45. *Solutions in Sulphuric Acid. Part XI.* The Densities and Viscosities of Some Sulphuric Acid Solutions.*

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The densities and viscosities of dilute solutions in sulphuric acid of water, sulphur trioxide, some alkali and alkaline-earth metal hydrogen sulphates, nitric acid, sulphuryl chloride, and a number of organic compounds have been measured at 25°. Apparent molal volumes of some of the cations have been calculated and they are discussed in terms of their solvation. The viscosities of some of the solutions are also briefly discussed.

THE measurement of the densities and viscosities of dilute solutions of a variety of solutes was originally undertaken to provide data necessary for the interpretation of the conductivity results presented in Part XII (*J.*, 1953, 221). The results obtained seemed, however, to be of sufficient interest to merit some independent discussion and they are accordingly presented here.

The only previous work on densities and viscosities of sulphuric acid solution has been concerned with the solutes water and sulphur trioxide, on which there is an extensive literature. No measurements of the densities or viscosities of solutions of other solutes appear to have been made.

EXPERIMENTAL

Sulphuric acid of minimum conductivity was prepared in a conductivity cell. A suitable quantity of the solute under investigation was added, the conductivity of the solution measured, and the concentration of the solute interpolated from a specific conductivity–concentration curve (Part XII, *loc. cit.*). Samples of the solution were transferred from the conductivity cell to the viscometer and pycnometer, the solution being protected throughout from contamination by atmospheric moisture. Further portions of the solute were then added, and the above procedure repeated. This method of determining the concentration of solutions from specific conductivity–concentration curves was easier and more rapid than making up each solution separately by weight, although the latter method was used in a few cases.

Densities were measured in a Sprengel-type pycnometer, and viscosities in simple Ostwald-type viscometers. The latter were calibrated by using suitable sucrose solutions of known viscosity (Bingham and Jackson, *Bur. Stand. Bull.*, 1917—18, **14**, 58).

Materials.—The preparation and purification of all the materials used is described in Parts X and XII (*locc. cit.*).

Results.—The density of sulphuric acid was found to be 1·8269 at 25° and its viscosity 24·54 centipoises at the same temperature. Table 1 contains the results of the measurements of the densities and viscosities of all the solutions investigated at 25°. These results are shown graphically in Figs. 1—7. Concentrations are expressed in molalities (m), *i.e.*, moles per 1000 g. of sulphuric acid. Viscosities are given in centipoises.

* Part X, preceding paper.

