

Research Article



Role of Cation and Anions (K^+ , $Cr_2O_7^{2-}$ and $P_2O_7^{4-}$) Towards ion Association and Solvation in Aqueous and Aqueous d-Mannitol Mixtures at Different Temperatures

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Accepted on: 19-03-2014; Finalized on: 31-05-2014.

ABSTRACT

The conductance of potassium dichromate and pyrophosphate has been measured in the concentration range of 1×10^{-3} to 6×10^{-2} mol dm^{-3} in aqueous and aqueous binary mixtures containing d-mannitol (5, 10, 15% (w/w)) at different temperatures (298.15-313.15K). The conductance data in all cases have been computed by Shedlovsky equation to obtain Λ_m^0 and K_A . Based upon the composition dependence of Walden product, the influence of the d-mannitol mixtures on the solvation of ions has been discussed. The values of the association constants, K_A , are used to obtain various thermodynamic parameters for the association process in the solution. It has been observed that the electronic contribution is totally negligible towards the standard transfer thermodynamic quantities.

Keywords: Aqueous d-mannitol, Association constant, Potassium dichromate and pyrophosphate.

INTRODUCTION

Mannitol, the sugar alcohol, is a white, crystalline solid with the chemical formula $C_6H_8(OH)_6$. It is usually isolated from the secretions of the flowering ash and called manna after its resemblance to the Biblical food. In plants, it is used to induce osmotic stress. It has several industrial uses, but is mainly used to produce tablets of medicine. Mannitol is also used as a facilitating agent for the transportation of pharmaceuticals directly into the brain. Mannitol is commonly used in the circuit prime of a heart lung machine during cardiopulmonary bypass.^{1,2} The presence of mannitol preserves renal function during the times of low blood flow and pressure, while the patient is on bypass. Mannitol is also the first drug of choice for the treatment of acute glaucoma in veterinary medicine. Mannitol increases blood glucose to a lesser extent than sucrose (thus having a relatively low glycemic index and is therefore used as a sweetener for people with diabetes, and in chewing gums.^{3,4} Because of its important applications in food, pharmaceutical industry and solubility in water, it is of great interest for many researchers to study the ion-solvent interaction for multi-charged electrolytes like potassium dichromate and pyrophosphate ions. The conductance studies of dichromate and pyrophosphate ion in different compositions of water with d-mannitol mixtures can be useful for obtaining information on the behavior of ions in solutions and the interactions of water and d-mannitol with each other and with the solute. The calculated values of association constant are well known to be composite quantity depending upon specific and non-specific solute-solvent interaction, and the separation of various interaction contributions are usually difficult. Since the composition of aquo-organo solvent is varied, in addition to the dielectric constant variation, there is also

variation of solvent-solvent interaction in aquo-organo solvent. The specific and non-specific solvation effects on the ion-association phenomena may be obtained from the studies on aquo-organo solvents. However, there is a possibility of preferential solvation in d-mannitol solution. The aim of present investigation is to study the role of ion-aqueous d-mannitol interactions characterizing the preferential solvation of the solute. In this paper, we report the molar conductance of potassium dichromate and pyrophosphate in water and water with d-mannitol mixtures which is measured at temperatures at 5K intervals ranging from 298.15K to 313.15K.

MATERIALS AND METHODS

All chemicals used were of GR or BDH., AnalaR grades. Conductivity water (Specific conductance $\sim 10^{-6}$ S cm^{-1}) was used for preparing water with d-mannitol (0, 5, 10 and 15 %, (w/w)) mixtures. The d-mannitol content in the mixed solvents was accurate to within $\pm 0.01\%$. The salt solutions were prepared on the molal basis and conversion of molal to molar was done by using the standard expression⁵ considering the density differences at the respective temperatures. The conductance measurements were made on a digital reading conductivity meter with a sensitivity of 0.1% and giving the conductance value of three digits. A conductivity cell with a platinized electrode (cell constant 1S cm^{-1}) was used. The measurements were made over the temperature range of 298.15 - 313.15 K ($\pm 0.05K$). The specific and molar conductance values are expressed in terms of S cm^{-1} and S $cm^2 mol^{-1}$, respectively. The ionic strengths of the solutions were kept as low as possible ($\sim 10^{-4}$ to 10^{-2} M). The experiment was carried out with different concentrations of solutions (ranging from 1×10^{-3} to 6×10^{-2} M in water, and 5.0, 10.0 and 15.0 wt% d-mannitol in water. The conductance of different



concentrations of potassium dichromate and pyrophosphate were measured making appropriate corrections for the conductance of the solvents concerned.

