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On Properties of Strong Electrolytes

II. The Densities of Aqueous Magnesium, Calcium, Strontium, and Barium Perchlorate Solutions

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The densities of aqueous magnesium, calcium, strontium, and barium perchlorate solutions were determined by the pycnometric method. The concentrations were varied from 0.001 to 0.07 M at 20° and 30°C and from 0.001 M to 2 M at 25°C, those of the calcium perchlorate solutions over the latter concentration range at 20°C also. The results could be represented by Root's equations,[1] the constants of which were evaluated by the method of least squares. The values 63.2, 69.0, 71.5, and 76.3 cm^3/mole, respectively, were obtained for the apparent molal volumes of magnesium, calcium, strontium and barium perchlorate in water at 25°C. These values are directly proportional to the crystal radii of the metal ions.

The present work is a continuation of our studies on the densities, viscosities, conductivities, refractions, and structures of metal perchlorate solutions. A smaller part of these results has been reported elsewhere.[2] The choice of metal perchlorate solutions as the objects of our studies is based on the fact that the perchlorate anion does not in general form complexes with metal ions. Metal perchlorate solutions are hence suitable for the study of solution properties without the disturbing effect of complex formation.

In this paper we report and discuss the results of density measurements on aqueous magnesium, calcium, strontium and barium perchlorate solutions.

EXPERIMENTAL

Magnesium, calcium, strontium, and barium perchlorate were prepared by adding almost equivalent amounts of concentrated perchloric acid (E. Merck AG, *pro analysi*, 70 %) to mixtures of conductivity water (distilled and deionized) and magnesium carbonate (E. Merck AG, *p.a.*), calcium carbonate (E. Merck AG, *p.a.*), strontium carbonate (J. T. Baker Chemical Co., analytical reagent), or barium carbonate (E. Merck AG, *p.a.*). The pH values of the resulting solutions were adjusted to about seven with magnesium, calcium, or strontium oxide (E. Merck AG, *p.a.*) or barium hydroxide

(E. Merck AG, *p.a.*), respectively. The solutions were allowed to stand overnight, filtered through a fine sintered glass (G4 or G5) disc and adjusted to pH 4–5 with dilute perchloric acid. The solutions were evaporated to a small volume and allowed to cool. The crystalline perchlorates (xH$_2$O) were separated from the mother liquors by filtering through a sintered glass (G3) disc. The products were recrystallized twice from conductivity water. Stock solutions of the recrystallized perchlorates were prepared in Pyrex bottles. The pH values of the stock solutions were adjusted to 4–5 with perchloric acid.

The concentrations of the stock solutions of the perchlorates at 20°C were determined by evaporating 5 ml volumes of the solutions to dryness in a Pyrex weighing glass in a drying oven, and then heating the residues in an electric oven continuously to 280°C for calcium perchlorate, to 250°C for barium perchlorate, and to 270°–400°C for strontium perchlorate, at which temperatures according to our thermograms the perchlorates are converted to their anhydrous forms. Magnesium perchlorate is converted to magnesium oxide at 900°C according to its thermogram. The samples were held at the given temperatures several hours, allowed to cool to room temperature in a desiccator and weighed. The constancy of the weight of the residue was confirmed by repeating the heating. The concentrations of the calcium and magnesium perchlorate solutions were checked also by titrating known volumes of the stock solutions with Titriplex. The concentrations of the strontium and barium perchlorate solutions were checked by the sulphate method. The concentrations determined by these methods differed in the fifth decimal. The concentrations of the stock solutions at 20°C as the mean values of at least four determinations were: $Mg(ClO_4)_2$ 2.656 M; $Ca(ClO_4)_2$ 4.1095 M (and the density $\varrho_{20/4}=1.63780$ g/cm^3), 3.0834 M ($\varrho_{20/4}=1.48512$) and 2.414 M; $Sr(ClO_4)_2$ 2.302 M; and $Ba(ClO_4)_2$ 3.509 M.

