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Volumetric study of strong electrolytes-Metal chlorides and metal sulphates in aqueous medium at different temperatures

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ABSTRACT

The apparent molar volume (V_ϕ) of strong electrolytes like Magnesium chloride, Zinc chloride, Strontium chloride, Cadmium chloride, Barium chloride, Magnesium sulphate and Zinc sulphate has been evaluated from the density data of their aqueous solutions at 298.15, 303.15, 308.15 and 313.15K. The apparent molar expansibility (E_ϕ) has been calculated from the apparent molar volume at these temperatures. The limiting apparent molar volume(V_ϕ^0),limiting apparent molar expansibility (E_ϕ^0) and the constants (S_V and S_E) have also been evaluated and discussed in the light of solute-solvent and solute-solute interactions .

Keywords: Strong electrolytes, Partial molar volume, partial molar expansibility, Limiting apparent molar volume

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INTRODUCTION

The dissolution of strong electrolytes in an aqueous medium causes a volume contraction due to ion-solvent interaction and the molecular interactions throws light for better understanding of the structural change occurred in solutions depending on the charge density [1,2]. The measurement of density of aqueous electrolyte solution leads an insight into the state of association of the solute and the extent of interaction of the solute with the solvent. The structural aspects of the solutions can be inferred from the density of solutions at different concentrations and temperatures. It also helps to understand ion-solvent and ion-ion electrostatic interactions in solutions. The volumetric properties like apparent and partial molar volume are the sensitive tools, which help in elucidating solvation behaviour of an electrolyte in aqueous solutions. From the theoretical point of view, the most useful quantities are the limiting values of the apparent molar volume and apparent molar expansibility, since these values depend only on the intrinsic size of the ion and on ion-solvent interactions. The variation of the apparent molar volume of electrolytes with temperature in aqueous solutions has been employed to study interactions in solutions by many authors [3-5]. In the literature, there are, however, few data on partial molar volumes of the alkali metal, ammonium and calcium salts reported at 298.15K [6,7]. Evaluation of apparent and partial molar quantities are of importance as they give a lot of information regarding ion-ion and ion-solvent interactions in various solutions.

The present work aims at determining the values of density of metal chlorides ($MgCl_2$,$ZnCl_2$,$SrCl_2$, $CdCl_2$ and $BaCl_2$) and metal sulphates ($MgSO_4$ and $ZnSO_4$) in aqueous medium at different temperatures ranging from 298.15K to 313.15K at an interval of 5K and related parameters, such as apparent molar volume (V_ϕ), apparent molar expansibility (E_ϕ), limiting apparent molar volume(V_ϕ^0) , limiting apparent molar expansibility (E_ϕ^0) and the constants (S_V & S_E) have been calculated along with the partial molar volume ($\bar{V}_2$) and molar expansibility($\bar{E}_2$) values to study the possible ion-ion and ion-solvent interactions in the solutions. The strong electrolytes used in the work have wide applications in medicine, industry, agriculture and environmental process.

EXPERIMENTAL SECTION

All metal chlorides and metal sulphates used were of GR or AR grades and dried over anhydrous $CaCl_2$ in vacuum desiccator before use. All solutions were prepared in conductivity water (Sp. cond.~ 10^{-6} $S.cm^{-1}$).The solutions were prepared on the molal basis and conversion of molality to molarity was done by using standard expression[8].The solute content of the solutions varied over a concentration range of $6.0x10^{-3}$ M to $8.0x10^{-2}$M.The densities of solutions were measured by using a specific gravity bottle (25 ml capacity).At least five observations were taken and the differences in any two readings did not exceed ±0.02%. Sufficient care was taken to avoid any entrapment of air bubble. Desired temperature was maintained by a thermostat with a precision of ±0.05 K.

Theoretical Aspects

The apparent molar volume $V_ϕ$ and apparent molar expansibility $E_ϕ$ are computed by the following relations[9]

$$V_ϕ=1000(cd_0)^{-1}(d_0-d)+Md_0^{-1} \qquad ....(1)$$

$$E_ϕ= \alpha_0 V_ϕ+(\alpha - \alpha_0)1000c^{-1} \qquad ....(2)$$

where c is the molar concentration,d_0 and d are the densities of solvent and solution, respectively, M is the molar mass of the solute, α_0 and α are the coefficients of thermal expansion of solvent and solution, respectively and calculated by following relations,

$$\alpha_0 = -1/d_0 (\partial d_0/\partial T)_p \qquad \text{and} \qquad \alpha = -1/d (\partial d/\partial T)_p$$

The $V_ϕ$ and $E_ϕ$ data have been fitted to the Masson equation by least squares method [9]

$$V_ϕ = V_ϕ^0+ S_V c^{1/2} \qquad ....(3)$$

$$E_ϕ = E_ϕ^0+ S_E c^{1/2} \qquad ....(4)$$

to obtain the limiting apparent molar volume($V_ϕ^0$), slope (S_V) of the $V_ϕ \sim c^{1/2}$ plot of Eq.(3),the limiting apparent molar expansibility($E_ϕ^0$) and slope(S_E) of the $E_ϕ \sim c^{1/2}$ plot of Eq.(4).

