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Partial Molar Volumes of Cobalt Nitrate and Nickel Nitrate in Water and Binary Aqueous Mixtures of DMSO at Different Temperatures

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Abstract

Partial molar volumes of Cobalt nitrate and Nickel nitrate have been determined in water and binary aqueous mixtures of dimethyl sulfoxide (5,7, 9 and 12% by weight of DMSO) at 308.15 K with the help of density measurements. Effect of temperature on the partial molar volumes was also studied for these salts in water and binary aqueous mixtures of DMSO. Results obtained have been analyzed by Masson's equation and the experimental values of slopes and partial molar volumes of these transition metal nitrates have also been interpreted in terms of ion-ion or ion – solvent interactions. Limiting molar expansibilities have also been determined which are interpreted in terms of structure making or breaking capacities of transition metal nitrates. In the present study both the transition metal nitrates have been found structure breaker in water and binary aqueous mixture of DMSO.

Keywords: Partial molar volumes, structure breaker, transition metal nitrates**.**

1. Introduction

In thermodynamic properties partial molar volume is one of the most important tool which is useful in elucidating the various types of interactions like ion-ion, ion - solvent and solvent – solvent interactions occurring in aqueous as well as non-aqueous solutions [1-10]. The structure and properties of the solutions can be determined by these interactions and appreciable work has been done for various electrolytes in different binary aqueous mixtures but less work is done for cobalt nitrate and nickel nitrate in binary aqueous mixtures of DMSO. So, the present study is to understand the interactions of cobalt nitrate and nickel nitrate in water and DMSO + water mixture. As we know that transition metal ions play an important role in different life systems as these are present in different minerals, vitamins, enzymes and proteins. Nickel is the most widely available metal ion for purifying histidine-tagged proteins and provides good binding efficiency to His-tagged proteins but also tends to bind nonspecifically to endogenous proteins that contain histidine clusters. On the other hand cobalt exhibits a more specific interaction with histidine tags, resulting in less nonspecific interaction. For this reason, cobalt is the preferred divalent cation for purifying His-tagged proteins when high purity is a primary concern. Cobalt is also used in the production of super alloys. Its primary use is in the preparation of alloys such as stainless steel. Applications of nickel have been found in petroleum industry, machinery and household appliances and chemical industry. The solvent Dimethyl sulfoxide which is used in the present study is a water miscible solvent and has wide applications in cell biology and has been used for over 50 years in a large variety of industrial applications.

2. Materials and methods

The reagents Cobalt nitrate [$Co(NO_3)_2 .6H_2O$, M.W.291.03g], Nickel nitrate [$Ni(NO_3)_2.6H_2O$, M.W. 290.79 g] and DMSO were of AR grade. These reagents were used after drying over anhydrous calcium oxide in a desiccator. Fresh triple distilled water was used as standard solvent for preparing binary aqueous mixtures of DMSO and other solutions. The binary aqueous mixtures of DMSO and five different concentrations of above mentioned transition metal nitrates were prepared by weight and the conversion of molality, (m) into molar concentration(C) was done by using the standard expression [11]:

$$C = \frac{\mathrm{md}1000}{1000 + \mathrm{mM}_2} \qquad (1)$$

Where, d is the density of solution and M_2 is the molecular weight of transition metal nitrate salts.

The density was measured with the help of an apparatus similar to the one reported by Ward and Millero [12]. 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. In the present studies a 37.433g float of volume 34.6429± 0.040023 cm^3 at 303.15K was used. The densities of different aqueous solution of transition metal nitrates 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 the densities of sample solution and of water respectively; w and w_0 are the weights of float in sample solution and water respectively and V_f is the float volume. The calibration of float was checked by measuring density of pure dioxane at 308.15K (our value d =1.02226 gcm^{-3} is in good agreement with literature valued=1.02230 gcm^{-3}) [13]. The accuracy in the density measurements was 1 x 10^{-4} gcm^{-3}.

