278. *Some Properties of the Calcium Salts of the Lower Fatty Acids. Part I. Viscosity.*

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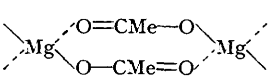
The viscosities of aqueous solutions of calcium acetate, propionate, *iso*butyrate, and *iso*valerate were measured, and the results considered from the point of view of the Einstein and Guth–Simha equations, usually applied to systems of larger molecules. The high viscosity of these salts suggests a similarity with the behaviour of more complex molecules, and the agreement with the above equations substantiates this.

The properties of the sols and gels formed when polar organic liquids are added to aqueous solutions of calcium acetate have been described by Thorne and Smith (*Kolloid-Z.*, 1929, **48**, 113) and by Smith (*ibid.*, 1931, **54**, 181, 284). The higher fatty acid salts of calcium, such as the propionate and the butyrate, form gels with organic liquids very much less readily, usually giving instead a fine-meshed mass of thin fibrous crystals. Hardly any other electrolytes are known to form gels in this way, and the question why calcium acetate should possess this remarkable property to such a considerable degree presents an interesting problem. Study of the gels themselves throws little light on the reason for their formation, and the present investigation was undertaken to discover whether this reason lay in the properties of the aqueous solutions.

Although the physical properties of aqueous solutions of alkali-metal salts of the fatty acid series have been extensively investigated, very little work has been undertaken upon the corresponding compounds of the alkaline earths. Only the lower members of this series are water-soluble to an appreciable extent, so that it was necessary to confine observations in aqueous solution to such salts as the formate, acetate, propionate, butyrate, and valerate. Except at very high dilution aqueous solutions of the alkali-metal salts of the higher fatty acids are colloidal electrolytes, micelle formation increasing with increase in the length of the carbon chain. The sodium salts of the lower members of the fatty acids appear not to form micelles, but the alkaline-earth salts contain twice as many carbon atoms as the corresponding sodium or potassium salts, and hence the onset of micelle or complex-anion formation may be expected at a much lower anionic weight. Rivett *et al.* (*J.*, 1926, 1063; 1928, 1950) suggested that in aqueous solutions of magnesium acetate complexes of the inset type are formed to an appreciable extent. Similar complexes in calcium acetate are a possibility which was kept in mind during this investigation. The known high viscosities of many solutions of electrolyte acetates suggest a high degree of solvation with, possibly, the formation of asymmetric complexes, and an attempt has been made to interpret viscosity data in this light.



Experimental.

Preparation and Purification of Materials.—The calcium acetate used was prepared by adding small amounts of AnalaR calcium carbonate to glacial acetic acid, well diluted with water, at room temperature. When an amount of calcium carbonate slightly in excess of the theoretical had been added, the mixture was set aside overnight, heated at 100° for 1—2 hours, filtered, and concentrated on a boiling water-bath until about 10% of the salt had been precipitated. The liquid was filtered whilst still hot (calcium acetate is less soluble in hot than in cold water). The precipitated calcium acetate was dissolved to saturation in cold water and the process of concentration repeated. The twice-precipitated salt was dried at the pump and heated to constant weight at 120° (Found : Ca, by precipitation as oxalate and titration with permanganate, 25·3—25·4%. Calc. for $C_4H_6O_4Ca$: Ca, 25·3%).

Calcium propionate and *iso*butyrate were prepared by twice crystallising commercial samples. Both are more soluble in water at 100° than at room temperature. After being heated to constant weight at 120°, both gave satisfactory analyses for calcium.

A commercial sample of *iso*valeric acid was redistilled and calcium *iso*valerate prepared from it as described for calcium acetate. Calcium *iso*valerate is more soluble in cold than in hot water. The twice-precipitated material, dried at 120°, contained the theoretical amount of calcium within 0·2%.