The partial molar volume ($\bar{V}_2$) and partial molar expansibility($\bar{E}_2$) have been calculated from the following relations[10]

$$\bar{V}_2 = V_ϕ+(1000-cV_ϕ)(2000+S_V c^{3/2})^{-1} S_V c^{1/2} \qquad ....(5)$$

$$\bar{E}_2 = E_ϕ+(1000-cE_ϕ)(2000+S_E c^{3/2})^{-1} S_E c^{1/2} \qquad ....(6)$$

The apparent molar volume at infinite dilution also called the limiting apparent molar volume is equal to the partial molar volume at infinite dilution $\bar{V}_2^0$.

RESULTS AND DISCUSSION

The values of density of the electrolytes i.e. Magnesium chloride, Zinc chloride, Strontium chloride, Cadmium chloride, Barium chloride, Magnesium sulphate and Zinc sulphate in aqueous solutions have been determined at four different temperatures. The values of density of all electrolytes in aqueous solutions show that, the density (d) increases with increase in concentration but decreases with increase in temperature. The increased value of density is attributed to the increase in hydrophilic interactions in the solutions. The values of density (d) were fitted to an equation of the form

$$d = d_o+Ac+Bc^{3/2}+Cc^2 \qquad ....(7)$$

where A, B and C are the empirical constants. The values of these constants are given in Table-1. The variation of $(d-d_0)/c$ vs $c^{1/2}$ decreases almost linearly for the aqueous solutions of all metal chlorides and metal sulphates at all temperatures agreeing fairly well with the Eq.(7).Typical plots are shown in Fig.1 (a)-(b) over the concentrations and temperature ranges studied.

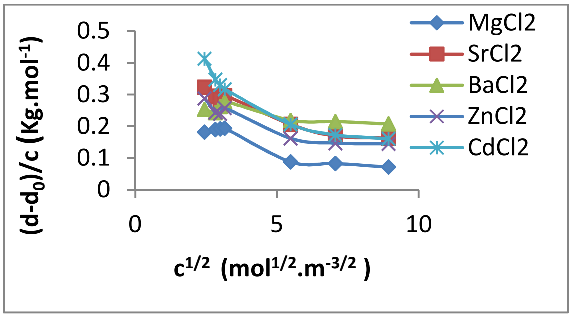

Fig.1(a) Plot of (d-d$_0$)/c vs c$^{1/2}$ in aqueous metal chlorides at 298.15K

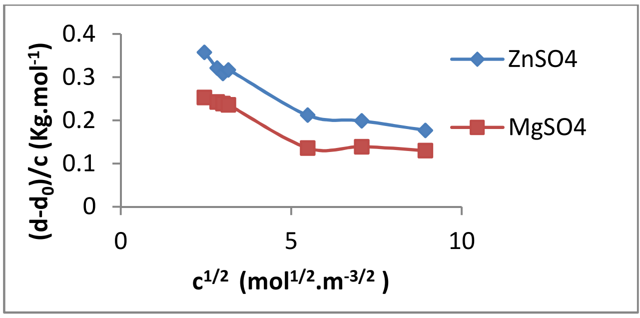

Fig.1(b) Plot of (d-d$_0$)/c vs c$^{1/2}$ in aqueous metal sulphates at 298.15K

Table-1. Values of empirical constants A,B and C of Eq.(7) for aqueous electrolyte solutions at different temperatures

Electrolytes	Temp./K	10^2A	10^3B	10^5C
$MgCl_2$	298.15	24.467	-21.589	15.087
	303.15	33.528	-33.798	56.257
	308.15	26.466	-23.238	20.498
	313.15	27.895	-23.356	-27.060
$ZnCl_2$	298.15	31.313	-21.583	37.090
	303.15	33.056	-23.667	22.777
	308.15	48.925	-44.862	94.965
	313.15	40.273	-33.545	59.652
$SrCl_2$	298.15	36.901	-25.620	28.273
	303.15	34.059	-22.384	1.402
	308.15	36.047	-25.674	56.868
	313.15	30.464	-18.591	44.842
$CdCl_2$	298.15	44.937	-36.371	67.056
	303.15	36.336	-26.075	19.069
	308.15	36.633	-25.819	50.439
	313.15	39.767	-29.636	51.617
$BaCl_2$	298.15	28.183	-8.927	-1.126
	303.15	34.614	-18.704	11.124
	308.15	45.608	-32.579	41.768
	313.15	41.548	-27.494	31.777
$MgSO_4$	298.15	29.702	-21.368	31.282
	303.15	32.949	-25.567	34.610
	308.15	31.789	-23.101	31.232
	313.15	32.577	-23.414	6.536
$ZnSO_4$	298.15	39.911	-27.311	38.492
	303.15	41.764	-29.764	21.600
	308.15	33.296	-19.276	23.728
	313.15	33.477	-19.343	7.022

The apparent molar volume(V_{ϕ}) have been calculated at each concentration (c) using density values of solutions (d) and solvent (d_o) by Eq (1).The values of V_{ϕ}^0 and S_v obtained from Eq.(3) are presented in Table-2.