Most of the studied solutions were prepared by weighing the required amounts of the stock solutions in calibrated (20°C) 100 ml volumetric flasks of Pyrex glass and filling the flasks to the mark with conductivity water. The volumes of the stock solutions required to prepare the highly dilute solutions were measured with an Agla microsyringe or with calibrated micro burettes. Two solutions of each concentration were prepared and measured.

The densities of the solutions were measured with two or three pycnometers of the Ostwald type made from Pyrex glass in water thermostats at 20°, 25°, and 30°±0.01°C. The errors in the density values due to the temperature deviations were a few units of the sixth decimal. The density values are means of at least five measurements. The water values of the pycnometers varied from 13.9303 to 15.2926 ml at 20°C. For water, the density values (ϱ_0) 0.99823, 0.99707 and 0.99567 (g/m^3) at 20°, 25°, and 30°C, respectively, were used.[3] All weights, volumes, concentrations, and densities were corrected to vacuum.[4]

RESULTS AND DISCUSSION

The results of the density measurements are given in Tables 1–4 and those at 25°C also graphically in Fig. 1. The results can be represented by Root's equation:[1]

$$\varrho=\varrho_0+aC-bC^{3/2} \tag{1}$$

where ϱ and ϱ_0 are the densities of a salt solution and water in g/cm^3, a and b are fitted constants and C is the salt concentration in moles/liter.

Eqn. (1) was fitted to the data in Tables 1–4 by the method of least squares using for ϱ_0 the above values for water at the different temperatures.[3] The calculated values of the constants a and b of eqn. (1) are shown in Table 5. Density values calculated from eqn. (1) using these values are included in Tables 1–4.

In studies of the structures of electrolyte solutions, the determination and theoretical calculation of the apparent molal volumes of electrolytes and the ionic molal volumes of the individual ions in aqueous solutions have been objects of interest during several decades.[5–9] The usual way to obtain the

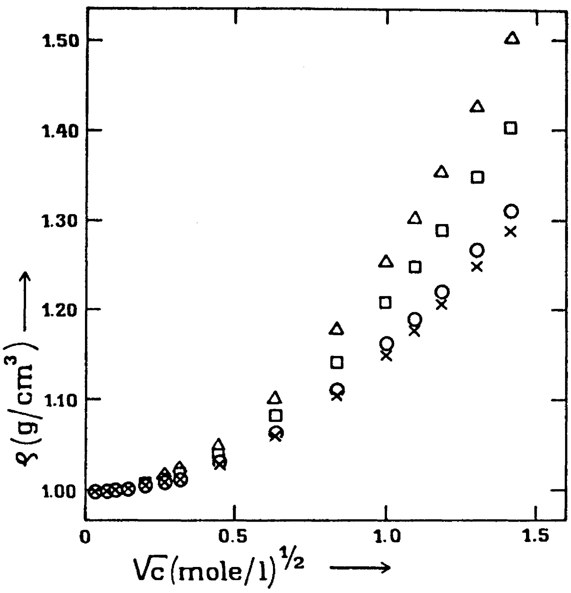

Fig. 1. The densities of aqueous magnesium, calcium, strontium, and barium perchlorate solutions at 25°C as functions of the square root of the molar concentration.
×, $Mg(ClO_4)_2$; ○, $Ca(ClO_4)_2$; □, $Sr(ClO_4)_2$; △, $Ba(ClO_4)_2$.

Table 1. Determined density values of aqueous magnesium perchlorate solutions at 20°, 25°, and 30°C and density values calculated from eqn. (1).

