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Studies on ion association and solvation of multi-charged electrolytes (potassium ferricyanide and ferrocyanide) in aqueous and aqueous D-fructose mixtures at different temperatures

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ABSTRACT

The conductance of potassium ferricyanide and ferrocyanide 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-fructose (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^{o}_{m} *and* $K_{A.}$ *Based upon the composition dependence of Walden product, the influence of the d-fructose 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-fructose, potassium ferrocyanide and ferricyanide, association constant.

INTRODUCTION

D-Fructose is a monosaccharide with molecular formula, $C_6H_{12}O_6$ or $HOCH_2$-(C=O)-$(CHOH)_3$-CH_2OH, whose five hydroxyl (-OH) groups are arranged in a specific way along its six-carbon backbone. Because of its highest solubility in water, it is of great interest for many researchers to study the ion-solvent interaction for multi-charged electrolytes like potassium ferricyanide and ferrocyanide ions in solution as well as in chemical and pharmaceutical research. The conductance studies of ferricyanide and ferrocyanide ion in different compositions of water with d-fructose mixtures can be useful for obtaining information on the behavior of ions in solutions and the interactions of water and d-fructose 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 water-soluble d-fructose solution. The aim of present investigation is to study the role of ion-water soluble d-fructose interactions characterizing the preferential solvation of the solute. In this paper, we report the molar conductance of potassium ferricyanide and ferrocyanide in water and water with d-fructose mixtures which is measured at temperatures at 5K intervals ranging from 298.15K to 313.15K.

EXPERIMENTAL SECTION

All chemicals used were of GR or BDH., AnalaR grades. Conductivity water (Specific conductance ~ 10^{-6} S cm^{-1}) was used for preparing water with d-fructose (0, 5, 10 and 15 %,(w/w)) mixtures .The d-fructose content in the mixed solvents was accurate to within ±0.01%. The salt solutions were prepared on the molal basis and conversion of molal to molar was done by using the standard expression [1] 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 dipping type conductivity cell with a platinised electrode (cell constant 1S cm^{-1}) was used. The measurements were made over the temperature range of 298.15-313.15 K (±0.05K). The specific and molar conductances 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 (~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-fructose in water. The conductance of different concentrations of potassium ferricyanide and ferrocyanide were measured making appropriate corrections for the conductance of the solvents concerned.

Table 1. Values of Λ^o_m (Sm^2mol^{-1}), K_A(m^3 mol^{-1}) and Λ^o_m η_o of Ferricyanide and Ferrocyanide in water and water and d-fructose mixtures at different temperatures

d-Fructose (wt%)	**Temperature (K)**	**Λ^o_m**	**K_A**	**Λ^o_m η_o**
$K_3[Fe(CN)_6]$				
0.0	298.15	535.6±6.1	31.82±1.99	4771.66
	303.15	581.2±6.3	29.11±1.91	4639.13
	308.15	641.3±6.6	30.86±1.96	4656.47
	313.15	703.1±6.9	35.58±2.01	4598.27
5.0	298.15	451.0±5.2	28.76±1.89	4399.95
	303.15	499.8±5.5	28.70±1.89	4196.82
	308.15	545.8±5.8	29.24±1.91	4189.01
	313.15	589.6±5.9	28.20±1.87	4085.92
10.0	298.15	394.1±4.8	26.68±1.82	4344.55
	303.15	439.5±5.1	27.63±1.85	4182.28
	308.15	481.7±5.3	27.40±1.85	4080.48
	313.15	520.6±5.5	27.30±1.84	3889.40
15.0	298.15	342.8±4.4	27.22±1.84	4397.09
	303.15	382.3±4.7	27.76±1.86	4277.17
	308.15	418.9±5.0	28.11±1.87	4190.67
	313.15	460.3±5.2	28.73±1.89	4018.41
$K_4[Fe(CN)_6]$				
0.0	298.15	663.0±7.0	40.59±2.25	5906.66
	303.15	737.1±7.6	45.22±2.37	5883.53
	308.15	801.9±7.9	45.71±2.39	5822.59
	313.15	872.3±8.3	48.44±2.46	5704.84
5.0	298.15	554.6±6.4	40.68±2.25	5410.67
	303.15	609.1±6.7	39.54±2.22	5114.61
	308.15	666.1±7.1	41.30±2.27	5112.31
	313.15	723.4±7.4	42.03±2.29	5013.16
10.0	298.15	488.1±6.1	43.42±2.32	5380.81
	303.15	543.0±6.5	44.70±2.36	5167.18
	308.15	592.9±6.8	44.81±2.37	5022.45
	313.15	647.5±7.1	45.40±2.38	4837.47
15.0	298.15	417.6±5.6	42.06±2.29	5356.55
	303.15	477.1±6.0	45.87±2.39	5337.79
	308.15	512.9±6.2	42.77±2.31	5131.05
	313.15	561.3±6.6	43.47±2.33	4900.14

RESULTS AND DISCUSSION

The experimental values of the conductance measurements for potassium ferricyanide and ferrocyanide in water and in three wt% compositions of water with d-fructose mixtures, after solvent correction, were analysed using Shedlovsky [2,3] equation. The limiting molar conductivity values Λ^o_m are obtained by using the value of ion-size parameter a_o = q as a_o = 0, q and 2q are very close to each other [4]. The calculated values of K_A, the ion association constant and Λ^o_m values in aqueous and in water- d-fructose -mixed solvents are given in Table 1 at experimental temperatures. Table 1 also contains the values of Walden product $\Lambda^o_m\eta_o$ for the multi-charged electrolytes at 298.15 K only.

