CCCLVII.—*The Effect of Electrolytes upon the Viscosity of Solutions of Sodium Palmitate.*

By James William McBain, Herbert James Willavoys, and Harold Heighington.

Many investigators have studied the viscosity of soap solutions and the effect of electrolytes thereon (Mayer, Schaeffer, and Terroine, *Compt. rend.*, 1908, **146**, 484; Bottazzi and Victoroff, *Atti R. Accad. Lincei*, 1910, (v), **19**, i, 659; Farrow, J., 1912, **101**, 354; Goldschmidt and Weissmann, *Z. Elektrochem.*, 1912, **18**, 380; *Koll. Z.*, 1913, **12**, 18; *Seifensieder Ztg.*, 1913, **40**, 263; Hatschek, *Koll. Z.*, 1913, **12**, 238; *Trans. Faraday Soc.*, 1913, **9**, 80; Kurzmann, *Koll.-Chem. Beih.*, 1914, **5**, 427; Arndt and Schiff, *ibid.*, 1914, **6**, 201; Goldschmidt, *Seifensieder Ztg.*, 1914, **41**, 337; Fischer and Hooker, *Chem. Eng.*, 1919, **27**, 223; Clarke, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, **6**, No. 1, 1; King, *J. Soc. Chem. Ind.*, 1922, **41**, 147T; Bircumshaw, J., 1923, **123**, 91; Prasad, *J. Physical Chem.*, 1924, **28**, 636; Freundlich and Schalek, *Z. physikal. Chem.*, 1924, **108**, 153; Freundlich and Kores, *Koll. Z.*, 1925, **36**, 241; Jajnik and Malik, *ibid.*, p. 322; Hahne, *Z. deut. Oel-Fett Ind.*, 1925, **45**, 245, 263, 274, 289, 308), but their work has always been broken off in the region where the viscosity was rising rapidly with increasing concentration of added salt. It remained for Miss A. M. King, in a communication from Bristol University (*J. Soc. Chem. Ind.*, 1922, **41**, 147T), to discover the remarkable fact that further addition of salt produces a sharp maximum of viscosity, which thereafter falls rapidly with still further addition. The last effect continues right up to the limit of possible existence of the soap solution as a single homogeneous phase. The present paper gives further information with regard to this effect (see, *e.g.*, Fig. 1).

Solutions of sodium palmitate at 80° and 90° were chosen for study because of the large amount of other information already available, and also because their properties are independent of time at these high temperatures.

Once again it is shown that, if sufficient care is taken to control the factors involved, even such a property as the viscosity of soap solution is definite and reproducible. For example, we have taken the viscosity of a solution $0{\cdot}5N_w$ with respect to both sodium chloride and sodium palmitate at 81·0° as a point of reference. Miss King published the values for its absolute viscosity in c.g.s. units, $\eta = 10{\cdot}63$ and $10{\cdot}54$; one of us (H. J. W.) obtained 10·07, another (H. H.) 10·06, and Mr. H. Horwood 10·39, all with different specimens of pure sodium palmitate. In other series of experiments, the viscosity of the original soap solution was first taken, then successive amounts of pure electrolyte were added, thus giving a range of viscosity readings up to the limit of existence of isotropic soap solutions. Thereupon, the final solution was diluted with successive portions of the original soap solution, retracing the curve, and yielding confirmatory values.

For details of the experimental method reference may be made to the communication cited. A Wenner stop-watch reading to 0·01 sec. was employed. Temperatures were read on standardised thermometers. The steel balls required were heated before being dropped through the tube in order to avoid solidification of the soap solution on them. All concentrations are expressed in weight normalities (N_w), *i.e.*, g.-mols. per 1000 g. of water.

The results were calculated according to the formula $\eta = K(s - D)T$, where K is the tube constant $\eta_1/(s - \sigma)T_1$, η is the viscosity of the soap solution in c.g.s. units, D its density, s the density of the steel ball, T and T_1 are the times of fall in soap solution and castor oil respectively, η_1 is the viscosity of castor oil $= 16{\cdot}46$ c.g.s. units at 14·1°, and σ the density of castor oil $= 0{\cdot}963$. The value of K depends upon the dimensions of the tubes and balls, and the values used are given in Table I.

TABLE I.

Calibration of the falling balls and tubes with castor oil (Kahlbaum).

