is still stable at the time of writing, about two years later. Similar anomalies have been observed by other workers in an even more accentuated manner probably owing to the fact that most of the emulsions previously studied were produced by shaking, stirring or grinding in a mortar, conditions more difficult to reproduce than those employed by us. For example, Seifrez (*J. Physical Chem.*, 1925, **29**, 839) working with petroleum emulsions seems to have experienced so much difficulty that he remarked, 'It is such idiosyncrasies of emulsions which try the patience of the investigator.'

As already mentioned, emulsions of two types have been obtained with every stabiliser used, the type depending upon the relative quantity of the two constituents. A fairly definite inversion point exists for each stabiliser, emulsions containing more petrol than the quantity corresponding with the inversion point being of the water in petrol type and *vice versa*. In the neighbourhood of the inversion point, emulsions of both types having the same composition could be obtained. There is a marked difference between the ammonium soaps and the other stabilisers, the reason for which is not apparent. With the former the inversion point is in the neighbourhood of 30 per cent. of petrol ; for the sodium and potassium salts of unsaturated acids it is at about 65 per cent., for potassium stearate the figure is 50 per cent., and for potassium palmitate 30 per cent. In the last case, however, petrol in water emulsions have been obtained with as much as 52 per cent. of petrol and one emulsion with 0·5 per cent. of potassium stearate was of the water in petrol type although containing only 33 per cent. of petrol. The inversion point did not appear to depend on the concentration of the stabiliser.

In general, the ammonium soaps gave more stable emulsions than the other stabilisers particularly as regards water in petrol emulsions. No emulsion of this type stable for an hour could be produced with the sodium or potassium salts of unsaturated acids, but more stable emulsions were obtained with potassium palmitate and stearate, probably because solutions of these have a tendency to set in a jelly. Except in these two cases the degree of unsaturation of the acid appeared to have little effect on stability.

It is clear from the above that the type of emulsion does not depend on the nature of the stabiliser, but on the relative proportion of the constituents. This is not in agreement with the adsorption film theory of Bancroft (*J. Physical Chem.*, 1913, **17**, 514) according to which a soap with a univalent cation should give only oil in water emulsions. The oriented wedge theory (cf. Finkle, Draper and Hildebrand, *J. Amer. Chem. Soc.*, 1923, **45**, 2780) also indicates that only one type of emulsion should be obtained and thus cannot satisfy the requirements of the present experiments. Clayton (*Emulsions and their Technical Treatment*, 1928, 51) suggests that these general theories may be modified by factors depending on the relative volumes of the solution, so that water in oil emulsions could be obtained with soap stabilisers if the original mixture contained a large excess of oil. This would indicate that the water in petrol emulsions were less stable than those of the reverse type, as found for the sodium and potassium soaps; but it does not account for the ammonium soaps, which in several cases gave equally stable emulsions of both types with the same volume composition, nor does it explain the existence of water in petrol emulsions with potassium palmitate and stearate containing only 30–40 per cent. of petrol.

Within the last few years several authors have described the preparation of emulsions of both types with the same stabiliser, among others Joshi (*Trans. Faraday Soc.*, 1925, **20**, 512) and Seifrez (*loc. cit.*). The former used olive, castor and paraffin oils with soap stabilisers; the latter, petroleum distillates of various densities stabilised with casein. In this case the type of emulsion depended upon the density of the oil. It is thus evident that the simple theories so far put forward are inadequate to explain observed facts and that the nature of an emulsion depends upon a number of complex factors which require a great deal more experimental work for their elucidation than has yet been conducted.

If the results of Table II for the stability of the emulsions be compared with the drop-numbers for the different stabilisers it appears that the most stable emulsions are obtained with the stabilisers which have the lowest drop-numbers, i.e., ammonium oleate and the ammonium soap from olive oil fatty acids. This is the reverse of what might be expected since it is usually considered that emulsification takes place most readily when the interfacial tension is lowest, i.e., when the drop-number is largest. On the other hand it is possible that, once the emulsion is formed, a high interfacial tension tends to prevent aggregation of the globules and thus conduces to stability.

The general relation between the composition of the emulsions and their viscosity has already been mentioned. In the case of petrol in water emulsions the viscosity rises very rapidly with increase in the quantity of disperse phase and it seemed possible that the values might agree with those calculated by Hatschek's equation (*Trans. Faraday Soc.*, 1913, **9**, 80),

$$n = A^{\frac{1}{3}}/(A^{\frac{1}{3}} - 1)$$

where n is the viscosity of the emulsion relative to that of the continuous phase and A is the ratio of the total volume of the emulsion to the volume of the dispersed phase. The calculated values are shown in Fig. I and it will be seen that they are much lower than the experimental figures in the region of high volume concentration to which the equation is considered particularly applicable.

The equation of Arrhenius (*Z. physical Chem.*, 1887, **I**, 285), $\log n = K/A$ with the above notation, contains an arbitrary constant K and hence can be fitted to the experimental values with some semblance of accuracy but an inspection of the curve in Fig. I for which K has the value 0·0186, p being the percentage of petrol and equal to $100/A$, shows that the equation cannot be regarded as representing the true nature of the results.

Over the stable range, the results for the initial viscosities may be represented by the parabolic equation

$$3n = 103 - 4{\cdot}83\,p + 0{\cdot}62\,p^2$$

but this expression has naturally no physical significance. In order to investigate the change in viscosity with concentration and represent the relation between these two factors by an equation, many results more concordant than those obtained in the present experiments are required and these are, unfortunately, extremely difficult to secure.

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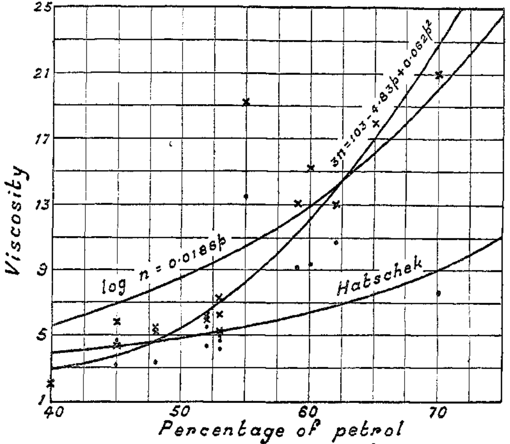
Fig. I



Crosses-initial viscosity : dots-final viscosity

Fig. II