It is clear from Table 1 that the values of Λ^o_m 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^o_m values are higher in case of ferrocyanide than ferricyanide. Hence we can conclude that higher is the charge and total no of ions, more is value of conductance. In both the cases, we observed that the Λ^o_m values in water in all temperatures are greater than that in all compositions of water with d-fructose mixtures, which indicates that d-fructose molecules hinder the mobility of ions in mixed solvents. As the weight percentage of d-fructose increases, more is the number of d-fructose molecules in solvent cage, hence less is the mobility of the ions.

The all time high value of Λ^o_m in water only for both the salts may be attributed to the fact that in spite of high dielectric constant of water, the potassium, ferricyanide and ferrocyanide ions have become highly hydrated which reflects 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 ferrocyanide ions and the interionic distance between them. Both the factors influence the hydrodynamic radii of the ions and thus influence the Λ^o_m values.

The association constant, $K_{A,}$ values of both potassium ferricyanide and ferrocyanide obtained show an irregular trend with increase in temperature and also with increase in d-fructose 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. The variation of the Walden product ($\Lambda^o_m\eta_o$) with composition at 298K is shown below in Figure 1.

It is found that the Walden product is higher in case of ferrocyanide ion than that of ferricyanide 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-fructose increases, there is a variation trend observed in Walden product values.

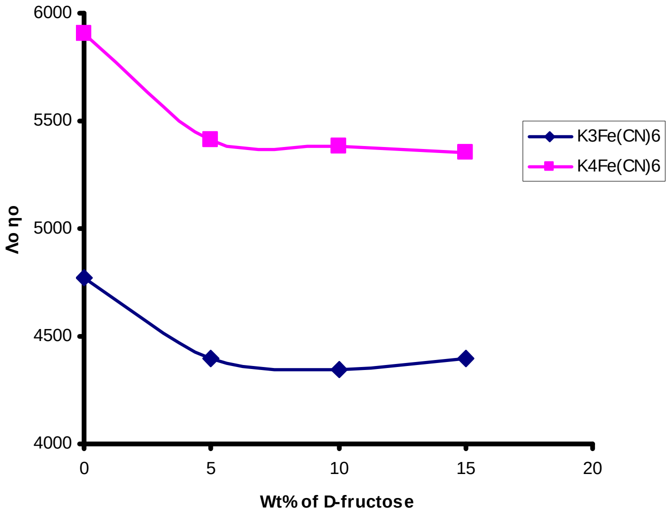

Figure 1. Plot of Walden products ($\Lambda o\ \eta_o$) vs. wt% of aqueous d-fructose solutions.

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 process [5] that takes place with the change in temperature, i.e.

$\Lambda^o_m = Ae^{-Es/RT}$ (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^o_m versus 1/T, the E_s values have been computed from the slope (-Es/20303R) and are given in Table 2.

The standard free energy change for the association process is calculated from equation (2) [6]

$\Delta G^o = - RT \ln K_A$ (2)

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

$\Delta G^o = \Delta H^o - T\Delta S^o$ (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^o, values are negative for both the salts in the solvent systems studied. This shows that the association process is favoured over the dissociation process in all the mixed solvents. The positive values of ΔH^o and ΔS^o (except one case) show that the association process is endothermic in nature and the randomness of ions in all the solvent systems.

Table 2. Thermodynamic Parameters ΔG^o (kJ mol^{-1}), ΔH^o (kJmol^{-1}), ΔS^o (Jmol^{-1}K^{-1}) and Es (kJmol^{-1}) at 25°C

d-Fructose (wt%)	ΔG^o	ΔH^o	ΔS^o	Es
$K_3[Fe(CN)_6]$				
0.0	-8.57	5.98	48.85	14.19
5.0	-8.32	-0.61	25.88	13.85
10.0	-8.14	0.97	30.56	14.40
15.0	-8.19	2.70	36.53	15.15
$K_4[Fe(CN)_6]$				
0.0	-9.18	8.42	59.05	14.09
5.0	-9.19	2.17	38.11	13.77
10.0	-9.34	2.11	38.44	14.53
15.0	-9.27	0.48	32.72	14.91

