95. *The Internal Phase and the Emulsifier as Factors determining the Viscosity of Oil-in-water Emulsions.*

By B. A. Toms.

An investigation of the influences of the internal phase and the emulsifier upon the viscosity of an emulsion has been made. Series of oil-in-water emulsions (all identical with one another as regards phase-ratio, external phase, type and concentration of emulsifier) were prepared with a variety of organic liquids as internal phases and a number of univalent soaps as stabilisers.

The viscosities of the emulsions were measured at 20°, and from the results obtained the active volume of the internal phase in each was calculated by means of Hatschek's formula : $\phi = (\eta' - \eta_e)^3/\eta'^3$.

An explanation, attributing the observed variations in viscosity to interactions between oil, soap, and water, is advanced.

The introduction of a numerical correction factor in the Hatschek equation is suggested.

Factors controlling the viscosity of a concentrated emulsion may be summarised under three heads : (1) the nature, amount, and degree of dispersion of the internal phase;

(2) the nature, amount, and phase-distribution of the stabilising agent; (3) the nature and amount of the external phase. In addition, account must also be taken of interactions between the constituents of the system. Although the known influence of paraffin-chain salts upon the mutual solubilities of organic substances and water (cf. Pickering, J., 1907, **91**, 2001; 1917, **111**, 86; Lester Smith, *J. Physical Chem.*, 1932, **36**, 1401, 1672, 2455; Lawrence, *Trans. Faraday Soc.*, 1937, **33**, 325) renders the possibility of such interaction specially important in emulsions of the oil–soap–water class, yet the relevant literature contains no record of any thorough investigation of this aspect of their viscosity. In these circumstances it was decided to study emulsion viscosity under conditions where, in particular, the influences of the internal phase and the emulsifying agent would be emphasised.

EXPERIMENTAL.

A. (1) *Emulsions.*—Attention was confined to oil-in-water systems of 50/50 phase-volume ratio. Arranged in order of increasing density, the oils used as internal phase were: (1) *n*-hexane, (2) *cyclo*hexane, (3) xylene, (4) toluene, (5) decalin, (6) benzene, (7) tetralin, (8) aniline, (9) chlorobenzene, (10) nitrobenzene, (11) chloroform. For stabilisation of the emulsions a series of ten univalent soaps, comprising the sodium and potassium salts of lauric, myristic, palmitic, stearic, and oleic acids, was selected. Since the characteristics of emulsions of different oils in water stabilised by a single agent, and those of a single oil stabilised by different agents, were found to vary widely, some difficulty was experienced in choosing an emulsifier concentration which would permit of the maximum number of reliable viscosity measurements being obtained. Eventually it was decided to employ two concentrations of each soap (0·001 and 0·002 mol. per 100 c.c. of emulsion) so that, in addition to studying the factors already specified, some check might be kept upon the influence of emulsifier concentration on viscosity.

(2) *Preparation of Emulsions.*—100 C.c. of each emulsion were prepared in a tall, glass-stoppered bottle of 250 c.c. capacity, and 50 c.c. of aqueous solution containing either 0·001 or 0·002 mol. of sodium or potassium hydroxide were measured into the bottle, followed by 50 c.c. of organic liquid containing the molar equivalent of a fatty acid.

Emulsification was carried out by hand-shaking, Briggs's "intermittent" technique (*J. Physical Chem.*, 1920, **24**, 120) being used with a "rest-interval" of 30 secs. In all cases not more than 6 shakes were needed to effect complete dispersal of the internal phase. Immediately after preparation, each emulsion was homogenised by passing it five times in quick succession through a hand-operated cream-making machine ("Pentecreme" pattern). It was then set aside for 24 hours before examination.

(3) *Description of the Emulsions.*—Wide variations in characteristics were observed amongst the emulsions. Of those suited to the purpose of the present investigation all except those stabilised by oleates creamed more or less rapidly, the rate of sedimentation decreasing in the following order of soaps: laurates, myristates, palmitates, stearates. Emulsions containing salts of oleic acid creamed slowly and were very stable. In general, of the emulsions stabilised by soaps of saturated fatty acids, those emulsified by laurates broke down most rapidly. Except in a few cases, enhanced stability, due to increasing the soap concentration from 0·001 to 0·002 mol. per 100 c.c. of emulsion, was not apparent during the 7 days following homogenisation.

