169. *Solutions in Sulphuric Acid. Part XXIX.*[1] *Densities and Apparent Molar Volumes of Some Electrolyte Solutions.*

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The densities of solutions of a number of electrolyte solutions in sulphuric acid at 25° are reported. The temperature-dependence of the densities of sulphuric acid and sodium and potassium hydrogen sulphate solutions has also been studied. Apparent molar volumes of some metal cations have been calculated from the densities. They are compared with the corresponding values in aqueous solutions and are discussed in terms of the solvation of the cations.

Solutions in sulphuric acid are most conveniently made up by weight, so that in order to obtain the volume concentrations needed for the interpretation of cryoscopic and conductivity measurements [1,2] it was necessary to obtain the densities of all the solutions studied by these methods. Densities can also be used to provide information on ion-solvent interaction. The densities of some electrolyte solutions have been measured at 25° by Gillespie and Wasif.[3] The present work extends these measurements to cover all the electrolyte solutions whose conductivities and freezing points have been measured.[1,2] The results obtained at 25° are given in Table 1 in the form of interpolated values at round

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[1] Part XXVIII, Bass, Gillespie, and Oubridge, preceding paper.

[2] Flowers, Gillespie, and Robinson, unpublished work.

[3] Gillespie and Wasif, *J.*, 1953, 215.

concentrations w (moles per kg. of solution). The densities of sulphuric acid and of solutions of sodium and potassium hydrogen sulphates were also measured at 5° intervals over the range 0—40°. In each case the densities were linear functions of the temperature:

$$\rho_t = \rho_{25} + a(25 - t) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where ρ_{25} is the density at 25° and t is the temperature in °c. The coefficient a was found to be the same for sulphuric acid and the two electrolyte solutions and almost independent of the concentration of the solutions up to $w = 0·5$. The mean value $a = (1·08 \pm 0·01) \times 10^{-3}$ was used in order to obtain the densities at 10° that were required for the interpretation of cryoscopic measurements.[1]

TABLE 1. *Interpolated densities at 25°.*

w	$LiHSO_4$	$NaHSO_4$	$KHSO_4$	$RbHSO_4$	$CsHSO_4$	$AgHSO_4$	$TlHSO_4$
0·05	1·828	1·830	1·830	1·8335	1·8360	1·835	1·843
0·10	1·829	1·833	1·834	1·8410	1·8463	1·846	1·860
0·15	1·829	1·836	1·838	1·8474	1·8562	1·857	1·879
0·20	1·830	1·839	1·841	1·8545	1·8660	1·869	1·898
0·25	1·831	1·842	1·845	1·8628	1·8759	1·881	1·918
0·30	1·832	1·845	1·849	1·8681	1·8858	1·893	1·938
0·35	1·832	1·848	1·852	1·8754	1·8957	1·906	1·957
0·40	1·833	1·851	1·856	1·8827	1·9055	1·919	1·978

w	NH_4HSO_4	H_3O,HSO_4	$Ca(HSO_4)_2$	$Sr(HSO_4)_2$	$Ba(HSO_4)_2$	$H_2S_2O_7$	$HB(HSO_4)_4$
0·05	1·828	1·8272	1·834	1·839	1·843	1·8276	1·831
0·10	1·828	1·8275	1·842	1·850	1·858	1·8290	1·835
0·15	1·829	1·8278	1·849	1·862	1·874	1·8307	1·840
0·20	1·830	1·8282	1·857	1·874	1·890	1·8323	1·844
0·25	1·830	1·8286	1·864	1·886	1·906	1·8336	1·849
0·30	1·831	1·8291	1·872	1·898	1·922	1·8344	1·853
0·35	1·832	1·8296	—	1·911	1·939	1·8360	—
0·40	1·832	1·8302	—	—	—	1·8373	—

w	$COMe_2$	$COPhMe$	$COPh_2$	$(p\text{-}Cl{\cdot}C_6H_4)_2CO$	$(p\text{-}Me{\cdot}C_6H_4)_2CO$	NH_2Ph	$NHPh_2$	NPh_3
0·05	1·8231	1·821	1·817	1·819	1·815	1·8223	1·815	1·812
0·10	1·8194	1·815	1·808	1·812	1·803	1·8196	1·803	1·797
0·15	1·8157	1·808	1·798	1·804	1·790	1·8131	1·791	1·783
0·20	1·8119	1·802	1·789	1·796	1·778	1·8085	1·779	1·768
0·25	1·8082	1·796	1·779	1·789	1·766	1·8035	1·766	1·754
0·30	1·8045	1·790	1·770	1·781	1·754	1·7983	1·754	1·739
0·35	1·8008	1·784	1·760	1·773	1·742	1·7931	1·742	1·724
0·40	1·7972	1·778	1·751	1·766	1·729	1·7878	1·730	1·709