Observer.	Temp.	Diam. of steel balls.	Density of balls.	T_1 (secs.).	Tube constant, K.
Horwood	14·1°	0·316 cm.	7·595	6·0	0·4136
,, ...	14·1	1/8 in.	7·720	6·2	0·3928
Heighington	14·1	1/8 in.	7·697	6·2	0·3943
Willavoys	15·7	0·163 cm.	7·554	29·32	0·0731

The results for 0·75, 1·0, and 1·5N_w-solutions of sodium palmitate with added sodium chloride are in Table II. The 1·5N_w-solutions are so viscous that for determining the density a specially wide pipette was employed, closed at the bottom with a flattened glass rod held in place by rubber tubing, and continued at the top with a small tube also held in place by rubber tubing so that when temperature equilibrium was attained this could be slipped off, leaving the pyknometer exactly filled with soap solution. Thereupon the tube was cooled and the contents were solidified for weighing.

Results for approximately 1·5N_w-sodium palmitate with added sodium carbonate or acetate at 81° are given in Table III.

Discussion.

The experimental results for added sodium chloride at 81° are shown in Fig. 1 and those for the acetate and carbonate in Fig. 2. The outstanding effect is that the addition of medium concentration of electrolyte enormously increases the viscosity of soap solution. Without salt, the viscosity is only a few centipoises, and it is increased 600—700-fold at the maxima by the addition of the salt. It may be recalled that with many soaps at lower temperatures the soap solutions in these intermediate concentrations of salt actually set to a jelly, but the effect there also passes through a maximum, and further addition of salt reliquefies the jelly.

The most striking feature of the curves is the existence of these sharp maxima at which the effect of salts is reversed, the viscosity with further increase of salt falling off as rapidly as it had risen. For example, in the curve for carbonate (Fig. 2) the highest viscosity measured was 102 poises, which fell on further addition of carbonate to 6 poises. With the most concentrated soap and sodium chloride, the fall is from 55 to 3 poises. The limited extent of the fall is, however, shown by the fact that when the soap solution contains all the salt that can be added without the formation of several layers, the viscosity is still 20—50 times higher than that of the original soap without salt.

TABLE II.

Viscosity and density of solutions of sodium palmitate containing various weight normalities of added sodium chloride at about 81·0°.

Observer.	Temp.	NaCl (N_w).	T (secs.).	Density (g./c.c.).	η.
		0·75N_w-Sodium palmitate.			
Horwood	81°	0·729	2·5	0·992	6·82
,, ...	,,	0·600	5·3	0·991	14·48
,, ...	,,	0·748	2·4	0·991	6·34
H. H.	,,	0·201	0·9	0·977	2·38
,, ...	,,	0·400	7·6	0·9850	20·11
,, ...	,,	0·500	6·99	0·9877	18·49
,, ...	,,	0·300	3·39	0·9823	8·96
,, ...	,,	0·600	5·2	0·9900	13·75
,, ...	,,	0·450	8·718	0·9864	23·07
H. J. W.	,,	0·440	57·74	0·981	27·74 *
,, ...	90	0·880	1·79	0·9872	0·73 †
		1·0N_w-Sodium palmitate.			
H. H.	81·00	0·880	0·98	1·00000	2·59
,, ...	81·26	0·6797	3·06	0·99805	8·08
,, ...	81·7	0·5771	5·42	0·99570	14·4
,, ...	81·63	0·46945	7·3	0·98805	19·3
,, ...	81·64	0·50000	7·24	0·98980	19·1
,, ...	81·65	0·37220	9·95	0·98645	26·3
,, ...	81·68	0·26205	11·23	0·98310	29·7
,, ...	81·76	0·14445	4·17	0·97910	11·0
,, ...	81·7	0·29000	10·47	0·98310	27·7
,, ...	81·7	0·25000	7·7	0·97530	20·4
,, ...	81·7	0·32000	11·1	0·98470	29·4
H. J. W.	80·96	0·3000	68·76	0·9826	33·0
,, ...	90·05	0·3000			10·2
H. H.	81·92	0·1445	4·76	0·9791	12·3
		1·50N_w-Sodium palmitate.‡			
H. J. W.	80·97	0·100	88·21	0·9740	39·54
,, ...	80·95	0·7500	11·60	1·005	5·55
,, ...	80·99	0·8700	6·45	1·016	3·08
,, ...	81·01	0·7120	12·45	1·001	5·96
,, ...	81·00	0·5658	26·06	0·9965	12·48
,, ...	90·06	0·4395	17·16	(0·9851)	8·24
,, ...	81·01	0·4395	41·53	0·9851	19·94
,, ...	81·03	0·3015	71·03	0·9614	34·23
,, ...	90·05	0·2660	29·75	0·9614	14·33
,, ...	81·00	0·2660	75·78	0·9458	36·59
,, ...	81·00	0·2431	85·38	0·9806	41·02
,, ...	80·99	0·2032	102·77	0·9651	49·49 §
,, ...	81·01	0·1845	105·27	0·9642	50·71 §
,, ...	81·00	0·1459	109·43	0·9692	52·65 §
,, ...	80·98	0·1049	83·48	0·9800	40·12
,, ...	80·94	0·08076	67·77	0·9740	32·59
,, ...	80·98	0·06503	83·32	0·9700	40·09
,, ...	81·02	0·04287	83·58	0·9600	40·28

