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Effect of Temperature on Partial Molar Volumes of Some Bivalent Transition Metal Chlorides and Magnesium Chloride in the Water-Rich Region of Binary Aqueous Mixtures of Ethanol.

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ABSTRACT

Partial molar volumes of five transition metal chlorides viz. manganese chloride, cobalt chloride, nickel chloride ,copper chloride ,cadmium chloride and magnesium chloride have been determined in water and in binary aqueous mixtures of ethanol (5%,10%,15%,20% and 35% w/w) from the solution densities at 303.15 K. The observed data has been analysed by using the Masson Equation and the obtained parameters S_v^* and φ_v^0 are interpreted in terms of solute-solute and solute-solvent interactions. The effect of temperature ranges from 298.15 to 318.15 K on partial molar volumes and limiting molar expansibility was also studied. In the present study, decrease in solute –solvent interactions has been noticed on increasing the content of ethanol in water. Structure making or breaking capacities of the electrolytes have been inferred from the sign $\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)_p$ i.e second derivative of partial molar volume with respect to temperature at constant pressure. All the electrolytes have been found to act as structure makers/promoters in water as well in aqueous mixtures of ethanol.

Key words: Ethanol+water, partial molar volumes, solute –solvent interactions, structure maker, transition metal chlorides.

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INTRODUCTION

Partial molar volume is one of the thermodynamic properties which have industrial and practical applications. It may be used to get information about how the various changes will influence a solution at equilibrium. Recently, the information of ionic solutions has increased immensely. Various types of interactions exist between the ions in solutions and of these solute – solute and solute – solvent interactions are of current interest in all branches of chemistry. Partial molar volumes of electrolytes is one of the tool to study the solute-solvent interactions [1-8].It has been realized that the solvation of solutes can be better understood in mixed solvent rather than a pure solvent.

Accurate aqueous data are needed in many fields besides chemistry including geology, oceanography, boiler engineering and oil recovery systems. These areas require aqueous data over wide range of temperature, pressure and composition. Due to the importance in geology, industrial and biological systems, a need has developed for accurate thermodynamic data for transition metal salts in aqueous solutions. In biological systems metals like copper, iron and manganese are required for various purposes, while other metals like nickel and cadmium can poison enzymes by substituting for their required metals. Transition metals are also important in geology because they are components of various minerals, while engineers are interested in their role in corrosion processes.

Appreciable work has been done in binary polar aqueous solvent mixtures but there is lack of study of transition metal chlorides in binary aqueous mixtures of ethanol. Present study is done to get information on the interactions of some of the transition metal chlorides in binary aqueous mixture of ethanol + water.

MATERIALS AND METHODS

Manganese chloride $MnCl_2.4H_2O$, cobalt chloride $CoCl_2.6H_2O$, nickel chloride $NiCl_2.4H_2O$,copper chloride $CuCl_2.5H_2O$,cadmium chloride $CdCl_2.2H_2O$ and magnesium chloride $MgCl_2.6H_2O$ were of Analytical grade with 99.99% purity were used after drying over P_2O_5 in a desiccator. Fresh triple distilled water was used as a standard solvent as well as for the preparation of different compositions of ethanol in water (5%, 10%, 15%, 20% and 35%w/w of ethanol).The binary aqueous mixture of ethanol as well as the solutions of transition metal chlorides of concentrations ranges from 0.005 to 0.01 mol Kg^{-1}were made by weight and the conversion of molalities (m) into molarities (C) was done using standard expression[9].

$$C = \frac{1000\, d\, m}{1000 + mM_2} \qquad (1)$$

Here, d is the density of solution and M_2 is the molecular weight of selected transition metal chlorides. The apparatus used for the determination of densities of transition metal chlorides solutions, was similar to one described by Ward and Millero [10].This apparatus consist of a glass float which is suspended with nylon thread from a balance pan into a cylindrical sample container. The sample container has a bakelite top and placed in a water bath. The whole assembly of sample container and water-bath was placed in thermostat whose temperature was controlled with the help of an electronic relay. The fluctuation in temperature was within $\pm$ 0.01K.The densities of different aqueous solution of transition metal chlorides were calculated with the help of the equation:

$$d - d_0 = \frac{(W_0 - W)}{V_f} \qquad (2)$$

Here, d and d_0 are densities of sample solution and of water respectively; w and w_0 are the weight of float in sample solution and in water respectively. The glass float of weight 28.8956g had a volume of 26.5148 $\pm$ 0.0048 cm^3.The accuracy of apparatus was checked by measuring the density of methanol d= 0.7868 gcm^{-3} at 298.15 K, which was is in good agreement with the literature value of methanol density value (d = 0.7865 gm^{-3}) [11].With the help of the measured solution density data, apparent molar volumes ϕ_v were calculated by using the following expression [12]:

$$\phi_v = \frac{M_2}{d_0} - \frac{1000}{c}\left[\frac{d - d_0}{d_0}\right] \qquad (3)$$

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where d and d_0 are the densities of solution and solvent respectively.