The *n*-hexoic acid available was a dark brown liquid which did not freeze at –15°. This was redistilled, the colourless middle fraction, b. p. 201—202°/760 mm., being collected. Thirty times its weight of water was added, and AnalaR calcium carbonate was used for neutralisation. Calcium hexoate is only slightly soluble in water, and the difference between the solubilities in 100 g. of cold and hot water is only about 0·4 g. The material was therefore recrystallised only once. When dried at 120°, it contained 14·7% of calcium (Calc. for $C_{12}H_{22}O_4Ca$: Ca, 14·8%).

It was most important to remove all excess of fatty acid from the salts by heating to constant weight. Excess of acid is liable seriously to affect the properties of the solutions, particularly their viscosity. The pH of the pure aqueous solutions is between 8 and 9, and the pH was found to be a good check on freedom from excess of acid.

Determination of Viscosity.—Viscosity measurements were carried out in an Ostwald-type capillary viscometer which had the following dimensions : capacity of the upper bulb, about 10 ml. ; radius of the capillary, 0·0201 cm. ; length of capillary, about 18 cm. ; time of flow for water at 18°, 185 seconds. Using the information given by De Jong ("First Report of Viscosity and Plasticity," Amsterdam, 1935, Chap. III), it was found that for this instrument the error due to eddying motion at the issuing jet should be less than 0·1%, and no kinetic energy correction was necessary.

The apparatus was cleaned with chromic acid solution before each day's determinations, and was kept filled with chromic acid when not in use. It was washed out with filtered water, and dried by passage of dust-free air. It was repeatedly re-calibrated by determining the time of flow for water. All determinations were carried out at a temperature kept within ±0·05° by a thermostat. Time of flow was determined to 0·1 second. In the calculation of the results, the densities determined by use of a 10-ml. pyknometer (repeatedly re-calibrated, constant ±0·002%) were employed. The results were not corrected for surface tension, but it appears that in an Ostwald viscometer of the usual shape this correction is small (Jones and Fornwalt, *J. Amer. Chem. Soc.*, 1938, **60**, 1683). The accuracy of the instrument was checked by measurement of the viscosity of sugar solutions at 15° and 30° (deviation from the International Critical Tables, –0·3% to –1·0%).

The solutions used were made by diluting known weights of saturated solutions with weighed quantities of water, and were checked against the concentrated solutions by evaporating 10-ml. portions to dryness, igniting and weighing the residue as calcium oxide.

RESULTS.

The viscosities of solutions of calcium acetate, propionate, *iso*butyrate, *iso*valerate, and *n*-hexoate without and with added salts are recorded in Tables I—III.

In Table V are given the viscosities of a saturated solution of calcium propionate at different temperatures. The solution was saturated at 18°, and hence is slightly supersaturated at 25° and 30°, although crystallisation did not commence until 40°.

TABLE I.

Viscosities of aqueous solutions at 18°.

G./l.	Molarity (c).	d^{18}_{18}.	η/η_0.	$(\eta/\eta_0 - 1)/c$.	G./l.	Molarity (c).	d^{18}_{18}.	η/η_0.	$(\eta/\eta_0 - 1)/c$.
Calcium acetate :					Calcium propionate :				
14·95	0·0945	1·0084	1·085	0·90	17·8	0·0954	1·0088	1·099	1·04
30·4	0·192	1·0168	1·163	0·85	38·0	0·204	1·0180	1·210	1·03
60·1	0·380	1·0328	1·335	0·88	88·8	0·477	1·0412	1·591	1·24
112	0·708	1·0590	1·659	0·93	147·5	0·792	1·0668	2·173	1·48
149	0·942	1·0770	2·030	1·09	224	1·203	1·0987	3·195	1·825
196	1·240	1·0992	2·537	1·24	253	1·359	1·1102	3·740	2·02
237	1·498	1·1172	3·167	1·45	322 *	1·729	1·1380	6·216	3·02
252	1·596	1·1252	3·414	1·51					
306 *	1·935	1·1475	5·144	2·14					
Calcium *iso*butyrate :					Calcium *iso*valerate :				
15·9	0·0741	1·0068	1·095	1·28	14·1	0·0580	1·0052	1·084	1·45
32·1	0·150	1·0134	1·194	1·29	29·3	0·121	1·0101	1·175	1·45
45·2	0·211	1·0186	1·290	1·37	55·7	0·230	1·0189	1·359	1·56
89·3	0·417	1·0358	1·648	1·55	88·3	0·364	1·0294	1·641	1·76
133	0·620	1·0522	2·085	1·75	125	0·518	1·0410	2·085	2·10
160	0·748	1·0620	2·480	1·98	154	0·638	1·0498	2·551	2·44
194	0·905	1·0741	3·017	2·23	190 *	0·784	1·0804	3·260	2·88
Calcium *n*-hexoate :									
9·4	0·346	1·0026	1·055	1·59					
18·1	0·0668	1·0053	1·106	1·59					
21·9 *	0·0810	1·0063	1·130	1·60					