The apparent molar volumes (ϕ_v) were calculated from the density data using the following expression [18] :

$$\phi_v = \frac{1000(d_0 - d)}{cd_0} + \frac{M_2}{d_0} \qquad (3)$$

where d_0 is the density of DMSO +water as solvent and d is the density of solution; C is the molar concentration of nitrate salts and M_2 is the molecular weight of transition metal nitrates. The density measurements were carried out in a well stirred water bath with a temperature control of ± 0.01 K.

3. Results and discussion

3.1 Effect of Concentration

The densities of aqueous solutions of cobalt nitrate and nickel nitrate in different compositions of DMSO + water (5, 7, 9 and 12%) at 308.15 K have been measured and were used to calculate the apparent molar volumes ϕ_v. The plot of ϕ_v verses $C^{1/2}$ were found to be linear in different compositions of DMSO + water. A sample plot for nickel nitrate in different compositions of DMSO + water at 308.15K is shown in figure 1. The partial molar volumes ϕ_v^0 were calculated by using least square fit to the linear plots of experimental values of $\phi_v$versus square root of molar concentration c and using Masson equation

$$\phi_v = \phi_v^0 + S_v^* C^{1/2} \qquad (4)$$

where ϕ_v^0 is the partial molar volume and S_v^* is the experimental slope.

Values of ϕ_v^0 and S_v are calculated and recorded in Table 1 in different compositions of binary aqueous mixture of DMSO at 308.15 K. It is clear, from table 1,that the values of slopes (S_v^*) are positive which indicate the presence of strong ion-ion interactions and these interactions decrease with increase in the amount of DMSO in water, which trait to the increase in solvation. Also from Table 1, it is clear that the ϕ_v^0 values are positive and increase in magnitude, in all the compositions of DMSO + Water at 308.15K for both the transition metals nitrates. The trend of ϕ_v^0values, for both the transition metal nitrates, with the increase of DMSO amount in water, shows that ion- solvent interactions increase on the addition of DMSO in water which indicates that solvent has less affinity for water. Also, on comparing the magnitudes of ϕ_v^0 values with the values of S_v^* ,

ϕ_v^0values are more in magnitudes than that of S_v^* of the same transition metal nitrates. This concludes that ion-solvent interactions dominate over the ion-ion interactions in DMSO + Water mixture at 308.15 K.The volume of transfer ($\Delta\overline{V}^0_{(tr))}$) has also been calculated by using the relation:

$$\Delta\overline{V}^0_{(tr)} = \Delta\phi^0_{v(MS)} - \phi^0_{v(W)} \qquad (5)$$

Here $\phi_v^0{}_{(MS)}$ and $\phi^0_{v(W)}$ are the partial molar volumes of transition metal nitrates in mixture of DMSO + water and water as solvents respectively.

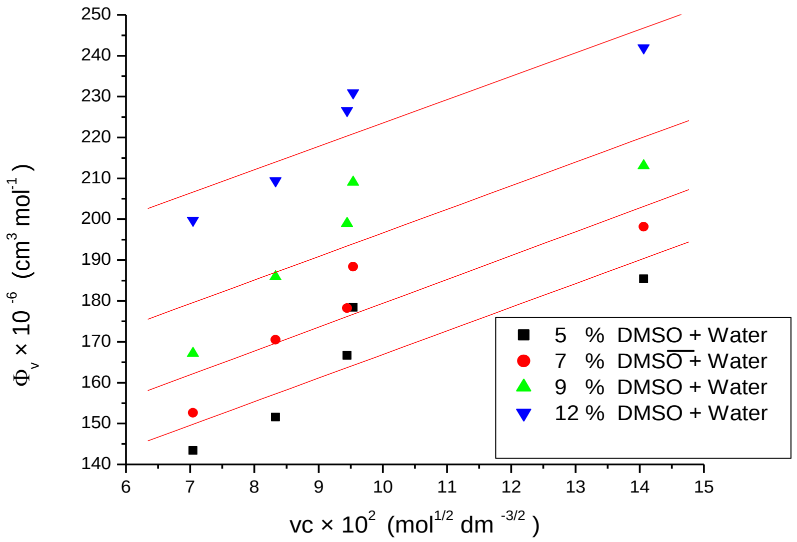

Figure 1: Plots of ϕ_v Vs $C^{1/2}$ for nickel nitrate in different compositions of DMSO+ Water at 308.15K

Table 1: Partial molar volumes (ϕ_v^0) and experimental slopes (S_v^*) for cobalt nitrate and nickel nitrate in different compositions of DMSO + Water mixture at 308.15 K.