With three exceptions, emulsions which could not be used were rejected because in the 24 hours following homogenisation "clotting" took place, the systems changing to a stiff, or semi-stiff, blancmange composed of groups of globules of disperse phase tightly packed together and embedded in soap gel. The tendency to clot was clearly determined by the nature of the internal phase and that of the soap. The character of these clotted emulsions altered notably as they aged: after 2 weeks' standing, complete breakdown had occurred in most cases, leaving a plug of solvated soap floating in portions of the free internal and external phases.

(4) *Measurement of Emulsion Viscosity.*—Despite some doubt as to the optimum conditions and the most suitable instrument for the measurement of emulsion viscosity, it is generally conceded that comparison of the viscosities of emulsions of closely similar composition may reasonably be attempted. Since, in the present investigation, the emulsions under consideration differed from one another only as regards the natures of the internal phase and emulsifying agent, it was decided to use a U-tube viscometer. All measurements were made at 20°, and 10 separate determinations of the time of flow of each emulsion were carried out and averaged.

The viscosities, expressed in centipoises, of all the emulsions examined are recorded in Table I, the internal phase in each case being designated by the number assigned to it on p. 543. The sub-headings (1) and (2), under which the results for each soap are set forth, correspond respectively to the two emulsifier concentrations used, *viz.*, 0·001 and 0·002 mol. of soap per 100 c.c. of emulsion.

TABLE I.

Ref. no. of internal phase.	η (centipoises).									
	Laurate.		Myristate.		Palmitate.		Stearate.		Oleate.	
	(1).	(2).	(1).	(2).	(1).	(2).	(1).	(2).	(1).	(2).
	Emulsions stabilised by sodium soaps.									
(1)	7·65	7·65	7·56	—(s)	—(s)	—(s)	—(s)	—(s)	6·99	6·92
(2)	7·64	8·01	8·09	—(s)	—(s)	—(s)	—(s)	—(s)	6·89	7·26
(3)	8·12	8·29	8·55	—(s)	—(s)	—(s)	—(s)	—(s)	7·43	7·27
(4)	7·85	8·41	8·44	—(s)	—(s)	—(s)	—(s)	—(s)	6·51	6·70
(5)	8·40	8·44	8·40	—(s)	—(s)	—(s)	—(s)	—(s)	8·26	8·52
(6)	7·35	7·77	—(s)	—(s)	—(s)	—(s)	—(s)	—(s)	6·22	6·46
(7)	8·46	8·69	8·66	9·19	—(s)	—(s)	—(s)	—(s)	8·48	8·64
(8)	7·64	7·31	8·89	8·28	—(s)	—(s)	—(s)	—(s)	9·72	10·5
(9)	8·01	8·46	8·52	—(s)	—(s)	—(s)	—(s)	—(s)	6·62	6·73
(10)	—(b)	7·78	—(s)	—(s)	—(s)	—(s)	—(s)	—(s)	7·96	7·96
(11)	—(b)	7·66	7·61	7·54	—(s)	—(s)	—(s)	—(s)	6·05	6·36
	Emulsions stabilised by potassium soaps.									
(1)	7·75	7·60	7·60	7·89	8·20	7·75	6·48	—(s)	6·94	6·90
(2)	7·64	7·90	7·92	8·33	8·12	8·16	—(c)	—(s)	6·87	7·03
(3)	8·00	8·25	8·31	8·84	8·33	8·49	7·29	8·37	7·27	7·23
(4)	7·99	8·14	8·02	8·60	7·99	8·36	6·86	7·93	6·70	6·92
(5)	8·56	8·64	8·34	8·82	8·96	9·22	8·72	—(c)	8·38	8·44
(6)	7·43	7·61	7·15	7·59	7·55	7·97	7·29	7·59	6·18	6·48
(7)	8·50	8·89	8·62	9·50	8·81	9·19	7·60	—(s)	8·37	8·77
(8)	7·27	6·65	8·73	8·24	—(c)	—(s)	—(c)	—(s)	9·32	10·4
(9)	7·94	8·43	8·39	8·81	8·32	8·63	7·23	8·14	6·58	6·87
(10)	—(b)	8·36	8·01	8·83	8·90	9·81	—(c)	—(s)	8·10	8·29
(11)	7·02	7·48	7·40	7·35	6·83	7·15	6·70	7·27	6·18	6·6

(b) = Unstable emulsion which broke within 24 hours of homogenisation.
(c) = Emulsion contained clots of soap-gel.
(s) = Emulsion stiffened, becoming semi-solid within 24 hours of homogenisation.