* Saturated solution.

TABLE II.

Viscosities of 1·828M-*calcium acetate, containing added salts, at* 18°.

Added sodium chloride, g./l. of water.	molarity.	d^{18}_{18}.	η/η_0.	Added calcium chloride, g./l. of water.	molarity.	d^{18}_{18}.	η/η_0.	Added sodium acetate, g./l. of water.	molarity.	d^{18}_{18}.	η/η_0.
0	0	1·1252	3·414	0	0	1·1252	3·414	0	0	1·1252	3·414
4·3	0·0524	1·1281	3·442	6·9	0·0622	1·1306	3·452	3·53	0·0604	1·1275	3·482
24·2	0·295	1·1344	3·636	25·9	0·233	1·1396	3·564	25·6	0·438	1·1382	3·584
63·0	0·768	1·1452	4·101	41·8	0·377	1·1475	3·629	47·3	0·809	1·1491	3·689
87·8	1·070	1·1499	4·395	63·2	0·569	1·1600	3·750	63·8	1·092	1·1568	3·772
				84·9	0·765	1·1695	3·859	85·0	1·454	1·1670	3·890

TABLE III.

Viscosities of 0·829M-*calcium* iso*butyrate, containing added salts, at* 18°.

Added sodium *iso*butyrate, g./l. of water.	molarity.	d^{18}_{18}.	η/η_0.	Added calcium chloride, g./l. of water.	molarity.	d^{18}_{18}.	η/η_0.
0	0	1·0620	2·480	0	0	1·0620	2·480
1·83	0·0166	1·0630	2·491	5·8	0·0523	1·0656	2·497
13·0	0·118	1·0661	2·583	8·8	0·0793	1·0673	2·502
25·0	0·227	1·0680	2·694	26·1	0·235	1·0785	2·563
46·9	0·426	1·0708	2·909	35·6	0·321	1·0842	2·601
				45·5	0·410	1·0905	2·635
				55·2	0·497	1·0956	2·663

The decrease of viscosity caused by addition of acid is shown in Table IV.

TABLE IV.

Viscosity of 1·828M-*calcium acetate in acid and alkaline media at* 18°.

Medium.	pH.	d^{18}_{18}.	η/η_0.	Medium.	pH.	d^{18}_{18}.	η/η_0.
N/50-NaOH	11·0	1·1244	3·374	N-HCl	4·8	1·1307	2·873
Water	8·3	1·1252	3·414	2N-HCl	3·7	1·1391	2·472
N/50-HCl	7·0	1·1254	3·341				

TABLE V.

Viscosity of saturated calcium propionate solution.

Temp., ° C.	15	18	25	30
η/η_0	6·518	6·216	5·650	5·207

DISCUSSION.

