

259. *Solutions in Selenic Acid. Part I. The Viscosities and Densities of Solutions in Selenic Acid.*

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The densities and viscosities of dilute solutions of water, alkali hydrogen selenates, nitric acid, and a few organic compounds in selenic acid at 35° have been determined. Apparent molal volumes of some of the cations have been calculated; they are discussed in terms of solvation. The viscosities of some of the solutions are interpreted as resulting from solvation.

LITTLE has been reported about the viscosities and densities of selenic acid solutions. Hetherington, Hub, and Robinson¹ investigated the system selenic acid–nitryl fluoride but not other solutes. Our work was directed mainly to the behaviour of the alkali-metal selenates in this solvent, as they affect the density and especially the viscosity in a way similar to that of alkaline-earth hydrogen sulphates in sulphuric acid.²

¹ Hetherington, Hub, and Robinson, *J.*, 1955, 4041.

² Gillespie and Wasif, *J.*, 1953, 215.

EXPERIMENTAL AND RESULTS

Selenic acid containing 92.4% of SeO_3 was used; it had m. p. $\sim 12.5^\circ$ and specific conductivity $0.182 \text{ ohm}^{-1} \text{ cm.}^{-1}$ at 35° . For solutions, the conductivity was measured and the concentration of the solute interpolated from unpublished specific conductivity-concentration curves. Samples of the solution were transferred from the conductivity cell to the viscometer and the pyknometer, with protection from atmospheric moisture. Further portions of the solute were then added and the procedures repeated. This method of determining the concentration of the solutions was easier and faster than making up each solution separately by weight, although the latter method was used in some cases.

Materials.—Ammonium, potassium, and sodium hydrogen selenate were recrystallised twice and kept under a vacuum at 50° over desiccants until of constant weight. Methyl alcohol was fractionated, a middle fraction of b. p. 65° being collected. Ethyl alcohol was refluxed with ethyl succinate and sodium for 4 hr. and the alcohol fractionated, a fraction of b. p. 78.2° being collected.³ Acetic acid was distilled from 100% sulphuric acid at room temperature. Benzoic acid was twice recrystallised from hot water and dried (m. p. 121°). AnalaR acetone was dried (K_2CO_3) and distilled, the fraction of b. p. 56.7 – 57° being collected. Nitric acid was prepared by the method of Hughes *et al.*⁴

Densities were determined in a Sprengel-type pyknometer, and viscosities in a simple Ostwald-type viscometer calibrated by means of sucrose solutions.⁵

Results.—The density of selenic acid was $2.5263 \text{ g. cm.}^{-3}$ and its viscosity 21.52 centipoises at 35° . These results are comparable with, and may be even higher than, those for sulphuric acid at the same temperature (d 1.8269, η 24.54 at 25°). Table 1 lists the densities and viscosities of a variety of solutes in selenic acid at 35° , shown graphically in Figs. 1 and 2, and those for sulphuric acid are in Figs. 3 and 4.

DISCUSSION

Figs. 1 and 4 show the densities of a number of solutes in selenic and sulphuric acid, respectively. It is seen that the alkali-metal salts in selenic and sulphuric acid increase the density but that ammonium hydrogen selenate in selenic acid decreases the density. For solutions of sulphuric acid it was noted⁵ that the effect of the different solutes is due to the cations present as most of the latter ionised in a simple way, giving one or more cations and the hydrogen sulphate anion. The differences for selenic acid solutions can be similarly explained when the mode of ionisation is known with certainty, as for nitric acid,⁶ water, and alkali-metal selenates,⁷ and our discussion will be mainly concerned with these solutes. Figs. 1 and 4 show that the effect of different solutes on the density of the solution, and consequently on the structure, depends on both the charge density and the shape of the solute molecule, as in sulphuric acid solutions.⁵ It appears that the two acid systems represent a very compact three-dimensional structure type. X-Ray studies show selenic⁸ and sulphuric acid⁹ are extensively hydrogen-bonded in the solid state. The selenate group is surrounded by two hydrogen bonds of 2.61 \AA and two of 2.68 \AA ; in sulphuric acid the hydrogen bonds around the sulphate group are 2.85 \AA in length; the average length is slightly smaller in selenic acid and this probably accounts for the higher density of selenic acid and illustrates a greater compactness in its structure and consequently greater sensitivity to the effects of different solutes.