* High value owing to slight fall in temperature.

† At 90°, hence about 2·2 at 81°.

‡ 1·5N_w-Sodium palmitate does not exist as a single homogeneous solution at 81°, but falls in the heterogeneous region—middle soap + isotropic solution (see McBain and Langdon, J., 1925, **127**, 863).

§ Small crystals developed (acid sodium palmitate).

TABLE III.

Viscosity and density of solutions of sodium palmitate containing various weight normalities of added salts at about 81°.*

Temp.	Added salt (N_w).	T (secs.).	Density (g./c.c.).	η.
1·491N_w-Sodium palmitate with addition of sodium carbonate.				
81·05°	0·1876	213·3	(1·000)	102·2
81·09	0·4764	108·0	1·016	51·50
80·99	1·2736	26·8	(1·000)	12·84
80·99	1·6228	12·54	(1·000)	6·01
	0·1000	Heterogeneous—two layers.		
1·47N_w-Sodium palmitate with addition of sodium acetate.				
81·01	0·09786	90·82	0·9712	43·69
81·02	0·1490	118·85	0·9815	57·12
81·02	0·2081	128·97	0·9825	61·95
81·01	0·2759	67·23	0·9842	32·28
81·00	0·3958	27·50	0·9851	13·20
	0·5837	Heterogeneous system—nigre and lye.		

* Experiments by H. J. W.

The higher the concentration of soap, the less salt is required to produce the maximum viscosity, as the following tabulation shows :

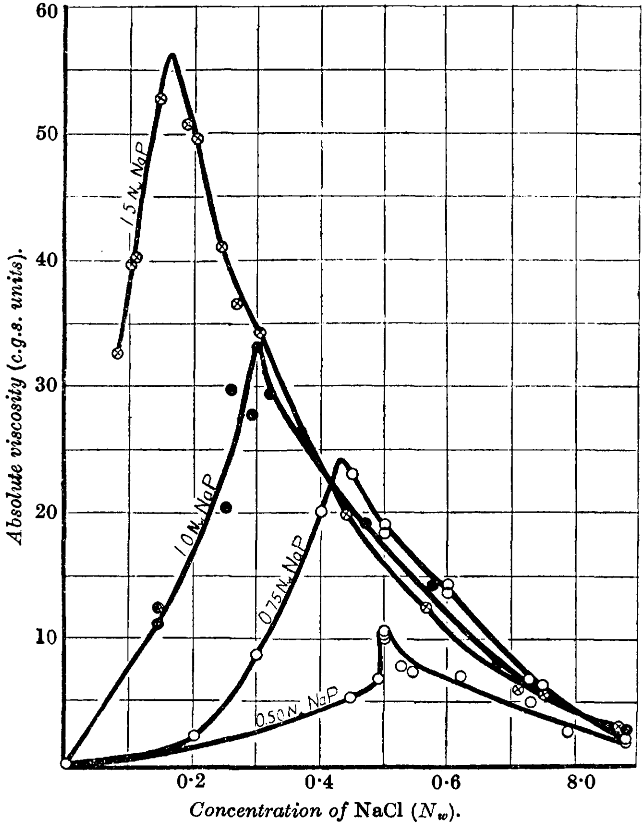
Conc. of soap (N_w)	0·5	0·75	1·0	1·5
Max. viscosity (poises)	10	24	33	56
Conc. (N_w) of salt at max. viscosity	0·50	0·43	0·30	0·16

The enormous increase in viscosity of a soap solution when moderate quantities of salt are added to it again shows the inadequacy of the emulsoid theory of colloids. In these strong soap solutions the soap is all in colloidal form already, before any salt is added. According to the emulsoid theory, addition of salt should shrink the globules of soap, and the viscosity should be diminished instead of being increased many hundred-fold. That the salt is less soluble in a soap-rich phase has been definitely proved by the numerous studies of phase-rule equilibria now available, and, indeed, by the experience of any soap boiler. This affords, therefore, yet another reason for replacing the emulsoid hypothesis by the view that the colloidal soap in solution is present in the form of solid particles or micelles.