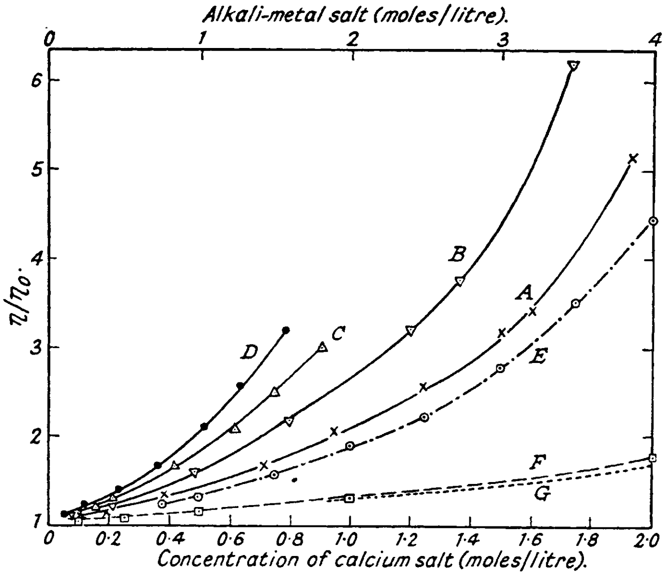
From Fig. 1 it will be seen that only at low concentrations is the viscosity linear with concentration, and that the relative viscosities of >1M-solutions rise steeply, reaching the order of 5 for saturated solutions.

Many electrolytes in very concentrated aqueous solution have viscosities several times greater than that of water. Thus the relative viscosities at 18° of 6M-calcium chloride and 10·03M-sodium hydroxide are 9·00 and 11·81 respectively. However, these solutions of acetates etc. are of the order of 2M. at the most, at which concentrations the other electrolytes mentioned have relative viscosities of 1·7 and 1·4 respectively.

The viscosity curve of sodium acetate is also plotted in Fig. 1 for comparison. The data for low concentrations was taken from the International Critical Tables, and a few determinations of the viscosity at higher concentrations were made by one of us (W. B. B.). The scale on abscissa has been doubled so that the concentration of acetate ions is comparable with that of the calcium salt. The viscosity of the sodium acetate is below that of the calcium at all concentrations, and the two curves are approximately parallel until the concentration of acetate ions reaches 3 g.-ions/l. Above this point, the viscosity of the calcium salt rises more steeply that that of the sodium. This is more clearly brought out in Fig. 3.

FIG. 1.

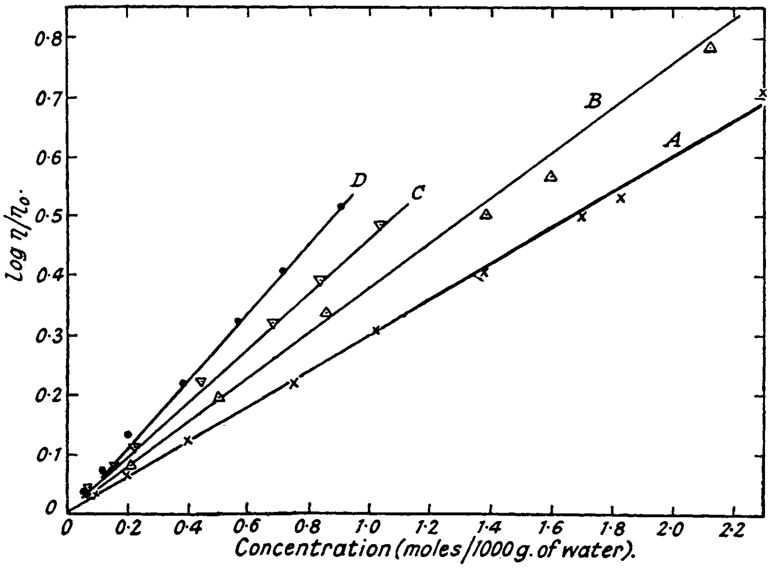
Viscosity of electrolyte solutions.



A = Calcium acetate. B = Calcium propionate. C = Calcium iso*butyrate. D = Calcium* iso*valerate. E = Sodium acetate. F = Calcium chloride. G = Lithium chloride.*

FIG. 2.