B. Before Hatschek's formula could be utilised (see p. 546), knowledge of the coefficients of viscosity of the several external phases employed in the present investigation had to be obtained. The viscosities of the appropriate 0·02M- and 0·04M-aqueous soap solutions were therefore measured at 20°, a Höppler viscometer being used, and each solution being allowed to age for 24 hours before examination.

Of the soap solutions prepared, only those of the laurates and oleates of sodium and potassium and potassium myristate were suited to viscometry; the others contained lumps of curdy material. The values of η, in centipoises, for the solutions examined are recorded in Table II.

The values of h (see p. 546), derived from data in Table I by substituting the appropriate values of η' and η_e in Hatschek's equation, are set forth in Table III, in which the headings (1) and (2) have the same significance as before.

TABLE II.

Viscosities of aqueous soap solutions at 20°.

	η (centipoises).	
Soap.	0·02M.	0·04M.
Sodium laurate	1·03	1·06
Potassium laurate	1·03	1·08
Potassium myristate	1·04	1·10
Sodium oleate	1·09	1·14
Potassium oleate	1·08	1·15

TABLE III.

Ref. no. of internal phase.	*h.*									
	Sodium soaps.				Potassium soaps.					
	Laurate.		Oleate.		Laurate.		Myristate.		Oleate.	
	(1).	(2).	(1).	(2).	(1).	(2).	(1).	(2).	(1).	(2).
(1)	1·30	1·28	1·20	1·16	1·30	1·26	1·29	1·27	1·20	1·16
(2)	1·30	1·31	1·19	1·20	1·30	1·29	1·31	1·31	1·20	1·17
(3)	1·33	1·33	1·24	1·20	1·32	1·31	1·34	1·34	1·24	1·19
(4)	1·31	1·34	1·15	1·14	1·32	1·30	1·32	1·33	1·18	1·16
(5)	1·35	1·34	1·30	1·30	1·36	1·34	1·34	1·34	1·32	1·29
(7)	1·27	1·29	1·12	1·12	1·28	1·26	1·25	1·25	1·12	1·11
(7)	1·35	1·35	1·32	1·31	1·36	1·36	1·36	1·40	1·32	1·31
(8)	1·30	1·25	1·40	1·42	1·26	1·18	1·37	1·30	1·38	1·41
(9)	1·32	1·34	1·16	1·15	1·32	1·33	1·34	1·34	1·17	1·15
(10)	—	1·29	1·29	1·26	—	1·32	1·32	1·34	1·30	1·28
(11)	—	1·28	1·10	1·11	1·24	1·25	1·27	1·23	1·12	1·13

DISCUSSION.

The data recorded in Table I are discussed under three heads.

A. (a) *Influence of the nature of the soap.* The substitution of potassium for sodium as basic radical produces no significant change in the viscosities of emulsions stabilised by laurates and oleates, but notable changes occur when the myristates, palmitates, or stearates are used. In these cases most of the emulsions stabilised by sodium soaps were semi-solid, whereas the majority of those emulsified with the potassium soaps were quite fluid. These differences may be ascribed to the fact that aqueous solutions of sodium soaps acquire a gel structure at much lower concentrations than their potassium counterparts. Also, since the laurates and oleates of both metals are more soluble than their myristates, palmitates, or stearates, gelation of aqueous solutions of the former does not occur at the low concentrations in which it is observed with the latter soaps.

In general, emulsions stabilised by oleates are less viscous than the others, and of the emulsions containing soaps of saturated acids, those emulsified by the laurates are the most fluid. Next in order of increasing viscosity come the emulsions prepared with the myristates, but little can be said about the relative viscosities of emulsions stabilised by palmitates and stearates though it would appear that these salts of potassium give emulsions with viscosities little different from those containing potassium myristate.

