ORIGINAL ARTICLE

Viscometric and Thermodynamic Studies of Ion-Ion and Ion-Solvent Interactions in the Solutions of Uni-univalent and Bi-univalent Electrolytes in Purely Aqueous and Aqueous L-sorbose Media at 293.15, 303.15 and 313.15K

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ABSTRACT

Viscosities (η) and apparent molar volume ($V\phi$) of solution of uni-univalent and bi-univalent electrolytes (NaCl, KCl, NH_4Cl, $NaNO_3$, KNO_3, NH_4NO_3, $BaCl_2$, $MgCl_2$, $Ba(NO_3)_2$ and $Mg(NO_3)_2$. In purely aqueous and 0.10 mol dm-3 aqueous L-sorbose solutions have been determined at 293.15, 303.15 and 313.15 K. These data have been used to calculate the constant of Jones-Dole and Massone's equation. Activation thermodynamic quantities ($\Delta\mu_1 0\#$, $\Delta\mu_2{}^{0\#}$, $\Delta S_2{}^{0\#}$, $\Delta H_2{}^{0\#}$) of viscous flow have also obtained. From the values of these parameters conclusions in regards to ion-ion and ion-solvent interactions have been obtained. It has also been found that all the electrolytes behave as structure makers in purely aqueous and aqueous L-sorbose solutions.
Key words: *viscosity, electrolyte, aqueous, L-sorbose*

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INTRODUCTION

Partial molar volumes of electrolytes provide valuables information about ion-ion, ion-solvent and solvent-solvent interaction[1,11]. This information is of fundamental importance for understanding the reaction rates and equilibria involving dissolved electrolytes.

The structural interactions of non-ionic solutes with ionic ones in different solvents are important in many fields of chemistry. The studies of such interactions of non-electrolytes with electrolytes in solution are very significant and useful for investigating their physico-chemical behaviour [12-21]. Robinson *et al* [22-23] and Vishnu *et al* [24-29] have studied aqueous and non-aqueous ternary system containing polyhydroxy compounds and electrolytes like alkali halides. Ultrasonic propagation parameters have been used to study interactions in binary [30-32] and ternary [33-35] systems in aqueous [36-37] and mixed aqueous [38] and non-aqueous [39-42] systems.

MATERIAL AND MATHODS

Pot.nitrate, Pot.chloride, Ammonium nitrate, Ammonium chloride, Barium chloride, Barium nitrate, Magnesium chloride, Magnesium nitrate, Sodium chloride and Sodium nitrate are of A.R. grade of E-Merk.

Freshly prepared double distilled water was used for preparing standard stock solutions of the electrolytes and non-electrolytes.

Density was measured by Picknometer and viscosity was measures by double walled Ostwald Viscometer.

Analysis of viscosity data by Jones-Dole equation

The viscosity data of solutions of electrolytes were fitted to Jones-Dole equation (a)

$$\eta/\eta_0 = \eta_{rel} = 1 + AC^{-1/2} + BC$$
$$\text{or } (\eta_{rel} - 1)/\sqrt{C} = A + B\sqrt{C}$$

Where η_0 and η are the viscosities of the solution and solvent respectively. η_{rel} is the relative viscosity of the system. C is the molar concentration of solution. A and B are the constants characteristic of ion-ion and ion-solvent interactions respectively.

Calculation of Apparent Molar Volume (V_ϕ)

It was calculated from the density data using the following expression-

$$V_\Phi = V_\phi^0 = Sv\sqrt{C}$$

Where V_ϕ^0 is the limiting apparent molar volume and is equal to partial molar volume V_2^0 at infinite dilution and Sv is the experimental slope.

Calculation of Enthalpy of Activation

The enthalpy of activation $\Delta H_2^{0\#}$ has been calculated with the help of the following equation

$$\Delta H_2^{0\#} = \Delta\mu_2^{0\#} + T\Delta S_2^{0\#}$$

Free energies of activation of viscous flow, $\Delta\mu_1^{0\#}$ and $\Delta\mu_2^{0\#}$, per mole of solvent and solute respectively have been calculated as below:

$$\Delta\mu_1^{0\#} = RT \ln (\eta o \bar{\upsilon}_1^0/\hbar N)$$
$$\Delta\mu_2^{0\#} = \Delta\mu_1^{0\#} + RT/\bar{\upsilon}_1^0 [1000B - (\bar{\upsilon}_1^0 - \bar{\upsilon}_2^0)]$$

Where and are the partial molar volumes of the solvent and solute respectively.