Application of Arrhenius equation.



A = Calcium acetate. B = Calcium propionate. C = Calcium iso*butyrate. D = Calcium* iso*valerate.*

A number of equations relating viscosity and solute concentration have been proposed, including :

(Einstein) $\eta/\eta_0 = 1 + k\phi$

(Guth and Simha) $\eta/\eta_0 = 1 + k\phi + K\phi^2$

(Arrhenius) $\log \eta/\eta_0 = Kc$

where ϕ is the volume fraction, and c the concentration.

Only Arrhenius's equation represents the data over the complete concentration range, as shown in Fig. 2, in which the logarithm of the relative viscosity is plotted against the molal concentration. Plots of viscosity against molarity depart appreciably from straight lines at higher concentrations.

The relation of the function $(\eta/\eta_0 - 1)/c$ to concentration is depicted in Fig. 3. In dilute solutions, the results agree with an equation of the Einstein form, but as the concentration rises, the curve corresponds to the Guth–Simha type, whilst at still higher values of the molar concentration, higher powers of c need to be added to the equation. In view of this, the Guth–Simha equation was solved for ϕ, and the function $(\eta/\eta_0 - 1)/\phi$ plotted against concentration (Fig. 4). It will be observed that the plots are almost linear over most of the range, suggesting that ratio of the concentration to the volume fraction is approximately constant, except for very dilute and very concentrated solutions. This corresponds to the constancy of the apparent degree of hydration inherent in the Guth–Simha equation; hydration is then responsible for the high viscosity (see Table VI.).

TABLE VI.

Moles/l.	η.	Guth–Simha, ϕ.	Volume fraction (v).	ϕ/v.	Apparent degree of hydration.
Calcium acetate :					
0·0945	1·085	0·029	0·0109	2·66	10·7
0·192	1·163	0·051	0·0220	2·32	8·48
0·380	1·335	0·0925	0·0435	2·12	7·3
0·708	1·659	0·145	0·0809	1·79	5·12
0·942	2·030	0·1952	0·108	1·81	5·4
1·240	2·537	0·252	0·142	1·78	5·18
1·498	3·167	0·312	0·1716	1·82	5·55
1·596	3·414	0·333	0·1822	1·83	5·58
1·935	5·144	0·461	0·2216	2·08	7·5
Calcium propionate :					
0·0954	1·099	0·0326	0·01416	2·30	10·17
0·204	1·21	0·0625	0·0302	2·07	8·9
0·477	1·591	0·1335	0·071	1·88	7·45
0·792	2·173	0·2125	0·1177	1·82	6·9
1·203	3·195	0·314	0·178	1·76	6·68
1·359	3·740	0·36	0·2018	1·79	7·07
1·729	6·216	0·525	0·256	2·05	9·27
Calcium *iso*butyrate :					
0·0741	1·095	0·0318	0·01258	2·52	14·42
0·150	1·194	0·0582	0·02543	2·28	12·42
0·211	1·290	0·0797	0·0358	2·22	11·64
0·417	1·648	0·1425	0·0708	2·02	9·6
0·620	2·085	0·2015	0·1052	1·92	8·88
0·748	2·480	0·246	0·127	1·935	9·15
0·905	3·017	0·298	0·1537	1·94	9·20
Calcium *iso*valerate :					
0·058	1·084	0·0284	0·0122	2·33	15·6
0·121	1·175	0·0536	0·0256	2·09	12·95
0·230	1·359	0·0934	0·0485	1·925	10·92
0·364	1·641	0·143	0·077	1·86	10·24
0·518	2·085	0·2015	0·109	1·845	10·18
0·636	2·581	0·254	0·134	1·895	10·88
0·784	2·88	0·326	0·165	1·975	11·9

According to Staudinger's theory, the limit of the function $(\eta/\eta_0 - 1)/c$, as c tends to zero, is proportional to the molecular weight of the solute, or in linear relation to it. Apart from the fact that the first members of an homologous series very often fail to obey the Staudinger law, no assistance can be expected from this approach in deciding whether or not association of the anions occurs, owing to the low dilutions used. The intrinsic viscosities of these substances have an approximately linear relation to the molecular weight; except, possibly, for the *iso*-compounds (Fig. 5).