Owing to ionisation to hydrogen selenate ion in each of the relevant solutions, their viscosities and densities are measures of the effect of the cations. The separate effect of the hydrogen selenate ion on these properties is of course not known, but we shall assume it to be negligible and treat all the changes as due to the cations. There is some justification for this in that the hydrogen selenate ion would be expected to fit easily into the

³ Smith, *J.*, 1927, 1288.

⁴ Hughes, Ingold, and Read, *J.*, 1950, 2400.

⁵ Bingham and Jackson, Nat. Bur. Standards U.S.A., Bull. No. 18-14-58 (1917).

⁶ Ingold, Millen, and Poole, *Nature*, 1956, 158, 480.

⁷ Wasif, unpublished work.

⁸ Bailey and Wells, *J.*, 1951, 968.

⁹ Finback, Rouning, and Vier, *Tidsskr. Kjemi, Bergvesen, Met.*, 1944, 426.

structure of the acid without causing much disturbance, and thus without much effect on the density and viscosity.

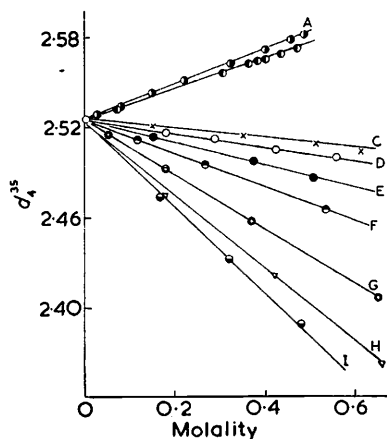


FIG. 1. Densities of selenic acid solutions at 35°.

Solutes: (A) KHSeO_4 . (B) NaHSeO_4 . (C) H_2O . (D) NH_4HSeO_4 . (E) MeOH . (F) AcOH . (G) EtOH . (H) Ac_2O . (I) BzOH .

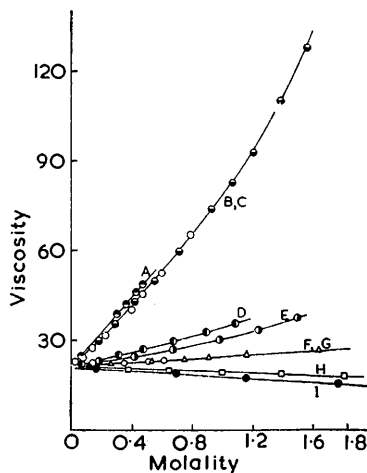


FIG. 2. Viscosities (centipoises) of selenic acid solutions at 35°.

Solutes: (A) NaHSeO_4 . (B, \circ) KHSeO_4 . (C, \ominus) NH_4HSeO_4 . (D) BzOH . (E) Ac_2O . (F, Δ) AcOH . (G, \circ) H_2O . (H) EtOH . (I) HNO_3 .

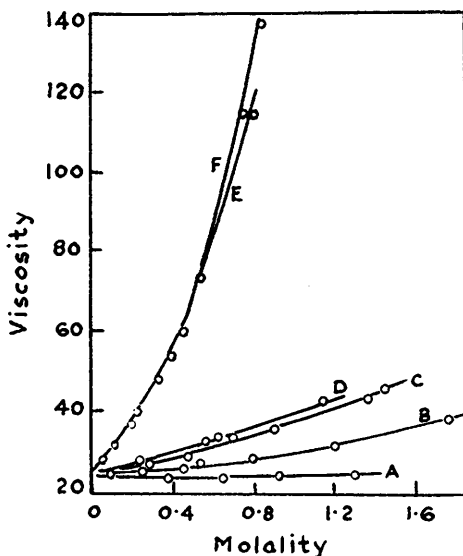


FIG. 3. Viscosities (centipoises) of sulphuric acid solutions at 25°.