Table1: Density (ρ) and apperent molar volumes (V_ϕ) of NaNO3 in water and in 0.10 mol dm-3 aqueous L-sorbose at different temperatures

Temperature 293.15K						
L-sorbose (mol dm-3)	0.0			0.10		
NaNO3 (mol dm-3)	P (gcm-3)	η (cp)	Vϕ (cm3mol-1)	H (cp)	P Gcm-3	Vϕ (Cm3mol-1)
0.0	0.9982	1.0020	-	1.0341	1.0063	-
0.2	1.0067	1.0789	42.63	1.1006	1.0109	61.82
0.4	1.0147	1.1801	43.93	1.1990	1.0161	60.07
0.6	1.0227	1.2387	44.22	1.2945	1.0251	53.30
0.8	1.0303	1.3103	45.02	1.3980	1.0337	50.40
1.0	1.0378	1.3737	45.45	1.49.45	1.0451	45.90
1.2	1.0456	1.4411	45.60	1.6054	1.0552	44.00
1.4	1.0603	1.4833	46.18	1.7458	1.0658	40.70
1.6	1.0603	1.5457	46.25	1.8275	1.0768	38.50
1.8	1.0674	1.6190	46.62	2.9883	1.0895	37.00
2.0	1.0748	1.6751	46.80	2.1260	1.1018	
Temperature 303K						
L-sorbose (mol dm-3)	0.0			0.10		
NaNO3 Mol dm-3)	P	η	Vϕ	H	P	Vϕ
0.0	0.9957	0.7977	-	0.8130	1.0004	-
0.2	1.0061	0.8798	22.60	1.0028	1.0080	36.34
0.4	1.0158	0.9541	24.20	1.0615	1.0197	26.30
0.6	1.0254	1.0251	25.10	1.0863	1.0308	23.90
0.8	1.0349	1.0840	25.90	1.1473	1.0428	21.60
1.0	1.0436	1.1423	26.70	1.2285	1.0545	20.47
1.2	1.0507	1.2171	28.80	1.3220	1.0672	18.89
1.4	1.0585	1.2668	29.78	1.4395	1.0796	18.00
1.6	1.0662	1.3284	30.58	1.5242	1.0928	16.80
1.8	1.0709	1.4176	32.90	1.5950	1.1085	14.51

2.0	1.0765	1.4168	43.28	1.6s889	1.1207	14.40

Temperature 313.15K

KCl (mol dm-3)	Urea (mol dm-3) 0.0			0.10		
	P (gcm-3)	η (cp)	Vφ (cm3mol-1)	H (cp)	P Gcm-3	Vφ (Cm3mol-1)
0.0	0.9922	0.6532	-	0.6963	0.9991	-
0.2	1.0018	0.7216	-	0.7408	1.0044	48.07
0.4	1.0108	0.7799	26.90	0.7482	1.0177	28.00
0.6	1.0197	0.8347	28.30	0.8217	1.0283	26.00
0.8	1.0281	0.8868	29.00	0.8927	1.0396	24.00
1.0	1.0353	0.9334	30.00	0.9582	1.0519	21.80
1.2	1.0436	0.9880	31.70	1.0210	1.0641	20.40
1.4	1.0506	1.0385	32.00	1.1247	1.0761	19.60
1.6	1.0585	1.1045	33.10	1.2043	1.0899	17.80
1.8	1.0652	1.1510	34.29	1.2667	1.1033	16.70
2.0	1.0730	1.1878	34.44	1.3553	1.1154	16.40

Table 2: Values of coefficient A and B of Jones-Dole Equation for the solutions of uni-univalent and bi-univalent electrolytes in water and in 0.10 mol dm-3 aqueous urea at different temperatures