TABLE 1. *Densities and viscosities of solutions in sulphuric acid.*

m	d_4^{25}	$\eta^{25°}$	m	d_4^{25}	$\eta^{25°}$	m	d_4^{25}	$\eta^{25°}$	m	d_4^{25}	$\eta^{25°}$
Solute : water.			Solute : NaHSO$_4$.			Solute : NH$_2$Ph.			Solute : COMe$_2$.		
0·0330	1·8271	24·47	0·2755	1·8437	27·49	0·0199	1·8242	24·60	0·0450	1·8235	24·12
0·0660	1·8273	24·07	0·4392	1·8531	29·45	0·0799	1·8197	24·80	0·1350	1·8176	23·13
0·1200	1·8280	23·90	0·6968	1·8665	33 70	0·1444	1·8140	25·00	0·1885	1·8129	22·62
0·1840	1·8281	23·63	0·9108	1·8784	35·91	0·2100	1·8081	25·23	0·2320	1·8097	22·19
0·2610	1·8287	23·22	1·365	1·8994	44·19	0·3570	1·7916	25·70	0·2950	1·8035	21·70
0·3440	1·8295	22·94	1·454	1·9064	46·13	0·4140	1·7875	25·90	0·3750	1·7995	21·19
0·4500	1·8313	22·40									
0·6106	1·8332	21·65	Solute : LiHSO$_4$.						Solute : *p*-C$_6$H$_4$Me·NO$_2$.		
			0·2491	1·8310	28·07	Solute : *o*-C$_6$H$_4$(NH$_2$)$_2$.			0·0325	1·8233	24·57
			0·5712	1·8455	32·74	0·0550	1·8269	26·43	0·0720	1·8168	24·60
Solute : disulphuric			0·6331	1·8484	33·78	0·1035	1·8270	27·85	0·1300	1·8080	24·62
acid, H$_2$S$_2$O$_7$.			1·127	1·8660	42·82	0·1500	1·8273	29·52	0·1980	1·8000	24·67
0·0190	1·8270	24·54				0·1958	1·8285	31·55	0·2900	1·7864	24·72
0·0470	1·8280	24·54	Solute : Ba(HSO$_4$)$_2$.			0·2400	1·8295	33·30	0·3850	1·7710	24·80
0·2250	1·8330	24·57	0·0650	1·8475	28·44	0·3124	1·8306	36·56			
0·3550	1·8360	24·66	0·1122	1·8612	31·34	0·3925	1·8308	41·00	Solute : CPh$_3$·OH.		
0·5360	1·8407	24·74	0·1997	1·8871	37·50				0·1190	1·8109	25·05
0·6920	1·8439	24·78	0·3917	1·9382	54·56				0·2050	1·7981	25·48
0·8350	1·8480	24·82	0·4486	1·9530	60·70	Solute : AcOH.			0·3420	1·7804	25·98
			0·7901	2·0361	114·90	0·0470	1·8253	24·43	0·5380	1·7593	26·93
						0·0830	1·8235	24·31			
Solute : NH$_4$HSO$_4$.			Solute : Sr(HSO$_4$)$_2$.			0·1100	1·8224	24·03	Solute : HNO$_3$.		
0·0964	1·8306	24·62	0·0616	1·8416	28·19	0·2430	1·8175	23·86	0·0388	1·8305	24·05
0·3741	1·8323	23·92	0·2266	1·8767	39·81	0·3570	1·8136	23·76	0·0680	1·8330	23·80
0·6556	1·8348	23·93	0·3250	1·8980	48·70	0·4275	1·8105	23·63	0·0975	1·8350	23·52
0·9245	1·8391	24·42	0·5366	1·9382	73·87	0·5740	1·8050	23·22	0·1480	1·8400	23·02
1·3000	1·8437	24·86	0·7568	1·9775	114·7				0·2000	1·8430	22·48
			0·8404	1·9920	137·7				0·2390	1·8492	22·02
						Solute : Ph·CO$_2$H.			0·3625	1·8600	20·80
Solute : KHSO$_4$.			Solute : NH$_2$Pr.			0·0450	1·8235	24·73			
0·2526	1·8446	25·23	0·0130	1·8255	24·46	0·0855	1·8190	25·13	Solute : SO$_2$Cl$_2$.		
0·4633	1·8578	26·14	0·0430	1·8224	24·32	0·1430	1·8120	25·31	0·0490	1·8260	24·13
0·5291	1·8622	26·89	0·0850	1·8168	23·96	0·2080	1·8071	25·69	0·0850	1·8256	23·92
0·8084	1·8780	28·30	0·1350	1·8107	23·72	0·2985	1·7996	26·13	0·1600	1·8240	23·40
1·199	1·8993	31·93	0·2030	1·8033	23·28	0·3720	1·7920	26·64	0·2350	1·8231	22·97
1·776	1·9276	38·84	0·3500	1·7850	22·80	0·4651	1·7832	27·25	0·3150	1·8217	22·55
									0·4012	1·8209	22·01

DISCUSSION

Although a large number of measurements have previously been made of the densities and viscosities of solutions of both water and sulphur trioxide in sulphuric acid (I.C.T., Vol. III, p. 57; Vol. V, p. 13; Landolt–Börnstein's " Physikalische-Chemische Tabellen," 1st edn., Vol. I, p. 397; 2nd edn., Vol. I, p. 135), relatively few values for the composition 100% H$_2$SO$_4$ have been recorded, and only one or two of these refer to 25°. Domke and Bein (Z. *physikal. Chem.*, 1905, **43**, 125) found the density of 100% H$_2$SO$_4$ to be 1·8270 at 25°, with which our value of 1·8269 is in good agreement. Bergius (*ibid.*, 1910, **72**, 357) found the viscosity of sulphuric acid to be 19·15 centipoises at 25°, and Dunstan (*J.*, 1908, **93**, 2179; *Proc.*, 1914, **30**, 104) obtained a value of 23·5 centipoises at the same temperature, both of which are lower than our value of 24·54. The value obtained by Bergius is certainly incorrect, and Dunstan's is probably somewhat in error, as it is very likely that his acid did not have exactly the composition 100% H$_2$SO$_4$, owing to the difficulty of adjusting the composition exactly to this value by ordinary chemical analysis.