(b) *Influence of the internal phase.* The viscosity of an emulsion is clearly influenced by the nature of its internal phase. Amongst the emulsions stabilised by a particular soap wide variation in viscosity is apparent, but if the results grouped under each soap are arranged in order of magnitude it is found that in no two cases is precisely the same sequence obtained. Hence the effect of a given oil is not specific but depends, in part, upon the nature and amount of the emulsifier. For instance, of the emulsions stabilised with 0·002 mol. of potassium laurate, that containing aniline as disperse phase is the least viscous, but the aniline emulsion has the greatest viscosity of those emulsified with either 0·001 or 0·002 mol. of potassium oleate.

The nature of these findings suggests that the internal phase probably exerts its influence on the viscosity of an emulsion by interacting with the film of emulsifier surrounding the globules.

(c) *Effect of varying the amount of emulsifier.* Increase of the soap concentration from 0·001 to 0·002 mol. per 100 c.c. of emulsion produces in most cases an increase in viscosity, the magnitude of which varies with the nature of both the internal phase and the soap. In a few cases a decrease in viscosity was found.

Some elucidation of this fact may be achieved by correlation with results obtained by Wilson and Parke (*Quart. J. Pharm.*, 1936, **9**, 188), who studied the effect of increasing the concentration of sodium oleate on the viscosity of a 70/30 benzene-in-water emulsion stabilised by that soap. It was found that the viscosity passed through a minimum when approximately 0·25 g. of soap was present in 100 c.c. of emulsion. Now, 0·25 g. of sodium oleate per 30 c.c. of aqueous phase corresponds to 0·42 g. (or *ca.* 0·0013 mol.)

per 50 c.c. of continuous phase. Thus, despite the disparity in phase-ratio between the emulsions studied by Wilson and Parke and those used in the present investigation, the physicochemical condition of the emulsifier is almost the same in both series. In these circumstances some comparison between their results and those described above seems possible.

It would appear that the viscosity of any one of the emulsions used in the present investigation is in the near neighbourhood of the minimum in the appropriate viscosity–concentration curve. In the majority of cases, where alteration of the soap concentration from 0·001 to 0·002 mol. per 100 c.c. of emulsion produces an *increase* in viscosity, it is evident that the emulsion of minimum viscosity in each of the several series must contain less than 0·002 (and, perhaps, less than 0·001) mol. of soap. Where a *decrease* in emulsion viscosity occurs on doubling the emulsifier concentration it is clear that the minimum in the appropriate curve must occur with more than 0·002 mol. of soap per 100 c.c. of emulsion.

On this basis two general conclusions may be derived from the results in Table I: (i) in emulsions of a particular oil in water stabilised by different soaps, the location of the minimum in the curve connecting emulsion viscosity and concentration of emulsifier varies with the nature of the soap; (ii) in emulsions stabilised by a single soap, but having different internal phases, the soap concentration producing the least viscous emulsion is different for different oils.

Further elucidation of these findings may be achieved by using an equation (Hatschek, *Kolloid-Z.*, 1911, **8**, 34) connecting the viscosity of an emulsion with that of its external phase and the volume-ratio of the internal phase, *viz.*, $\phi = (\eta' - \eta_e)^3/\eta'^3$ where η' and η_e are the coefficients of viscosity of the emulsion and of the external phase, respectively, and ϕ = (Volume of globules)/(Total volume of emulsion). The accuracy of this formula, which implies that the internal phase influences the viscosity of an emulsion by virtue of its volume concentration alone, was investigated by Sibree (*Trans. Faraday Soc.*, 1930, **26**, 26; 1931, **27**, 161), who found that if the volume ratio of the globules in an emulsion be calculated from the above formula it is almost always greater than its actual value, provided that this latter is at least 0·5; in the emulsions he examined, the ratio of calculated to actual volume ratio was usually equal to *ca.* 1·3 : 1. Concerning this ratio, which he designated by *h*, Sibree remarked: "If we assume the formula (*i.e.*, Hatschek's) to be correct, these figures indicate that the active volume of the disperse phase is throughout about 30 per cent. greater than that of the paraffin itself." The general implication of Sibree's findings, *viz.*, that the viscosity of an emulsion is dependent upon the *active* bulk of the internal phase, is clearly of considerable value for, by determining *h*, a measure of such interaction as may have occurred amongst the components of an emulsion is obtained.