$C\times10^3$	20°		25°		30°	
	$\varrho_{exp.}$	$\varrho_{calc.}$	$\varrho_{exp.}$	$\varrho_{calc.}$	$\varrho_{exp.}$	$\varrho_{calc.}$
0.9993	0.99835	0.99837	0.99724	0.99709	0.99586	0.99582
4.996	0.99890	0.99890	0.99780	0.99787	0.99625	0.99642
9.992	1.0000	0.99958	0.99873	0.99866	0.99705	0.99715
19.985	1.0013	1.0012	1.0004	1.0003	0.99847	0.99859
39.970	1.0039	1.0044	1.0031	1.0034	1.0015	1.0014
69.947	—	—	1.0079	1.0081	1.0061	1.0054
69.950	1.0093	1.0095	—	—		
99.920			1.0129	1.0128		
199.85			1.0278	1.0282		
399.70			1.0587	1.0586		
699.47			1.1034	1.1033		
999.25			1.1468	1.1471		
1199.1			1.1756	1.1759		
1398.9			1.2060	1.2044		
1698.7			1.2485	1.2467		
1998.5			1.2876	1.2885		

Table 2. Determined density values of aqueous calcium perchlorate solutions at 20°, 25°, and 30°C and density values calculated from eqn. (1).

20°			25°			30°		
$C\times10^3$	$\varrho_{exp.}$	$\varrho_{calc.}$	$C\times10^3$	$\varrho_{exp.}$	$\varrho_{calc.}$	$C\times10^3$	$\varrho_{exp.}$	$\varrho_{calc.}$
1.001	0.99832	0.99841	1.000	0.99725	0.99725	1.000	0.99590	0.99586
5.005	0.99950	0.99912	4.996	0.99807	0.99798	4.996	0.99643	0.99657
10.008	1.0001	1.0000	9.993	0.99903	0.99888	9.993	0.99732	0.99743
20.020	1.0019	1.0018	19.990	1.0006	1.0007	19.99	0.99862	0.99905
40.037	1.0054	1.0053	39.97	1.0041	1.0042	39.97	1.0021	1.0020
70.067	1.0106	1.0105	69.95	1.0088	1.0095	69.95	1.0072	1.0061
100.15	1.0153	1.0157	99.92	1.0137	1.0147			
200.35	1.0320	1.0328	199.9	1.0305	1.0318			
400.70	1.0654	1.0665	399.7	1.0631	1.0649			
701.23	1.1149	1.1158	699.5	1.1103	1.1127			
1001.8	1.1629	1.1642	999.3	1.1592	1.1589			
1202.2	1.1949	1.1959	1199.1	1.1894	1.1888			
1402.5	1.2274	1.2273	1399.0	1.2205	1.2181			
1703.0	1.2749	1.2738	1698.7	1.2669	1.2612			
2003.5	1.3212	1.3196	1998.5	1.3106	1.3031			

Table 3. Determined density values of aqueous strontium perchlorate solutions at 20°, 25°, and 30°C and density values calculated from eqn. (1).

$C\times10^3$	20°		25°		30°	
	$\varrho_{exp.}$	$\varrho_{calc.}$	$\varrho_{exp.}$	$\varrho_{calc.}$	$\varrho_{exp.}$	$\varrho_{calc.}$
0.9991	0.99838	0.99841	0.99720	0.99727	0.99597	0.99591
4.996	0.99923	0.99919	0.99813	0.99807	0.99664	0.99682
9.992	1.0005	1.0002	0.99919	0.99906	0.99766	0.99789
19.98	1.0025	1.0023	1.0014	1.0011	0.99990	0.99990
39.97	1.0068	1.0067	1.0056	1.0051	1.0041	1.0035
69.94	1.0125	1.0138	1.0111	1.0111	1.0097	1.0083
99.92			1.0184	1.0172		
199.8			1.0393	1.0376		
399.7			1.0817	1.0788		
699.4			1.1414	1.1414		
999.2			1.2069	1.2048		
1199.0			1.2470	1.2474		
1398.9			1.2892	1.2902		
1698.6			1.3488	1.3549		
1998.4			1.4022	1.4201		

values of the apparent molal volumes of electrolytes is to calculate them from the density values of solutions of the electrolyte. Values of the apparent molal volumes of electrolytes calculated on the basis of the additivity of the ionic molal volumes vary depending on the chosen standard ionic volume scale. An agreement in respect of this standard ionic volume scale has not yet been reached.[5-9]

Table 4. Determined density values of aqueous barium perchlorate solutions at 20°, 25°, and 30°C and density values calculated from eqn. (1).