RESULTS AND DISCUSSION

The experimental values of the conductance measurements for potassium dichromate and pyrophosphate in water and in three wt% compositions of water with d-mannitol mixtures, after solvent correction,

were analyzed using Shedlovsky⁶⁻⁷ equation. The limiting molar conductivity values Λ_m^0 are obtained by using the value of ion-size parameter $a_0 = q$ as $a_0 = 0$, q and $2q$ are very close to each other.⁸ The calculated values of K_A , the ion association constant and Λ_m^0 values in aqueous and in water- d-mannitol-mixed solvents are given in Table 1 at experimental temperatures. Table 1 also contains the values of Walden product $\Lambda_m^0 \eta_0$ for the multi-charged electrolytes at 298.15 K only.

Table 1: Values of Λ_m^0 ($\text{Sm}^2\text{mol}^{-1}$), K_A ($\text{m}^3 \text{mol}^{-1}$) and $\Lambda_m^0 \eta_0$ of Potassium Dichromate and Pyrophosphate in water and water and Mannitol mixtures at different temperatures.

Mannitol (wt%)	Temperature (K)	Λ_m^0	K_A	$\Lambda_m^0 \eta_0$
$\text{K}_2\text{Cr}_2\text{O}_7$				
0.0	298.15	88.25±0.8	2.30±0.1	786.21
	303.15	92.96±0.8	2.01±0.2	742.01
	308.15	98.33±0.7	1.47±0.2	713.97
	313.15	104.6±0.8	1.44±0.2	684.08
0.5	298.15	84.88±1.6	18.30±0.3	903.97
	303.15	89.72±1.6	17.64±0.2	851.44
	308.15	91.17±2.0	16.77±0.7	774.03
	313.15	102.2±1.8	17.40±0.4	796.13
10.0	298.15	76.65±1.7	27.08±0.4	928.23
	303.15	79.39±1.8	29.10±0.5	862.96
	308.15	84.71±1.9	30.72±0.6	831.01
	313.15	91.19±2.0	30.49±0.5	828.01
15.0	298.15	69.05±1.7	24.67±0.6	998.46
	303.15	73.61±1.8	30.45±0.7	962.81
	308.15	78.96±1.9	29.16±0.6	945.15
	313.15	84.82±2.0	31.43±0.5	945.74
$\text{K}_4\text{P}_2\text{O}_7$				
0.0	298.15	174.6±2.7	57.96±0.3	1555.51
	303.15	214.1±3.6	127.1±0.4	1708.94
	308.15	231.9±3.7	130.4±0.4	1683.82
	313.15	248.8±3.9	129.3±0.5	1627.15
0.5	298.15	166.6±3.0	84.94±0.3	1774.29
	303.15	208.1±3.8	185.8±0.7	1974.86
	308.15	226.4±4.0	184.0±0.8	1922.13
	313.15	243.3±4.1	178.1±0.8	1895.30
10.0	298.15	163.9±3.0	111.9±0.1	1984.82
	303.15	201.8±3.7	203.7±0.8	2193.56
	308.15	215.6±3.8	175.1±0.7	2115.03
	313.15	228.3±4.1	183.4±0.9	2072.96
15.0	298.15	160.7±3.2	177.8±1.0	2323.72
	303.15	196.5±3.9	293.8±1.1	2570.22
	308.15	209.6±4.0	264.1±1.3	2508.91
	313.15	223.8±4.2	241.3±1.2	2495.37

It is clear from Table 1 that the values of Λ_m^0 increase regularly with an increase in temperature for both the electrolytes indicating less solvation or higher mobility of the ions in all the solvent systems studied. This is due to the fact that the increased thermal energy results in greater bond breaking and variation in vibrational, rotational and translational energy of the molecules that lead to higher frequency and hence, higher mobility of ions. It is observed that the Λ_m^0 values for pyrophosphate are higher than those of dichromate. Hence we can conclude that the value of conductance increases with the charge and total number of ions. The solvation of potassium ion in water+ d-mannitol mixture is shown in figure 1. For simplicity, only one potassium ion, six H₂O and two mannitol molecules are shown in the figure.