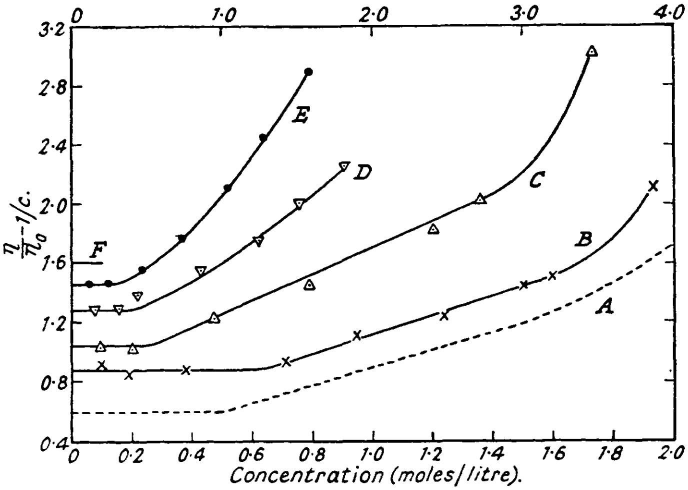
Inserting the numerical coefficients usually employed in the Guth–Simha equation, thus :

$$14{\cdot}1\phi^2 + 2{\cdot}5\phi + 1 - \eta/\eta_0 = 0$$

and solving for ϕ gives the results shown in Table VI. The volume fraction, given in column 4, was calculated from the molar volume in the solid state. This was chosen in preference to the apparent molar volume calculated from the densities of the solution, because the latter includes the effect of the " tightening " of the water structure around the hydrated ions. Whilst it is realised that the volume of the ions in solution may not be the same as that in the solid, it is probable that at each concentration, these two volumes are in the same ratio to each other.

FIG. 3.

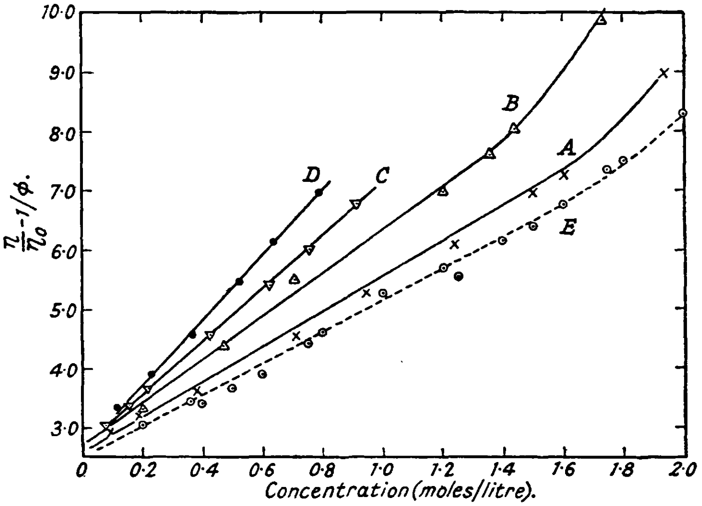
Application of Guth–Simha equation.



A = *Sodium acetate.* *B* = *Calcium acetate.* *C* = *Calcium propionate.* *D* = *Calcium* iso*butyrate.* *E* = *Calcium* iso*valerate.* *F* = *Calcium hexoate.*

FIG. 4.

Application of Guth–Simha equation.