Superficially, the curves look like any of Loeb's for the Donnan equilibrium. However, they differ in two respects. In the first place, Loeb's experiments never involved more than a five-fold increase in viscosity, whereas these involve increases of a higher order of magnitude. In the second place, Loeb's maxima arose from the fact that he was adding an acid or an alkali to an amphoteric colloid and producing colloidal electrolyte with high conductivity, osmotic activity, etc., whereas here, salts are being added and should have a uniformly depressing action on the viscosity, as was indeed observed by Loeb for salts when added to the systems he studied.

The problem then is to explain why fully formed colloid may have its viscosity increased many hundred-fold through the addition of salt. The only possible explanation seems to be the general hypothesis advanced by one of us (McBain, *J. Physical Chem.*, 1926, **30**, 239), that the viscosity of a reversible colloid, such as nitrocotton, soap, rubber, or protein, is not to be accounted for by the individual particles (micelles) either through their number or individual bulk, but that it is due to their loose aggregation into structures which effectively enmesh large tracts of the solvent or solution.

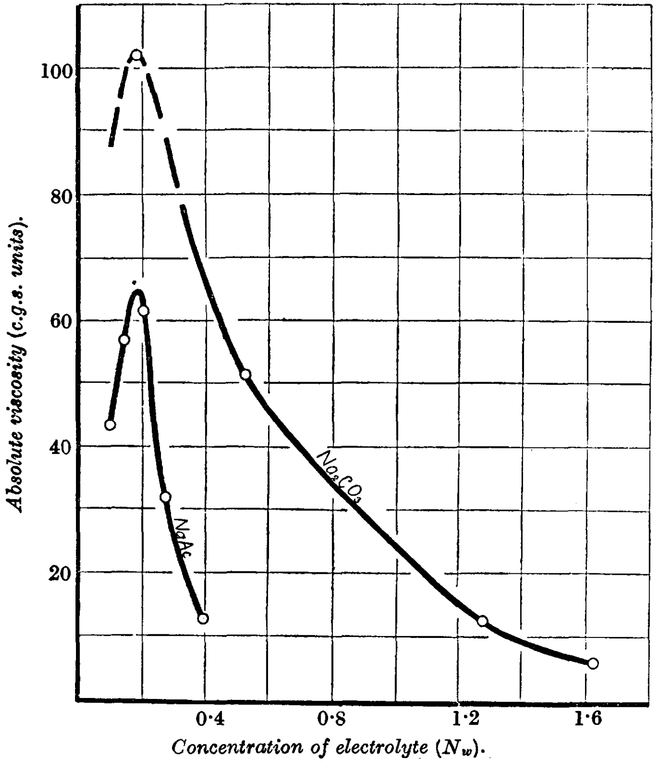
FIG. 1.



The viscosity of solutions of sodium palmitate at 81° as affected by addition of sodium chloride up to the maximum amount which can be added without salting out the solution into two layers.

Hatschek (*J. Physical Chem.*, 1927, **31**, 353) has recently published a communication which is ostensibly an attack upon McBain's general hypothesis of aggregation, but which is really an adoption and endorsement of one particular form of the general hypothesis, being a modification of that of Loeb. In general, there is a great variety of possible forms of aggregation. For example, if all the particles were to be joined end to end to form innumerable filaments, the medium in which they lay could be so effectively enmeshed as to have the properties of a jelly. Another form of loose ramifying aggregation is that of a pile of brushwood, or again seaweed in a rock pool. Hatschek would prefer to specify only one kind of ramifying aggregate like a lot of separate bushes not entangled but separate from each other, so that each aggregate could be treated approximately as a polyhedron, or even as a sphere. To call this loose ramifying aggregate the micelle is to introduce fresh confusion into the subject. We should prefer to retain the general hypothesis,

FIG. 2.



The viscosity of solutions of 1·5N$_w$-*sodium palmitate at* 81° *over the whole range of existence of isotropic solution in the presence of sodium acetate and sodium carbonate, respectively.*

which includes Hatschek's as one possibility. We use the term micelle to indicate each of the single ultimate particles of colloid.