DMSO + Water (wt.%)	**Cobalt nitrate**			**Nickel nitrate**		
	ϕ_v^0 **(cm^3 mol^{-1})**	S_v^* **(cm^{3}dm$^{1/2}$mol$^{-3/2}$)**	$\Delta\overline{V}^0_{(tr)}$ **(cm^3 mol^{-1})**	ϕ_v^0 **(cm^3 mol^{-1})**	S_v^* **(cm^{3}dm$^{1/2}$mol$^{-3/2}$)**	$\Delta\overline{V}^0_{(tr)}$ **(cm^3 mol^{-1})**
0 (Water)	40.40	8.29	------	29.42	6.95	-----
5	64.85	6.26	24.45	106.5	5.98	77.08
7	65.86	6.21	25.46	119.0	5.96	89.58
9	72.33	5.69	31.93	136.4	5.94	106.98
12	78.17	5.65	37.77	164.0	5.80	134.58

The values of volume of transfer of transition metal nitrates were recorded in table 1.It is clear from Table.1 that $\Delta\overline{V}^0_{(tr))}$ values continuously increase in magnitude with the increase in the content of DMSO in water. The increase in $\phi_v^0$and $\Delta\overline{V}^0_{(tr)}$ may be trait to the decrease in electrostriction in the presence of DMSO.The electrostriction effect, which leads to the contraction in the volume of the solvent, is enhanced in the mixed solvents as compared to pure water. This electrostriction effect, again confirms the earlier conclusion of lesser affinity of DMSO for water. It is also clear that as NO_3^- ion is common in both transition metal nitrates, the values of volume of transfer in a particular composition of DMSO + water , the electrostriction for these cations follows the order as : $Ni^{2+} > Co^{2+}$. This indicates that Co^{2+} ion is more solvated by DMSO + water mixture and Ni^{2+} is less. So the solvation of these cations follows the trend: $Ni^{2+} < Co^{2+}$. Also; ΔV^0_{tr} values, for each transition metal nitrates rises with the increase of DMSO amount in water, which may be trait to the decrease in solvent – solvent interactions between DMSO + water.

3.2 Effect of temperature:

Since the behaviour of the both the electrolytes was found to be linear and same in different composition of DMSO + water at 308.15 K, so only one composition system (5% w/w) has been selected for studying the effect of temperature. The experimentally determined values for the five different concentrations of both the transition metal nitrates at four equidistant different temperatures (303.15 – 318.15K) have been used to calculate the partial molar volume $\phi_V^0$of the salts.The plot of apparent molar volume ϕ_V against the $C^{1/2}$ were found to be linear with the positive slopes in water as well as in aqueous solutions of DMSO as shown in Figure. 2 for cobalt nitrate as sample plot.