B. Despite the similarity in the recorded values of *h* (in all cases it is very close to 1·3, as found by Sibree who worked with emulsions of a different character), certain significant variations are noticeable, suggesting that differences in the active volume of the internal phase exist among the emulsions examined.

(a) *Influence of the emulsifier on the value of* h. Variations due to the substitution of potassium for sodium as basic radical are without significance, being of the order of 1% in most cases; but alteration of the fatty acid radical of the soap produces notable change, of the order of 10—20%, in the value of *h* for a particular oil–water system: whereas soaps of the saturated acids (lauric and myristic) give emulsions for which the mean value of *h* is close to 1·3, yet those of oleic acid seem to stabilise emulsions in which the active volume of the internal phase is rather smaller, *h* approximating more nearly to 1·2.

Increase of the concentration of emulsifier from 0·001 to 0·002 mol. per 100 c.c. of emulsion appears to cause little change in the active volume of the disperse phase.

(b) *Influence of the internal phase on the value of* h. The data show very clearly that notable changes in the active volume of the disperse phase stabilised by a particular soap result from alteration of the organic liquid emulsified.

It may therefore be concluded that the active volume of the internal phase in an oil-in-water emulsion depends upon (i) the nature of the emulsifying agent (where water-soluble soaps are used, it depends on the nature of the fatty acid radical but is independent of the basic radical), and (ii) the nature of the oil used as internal phase.

A partial explanation of these findings can be based upon the mutual solubilities of organic liquids, soaps, and water. It is now abundantly clear (cf. Wellman and Tartar, *J. Physical Chem.*, 1930, **34**, 379; Lester Smith, *loc. cit.*) that in the system organic liquid–soap–water profound changes in both the physicochemical condition and phase distribution of each component may be brought about by suitable means. From the standpoint of the present investigation the fate of the soap is primarily of interest since a film of it, adsorbed at the liquid–liquid interface, determines the main characteristics of an emulsion.

In all emulsions used in the present investigation the external phase consisted of an aqueous soap solution either 0·02M or 0·04M in concentration. According to McBain and Jenkins (J., 1922, **121**, 2325) and Hartley (" Aqueous Solutions of Paraffin-chain Salts," Paris, 1936), solutions of these concentrations contain colloidal material. In the case of lower soaps, in the more dilute solution, much of this is probably composed of acid soap produced by hydrolysis, but with the higher soaps, formation of both neutral colloid and ionic micelles has commenced at these concentrations.

When globules of an organic liquid are distributed throughout such solutions, adsorption of soap at the liquid–liquid interface occurs and a film is formed. Subsequently, one or more of the following actions may take place: (1) Part of the soap, in the form of re-orientated micelles, may cross the interface and enter the oil globules, there forming a gel of solvated soap (Wellman and Tartar, *loc. cit.*); this, coupled with such change as it may cause in the packing, and hence the rigidity, of the interfacial film, is likely to alter the deformability, if not the actual bulk, of the globules. (2) Alteration of the mutual dispersion of the internal and external phases, caused by the soap (cf. Lester Smith, *loc. cit.*), may change the phase-volume ratio of the system. (3) Transfer of organic liquid across the interface may result in peptisation of the soap micelles in the aqueous external phase (Lawrence, *loc. cit.*). Any one of these effects will in some measure control the viscosity of the system (cf. Schulman and Cockbain, *Trans. Faraday Soc.*, 1940, **36**, 651; Richardson, *Kolloid-Z.*, 1933, **65**, 32; Lawrence, *Proc. Roy. Soc.*, 1935, *A*, **148**, 59), and it is thus clear, from the results now obtained, that the natures of the internal phase and of the emulsifier must be regarded as factors of importance in determining the viscosity of an emulsion. The data recorded above, coupled with those of Sibree (*loc. cit.*), indicate that the accuracy of Hatschek's equation for the viscosity of an emulsion will be enhanced by the introduction of a numerical correction factor, giving

$$\phi = 1{\cdot}3\ (\text{Volume of globules})/(\text{Total volume of emulsion}).$$

THE QUEEN'S UNIVERSITY OF BELFAST.

[*Received, May 22nd*, 1941.]