Attention may be directed to another influence which greatly enhances the effect of the presence of either particles or ramifying aggregates in their influence upon the apparent viscosity of the system. Hatschek has demonstrated that even in a suspension in which aggregation does not occur and in which hydration in the chemical sense is absent, the system does not show a true viscosity coefficient like a pure liquid, but the viscosity coefficient obtained is a function of the rate of shear. He has been at a loss to account for this effect, and similarly Porter and Rao (*Trans. Faraday Soc.*, 1927, **23**, 311) were unable to offer an explanation, but made a purely empirical attempt to obtain an equation to fit the results. As part of a general theorem relating to the structure of surfaces, one of us (J. W. McB.) and G. P. Davies (Address to the Mid-West Regional Meeting of the American Chemical Society, Madison, June, 1926; *J. Amer. Chem. Soc.*, 1927, **49**, 2230) have shown that this effect is a necessary result. On the basis of accurate absolute measurements on the amount of adsorption, now available for the first time, and of a survey of the results obtained in such fields as that of adhesives, etc., the authors concluded that any surface possesses considerable depth due to chains of oriented molecules extending inwards from points on the outer unimolecular layer. The effective length of these chains is conditioned by thermo-vibration and, of course, by rate of shear, the latter accounting for the results obtained by Hatschek and Porter. Hence a liquid in the neighbourhood of surfaces such as those of particles, filaments, or ramifying aggregates is semi-rigid, enhancing greatly the effectiveness of the aggregates in immobilising liquids, and producing a high apparent viscosity.

According to previous studies of soap, it is the neutral micelle, and not the ionic micelle, that has the power of forming ramifying aggregates. Salt does promote the formation of neutral micelles at the expense of ionic micelles, but this effect is too unimportant for our present purpose. We should ascribe the aggregation of the neutral micelles to partial dehydration on the addition of salt owing to the lowering of the vapour pressure of the solution. This is the first main factor involved in the action of salts upon soap solutions.

The maximum and the subsequent lowering of viscosity have still to be explained, and any explanation has to be sufficiently general to account for the salting out and phase-rule equilibria of soap, together with the formation of liquid crystals. We would seek this in a combination of the principles of dehydration through lowering of vapour pressure (as above), of orientation of like molecules when held sufficiently close together, and of the principle underlying the Donnan equilibrium. The dehydration facilitates aggregation by exposing unsaturated valence bonds (compare McBain, *J. Physical Chem.*, *loc. cit.*), thus tending to make the aggregates denser and less voluminous. The principle of constancy of ionic product, as exemplified by solubility of precipitates, utilised by Donnan and generalised by Wilson, must now be made use of to explain further the effect of salts upon the charges and the volumes within the colloidal aggregates.

Almost all surfaces, even those of the neutral micelles, show slight electrical charges (see Laing, *J. Physical Chem.*, 1924, **28**, 673). Particles of like charge tend to repel each other, probably not merely through direct electrostatic repulsion (the usual belief), but also through the excess osmotic pressure set up in the neighbourhood of all charges through the Donnan equilibrium. The effect of large excess of salt is two-fold : first, to reduce these charges, and, secondly, to minimise their effect upon the Donnan osmotic pressure in their neighbourhood. These two influences contribute to the collapse, or rather the closer packing, of the structures built up from the micelles, thus reinforcing the effect of increased intensity of aggregation. This releases a part of the liquid, or better, less of it is immobilised, and hence the apparent viscosity falls. This would appear to explain the decline in viscosity that occurs in more concentrated solutions of salts, whilst still leaving the viscosity higher than that of the original soap solution. This explanation embraces that given by Laing and McBain (J., 1920, **117**, 1507) for the formation of true soap jellies which occur in the middle of the isotropic region and are liquefied by excess of added salt. It should be noted that the curves in Fig. 1 cover practically the whole field of the possible existence of isotropic solutions of sodium palmitate (compare McBain and Langdon, *loc. cit.*). Throughout, the chief factor involved in apparent viscosity of colloids is the extent to which the solution or solvent is immobilised through entanglement in colloidal structures.