RESULTS AND DISCUSSIONS

Table 1: Limiting apparent molar volumes and experimental slopes for some transition metal chlorides in water and in different compositions of ethyl alcohol + water at 303.15K

Ethanol + water (% w/w)	ϕ_v^0 (cm^3mol^{-1})	S_v^* ($cm^3dm^{3/2}mol^{-3/2}$)	ΔV_{tr}^0 (cm^3mol^{-1})
Manganese chloride			
0(water)	69.39	1.112	----
5	53.93	0.370	-15.46
10	49.57	0.439	-19.82
15	46.57	0.437	-22.82
20	44.24	0.447	-25.15
35	39.91	0.528	-29.48
Cobalt chloride			
0(water)	120.51	0.519	----
5	138.15	0.626	17.64
10	131.43	0.652	10.92
15	130.13	0.658	9.62
20	127.23	0.697	6.72
35	125.21	0.698	4.70
Nickel chloride			
0(water)	83.88	0.865	----
5	109.92	0.534	26.04
10	104.64	0.675	20.76
15	102.60	0.684	18.72
20	99.56	0.731	15.68
35	96.40	0.862	12.52
Copper chloride			
0(water)	41.01	0.538	----
5	69.19	0.456	28.18
10	64.45	0.467	23.44
15	59.85	0.477	18.84
20	57.56	0.503	16.55
35	55.73	0.546	14.72
Cadmium chloride			
0(water)	60.80	0.668	----
5	57.02	0.497	-3.77
10	50.21	0.694	-10.59
15	47.24	0.756	-13.55
20	42.49	0.836	-18.30
35	38.97	0.861	-21.82
Magnesium chloride			
0(water)	138.39	0.654	----
5	146.45	0.634	8.06
10	142.07	0.702	3.68
15	139.52	0.767	1.13
20	135.79	0.824	-2.60
35	133.12	0.847	-5.27

The densities of aqueous solutions of manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in water and in ethanol + water of different compositions (5% - 35% by weight of ethanol in water) have been used to calculate apparent molar volumes (ϕ_v) at 303.15 K

of all transition metal chlorides taken for study by using equation 3. It has been found that the plots of apparent molar volumes ϕ_v verses square root of concentrations √C were found to be linear without scattering , with positive slopes in water as well as in ethanol + water of mentioned compositions. A sample plot for manganese chloride in different compositions of ethanol + water at 303.15 K is shown in fig.1.

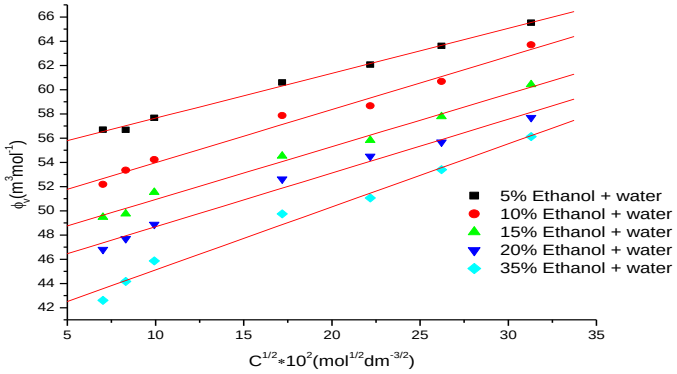

Fig.1. Plot of φ_v Vs $C^{1/2}$ of manganese chlorides in different compositions of ethanol + water at 303.15 K

The partial molar volumes ϕ_v^0 and experimental slopes S_v^* values were calculated by using the Massion's equation [13]:

$$\phi_V = \phi_v^0 + S_v^*\sqrt{C} \qquad (4)$$

The obtained values of ϕ_v^0 and S_v^* in water and in 5%,10%,15%,20% and 35% of ethanol + water at 303.15 K are recorded in table 1.