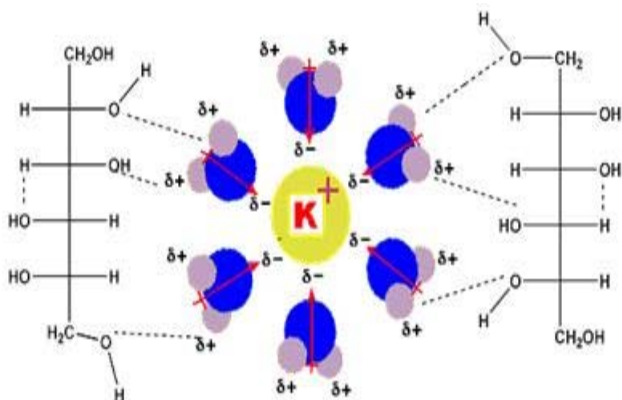


Figure 1: Schematic representation of solvation of potassium ion in water+ d-mannitol solvent

In both the cases, we observed that at all temperatures; the Λ_m^0 values in water are greater than those in all compositions of water+ d-mannitol mixtures, which indicate that d-mannitol molecules hinder the mobility of ions in mixed solvents. As the weight percentage of d-mannitol increases, more is the number of d-mannitol molecules in solvent cage, hence less is the mobility of the ions.

The all time high value of Λ_m^0 in water for both the salts may be attributed to the fact that in spite of high dielectric constant of water, the potassium, dichromate and pyrophosphate ions have become highly hydrated. It reflects on the factors affecting their effective size and strength of the columbic field in the range of the hydration shell. The factors that affect the size of the ions can be the radii of the strongly hydrated potassium and pyrophosphate ions and the interionic distance between them. Both the factors influence the hydrodynamic radii of the ions and thus influence the Λ_m^0 values. The schematic solvation process of pyrophosphate anion in water+d-mannitol mixture is shown in figure 2. For simplicity, only one pyrophosphate ion, six H₂O and two mannitol molecules are shown.

The association constant, K_A values of both potassium dichromate and pyrophosphate obtained show an irregular trend with increase in temperature and also with

increase in d-mannitol percentage. This may be attributed to the varying degree of exothermic ion-pair association caused due to difference in ionic stability, specific ion-solvent and solvent-solvent interactions.

It is found that the Walden product is higher in case of pyrophosphate ion than that of dichromate ion. The higher value of Walden product indicates weak solvation of the ions. It is known that the variation of Walden product reflects the change of solvation. As the weight percentage of d-mannitol increases, there is a variation trend observed in Walden product values.

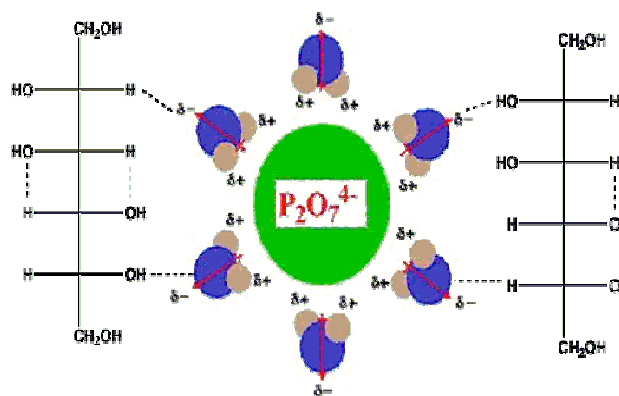


Figure 2: Schematic representation of solvation of P₂O₇⁴⁻ ion in water+d-mannitol solvent

Since the conductance measurements of an ion depend upon mobility, it is quite reasonable to treat the conductance data similar to the one employed for the rate process⁹ that takes place with the change in temperature, i.e.

$$\Lambda_m^0 = Ae^{-E_s/RT} \dots\dots\dots(1)$$

Where A is the frequency factor, R the gas constant and E_s the Arrhenius activation energy of the transport process. From the plot of log Λ_m^0 versus 1/T, the E_s values have been computed from the slope (-E_s/2.303R) and are given in Table 2.

Table 2: Thermodynamic Parameters ΔG^0 (kJ mol⁻¹), ΔH^0 (kJmol⁻¹), ΔS^0 (Jmol⁻¹K⁻¹) and E_s (KJmol⁻¹) at 25°C

D-Mannitol (wt%)	ΔG^0	ΔH^0	ΔS^0	E _s
K₂Cr₂O₇				
0.0	-2.07	-26.56	-82.16	8.81
5.0	-7.21	-3.19	13.47	8.88
10.0	-8.17	6.39	48.89	9.07
15.0	-7.94	10.68	62.50	10.66
K₄P₂O₇				
0.0	-10.06	38.14	161.6	17.81
5.0	-10.98	35.23	155.0	19.01
10.0	-11.69	20.91	109.3	16.52
15.0	-12.85	12.84	86.18	16.49

The standard free energy change for the association process¹⁰⁻¹¹ is calculated from equation (2)

$$\Delta G^{\circ} = - RT \ln K_A \dots\dots\dots (2)$$

The heat of association, ΔH° , is calculated from the slope of the plot of $\ln K_A$ versus $1/T$ and the entropy change, ΔS° , from Gibbs-Helmholtz equation,

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \dots\dots\dots (3)$$

The values of the standard thermodynamic parameters are given in Table 2 at 25°C only.