The transfer thermodynamic quantities, e.g., ΔG^o_t, ΔH^o_t and ΔS^o_t for potassium ferrocyanide and ferricyanide in 5, 10, 15 wt% of d-fructose solutions at 25°C only 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) → MX(s), has been calculated in mole fraction scale because it will eliminate free energy changes and is given by

$\Delta G^o_t = ({}^s\Delta G^o_N - {}^w\Delta G^o_N)$ (4)

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

$\Delta G^o_N = \Delta G^o_m - (\nu\text{-}1) \times 2.303\ RT \log (0.001\ M_{av})$ (5)

where ν 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^o_t) and enthalpy change (ΔH^o_t) of transfer process have been derived by means of the following equations

$\Delta S^o_t = - d(\Delta G^o_t)/dT$

and

$\Delta H^o_t = \Delta G^o_t + T\,\Delta S^o_t$ (6)

The negative values of ΔG^o_t (excepting in 5.0 and 10wt% d-fructose for potassium ferricyanide) 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^o_t and ΔS^o_t are found to be negative in both the salts. The negative values of ΔH^o_t and ΔS^o_t suggest that when a bulky organic molecule like d-fructose, 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 grater 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 as[7-9]

$\Delta X^o_t = \Delta X^o_{t,el} + \Delta X^o_{t,ch}$ (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 $\Delta G^o_{t,el}$ and $\Delta S^o_{t,el}$ are calculated by means of Born equation:

$\Delta G^o_{t,el} = (Ne^2/2)\,(\varepsilon_s^{-1} - \varepsilon_w^{-1})(r_+^{-1} + r_-^{-1})$

and

$\Delta S^o_{t,el} = -\,(Ne^2/2)\,(r_+^{-1} + r_-^{-1})\,(\varepsilon_s^{-1}\,\theta_s^{-1} - \varepsilon_w^{-1}\,\theta_w^{-1})$ (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. $\theta_s = d\ln \varepsilon_s/dT$ and $\theta_w = d\ln \varepsilon_w/dT$, 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-fructose mixtures are taken from the literature [10].

Table 3. Standard transfer thermodynamic quantities ΔG^o_t (kJ mol^{-1}), ΔH^o_t (kJmol^{-1}), ΔS^o_t (Jmol^{-1}K^{-1}) at 298.15K

d-fructose (wt%)	ΔG^o_t	$\Delta G^o_{t,el}$	$\Delta G^o_{t,ch}$	ΔS^o_t	$\Delta S^o_{t,el}$	$\Delta S^o_{t,ch}$	ΔH^o_t	$\Delta H^o_{t,el}$	$\Delta H^o_{t,ch}$
$K_3[Fe(CN)_6]$									
5.0	0.047	2.21×10^{-18}	0.047	-22.29	-6.53×10^{-16}	-22.29	-6.599	-1.94×10^{-13}	-6.596
10.0	0.013	4.41×10^{-18}	0.013	-16.91	-1.23×10^{-15}	-16.91	-5.030	-3.66×10^{-13}	-5.028
15.0	-0.270	9.64×10^{-18}	-0.270	-10.10	4.08×10^{-15}	-10.10	-3.282	1.21×10^{-12}	-3.281
$K_4[Fe(CN)_6]$									
5.0	-0.275	2.23×10^{-18}	-0.275	-20.05	-6.53×10^{-16}	-20.05	-6.254	-1.94×10^{-13}	-6.251
10.0	-0.731	4.46×10^{-18}	-0.731	-18.69	-1.23×10^{-15}	-18.69	-6.304	-3.66×10^{-13}	-6.301
15.0	-0.965	9.75×10^{-18}	-0.965	-23.39	4.08×10^{-15}	-23.39	-7.942	1.21×10^{-12}	-7.938

From equation (7), the value of $\Delta G^o_{t,ch}$ is determined from the values of ΔG^o_t and $\Delta G^o_{t,el}$ and so is the value of $\Delta S^o_{t,ch}$. Thus, from the values of $\Delta G^o_{t,ch}$ and $\Delta S^o_{t,ch}$, the value of $\Delta H^o_{t,ch}$ has been computed [11-16]. All these computed values are given in Table 3.

The observed negative values of $\Delta G^o_{t,ch}$ (except 5 and 10wt% of potassium ferricyanide) 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 $\Delta S^o_{t,ch}$ and $\Delta H^o_{t,ch}$ are also found to be negative in all cases. Thus, the chemical contribution towards Gibbs free energy, entropy and enthalpy changes accompanying the transfer process of ferricyanide and ferrocyanide (since the cation is same, K^+) ions from water to water and d-fructose mixtures suggest that the aqueous d-fructose is a stronger solvating agent than simple water.

CONCLUSION

In this paper, the molar conductance of potassium ferricyanide and ferrocyanide in water and water with d-fructose 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 ferrocyanide), more is value of conductance. As the weight percentage of d-fructose increases, more is the number of d-fructose molecules in solvent cage, hence less is the mobility of the ions. This lead to low value of conductance at higher weight percentage of d-fructose 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.

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