With the exception of disulphuric acid and sulphuryl chloride, all the solutes we are considering ionise as hydrogen sulphates. Thus the effects of all these solutes on the viscosity and density are a measure of the relative effects of their cations. The separate effect of the hydrogen sulphate ion on these properties is of course not known, but for convenience we will assume it to be negligibly small and treat all the changes observed as being due to the cations. There is some justification for this assumption in that the hydrogen sulphate ion would be expected to fit easily into the structure of the acid without causing much disturbance and, since the effect of solute on the density and viscosity is

largely due to the changes that they cause in the structure of the solvent, it is reasonable to assume that the effect of the hydrogen sulphate will be rather small.

Densities and Apparent Molal Volumes.—It is clear from Figs. 1—4 that inorganic cations generally cause an increase in the density, this increase being roughly proportional
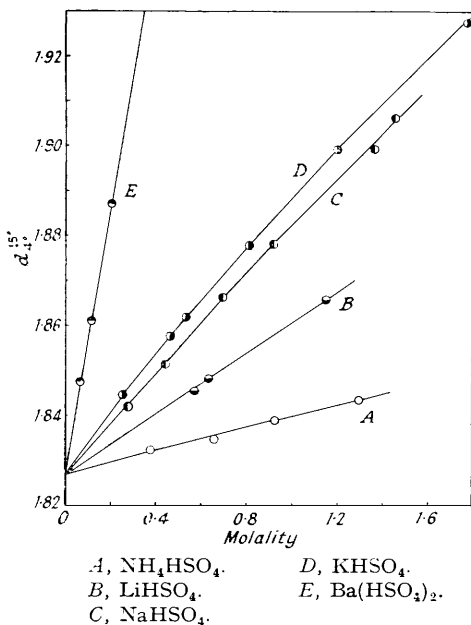
FIG. 1. *Densities of solutions at 25°.*
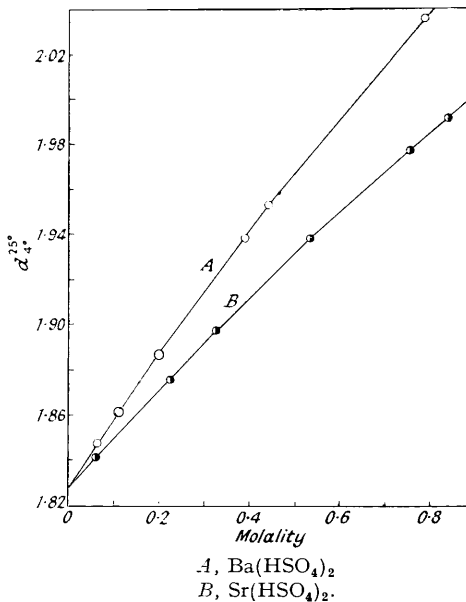
FIG. 2. *Densities of solutions at 25°.*

A, NH₄HSO₄.　　*D*, KHSO₄.
B, LiHSO₄.　　*E*, Ba(HSO₄)₂.
C, NaHSO₄.

A, Ba(HSO₄)₂.
B, Sr(HSO₄)₂.

FIG. 3. *Densities of solutions at 25°.*

FIG. 4. *Densities of solutions at 25°.*

A, *o*-C₆H₄(NH)₂.　　*D*, NH₂Ph.
B, AcOH.　　*E*, NH₂Prⁿ.
C, COMe₂.　　*F*, *p*-C₆H₄Me·NO₂.

A, HNO₃.　　*C*, H₂O.
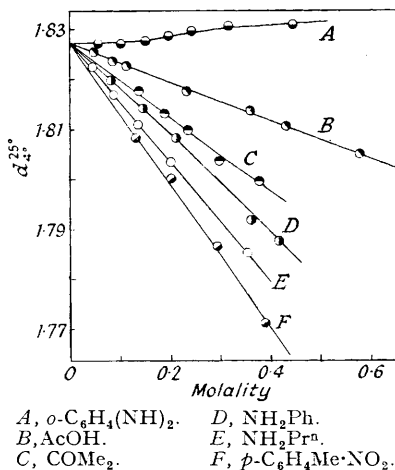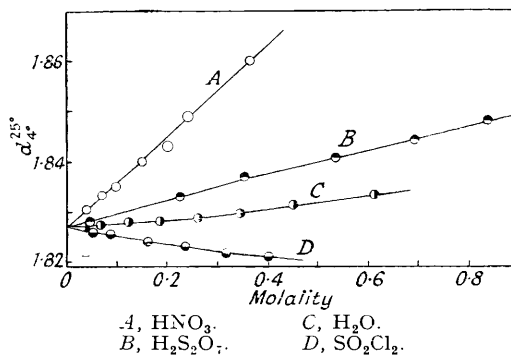*B*, H₂S₂O₇.　　*D*, SO₂Cl₂.