From table 1, it is clear that the values of slopes S_v^* are positive in water as well as in all prepared compositions of ethanol + water at 303.15 K. These positive values of slopes S_v^* of transition metal chlorides indicates the presence of strong solute – solute interactions in both the solvent systems. Also, it is clear from table 1, that the magnitude of S_v^* of each electrolyte increases with the increase in the amount of ethanol in water. This reveals that solute – solute interactions become more strengthened and decrease in the solvation of ions with increase amount of ethanol in water. Reason for the positive S_v^* values of all transition metal chlorides taken for the present study in the different compositions of ethanol + water is due to partial dissociation of these transition metal chlorides, which shows the absence of an intrinsic penetration.

Also it is clear from table 1 that the values of ϕ_v^0 are also positive in both water and in ethanol + water systems for all the transition metal chlorides. This indicates the presence of strong solute- solvent interactions. From table 1, it is also clear that the magnitude of ϕ_v^0 values for each transition metal chloride decreases on the addition of ethanol in water which shows that solute – solvent interactions are weakened on the addition of ethanol in water. On comparing the magnitudes of ϕ_v^0 values with S_v^* values, ϕ_v^0 values are greater in magnitude than that of S_v^*values of for the same transition metal chloride. This suggests that solute – solvent interactions dominates over solute – solute interactions in all ethanol + water compositions at 303.15 K.

The volume of transfer $\Delta V_{tr}^0 = \phi_{v(MS)}^0 - \phi_{v(w)}^0$ has been recorded in table 1. Here, $\phi_{v(MS)}^0$ and $\phi_{v(w)}^0$are the partial molar volumes of transition metal chlorides in mixed solvent system (ethanol + water) and in water respectively. The decrease in the ΔV_{tr}^0 and ϕ_v^0 values with increase in the amount of ethanol in water ; for all the transition metal chlorides , may be trait to the increase in electrostriction in the presence of ethanol. This electrostriction effect, which causes the contraction in the volume of the solvent, increases with the increase in the content of ethanol in water. This reflects the improvement in the solute –solvent interactions from change of water as a solvent to ethanol + water solvent.

As the chloride ion is common in all the transition metal chlorides so it is also clear that the volumes of transfer ΔV_{tr}^0 values in a particular composition of ethanol + water; the electrostriction for these transition metal cations follows the order: Mn^{2+} >Cd^{2+}>Mg^{2+}>Co^{2+}> Ni^{2+}> Cu^{2+}; so we can say that Cu^{2+} ion is

preferentially solvated by ethanol + water mixture and order of preferential salvation of these cations follows the order Cu^{2+} >Ni^{2+} Co^{2+} >Mg^{2+} >Cd^{2+} >Mn^{2+}.

As the magnitudes of ΔV_{tr}^{0} for each transition metal chlorides decreases as shown in table 1 with the increase in the amount of ethanol in water,so it cause decrease in the solvation of a particular cation with the increase of ethanol in water.

Effect of temperature on partial molar volumes

Table 2: Values of limiting apparent molar volume ϕ_v^0, experimental slopes S^*_v and limiting molar volumes of expansibilities ϕ_E^0 for some transition metal salts in water and in 5% w/w ethanol + water at different temperatures

Temperature K	ϕ_v^0 (cm^3mol^{-1})	S^*_v ($cm^3dm^{3/2}mol^{-3/2}$)	ϕ_E^0 ($cm^3mol^{-1}K^{-1}$)
		Manganese chloride	
298.15	78.40	0.803	-2.01
303.15	69.39	1.112	-1.59
308.15	61.62	1.332	-1.16
313.15	56.82	1.350	-0.74
318.15	44.33	1.488	-0.32
		Cobalt chloride	
298.15	127.20	0.440	-1.34
303.15	120.51	0.519	-1.33
308.15	114.19	0.600	-1.31
313.15	107.63	0.627	-1.30
318.15	97.93	0.649	-1.29
		Nickel chloride	
298.15	91.81	0.679	-1.83
303.15	83.88	0.865	-1.33
308.15	67.02	0.914	-0.83
313.15	64.06	0.928	-0.34
318.15	55.53	0.964	0.15
		Copper chloride	
298.15	47.26	0.512	-1.54
303.15	41.01	0.538	-0.94
308.15	30.03	0.664	-0.34
313.15	29.78	0.676	0.24
318.15	22.16	0.697	0.84
		Cadmium chloride	
298.15	71.08	0.656	-2.27
303.15	60.80	0.668	-1.83
308.15	53.98	0.798	-1.39
313.15	48.11	0.808	-0.95
318.15	37.94	0.933	-0.51
		Magnesium chloride	
298.15	153.80	0.497	-3.29
303.15	138.39	0.654	-2.87
308.15	131.82	0.906	-2.44
313.15	120.63	0.975	-2.02
318.15	114.71	0.994	-1.60

