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A STUDY OF ION SOLVENT INTERACTION OF BINARY ELECTROLYTES IN METHANOL + WATER SYSTEM AT DIFFERENT TEMPERATURES

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Ion-solvent interaction binary electrolytes in methanol-water mixtures at temperatures 30, 35 and 40°C have been studied. The results indicate strong alignment of solvent molecule with the ions which promotes the structure of solvent molecule. The ion-solvent interaction in the order Mg^{++} ? Mn^{++} > Zn^{++}. The solute-solvent interaction coefficient of cations is found to increase with increasing temperatures.

INTRODUCTION

Earlier one of the authors has studied the solute-solvent interaction in binary mixtures of polar-polar and polar-non-polar liquids through viscosity dielectric and ultrasonic studies. The complexities in liquid arising from molecular interactions owing to closeness of molecules and gas like behaviour due to lack of long range order forces the experimentalists to confirm the nature of interaction between solute-solvent, ion-solvent through other studies like I.R. spectra, conductance measurement besides the above three studies. The findings obtained through these experiments are compared to clear picture of the inrteraction in binary mixture. As a part of our programme of studying solute-solvent interactions in mixed solvent the present work aims at measuring the density of solutions of magnesium, manganese and zinc sulphate in varying ranges of concentration of aqueous methanol at temperature 30°, 35° and 40°C.

EXPERIMENTAL

All the salts used are of E. Merck Extra-Pure Varieties. This viscosmetric apparatus and the technique are the same as that of Chakravarty and Prasad. The densities of the solutions and solvents are determined with the help of pyknometer of (50 cm^3 capacity) with buoyancy

correction and is same as that are. The accuracy in the measurement of density is 0.0002 gm/cm^3.

Theory

The apparent molar volume and has been calculated from the density data with the help of equation.

$$\phi = (M_2/\rho) - [(\rho - \rho_0)/ \rho_0] \times 10^3/C$$

where M_2 is molecular weight of solute ρ_0 and ρ are the densities of pure solvent and solution respectively and C is the molar concentration.

r_+ and r_- are the ionic radii of the cations (*i.e.* Zn^{++}, Mn^{++} and Mg^{++} and anion SO_4^{--} have been calculated from the equation of Andrew *et al* as

$$\phi = 6.47(r_+^3 + r_-^3)$$

where the terms have their usual significance.

The partial molar volume of the solute V_+ has been evaluated using equation of Coutre and Laidler's equation.

$$V^{-}_{++} = 16 + 4.9r_+^3 - (20/Z_{++})$$

Viscosity has been analysed in terms of Jones – Dole equation.

$$\eta_r = 1 + A\sqrt{C} + BC$$

and plotting graph $[(\eta_r-1) / C^{1/2}]$ vs $C^{1/2}$, which is linear, where η_r = coefficient of viscosity,

where A and B are the interaction forces in the viscosity and solute-solvent interaction coefficient.

C = the concentration of the solution electrolyte ml^{-1}.

The solute-solvent interaction coefficient of individual cations B^{++} can evidented in the S.P. Mallik eq.

$$B_{++} = 2.79\ V_{++} - 0.018$$

where V_{++} = the partial molar volume.

Results and discussion

For ionic radius of SO_4^{--} : Using the eq. Andere *et al*, the rSO_4^{--} have been calculated $\phi = 6.47\ (r^3_+ + r^3_-)$ with the crystallographic radius data of the cation and tabulated at the table 1.

It has confirmed that in each compound ($MgSO_4$, $MnSO_4$ and $ZnSO_4$) the radius of SO_4^{--} is increasing with increasing temperature.

for each case, $r^{--}_{SO_4\ 40°} > r^{--}_{SO_4\ 35°} > r^{--}_{SO_4\ 30°}$

It has been authentic experimented that with increasing the methanol content in the mixture, the radium of SO_4^{--} radical also increasing in case of the three compounds $MgSO_4$, $MnSO_4$ and $ZnSO_4$ we have analysed.

$$r^{--}_{SO_4\ C_2H_5OH\ 30°} > r^{--}_{SO_4\ C_2H_5OH\ 20°} > r^{--}_{SO_4\ C_2H_5OH\ 10°}$$

Partial Molar Volume for Cations : Partial molar volume of the three cations viz. Mg^{++}, Mn^{++} and Zn^{++} are calculated by using the laidlens eq. $V_{++} = 16 + 4.9\ r^3_{++} - 20/Z_{++}$ and tabulated ion table No. 1. It has been analysed that the particular molar volume of each cation is increasing with increasing temperature but inert towards with increasing the methanol content.