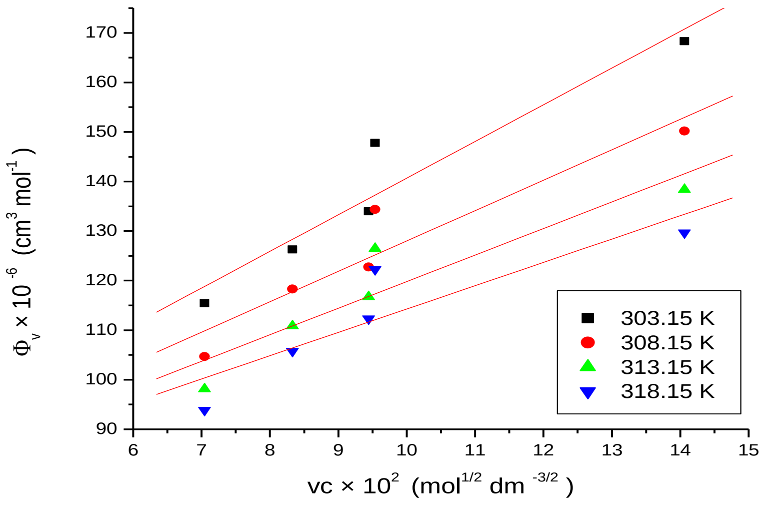

Figure 2: Plots of ϕ_v Vs $C^{1/2}$ for Cobalt nitrate in 5% DMSO + water mixture at different temperatures.

Table 2: Partial molar volumes, (ϕ_V^0) and experimental slopes, (S_V^*) for cobalt nitrate and nickel nitrate in water and 5% (w/w) DMSO + water mixture at different temperatures.

Temperature (K)	Cobalt nitrate (in water)		Nickel nitrate (in water)	
	ϕ_V^0 ($cm^3\ mol^{-1}$)	S_V^* ($cm^3 dm^{1/2} mol^{-3/2}$)	ϕ_V^0 ($cm^3\ mol^{-1}$)	S_V^* ($cm^3 dm^{1/2} mol^{-3/2}$)
303.15	38.79	9.17	26.39	7.74
308.15	40.40	8.29	29.42	6.95
313.15	42.03	7.66	32.61	6.36
318.15	42.92	6.83	38.90	5.32
Temperature (K)	Cobalt nitrate in 5% (w/w) DMSO +water		Nickel nitrate in 5% (w/w) DMSO +water	
	ϕ_V^0 ($cm^3\ mol^{-1}$)	S_V ($cm^3 dm^{1/2} mol^{-3/2}$)	ϕ_V^0 ($cm^3\ mol^{-1}$)	S_V ($cm^3 dm^{1/2} mol^{-3/2}$)
303.15	64.68	7.53	98.5	6.060
308.15	64.85	6.26	106.5	5.981
313.15	64.94	5.50	117.6	5.770
318.15	65.41	4.85	129.1	5.244

It is evident from table 2 that the values of $S_V^*$are positive and decrease for both the transition metal nitrates in water and in 5% DMSO + Water mixture at all temperatures. The decrease in S_V^*values of transition metal nitrates indicates the presence of weak ion-ion interactions and these values further decreases with the increase in temperature trait to decrease in ion-ion interactions and attributes the increase in the solvation of transition metal ions with rise in temperature. Also it is clear from Table 2, that the values of ϕ_v^0 increase with increase in temperature ,for both the transition metal nitrates in DMSO + water (5% w/w) mixture , thereby showing that ion – solvent interactions are strengthened with increase in temperature. The increase in ϕ_v^0values may be trait to increase in solvation of transition metal nitrates with rise in temperature.

It has been found that only S_v^* is not only one parameter for determining the structure making or breaking nature of any solute. Limiting molar expansibilities (ϕ_E^0) is another parameter, which determines the structure making or breaking capacity of any solute in any of the solvent developed by Hepler [14].

The temperature dependence of ϕ_v^0in water [relations (6) and (7)] and 5% DMSO + water [relations (8) and (9)] for cobalt nitrate and nickel nitrate can be expressed by the following relations:

$$\phi_v^0 = -731.417 + 4.72T - 0.0072T^2 \text{ for cobalt nitrate} \quad (6)$$

$$\phi_v^0 = -3201.34 + 20.53T - 0.032T^2 \text{ for nickel nitrate} \quad (7)$$

$$\phi_v^0 = -258.8 + 1.67T - 0.002T^2 \text{for cobalt nitrate} \quad (8)$$

$$\phi_v^0 = -3654.42 + 22.99 - 0.035\,T^2 \text{ for nickel nitrate} \quad (9)$$

Limiting molar expansibilities $\phi_E^0 = \left[\frac{\partial \phi_v^0}{\partial T}\right]_P$,which is temperature dependence function of ϕ_v^0 ,is calculated for both the transition metal nitrates by using relations (6) to (9)and are given in Table 3.