In 5% Ethanol+water			
		Manganese chloride	
298.15	57.68	0.424	-1.34
303.15	51.51	0.464	-1.12
308.15	46.32	0.517	-0.91
315.15	42.30	0.540	-0.69
318.15	40.70	0.556	-0.48
		Cobalt chloride	
298.15	142.91	0.525	-0.98
303.15	138.55	0.612	-0.75
308.15	135.89	0.680	-0.52
313.15	133.87	0.693	-0.28
318.15	131.59	0.703	-0.05
		Nickel chloride	
298.15	111.02	0.627	-0.96
303.15	106.74	0.639	-0.74
308.15	104.73	0.665	-0.51
313.15	102.71	0.677	-0.29
318.15	100.14	0.687	-0.06
		Copper chloride	
298.15	73.21	0.466	-0.96
303.15	68.45	0.499	-0.93
308.15	66.66	0.526	-0.90
313.15	62.19	0.533	-0.87
318.15	59.75	0.595	-0.84
		Cadmium chloride	
298.15	57.30	0.505	-0.734
303.15	53.63	0.626	-0.733
308.15	51.51	0.643	-0.732
313.15	47.85	0.650	-0.731
318.15	44.33	0.673	-0.730
		Magnesium chloride	
298.15	150.53	0.631	0.98
303.15	146.32	0.645	-0.70
308.15	142.03	0.663	-0.41
313.15	140.64	0.673	-0.13
318.15	135.53	0.798	-0.14

As the behaviour of each electrolyte was found to be linear and same in all the prepared compositions of ethanol + water at 303.15K so only one composition 5% w/w of ethanol +water has been taken for studying the effect of temperature. The densities for seven different concentrations 0.005, 0.007, 0.01, 0.03, 0.05, 0.07 and 0.1 mol Kg^{-1} of transition metal chlorides were calculated at five different temperatures 298.15,303.15,308.15,313.15 and 318.15 K. The plots of ϕ_v verses √C have been found to be linear with the positive slopes values in water as well as in ethanol + water mixtures. A sample plot for manganese chloride is shown in fig 2.

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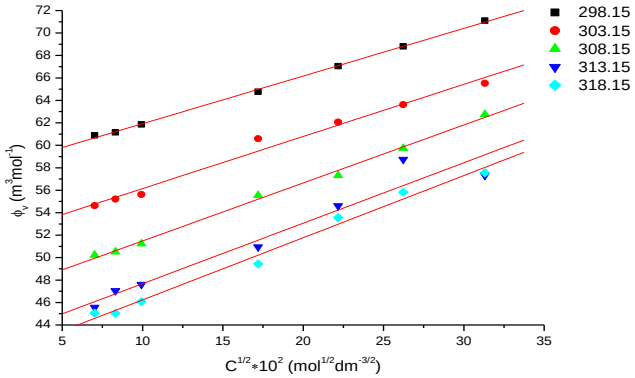

Fig. 2. Plot of ϕ_v Vs $C^{1/2}$ for manganese chloride in 5% binary mixture of ethanol + water at different temperatures.

The experimental slopes S_v^* and partial molar volumes ϕ_v^0 values at different temperatures has been obtained by using a least square fit to the plot of ϕ_v verses √C , were reported in table 2.

It is clear ,from table 2 ,that the values of S_v^* are positive for all the transition metal chlorides in water and in 5% ethanol + water at all the selected temperatures indicating the presence of strong solute-solute interactions which further increases with the increase in temperature.

Also, it is clear from table 2, that the values of ϕ_v^0 decreases with increase in temperatures for selected transition metal chlorides in 5% w/w ethanol + water, showing that solute – solvent interactions are weakened with increase in temperatures. This decrease in ϕ_v^0 values may be leads to decrease in solvation.