Solutes: (A) NH_4HSO_4 . (B) KHSO_4 . (C) NaHSO_4 . (D) LiHSO_4 . (E) $\text{Ba}(\text{HSO}_4)_2$. (F) $\text{Sr}(\text{HSO}_4)_2$.

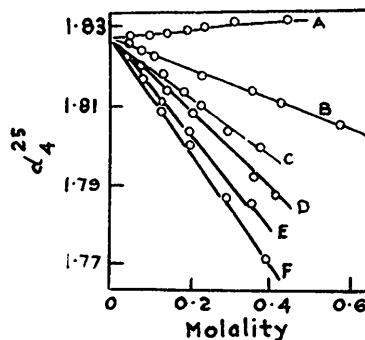


FIG. 4. Densities of sulphuric acid solutions at 25°.

Solutes: (A) $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$. (B) AcOH . (C) COMe_2 . (D) NH_2Ph . (E) NH_2Pr^n . (F) $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$.

Fig. 1 shows that sodium and potassium hydrogen selenate increase the density while the ammonium salt decreases it. The change in density is roughly proportional to the concentration over the range investigated.

TABLE 1.

Viscosities and densities of some selenic acid solutions.*

Ammonium hydrogen selenate			Potassium hydrogen selenate			Sodium hydrogen selenate		
<i>C</i>	d_4^{35}	Viscosity	<i>C</i>	d_4^{35}	Viscosity	<i>C</i>	d_4^{35}	Viscosity
0.1813	2.5176	30.00	0.02507	2.5291	22.50	0.06819	2.5325	25.50
0.2927	2.5125	36.00	0.07739	2.5350	24.51	0.3037	2.5570	39.00
0.4234	2.5066	43.31	0.1388	2.5431	27.50	0.3633	2.5630	42.30
0.5584	2.5000	50.71	0.2203	2.5515	31.60	0.4021	2.5731	49.09
0.7160	2.4927	60.75	0.3981	2.5713	40.03			
0.9135	2.4840	74.30	0.4856	2.5950	45.70			
1.0690	2.4771	85.80						
Acetic anhydride			Benzoic acid			Nitric acid		
<i>C</i>	d_4^{35}	Viscosity	<i>C</i>	d_4^{35}	Viscosity	<i>C</i>	d_4^{35}	Viscosity
0.1767	2.4750	22.90	0.1652	2.4750	23.43	0.1574	2.5151	21.08
0.4141	2.4210	24.85	0.3131	2.4331	25.30	0.6908	2.4725	19.29
0.6682	2.3631	27.00	0.4740	2.3900	27.00	1.1480	2.4375	17.57
0.9840	2.2852	30.41	0.6824	2.3252	29.87	1.7790	2.3920	15.80
Acetic acid			Water			Methyl alcohol		
<i>C</i>	d_4^{35}	Viscosity	<i>C</i>	d_4^{35}	Viscosity	<i>C</i>	d_4^{35}	Viscosity
0.1103	2.5133	21.80	0.1500	2.5211	21.94	0.1500	2.5142	
0.2659	2.4965	22.30	0.3501	2.5145	22.50	0.3750	2.4971	
0.5310	2.4467	23.26	0.5100	2.5089	22.90	0.5000	2.4862	
0.7430	2.4370	23.90	0.6100	2.5038	23.24	0.6361	2.4700	
0.9035	2.4245	24.63				0.9341	2.4241	
1.1650	2.4000	25.50				1.3270	2.4076	

* *C* = mole per kg. of solvent. Viscosity in centipoises. d = density referred to water at 4°.