From Table 2, it is evident that the activation energy, E_s , is positive for both the salts in all solvents. The free energy change, ΔG° , values are negative for both the salts in the solvent systems studied. This shows that the association process is favored over the dissociation process in all the mixed solvents. The positive values of ΔH° and ΔS° (except three cases) show that the association process is endothermic in nature and the randomness of ions in all the solvent systems.

The transfer thermodynamic quantities, e.g., ΔG°_t , ΔH°_t and ΔS°_t for potassium dichromate and pyrophosphate in 5, 10, 15 wt% of d-mannitol solutions at 25°C are given in Table 3. The effect of solvent on these quantities may be explained on the basis of the magnitude and sign of these quantities.

The free energy change for the transfer process, $MX(w) \rightarrow MX(s)$, has been calculated in mole fraction scale because it will eliminate free energy changes and is given by

$$\Delta G^{\circ}_t = (\Delta G^{\circ}_N - {}^w\Delta G^{\circ}_N) \dots\dots\dots (4)$$

where the superscripts w and s refer to water and mixed solvents, respectively, and ΔG° values are given in mole fraction scale, as

$$\Delta G^{\circ}_N = \Delta G^{\circ}_m - (v-1) \times 2.303 RT \log (0.001 M_{av}) \dots (5)$$

where v is the number of moles of ion produced from one mole of salt and M_{av} is the average molar mass of the concerned solvent.

The entropy change (ΔS°_t) and enthalpy change (ΔH°_t) of transfer process have been derived by means of the following equations

$$\Delta S^{\circ}_t = - d(\Delta G^{\circ}_t)/dT$$

$$\text{and } \Delta H^{\circ}_t = \Delta G^{\circ}_t + T \Delta S^{\circ}_t \dots\dots\dots (6)$$

The negative values of ΔG°_t in all cases indicate that the overall effect of permittivity as well as of chemical nature

(Which mainly reflects the relative basicity and solvating capacity) of the solvent makes the transfer of the solute (both cations and anions) from water to the mixed solvent favorable. In this case, the ions (of the solute) appear to be in a lower free energy state in the mixed solvent than in water, and hence the transfer is spontaneous.

The values of ΔH°_t and ΔS°_t are found to be negative in case of pyrophosphate salt. The negative values of ΔH°_t and ΔS°_t suggest that when a bulky organic molecule like d-mannitol, is added to a highly polar water molecule, the mixed solvent becomes less associated than pure water.

Thus, the transferred ion breaks more structure in pure water than in the mixed solvent. This is further supported by the fact that the transfer process is the structure forming process including the solvation of ions which is exothermic accompanied by entropy decrease. The negative entropy of the transfer of solutes (i.e. ions of the solutes) can probably be attributed to a greater structure formation in the mixed solvent than in water. Consequently, the degree of solvent orientation is more in the mixed solvent than in aqueous medium.

Considering the transfer thermodynamic quantities comprising of two parts, namely, electrostatic (el) arising from the difference in the dielectric constants of the solvents, and chemical (ch) which reflects the chemical nature of the solvent including basicity as well as the solvating capacity of the solvent as¹²

$$\Delta X^{\circ}_t = \Delta X^{\circ}_{t,el} + \Delta X^{\circ}_{t,ch} \dots\dots\dots (7)$$

Where X stands for G, H or S.