Table 3: Variation of limiting apparent molar volume expansibilities(ϕ_E^0) for cobalt nitrate and nickel nitrate in 5% (w/w) DMSO + Water mixture at different temperatures.

Temperature (K)	Cobalt Nitrate in water ϕ_E^0($cm^3\ mol^{-1}\ K^{-1}$)	Nickel Nitrate in water ϕ_E^0($cm^3\ mol^{-1}\ K^{-1}$)
303.15	0.36	1.13
308.15	0.29	0.81
313.15	0.22	0.49
318.15	0.14	0.17
Temperature (K)	Cobalt Nitrate in 5% (w/w) DMSO + Water ϕ_E^0($cm^3\ mol^{-1}\ K^{-1}$)	Nickel Nitrate in 5% (w/w) DMSO + Water ϕ_E^0($cm^3\ mol^{-1}\ K^{-1}$)
303.15	0.46	1.77
308.15	0.44	1.42
313.15	0.42	1.07
318.15	0.40	0.72

From table 3, ϕ_E^0 values for transition metal nitrates at different temperatures are positive and decrease in magnitude with rise in temperature showing that both these transition metal nitrates do not behaving like that of symmetrical tetra alkyl ammonium salts [15] but like those of common salts [16,17] because in the case of common electrolytes the molar volume expansibilities should decrease with the rise in temperature. The variation of $\phi_E^0$with temperature, for both the transition metal nitrates is linear and a sample plot for cobalt nitrate is shown in figure 3.

Hepler has developed a technique of examining the sign of $[\partial^2\phi_v^o/\partial T^2]_p$ i.e. second derivative of partial molar volume with respect to temperature at constant pressure, for various solutes in terms of long range structure making and breaking capacity of the solutes in aqueous solutions using the general thermodynamic expression [14]:

$$[\partial C_P / \partial P]_T = - T\,[\partial^2\phi_v^o / \partial T^2]_p \quad (10)$$

On the basis of this expression, it has been deduced that both the salts are structure breakers in water as well as in binary aqueous mixtures of DMSO.

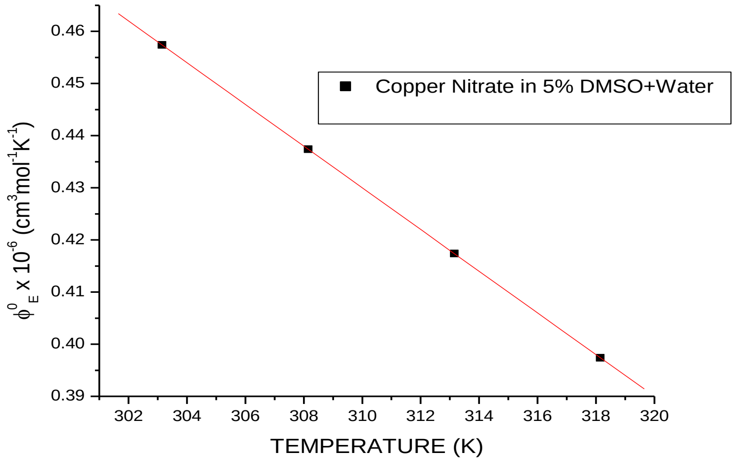

Figure 3: Variation of ϕ^0_E with temperature for cobalt nitrate in 5% DMSO + Water mixture.

Conclusion

1. By using the Masson's equation behavior of cobalt nitrate and nickel nitrate has been analysed in water and DMSO + Water mixtures.
2. Effect of concentration of DMSO in water was also analysed and it has been found that ion solvation increases with the increase in concentration of DMSO in water.
3. Effect of temperature was also analysed and in the present study both the transition metal nitrates have been found structure breaker in water and DMSO + Water mixture.

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