A = *Calcium acetate.* *B* = *Calcium propionate.* *C* = *Calcium* iso*butyrate.* *D* = *Calcium* iso*valerate.* *E* = *Sodium acetate.*

Hence although the actual numerical results set out in the last three columns of Table VI are likely to be very approximate, the trend indicated reflects a change in the internal condition of the solution.

Over a wide range of concentration, the ratio ϕ/v is approximately constant. Since the volume fraction v calculated from the molar volume in the solid state is proportional to the molarity, it can be a constant fraction of the Guth–Simha ϕ only whilst the apparent degree of hydration is constant. At low concentrations, this degree of hydration is high, but it falls rapidly as the concentration increases to a more or less constant value. It is not unreasonable

FIG. 5.

Staudinger's rule.

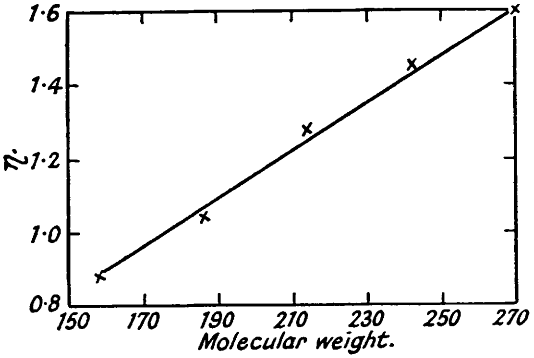
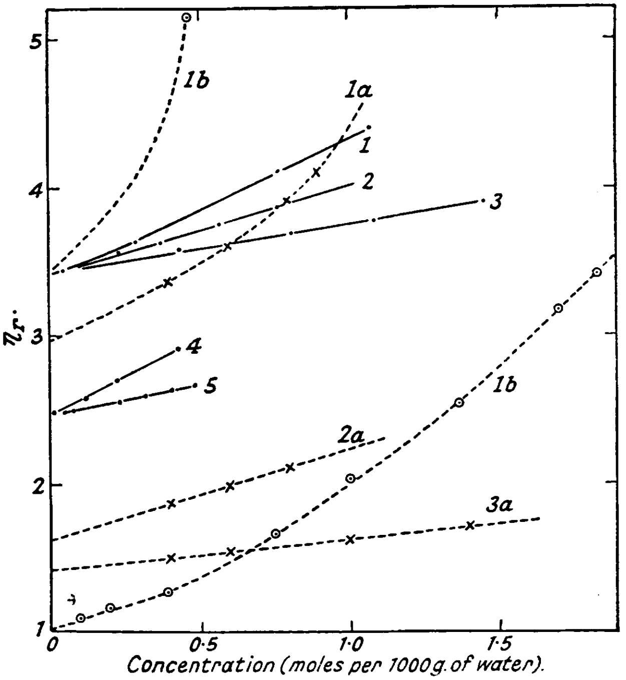


FIG. 6.

Viscosity of mixed solutions.



Calcium acetate solution containing (1) *sodium acetate,* (2) *calcium chloride, and* (3) *sodium chloride. Calcium* iso*butyrate solution containing* (4) *sodium* iso*butyrate, and* (5) *calcium chloride.* (1*a*) *Sodium acetate solution,* 3·65 M. *and higher.* (2*a*) *Calcium chloride solution,* 1·83 M. *and higher.* (3*a*) *Sodium chloride solution,* 3·65 M. *and higher.* (1*b*) *Calcium acetate solution.*

to assume that this corresponds to a real decrease in the hydration of the ions. However, the increase of viscosity at the higher concentrations is not likely to be due to any increase of real hydration, since the water is becoming scarcer. Since also the mere aggregation would not in itself increase viscosity, it may be assumed that this increase is caused by a development of symmetry of either shape or charge distribution, factors which would increase the internal friction. It is also noticeable that the apparent degree of hydration is greater with the higher fatty acid salts. Since the anions depart more and more from hydrophilic character with increase of chain length, and the degree of hydration of the cation may be assumed uninfluenced by the anion, any increase of hydration is unlikely unless something in the nature of micelle formation, entrapping water, occurs. The increased viscosity again may be attributed to the increased asymmetry of the anion or anionic complex. This anionic complex may be of the same nature as the Debye–Hückel ionic atmospheres, for the same changes in apparent degree of hydration are shown by quite simple salts, although at higher concentrations. As the viscosity of these simple salts is invariably lower, the apparent degree of hydration is lower, often lower than that deduced from other measurements. Since fatty-acid ions are less likely to be hydrated than those derived from inorganic acids, the high viscosity of the calcium salts of these fatty acids must be attributed to a developing asymmetry of the anion complexes.