The plot of $\phi_v$verses √C at different temperature showed the positive slopes values indicated that transition metal chlorides taken in 5% ethanol + water composition are not fully ionised. This indicates the absence of intrinsic penetration which leads to positive slopes in plot of apparent molar volumes verses square root of concentrations.

The temperature dependence of ϕ_v^0 in water for selected transition metal chlorides and magnesium chloride can be computed by the following equations:

$\phi_v^0 = 4425.42 - 27.14\,T + 0.042T^2$ for manganese chloride (5)
$\phi_v^0 = 643.41 - 2.11\,T + 1.3 \times 10^{-3}T^2$ for cobalt chloride (6)
$\phi_v^0 = 5065.59 - 31.53\,T + 0.049T^2$ for nickel chloride (7)
$\phi_v^0 = 5831.60 - 37.25\,T + 0.050T^2$ for copper chloride (8)
$\phi_v^0 = 4679.46 - 37.25\,T + 0.040T^2$ for cadmium chloride (9)
$\phi_v^0 = 4886.95 - 28.45\,T + 0.040T^2$ for magnesium chloride (10)

and in 5% ethanol + water the transition metal chlorides has following equations:

$\phi_v^0 = 2365.18 - 14.13\,T + 0.021T^2$ for manganese chloride (11)
$\phi_v^0 = 2517.88 - 14.94\,T + 0.023T^2$ for cobalt chloride (12)
$\phi_v^0 = 2408.91 - 14.44\,T + 0.022T^2$ for nickel chloride (13)
$\phi_v^0 = 623.73 - 2.72\,T + 2.9 \times 10^{-2}\,T^2$ for copper chloride (14)
$\phi_v^0 = 284.21 - 0.78\,T + 9.0 \times 10^{-5}\,T^2$ for cadmium chloride (15)
$\phi_v^0 = 2950.40 - 17.79\,T + 0.028T^2$ for magnesium chloride (16)

The partial molar volume expansibilities , $\phi_E^0 = \left[\frac{\partial \phi_v^0}{\partial T}\right]_P$ values were calculated using equations numbered as (5) to (16), for selected transition metal chlorides, in water and in 5% w/w ethanol + water has been noted in table 2. It is clear, from table 2, that the values of ϕ_E^0 for all the selected transition metal chlorides at different temperatures are negative but increase in the magnitude with rise in temperatures shows that these transition metal chlorides are behaving like symmetrical tetra alkyl ammonium salts [14]. The increase in the magnitude of ϕ_E^0 values indicates the absence of "packing effect" [14-15]. The variation of ϕ_E^0

with temperature has been found to be linear in water as well as in 5% w/w ethanol + water for all the transition metal chlorides. Fig 3 showed the variation of ϕ_E^0 verses temperatures in water and 5% w/w ethanol+ water.

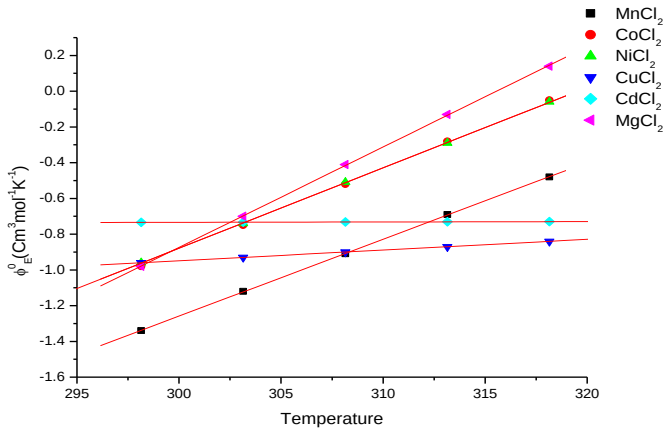

Fig. 3. Plot of ϕ_E^0 verse temperature for manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in 5% ethanol + water.

Hepler [16] has given a method of examine the sign of $\left[\frac{\partial \phi_v^0}{\partial T}\right]_P$ for various solutes in terms of long range structure maker/breaker behaviour of the solutes in aqueous solution using general thermodynamic relation: $(\partial Cp)/\partial P) = -\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right) p$

With the help of this relationship; it has been derived that the structure maker solutes should have positive values, while structure breaker solute has negative values. In the present case, $\phi_E^0 = -\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right) p$ for transition metal chlorides are positive in water as well as in 5% w/w ethanol + water. This reveals that all the selected transition metal chlorides acts as structure promoters in both the solvent systems.

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