Density may be conveniently and exactly discussed in terms of the apparent molal volume ϕ of the solutes, rather than in terms of density, to which it is related by the equation

$$\phi = \frac{1000}{m} \left(\frac{1}{\rho} - \frac{1}{\rho_1} \right) + \frac{M}{\rho},$$

where M = molecular weight of the solute, m = molality, and ρ and ρ_1 = density of the solution and solvent, respectively. Apparent molal volumes, calculated in this way, are given in Table 2, showing no marked change of the apparent molal volume with concentration, although in some cases there seem to be small but fairly regular increases with increasing concentration. If we assume that the apparent molal volume occupied by a

TABLE 2.

Apparent molal volumes of ammonium, potassium, and sodium hydrogen selenate in selenic acid.

Ammonium			Potassium			Sodium		
<i>m</i>	d_4^{35}	ϕ	<i>m</i>	d_4^{35}	ϕ	<i>m</i>	d_4^{35}	ϕ
0.3626	2.5176	67.31	0.0501	2.5291	60.64	0.1364	2.5325	58.62
0.5854	2.5125	68.03	0.1548	2.5350	62.55	0.6074	2.5570	57.23
0.8464	2.5066	68.26	0.2776	2.5431	61.86	0.7266	2.5630	57.03
1.1168	2.5000	68.46	0.4406	2.5515	62.46			
1.4320	2.4927	68.72						Average 57.62
		Average 68.15			Average 61.87			

hydrogen selenate ion in solution is the same as that (56.23 cm.³) of a selenic acid molecule (see above), we calculate the apparent molal volume of the cations in the solutions to be those given in Table 3. This Table shows small or negative values for the contraction volumes of the ions NH₄⁺, Na⁺, and K⁺. The last two decrease rather than increase the volume when in solution in selenic acid. This can be attributed to their effect on the solvent, which may be described as solvation, the selenic acid molecules that are bound strongly to the cations occupying less volume than the free solvent molecules.

TABLE 3.

Apparent molal volumes and solvation numbers of the alkali-metal ions.

Solute	Mean ϕ (cm. ³)	Mean ϕ_+ (cm. ³)	r_+ (Å)	V_+ (cm. ³)	Contraction $V_+ - \phi_+$	Solvation number
NH ₄ HSeO ₄	68.15	11.92	1.48	8.2	-3.72	—
KHSeO ₄	61.87	5.64	1.33	5.9	+0.26	1.0
NaHSeO ₄	57.62	1.39	0.95	2.2	+0.81	3.0

Knowing the true volumes of the alkali-metal cations we can calculate the contractions they produce in the solvent by subtracting these volumes from the apparent molal volumes. Assuming that the larger the contraction the more strongly is the ion solvated, we see that the extent of solvation increases in the direction NH₄⁺ < K⁺ < Na⁺.

The degree of solvation of the sodium and the potassium cation can also be expressed as solvation numbers. The ammonium ion did not cause a contraction although its effect on viscosity could not be ignored. If we assume a solvation number of one for the potassium ion, the sodium ion would then have a solvation number of approximately three. This trend is similar to, though not identical with, that for solutions of the sulphates of the same ions in sulphuric acid, for which the solvation numbers⁵ are NH₄⁺ 1.0, K⁺ 2.0, and Na⁺ 3.0.

An attempt to calculate the apparent molal volumes of the nitronium and the hydroxonium ion in selenic acid gave values of 16.55 and 19.08 cm.³, respectively.

Fig. 2 shows that alkali hydrogen selenates increase the viscosity of selenic acid while organic solutes vary in their behaviour. There is no doubt that the changes noted must be due to corresponding changes in the structure of the solvent due to solvation, disruption, or some other process that might affect the state of the solvent molecules.

A more detailed interpretation of the viscosity and the density of the solutes investigated in this system cannot be provided at the present stage of this work.