Table 1

Salt	**Wt. of ethanol in the solvent**	**Temperature**	**ϕ**	**γ_{++}**	**γSO_4^{--}**	**V_{++}**	**B_{++}**
$MgSO_4$	10%	30°C	135	0.82	2.728	16.699	46.572
		35°C	142	0.85	2.773	17.00	47.412
		40°C	150	0.865	2.824	17.17	47.886
	20%	30°C	142	0.82	2.776	16.699	46.572
		35°C	146	0.85	2.799	17.00	47.412
		40°C	155	0.865	2.837	17.17	47.886
	30%	30°C	150	0.82	2.828	16.699	46.572
		35°C	162	0.85	2.901	17.00	47.412
		40°C	178	0.865	2.994	17.17	47.887
Salt	Wt. of ethanol in the solvent	Temperature	ϕ	γ_{++}	γSO_4^{--}	V_{++}	B_{++}
$MnSO_4$	10%	30°C	130	0.80	2.70	17.637	49.189
		35°C	134	0.82	2.721	17.73	49.448
		40°C	140	0.846	2.764	18.095	50.447
	20%	30°C	138	0.80	2.750	17.637	49.189
		35°C	144	0.82	2.789	17.73	49.448
		40°C	156	0.846	2.864	18.095	50.447
	30%	30°C	142	0.80	2.777	17.637	49.448
		35°C	152	0.82	2.841	17.73	49.448
		40°C	166	0.846	2.926	18.095	50.447
$ZnSO_4$	10%	30°C	147	0.74	2.816	17.271	48.168
		35°C	152	0.76	2.845	17.366	48.333
		40°C	156	0.77	2.870	17.520	48.870
	20%	30°C	151	0.74	2.841	17.271	48.168
		35°C	157	0.76	2.878	17.366	48.333
		40°C	162	0.77	2.96	17.520	48.870
	30%	30°C	160	0.74	2.89	17.271	48.168
		35°C	168	0.76	2.944	17.366	48.333
		40°C	172	0.77	2.96	17.520	48.870

So, V_{++} (40°C) > V_{++} (35°C) > V_{++} (30°C) has been evidented.

Andrew, Johnson and Lyons have stated that ionic redii can be calculated from the equation.

$$= 6.47 (r^3_+ + r^3_-)$$

Viscosity : The viscosity data were analysed in terms of Jones-Dole equations, as the plots of ($\eta_r - 1$ vs $C^{1/2}$) / $C^{1/2}$ were linear. The intercept and the slope of the above plots gave the values of A and B respectively and tabulated in tables 2 and 3.

Table 2. A × $10^3/L^{1/2}$ $mol^{-1/2}$

Wt.% of ethanol	$MgSO_4$			$MnSO_4$			$ZnSO_4$		
	30°C	35°C	40°C	30°C	35°C	40°C	30°C	35°C	40°C
10	10.50	9.0	8.0	12.0	10.0	9.0	32.0	30.0	29.0
20	20.0	18.0	15.0	28.0	26.0	25.0	35.0	32.0	30.0
30	32.0	30.0	28.0	42.0	39.0	39.0	40.0	38.0	35.0

Table 3. B/L Mol^{-1}

Wt. ethanol	$MgSO_4$			$MnSO_4$			$ZnSO_4$		
	30°C	35°C	40°C	30°C	35°C	40°C	30°C	35°C	40°C
10	0.401	0.436	0.452	0.430	0.468	0.509	0.462	0.481	0.655
20	0.474	0.525	0.569	0.515	0.569	0.620	0.528	0.625	0.65
30	0.509	0.532	0.680	0.529	0.474	0.698	0.572	0.683	0

For 'A' Values : The different 'A' values for the three salts are positive which indicates ion-ion interaction and is found to be of the order : $Zn^{++} > Mn^{++} > Mg^{++}$. The A value is also found to increase with the increase in methanol content in the medium. This may be attributed due to change in the mobility of the ions with a change in the dielectric constant of the medium. Positive 'A' value suggested strong ion-ion interaction, possibly due to cation- cation and cation-anion penetrations suggested by Gopal *et al.*

For 'B' Values : The positive 'B' values indicate strong alignment of the solvent molecules with the ions which undoubtedly promote the structure of the solvent molecules in its immediate vicinity. Thus the next structure forming is found to be of the order $Zn^{++} > Mn^{++} > Mg^{++}$ and ion solvent interaction is of reverse order *i.e.* $Mg^{++} > Mn^{++} > Zn^{++}$. The increase in B coefficients increase in ethanol content of the solvent, may be attributed due to large size of the molecule and also to the strong association through hydrogen bonding for solute solvent interaction coefficient of cations. The solute interaction coefficient B_{++} of the three cations (Mg^{++}, Mn^{++}, Zn^{++}) are tabulated at due table No.1 by using the S.P.Mallick eq.

$$B_{++} = 2.79\ V_{++} - 0.018.$$

It has been confirmed that, in each case solute-solvent interaction coefficient of cations (B_{++}) are markedly increasing with increasing the temperature.

But with changing the methanol content, the solute solvent interaction coefficient of cations B_{++} remains the same have showed that determined impact with increasing the methanol content in the mixture.

So, $\underset{45°C}{B_{++}} > \underset{35°C}{B_{++}} > \underset{30°C}{B_{++}}$

has been observed whereas

$$\underset{10\%C_2H_5OH}{B_{++}} = \underset{20\%C_2H_5OH}{B_{++}} = \underset{30\%C_2H_5OH}{B_{++}}$$

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