The positive values of S_v for all metal chlorides and metal sulphates in aqueous solutions at the experimental temperatures show the presence of strong ion-ion (solute-solute) interactions varying with change of temperature and nature of electrolytes [11]. The V_{ϕ}^0 values are negative for all the electrolytes in aqueous solutions at all the experimental temperatures. As V_{ϕ}^0 measures ion-solvent (solute-solvent) interaction in a solution, the negative values of V_{ϕ}^0 indicate weaker ion-solvent interaction and electrostrictive solvation of ions. So, it provides evidence of electrostriction and it increases with increase in temperature (except in few cases) [12].

The values of E_{ϕ}^0 and S_E have been calculated from Eq.(4) and presented in Table-2 . The E_{ϕ}^0 gives an idea about caging or packing effect. The value of E_{ϕ}^0 for all the electrolytes increases with temperature indicating the presence of caging or packing effect [13,14]. As observed the values of E_{ϕ}^0 are positive for $SrCl_2$,$CdCl_2$, and $ZnSO_4$ but negative for $MgCl_2$,$ZnCl_2$,$BaCl_2$ and $MgSO_4$ in aqueous solutions at all experimental temperatures. So the positive values of E_{ϕ}^0 indicate structure making (hydrophilic) effect where as negative values do not favour the structure making (hydrophobic) effect in aqueous solutions. As expected, the partial molar expansibility ($\bar{E}_2$) decreases with concentration but increases with temperatures.

Table-2.Values of parameters $V_{\phi}^{0}(m^3mol^{-1})$, $S_V(m^{9/2}mol^{-3/2})$, $E_{\phi}^{0}(m^3mol^{-1}K^{-1})$ and $S_E(m^{9/2}mol^{-3/2}K^{-1})$ for aqueous electrolyte solutions at different temperatures.

Electrolytes	Temp./K	$V_{\phi}^{0}x10^3$	S_Vx10^4	$E_{\phi}^{0}x10^3$	S_Ex10^4
$MgCl_2$	298.15	-245.28	216.508	-2.460	1.336
	303.15	-336.63	339.439	-2.489	1.376
	308.15	-266.15	233.765	-2.466	1.341
	313.15	-281.03	235.388	-2.471	1.342
$ZnCl_2$	298.15	-313.89	216.453	-6.209	8.155
	303.15	-331.85	237.691	-6.215	8.161
	308.15	-492.02	451.292	-6.267	8.231
	313.15	-405.74	338.067	-6.239	8.194
$SrCl_2$	298.15	-369.91	256.939	4.065	-4.539
	303.15	-341.90	224.806	4.074	-4.550
	308.15	-362.45	258.264	4.068	-4.538
	313.15	-306.86	187.360	4.086	-4.561
$CdCl_2$	298.15	-450.48	364.761	3.163	-4.266
	303.15	-364.74	261.878	3.191	-4.299
	308.15	-368.32	259.711	3.190	-4.300
	313.15	-400.59	298.670	3.179	-4.287
$BaCl_2$	298.15	-282.43	89.534	-9.128	12.476
	303.15	-347.43	187.844	-9.149	12.508
	308.15	-458.58	327.726	-9.185	12.554
	313.15	-418.51	277.087	-9.172	12.537
$MgSO_4$	298.15	-297.75	214.294	-2.120	1.515
	303.15	-330.79	256.775	-2.131	1.529
	308.15	-319.67	232.390	-2.127	1.521
	313.15	-328.19	235.965	-2.130	1.522
$ZnSO_4$	298.15	-400.10	273.900	4.044	-5.156
	303.15	-419.28	298.926	4.037	-5.148
	308.15	-334.78	193.911	4.065	-5.182
	313.15	-337.22	194.942	4.064	-5.182

It is observed that the partial molar volume $\bar{V}_2$ is negative for all electrolytes in aqueous solutions at all temperatures and increases with increase in concentration. The increased value of $\bar{V}_2$ with concentration is owing to the structure breaking of the solvent molecules in concentrated solutions of high charge density ions.

The measured partial molar volume can be considered to be a sum of the geometric volume of the solute and changes in the solvent due to its interaction with solvent. This simple approach has been widely used in many models[15] to interpret partial molar volume for a broad range of solutes.

CONCLUSION

The results of the present investigation on strong electrolytes-metal chlorides and metal sulphates in aqueous solutions reveal that the electrolytes which show strong ion-ion interaction have weak ion-solvent interaction and vice-versa. The presence of caging or packing effect in the above solutions are indicated by the increase value of E_{ϕ}^{0} with temperatures.

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