to the concentration, while organic cations generally cause a decrease, this again being roughly proportional to the concentration over the range investigated. It may also be seen that bivalent ions cause a larger increase in the density than univalent ions, and this is to some extent confirmed by the data given in Fig. 3, where it may be seen that the bivalent *o*-phenylenediamine cation is the only organic cation to cause an increase in the density. The density changes can be more conveniently and exactly discussed in terms of the apparent molal volumes of the solutes rather than in terms of the densities them-

selves. The apparent molal volume ϕ is related to the density of the solution ρ by the equation

$$\phi = \frac{1000}{m}\left\{\frac{1}{\rho} - \frac{1}{\rho_1}\right\} + \frac{M_2}{\rho}$$

where M_2 is the molecular weight of the solute, ρ_1 the density of the solvent, and m the molality of the solute. By use of this equation, the apparent molal volumes given in Table 2 were calculated. It can be seen that there is no very marked change of the apparent molal volume with concentration, although in some cases there seems to be a small but fairly regular increase with increasing concentration.
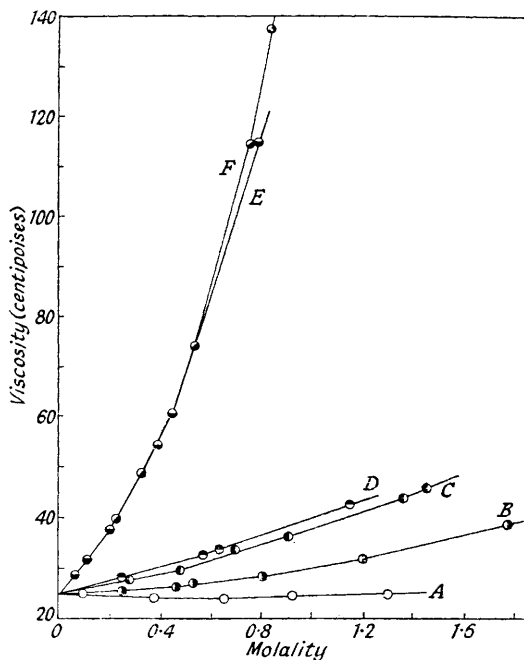

FIG. 5. *Viscosities of solutions at* 25°.

A, NH_4HSO_4. D, $LiHSO_4$.
B, $KHSO_4$. E, $Ba(HSO_4)_2$.
C, $NaHSO_4$. F, $Sr(HSO_4)_2$.

If we make the assumption that the apparent volume occupied by a hydrogen sulphate ion in solution is the same as that of a sulphuric acid molecule, which, in view of our earlier assumption that it causes little disturbance to the structure of sulphuric acid, is not unreasonable, we can easily calculate the apparent molal volumes of the cations in the

TABLE 2. *Apparent molal volume of some hydrogen sulphates.*

m	d_4^{25}	ϕ (cm.³)	m	d_4^{25}	ϕ (cm.³)	m	d_4^{25}	ϕ (cm.³)	m	d_4^{25}	ϕ (cm.³)
Solute : NH_4HSO_4.			Solute : $KHSO_4$.			Solute : HNO_3, *i.e.*,			Solute :		
0·3741	1·8323	58·5	0·2526	1·8446	52·9	$(NO_2)(H_3O)(HSO_4)_2$.			$o\text{-}C_6H_4(NH_3)_2(HSO_4)_2$.		
0·6556	1·8348	59·1	0·4633	1·8578	53·8	0·0690	1·8330	115	0·2035	1·8285	164
0·9245	1·8391	58·6	0·5291	1·8622	53·6	0·0994	1·8350	117	0·2519	1·8295	163
1·3000	1·8347	58·6	0·8084	1·8780	54·1	0·1525	1·8400	115	0·3329	1·8306	163
			1·199	1·8993	54·3	0·2082	1·8430	118	0·4252	1·8308	163
Solute : $NaHSO_4$.			1·776	1·9276	54·5	0·2508	1·8492	114			
0·2755	1·8437	46·6				0·3903	1·8600	114			
0·4392	1·8531	46·6	Solute : $LiHSO_4$.						Solute : $Ph\cdot NH_3,HSO_4$.		
0·9110	1·8784	47·4	0·5712	1·8455	46·8				0·2144	1·8081	132
1·364	1·8998	47·8	0·6331	1·8484	46·3				0·3516	1·7916	137
1·453	1·9064	47·4	1·127	1·8660	45·8				0·4326	1·7875	135