The purpose of determining the densities and viscosities of mixed solutions, recorded in Tables II—III, was to study the influence of a common ion. Sodium chloride was used for control experiments to assess the effect of increasing the ionic strength. The results are depicted graphically in Fig. 6 and, for comparison, the viscosities of solutions of the pure added salts over the same concentration range are added.

FIG. 7.

Viscosity and pH.

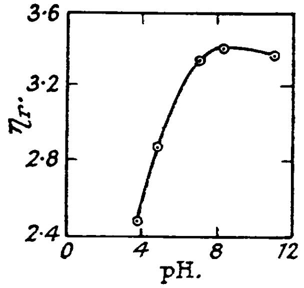
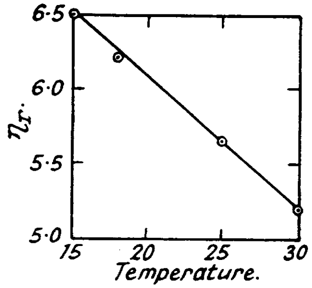


FIG. 8.

Viscosity and temperature.



It will be observed that the curve for the pure added electrolytes lies roughly parallel to the curves for the mixed solutes, suggesting that these added ions have little effect on the viscosities of calcium acetate and *iso*butyrate. Were the high viscosity due in any large degree to the presence of undissociated salt, then the common ion, by decreasing dissociation, should markedly increase the viscosity. Another factor which may not be without influence is the partial dehydration of the calcium acetate by the added electrolyte. Not only is this likely, but the eventual salting-out of the acetate suggests that it is actually occurring. This would reduce the viscosity, or at least maintain it constant, so that the increase observed is due solely to the added electrolyte. The rate of increase of viscosity of pure sodium acetate solution is greater than that of the mixed solution.

The decrease in viscosity of calcium propionate with rise of temperature (Fig. 8) points to the salt not being ionised in moderately concentrated solution, so that added ions would have no effect. On the other hand, the decrease of viscosity with increasing acidity (Fig. 7) is characteristic of an ionic system. " Neutral " calcium acetate solution (slightly alkaline owing to hydrolysis) shows maximum viscosity.

The addition of ethanol and *iso*propanol to aqueous solutions of calcium acetate, whilst causing certain irregularities in the viscosity, produces, in general, a preliminary diminution in the viscosity owing to dehydration, followed by an increase owing to the coalescence of the anionic complexes.

Conclusion.—The evidence on whether the high viscosity of these solutions is due to the anion or the un-ionised salt seems to be conflicting. Thus whilst neutral salts have little or no influence, pH of the medium is an important factor. The rapid increase at high concentration points to the formation of asymmetric anionic complexes, similar to, but simpler than, the micelles formed in soap solutions. These grow rapidly at higher concentrations and on dehydration (leading to salting out as gels or gelatinous precipitates), but are reduced by acidity or alkalinity (giving rise to acetic acid or alkali acetate).

Since high viscosity is characteristic of acetates etc. in concentrated solution, it may be concluded that it is the anions which are responsible. Compared with cations, these ions are not likely to be heavily hydrated, but anything in the nature of a micelle would entrap water, keeping the micelle small but giving a high viscosity. Removal of this water would permit agglomeration of the micelles, without necessarily increasing viscosity, any asymmetry effect being counteracted by dehydration of the micelles.

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