$C\times 10^3$	20°		25°		30°	
	$\varrho_{exp.}$	$\varrho_{calc.}$	$\varrho_{exp.}$	$\varrho_{calc.}$	$\varrho_{exp.}$	$\varrho_{calc.}$
0.9991	0.99841	0.99845	0.99729	0.99732	0.99600	0.99595
4.996	0.99947	0.99937	0.99833	0.99833	0.99686	0.99705
9.991	1.0008	1.0006	0.99970	0.99958	0.99804	0.99837
19.98	1.0035	1.0032	1.0022	1.0021	1.0013	1.0010
39.97	1.0086	1.0088	1.0074	1.0072	1.0061	1.0059
69.94	1.0173	1.0181	1.0153	1.0148	1.0133	1.0129
99.91			1.0228	1.0224		
199.8			1.0484	1.0477		
399.7			1.0999	1.0985		
699.4			1.1763	1.1782		
999.1			1.2516	1.2512		
1199.0			1.3007	1.3022		
1398.8			1.3521	1.3532		
1698.5			1.4251	1.4299		
1998.3			1.4993	1.5066		

Following the above mentioned procedure we have calculated on the basis of the experimental results in Tables 1–4 the values of the apparent molal volumes of the studied electrolytes in aqueous solutions at 25°C and those of calcium perchlorate at 20°C also from the usual equation:

$$\Phi = \frac{\mathrm{M}}{\varrho_0} - \left(\frac{\varrho}{\varrho_0} - 1\right)\frac{10^3}{C} \text{ (cm}^3\text{/mole)} \qquad (2)$$

where M is the molecular weight of the solute and the other symbols have their above-mentioned meanings. Only the density values for concentrations $C \geq 0.1$ mole/liter were used, because the density values at lower concentrations are not accurate enough for this purpose. The data at 25°C are presented graphically in Fig. 2. The mentioned inaccuracy of the values at low concentrations is obvious.

During the third decade of this century, Masson [10] observed that the apparent molal volume of an electrolyte, at least at low concentrations, is a function of the square root of the molar concentration of the salt. This was confirmed theoretically by Redlich and Rosenfeld.[11] To fit the data at higher concentrations, it is suitable to use the expanded equation:

$$\Phi = \Phi_0 + \alpha\sqrt{C} + \beta C \qquad (3)$$

The present data (Fig. 2) seem to exhibit this dependence on the molar concentration over the studied concentration ranges. The equations for the lines in Fig. 2 were calculated by the method of least squares on the basis of the calculated values of Φ ($C \geq 0.1$) from eqn. (2). For α, we used the theoretical values,[12] which are given together with the calculated values of Φ_0 and β in Table 6. The constants of eqn. (3) for calcium perchlorate solutions at 20°C are also given in Table 6.

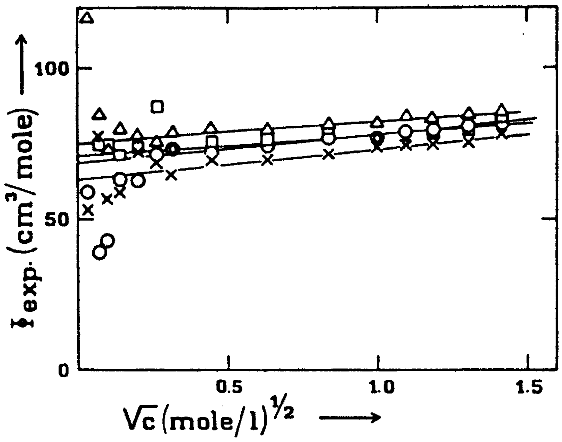

Fig. 2. The apparent molal volumes of magnesium, calcium, strontium and barium perchlorate in aqueous solutions at 25°C as functions of the square root of the molar concentration.