Apparent Molar Volumes.—From the densities at 25° apparent molar volumes were calculated by means of the expression

$$\phi_v = M/\rho^\circ + 10^3(1/\rho - 1/\rho^\circ)/w \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where M is the molecular weight of the solute, ρ is the density of the solution and ρ° is the density of the pure solvent. The densities were not sufficiently accurate to give reliable values of the apparent molar volumes at concentrations less than $w = 0·1$. At higher concentrations the apparent molar volumes were either independent of the concentration or varied only slowly and almost linearly with concentration up to $w = 0·5$. When necessary a value of the apparent molar volume at $w = 0$ was obtained by linear extrapolation. Values are given in Table 2. In aqueous solutions the apparent molar volume is a linear function of $c^{\frac{1}{2}}$, and by extrapolation to $c = 0$ the partial molar volume can be obtained. It was not possible to obtain such a plot from our data, partly because they were not sufficiently accurate at low concentrations, and partly because of the complication of the relatively high ionic strength of the pure solvent.

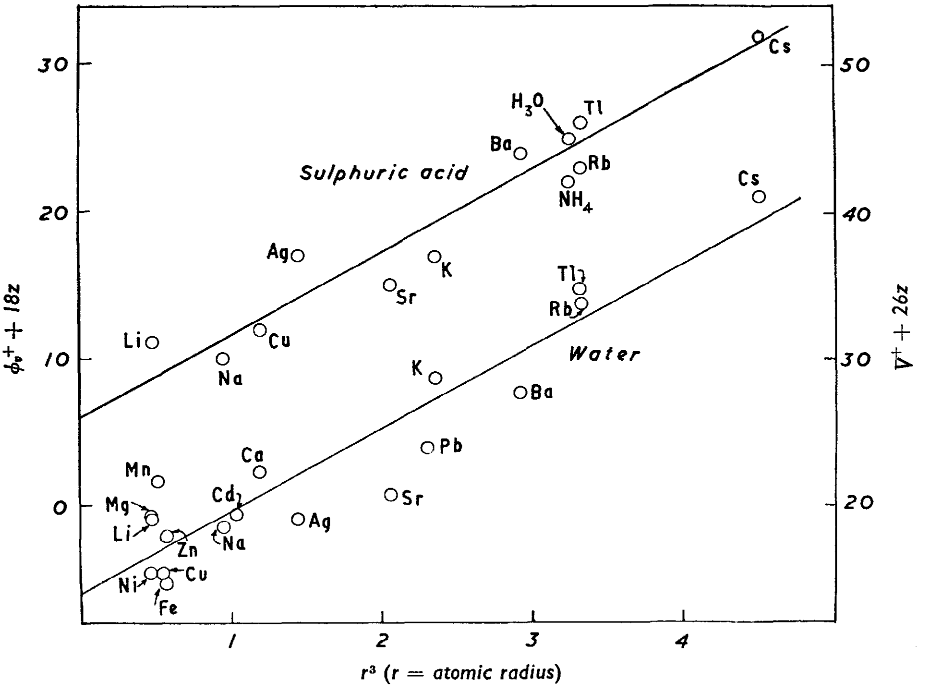
If it is assumed that the apparent molar volume of the hydrogen sulphate ion is the same as that of sulphuric acid,[3] *i.e.*, 54 c.c., the apparent molar volumes of the cations

(ϕ_v^+) may be calculated, and these are given in Table 2. They may be compared with the partial molar volumes in aqueous solution[4] [$\bar{V}^+(H_2O)$] which are also given in this Table. The close similarity in the values for univalent ions in the two solvents is remarkable—the difference in the case of H_3O^+ is not particularly surprising in view of the special relation of H_3O^+ to the water structure. This agreement may be regarded as supporting the assumptions on which these values are based, namely, that[4] the partial molar volume of the hydrogen ion (H^+) in aqueous solution is 6 c.c., and that[3] the apparent molar volume of the hydrogen sulphate ion in sulphuric acid is 54 c.c. For bivalent ions the partial molar volumes in water are smaller than the apparent molar volumes in sulphuric acid.