solutions we have investigated. The values given in col. 3 of Table 3 were calculated by using a value of 54 c.c., the molal volume of sulphuric acid, for the apparent molal volume of the hydrogen sulphate ion. We see that very small or negative values for the apparent

molal volumes are obtained. In other words, the cations produce in most cases a decrease and not an increase in volume when in solution in sulphuric acid. This can be attributed to their effect on the solvent, which we describe as solvation, the sulphuric acid molecules that are bound strongly to the cations occupying less volume than the free solvent molecules.

TABLE 3. *Apparent molar volumes and solvation numbers of alkali and alkaline-earth cations.*

| Solute	Mean ϕ (cm.³)	Mean ϕ_+ (cm.³)	r_+ (Å)	V_+ (cm.³)	Contraction volume, $(V_+ - \phi_+)$ (cm.³)	Solvation number
NH₄HSO₄	59	5	1·48	8·2	3	(1)
KHSO₄	54	0	1·33	5·9	6	2
NaHSO₄	47	− 7	0·95	2·2	9	3
LiHSO₄	46	− 8	0·60	0·5	9	3
Ba(HSO₄)₂	89	−19	1·35	6·1	25	8
Sr(HSO₄)₂	86	−22	1·13	3·6	25	8

If we know the true volume of a cation we can calculate the contraction that it produces in the solvent by subtracting this true volume from its apparent molal volume. For the alkali and alkaline-earth metal ions we may assume that an approximate value of their true volumes may be obtained from their crystal radii. The volumes obtained in this way are given in col. 5 of Table 3, and the " contraction volumes " calculated from them

FIG. 6. *Viscosities of solutions at 25°.*

A, H₂O.   *C*, SO₂Cl₂.
B, H₂S₂O₇.   *D*, HNO₃.
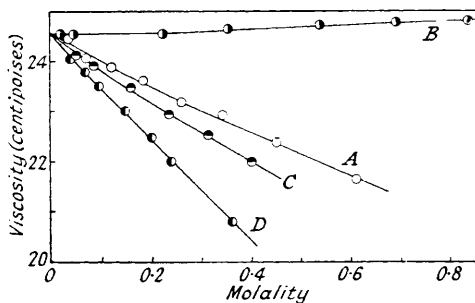
in col. 6. Assuming that the larger the contraction produced by the ion the more strongly is it solvated, we see that the extent of solvation increases in the series

$$NH_4^+ < K^+ < Na^+ < Li^+ < Ba^{++} < Sr^{++}$$
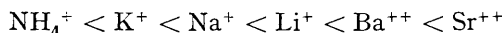
With the exception of the ammonium ion, whose transport number was not measured, this is the same order as is suggested by the transport numbers of these ions (Part X, *loc. cit.*) and as has been found from the extent of solvation of these ions in aqueous solutions. It seemed worth while to attempt to express the degree of solvation of these cations in terms of solvation numbers in order that a more exact comparison might be made with other methods of estimating the extent of solvation. If we assume a value of unity for the solvation number of the ammonium ion as is obtained from cryoscopy (Part I, *loc. cit.*) we may then assume that the 3 c.c. volume contraction produced by the ammonium ion corresponds to one unit of solvation; thence the potassium ion, which produces a contraction of 6 c.c., has a solvation number of 2. The values listed in col. 7 of Table 3 were all calculated in this manner. The value found for the potassium ion agrees with that obtained by cryoscopy.

The apparent molal volumes of some of the other solutes investigated are given in Table 4. Mean apparent molal volumes of their cations have been calculated in the same way as before on the assumption that the molal volume of the hydrogen sulphate ion is 54 c.c. In order to interpret these values in terms of solvation, it is necessary to make some assumption about the true volumes of the cations, and this is more difficult to do than for the alkali and alkaline-earth metal ions. The volume of the hydroxonium ion will probably not differ greatly from that of the ammonium ion, which is given in Table 3 as 8·2 c.c. Hence from the apparent molal volume of the hydroxonium ion, given in Table 4 as 7 c.c., it follows that the hydroxonium ion causes a solvent contraction of ∼1 c.c.,

corresponding to a solvation number of 0·4. A value of unity for this solvation number was obtained from cryoscopy (Part II, *loc. cit.*). Nitric acid is known from conductivity, cryoscopic, and other evidence (Gillespie and Millen, *Quart. Reviews*, 1948, **2**, 277) to ionise