When aggregation, brought about through dehydration and segregation as detailed above, becomes extreme, and the micelles are therefore more tightly packed in clumps, the tendency towards orientation must strongly assert itself (orientation of molecules accounts for the existence of micelles in the first place). Excess of salt always produces neat soap and lye, the latter being an ordinary salt solution containing most of the salt and scarcely any soap; the neat soap is liquid crystal. The common feature of all present hypotheses regarding the structure of liquid crystals is that they are full of tracts in which molecules or micelles are in an approximately parallel arrangement.

Whilst the above description appears to afford a reasonable explanation of the phenomena here discussed, searching tests are required to afford independent proof of the truth of each of the mechanisms involved. Again, far too little is known with regard to the structure of liquid crystals. Indeed, soap solutions afford the only examples of liquid crystals readily accessible for experimental study. The position of middle soap has still to receive adequate explanation. If a soap solution containing no added salt is sufficiently concentrated, middle soap separates as a new phase, and, within a certain range of concentration, soap solutions consist only of this form. Middle soap is a colloidal electrolyte, just like the isotropic solutions it has replaced. A small amount of salt may be added to middle soap, but it is destroyed by further salt, being replaced by isotropic soap solution. This is the significance of the curves for $1{\cdot}5N_w$-sodium palmitate in Figs. 1 and 2, which necessarily have their beginning as shown in the diagrams in the presence of the necessary minimum of salt. The pure $1{\cdot}5N_w$-sodium palmitate is middle soap; it turns into isotropic soap solution upon the addition of the requisite amount of salt, and the viscosity shortly thereafter passes through a maximum as shown in the diagrams. It throws a severe strain upon our explanation (detailed above) to account for these phenomena, because they ended in the production of liquid crystal through excess of salt, with the elimination as a separate phase of most of the water and salt, whereas here the $1{\cdot}5N_w$-sodium palmitate begins as liquid crystal, although retaining all the water with it in one homogeneous phase.

The existence of middle soap as liquid crystal is quite evidently due to mere contiguity of the particles on account of the very high concentration of soap. We have to suppose that this orientation is almost tantamount to coalescence, because no negative ions, other than a trace of hydroxyl ion (and of course the ionic micelles), are present to keep the particles apart. Addition of a small amount of salt supplies this defect, and the tracts of parallel orientation are disbanded with the formation of isotropic solution, although the apparent viscosity is already extremely high and aggregation or linkage is already at an advanced stage. Thereafter, but little salt is required to produce the maximum and the other specified effects.

Comparison of the effects due to the three salts is interesting, but in view of the explanations above it cannot be expected to be of direct significance. The two univalent salts, chloride and acetate, are fairly similar in the position and value of the maximum viscosity, that for sodium acetate being slightly higher and requiring rather more acetate, sodium acetate being a weaker electrolyte than sodium chloride. The bivalent sodium carbonate gives twice as high a maximum viscosity as the chloride and twice as much of it is required for salting out the palmitate into two layers. However, the acetate is exceptionally effective in salting out, $0{\cdot}57N_w$ being sufficient as compared with $0{\cdot}88N_w$ for the chloride and $1{\cdot}7N_w$ for the carbonate. McBain and Pitter (J., 1926, 893), in comparing a large number of salts, pointed out that apparently the single factor most effective in salting out is the concentration of the sodium ion. We suspect that the high viscosity in the presence of the carbonate may be due to its alkalinity, because we have found with various other samples of sodium palmitate that a slight excess of alkalinity very greatly increases the viscosity. Thus, if the sodium palmitate contains about one equiv. per cent. excess of sodium hydroxide, all the maxima of viscosity are roughly 1·7 times greater.

The futility of attempting to apply any of the usual empirical formulæ to our results is evident from the shape of the curves and also from the fact that the right-hand descending portions of the viscosity curves approximately coincide, *i.e.*, the viscosities are there nearly independent of the amount of soap present.

All the work here described was carried out at the University of Bristol.

Summary.

1. The viscosity of solutions of sodium palmitate has been studied over most of the range of existence of isotropic soap solutions in the presence of sodium chloride, acetate, and carbonate.

2. Addition of electrolytes increases the viscosity to a maximum value many hundred times greater than that of the original soap solution. Further salt decreases the viscosity almost equally rapidly until the salting out concentration is reached.

3. The results are discussed on the basis of the general explanation put forward by McBain for the high apparent viscosity of reversible sols and jellies. The rise in viscosity is in the opposite direction to that predicted by the Donnan equilibrium, and exceeds by a hundredfold the viscosity effects observed by Loeb, although the Donnan equilibrium may well be one of the factors involved.

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