TABLE 2. *Apparent molar volumes and solvation numbers of cations in solutions of their hydrogen sulphates.*

Cation	ϕ_v (c.c./mole)	ϕ_v^+ (c.c./mole)	$\bar{V}^+_{H_2O}$ (c.c./mole)	r (Å)	V^+ ($2{\cdot}5r^3$) (c.c./mole)	δV (c.c./mole)	s	s_{cryos}
Li	47	−7	−7·0	0·78	1·2	−8	2	2·3
Na	46	−8	−7·5	0·98	2·4	−10	3	3·0
K	53	−1	1·7	1·33	5·9	−7	2	2·1
Rb	59	+5	7·7	1·49	8·3	−3	1	—
Cs	68	+14	15·1	1·65	11·3	+3	0	—
Ag	53	−1	−7·0	1·13	3·6	−5	1·5	2·1
Tl	62	8	7·7	1·49	8·3	0	0	—
NH_4	59	5	—	1·48	8·2	−3	1	1·2
H_3O	61	7	12·0	1·48	8·2	−1	0·3	1·8
Ca	84	−24	−29·7	1·06	3·0	−27	8	—
Sr	87	−21	−30·2	1·27	5·8	−27	8	—
Ba	96	−12	−24·3	1·43	7·4	−19	5	6·5

Apparent molar volumes of cations in sulphuric acid and partial molar volumes of cations in water.



Couture and Laidler[4] showed that the partial molar volumes of ions in aqueous solution

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[4] Couture and Laidler, *Canad. J. Chem.*, 1956, **34**, 1209.

are proportional to the ionic charge and the cube of the crystal radius.[5] A similar relation appears to hold for apparent molar volumes of cations in sulphuric acid as is shown by the plot of $\phi_v + 18z$ against r^3 in the Figure, where z is the ionic charge. The straight line shown has a slope of 5·6 and an intercept of 6 c.c. The mean deviation in the volumes is 1·6 c.c. Thus the following empirical relation holds between the apparent molar volumes of the cations and their crystal radii and charge:

$$\phi_v^+ = 6 + 5{\cdot}6r^3 - 18z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Couture and Laidler [4] have given the relation

$$\bar{V}^+ = 16 + 4{\cdot}9r^3 - 26z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

for the partial molar volumes of cations in aqueous solution. However, on replotting their values for uni- and bi-valent ions it was found that a straight line could be drawn through them having the same slope as that for the apparent molar volumes in sulphuric acid and corresponding to the relation:

$$\bar{V}^+ = 14 + 5{\cdot}6r^3 - 26z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The mean deviation in the volumes is 2·1 c.c., compared with 2·4 c.c. for Couture and Laidler's relation (equation 4). Thus for univalent ions identical relations appear to hold for sulphuric acid solutions and for aqueous solutions. The physical significance of these empirical relations is not clear.

Solvation Numbers.—If we follow Eucken [6] and Gillespie and Wasif's treatment [3] we can relate the apparent contraction in the solvent ($\delta v = \phi_v^+ - v^+$) to the primary solvation number of the cation. By assuming a solvation number for one cation, values for other cations may be obtained provided that the solvent contraction is proportional to the extent of solvation, *i.e.*, that $\delta V = s\delta V_0$ where δV_0 is the contraction produced per solvent molecule in the solvation shell, and s is the solvation number of the cation. If we take the solvation number of the sodium ion to be 3·0 from cryoscopy,[1] then $\delta V_0 = 3{\cdot}5$ c.c./mole. The solvation numbers of the other cations deduced on this basis are given in Table 2. The values obtained by cryoscopy,[1] which are also given, agree well with these. The cæsium ion produces an apparent expansion in the solvent. It is presumably very little, if at all, solvated and the apparent expansion might be explained if the solvent structure is broken by the large ion or, perhaps more plausibly, if the actual volume of the ion is greater than that calculated from its crystal radius.[7] A radius in solution of 1·77 compared with the crystal radius of 1·65 Å would account for the observed apparent molar volume. Even if no precise significance can be attached to our values of the solvation numbers the values of δV_0 give an indication of the relative extents of interaction between the ions and the solvent.

Experimental.—Densities were measured by using either the float densitometer, described previously,[8] or a 10 c.c. specific-gravity bottle. Temperature coefficients were studied by using a small dilatometer that had been calibrated with water. Preparation and purification of sulphuric acid and the various solutes are described elsewhere.[1,2,9]

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[5] Goldschmidt, *Skrifter Norske Videnskap. Akad., Oslo I, Matem.-Naturvid. Klasse*, 1926, No. 2.
[6] Eucken, *Z. Elektrochem.*, 1948, **51**, 6.
[7] Gurney, "Ionic Processes in Solution," McGraw-Hill, New York, 1953.
[8] Flowers, Gillespie, Oubridge, and Solomons, *J.*, 1958, 667.
[9] Bass and Gillespie, *J.*, 1960, 814.