TABLE 4. *Apparent molal volumes of water, nitric acid, aniline, and o-phenylenediamine.*

Solute	Mean ϕ (cm.³)	Mean ϕ_+ (cm.³)
Water, $(H_3O)(HSO_4)$	61	7
Nitric acid, $(NO_2)(H_3O)(HSO_4)_2$	115	7
Aniline, $Ph \cdot NH_3HSO_4$	135	81
o-Phenylenediamine, $[C_6H_4(NH_3)_2](HSO_4)_2$	163	57

according to the equation $HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$. Hence, the apparent molal volume of the cations listed in Table 4 is actually the sum of the apparent molal volumes of the nitronium and hydroxonium ions. From the apparent molal volume of the hydroxonium ion also given in this table, it may be seen that the nitronium ion has a mean apparent molal volume of 0 c.c. It is difficult to make any reasonable assumption
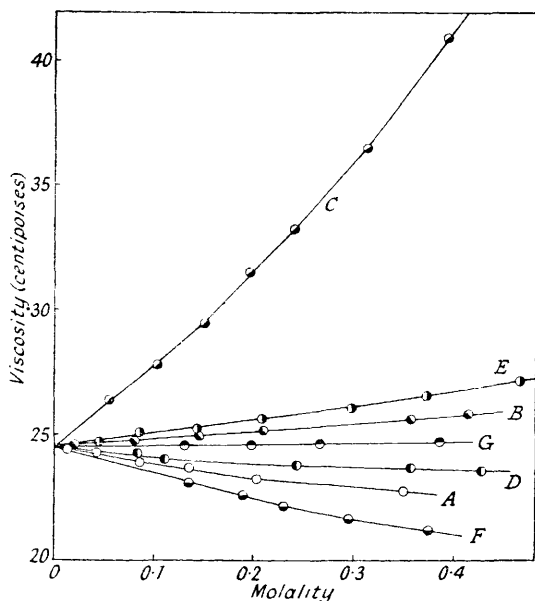

FIG. 7. *Viscosities of solutions at 25°.*

A, NH_2Pr^n.
B, NH_2Ph.
C, $o\text{-}C_6H_4(NH_2)_2$.
D, AcOH.
E, $Ph \cdot CO_2H$.
F, $COMe_2$.
G, $p\text{-}C_6H_4Me \cdot NO_2$.

about the true molal volume of the nitronium ion and hence to calculate the solvation number, but its zero apparent molal volume leaves no doubt that it is solvated. Cryoscopic measurements (Part III) have given a value of 2 for the solvation number of the nitronium ion.

A comparison of aniline and o-phenylenediamine is of some interest. The true volumes of their cations would be expected to be rather similar, with the o-phenylenediamine having the slightly greater volume. The apparent molal volume of the o-phenylenediamine cation is, however, considerably less than that for the anilinium ion, which can be attributed to the greater solvation of the doubly charged o-phenylenediamine cation.

Viscosities of Solutions.—It may be seen from Fig. 5 that inorganic cations generally increase the viscosity of sulphuric acid, the effect of the bivalent ions being particularly great, although the ammonium ion gives a slight initial decrease followed by a slight increase with increasing concentration. The organic cations that we have investigated do not, as may be seen from Figs. 6 and 7, cause very large changes in the viscosity, with the exception of the cation of o-phenylenediamine, which gives a rather large increase comparable to that produced by the bivalent inorganic cations.

These viscosity changes may be explained in terms of the effects of the cations on the structure of the solvent. The small inorganic cations cause a " tightening " of the structure of the solvent around the ion, pulling the solvent molecules strongly together,

considerably restricting their freedom of movement, and thus increasing the viscosity. It is reasonable to expect, therefore, that their effect will be related to their degree of solvation and indeed it may be seen from Fig. 5 that the order of increasing viscosity of their solutions is the same as that of their degree of solvation as derived from density measurements, namely,

$$NH_4^+ < K^+ < Na^+ < Li^+ < Ba^{++} < Sr^{++}$$
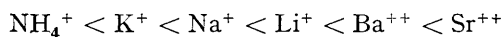
In addition to the effect caused by their solvation, the large organic cations will tend to disrupt the structure of the surrounding solvent, as they will not fit easily into it, and this will probably be accompanied by a decrease in viscosity. A more detailed interpretation of the viscosities that we have determined does not seem possible at the present stage of our knowledge of these solutions.

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