Assuming that the radii of the ions do not change with the change of the solvent, the values of $\Delta G^{\circ}_{t,el}$ and $\Delta S^{\circ}_{t,el}$ are calculated by means of Born equation:

$$\Delta G^{\circ}_{t,el} = (Ne^2/2) (\epsilon_s^{-1} - \epsilon_w^{-1})(r_+^{-1} + r_-^{-1}) \text{ and}$$

$$\Delta S^{\circ}_{t,el} = - (Ne^2/2) (r_+^{-1} + r_-^{-1}) (\epsilon_s^{-1} \theta_s^{-1} - \epsilon_w^{-1} \theta_w^{-1}) \dots\dots (8)$$

Where r_+ and r_- are the radii of cation and anion, respectively, ϵ_s and ϵ_w are the dielectric constants of the mixed solvent and water, respectively. $\theta_s = d \ln \epsilon_s / dT$ and $\theta_w = d \ln \epsilon_w / dT$, the temperature coefficients of the corresponding solvents. N is the Avogadro number and e is the electronic charge. The values of the dielectric constants of water and that of the water and d-mannitol mixtures are taken from the literature.¹³

From equation (7), the value of $\Delta G^{\circ}_{t,ch}$ is determined from the values of ΔG°_t and $\Delta G^{\circ}_{t,el}$ and so is the value of $\Delta S^{\circ}_{t,ch}$. Thus, from the values of $\Delta G^{\circ}_{t,ch}$ and $\Delta S^{\circ}_{t,ch}$, the value of $\Delta H^{\circ}_{t,ch}$ has been computed. All these computed values are given in Table 3.

The observed negative values of $\Delta G^{\circ}_{t,ch}$ suggest that the mixed solvents possess larger solvating capacity towards the ions and are more basic than the water. It is also found that the electronic contribution is totally negligible in all cases. The values of $\Delta S^{\circ}_{t,ch}$ and $\Delta H^{\circ}_{t,ch}$ are also found to be negative in case of potassium pyrophosphate. Thus, the chemical contribution towards Gibbs free energy, entropy and enthalpy changes accompanying the transfer process of dichromate and pyrophosphate (since the cation is same, K^+) ions from water to water and d-mannitol mixtures suggest that the aqueous d-mannitol is a stronger solvating agent than simple water.



Table 3: Standard transfer thermodynamic quantities ΔG_t^0 (kJ mol⁻¹), ΔH_t^0 (kJmol⁻¹), ΔS_t^0 in (Jmol⁻¹K⁻¹) at 298.15K

D-Mannitol (wt%)	ΔG_t^0	$\Delta G_{t,el}^0$	$\Delta G_{t,ch}^0$	ΔS_t^0	$\Delta S_{t,el}^0$	$\Delta S_{t,ch}^0$	ΔH_t^0	$\Delta H_{t,el}^0$	$\Delta H_{t,ch}^0$
K₂Cr₂O₇									
5.0	-5.337	3.42×10 ⁻¹⁸	-5.337	96.89	-6.43×10 ⁻¹⁸	96.89	23.552	-1.91×10 ⁻¹⁵	23.538
10.0	-6.529	5.90×10 ⁻¹⁸	-6.529	133.0	-7.16×10 ⁻¹⁵	133.0	33.129	-2.13×10 ⁻¹²	33.109
15.0	-6.535	8.50×10 ⁻¹⁸	-6.535	147.3	1.10×10 ⁻¹⁴	147.3	37.401	3.28×10 ⁻¹²	37.378
K₄P₂O₇									
5.0	-1.116	2.97×10 ⁻¹⁸	-1.116	-5.89	-5.58×10 ⁻¹⁸	-5.89	-2.875	-1.66×10 ⁻¹⁵	-2.874
10.0	-2.046	5.12×10 ⁻¹⁸	-2.046	-50.75	-6.21×10 ⁻¹⁵	-50.75	-17.180	-1.85×10 ⁻¹²	-17.173
15.0	-3.432	7.38×10 ⁻¹⁸	-3.432	-73.19	9.57×10 ⁻¹⁵	-73.19	-25.255	2.85×10 ⁻¹²	-25.244

CONCLUSION

The molar conductance of potassium dichromate and pyrophosphate in water and water with d-mannitol mixtures has been measured at temperatures ranging from 298.15K to 313.15K. As the temperature increases, the conductance value goes on increasing. Higher is the charge and total no of ions (in case of pyrophosphate), more is value of conductance. As the weight percentage of d-mannitol increases, more is the number of d-mannitol molecules in solvent cage, hence less is the mobility of the ions. This leads to low value of conductance at higher weight percentage of d-mannitol in comparison to water. The ion-association constant and thermodynamic parameters as well as transfer thermodynamic quantities have been calculated and their roles towards solvation have been discussed.

Acknowledgement: The authors would like to thank Department of Chemistry, ITER, Siksha 'O' Anusandhan University, Bhubaneswar, for providing financial, infrastructural support and experimental facilities.

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Source of Support: Nil, Conflict of Interest: None.