×, $Mg(ClO_4)_2$; ○, $Ca(ClO_4)_2$; □, $Sr(ClO_4)_2$; △, $Ba(ClO_4)_2$.

In Table 7 the present Φ_0 values can be compared with previously reported values calculated from the partial molal volumes of the ions based on different standard scales [7-9] and with the crystal radii of the metal ions.[13] The present Φ_0 values are in best agreement with those presented in the third and fourth columns of Table 7. The almost linear relationship between the apparent molal volumes and the crystal radii of the metal ions is seen in Fig. 3. A poorer linear relationship is found between Φ_0 and $r^3_{M^{2+}}$ (Å³).

Table 5. The values of the constants *a* and *b* of eqn. (1) calculated on the basis of the experimental data in Tables 1—4.

Constant	$Mg(ClO_4)_2$			$Ca(ClO_4)_2$		
	20°	25°	30°	20°	25°	30°
a	0.13427	0.16048	0.15391	0.17834	0.18304	0.19272
b	−0.09903	0.01036	0.05419	0.01268	0.02116	0.16633
	$Sr(ClO_4)_2$			$Ba(ClO_4)_2$		
	20°	25°	30°	20°	25°	30°
a	0.17993	0.19866	0.24731	0.20706	0.25272	0.28744
b	−0.16029	−0.00922	0.25212	−0.29242	−0.00160	0.15516

Table 6. The values of the constants Φ_0, α, and β of eqn. (3).

Salt	Φ_0	α	β
	25°C		
$Mg(ClO_4)_2$	63.33	9.706	0.120
$Ca(ClO_4)_2$	68.64	9.706	−0.370
$Sr(ClO_4)_2$	70.62	9.706	−1.670
$Ba(ClO_4)_2$	74.77	9.706	−2.031
	20°C		
$Ca(ClO_4)_2$	66.12	9.259	−0.808

Table 7. Experimental (this work) and calculated (literature values) apparent molal volumes Φ_0 (cm^3/mole) of magnesium, calcium, strontium, and barium perchlorates in water at 25°C and the crystal radii of the metal ions.[13]

Salt	This work	Fajans & Johnson [7]	Stokes & Robinson [8]	Mukerjee [9]	Crystal radius of metal ion in Å
$Mg(ClO_4)_2$	63.33	67.6	65.4	71.9	0.65
$Ca(ClO_4)_2$	68.64	70.0	69.84	75.1	0.99
$Sr(ClO_4)_2$	70.62	70.6	69.53	74.6	1.13
$Ba(ClO_4)_2$	74.77	75.8	75.19	80.5	1.35

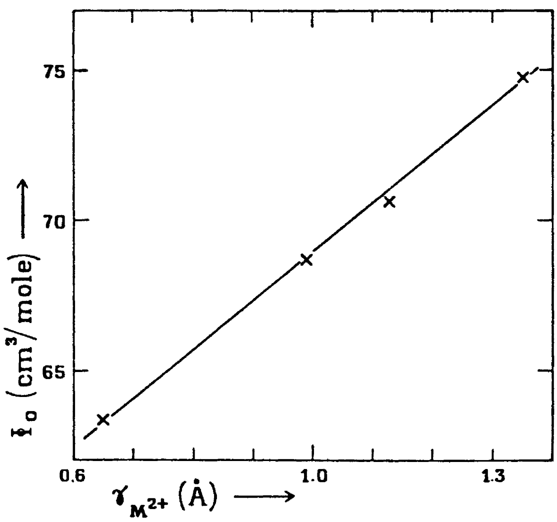

Fig. 3. Φ_0 as a function of the crystal radius of the metal ion for magnesium, calcium, strontium, and barium perchlorate at 25°C.

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