Temperature 293.15K

Electrolytes	A (dm$^{3/2}$mol$^{-1/2}$) Water	0.10 mol dm^{-3} Urea	B (dm³mol^{-1}) Water	0.10 mol dm^{-3} Urea
NaCl	0.1072	-0.0529	0.1945	0.3435
KCl	0.1051	-0.0939	0.3317	0.6527
NH₄Cl	0.0618	-0.1573	0.3323	0.5309
NaNO₃	0.1184	-0.0673	0.2504	0.4718
KNO₃	-0.1777	-0.1448	0.2954	0.2326
NH₄NO₃	-0.1805	-0.1872	0.3470	0.3453
BaCl₂	0.1194	-0.0987	0.2345	0.5265
MgCl₂	-0.1082	-0.0981	0.2817	0.4972
Ba(NO₃)₂	-0.4133	-0.1654	0.3021	0.3703
Mg(NO₃)₂	-0.0991	-0.0986	0.3027	0.4212

Temperature 303.15K

Electrolytes	A (dm$^{3/2}$mol$^{-1/2}$) Water	0.10 mol dm^{-3} Urea	B (dm³mol^{-1}) Water	0.10 mol dm^{-3} Urea
NaCl	0.0763	-0.0709	0.2093	0.3669
KCl	0.0930	-0.1242	0.3667	0.6596
NH₄Cl	0.0372	-0.1759	0.3419	0.5969
NaNO₃	0.0971	-0.0881	0.2612	0.5322
KNO₃	-0.1880	0.1028	0.3140	0.2423
NH₄NO₃	-0.1856	0.1137	0.3866	0.3638
BaCl₂	-0.1041	-0.1007	0.2641	0.5336
MgCl₂	-0.1105	-0.1227	0.3244	0.5265
Ba(NO₃)₂	-0.4248	-0.1803	0.3226	0.3902
Mg(NO₃)₂	-0.1005	-0.1464	0.3403	0.4431

Temperature 213.15K

Electrolytes	A (dm$^{3/2}$mol$^{-1/2}$) Water	0.10 mol dm^{-3} Urea	B (dm³mol^{-1}) Water	0.10 mol dm^{-3} Urea
NaCl	0.0610	-0.1030	0.2132	0.3730
KCl	0.0622	-0.1973	0.3784	0.6734
NH₄Cl	0.0269	-0.1852	0.3360	0.6017
NaNO₃	0.0922	-0.0931	0.2876	0.5721
KNO₃	-0.1908	-0.0666	0.3529	0.2555
NH₄NO₃	-0.2167	-0.0672	0.4203	0.4000
BaCl₂	-0.0978	-0.1048	0.2964	0.5440
MgCl₂	-0.1388	-0.1471	0.3530	0.5479
Ba(NO₃)₂	-0.4734	-0.1895	0.3883	0.4102
Mg(NO₃)₂	-0.1217	-0.1655	0.3527	0.4809

Table 3: Values of Vφ and Sv for the solutions of uni-univalent and bi-univalent electrolytes in water and 0.10 mol dm-3 aqueous urea at different temperatures

Temperature 293.15K				
Urea Electrolyte	$V_{\phi}°$ (cm³Mol⁻¹)		S_v(cm³dm^{1/2}mol^{-3/2})	
	0.0	1.0	0.0	1.0
NaCl	4.89	20.97	8.15	-8.16
KCl	14.36	33.69	11.09	-14.86
NH₄Cl	24.16	61.40	11.94	-21.56
NaNO₃	41.49	73.96	3.82	-22.48
KNO₃	52.35	57.23	-11.59	17.75
NH₄NO₃	35.37	44.47	-8.73	30.26
BaCl₂	144.19	172.82	13.62	-16.45
MgCl₂	185.08	193..20	-16.20	-23.49
Ba(NO₃)₂	169.77	201.52	-13.92	-6.83
Mg(NO₃)₂	186.84	193.17	-13.38	-16.12
Temperature 303.15K				
Urea Electrolyte	$V_{\phi}°$ (CM³Mol⁻¹)		S_v(cm³dm^{1/2}mol^{-3/2})	
	0.0	1.0	0.0	1.0
NaCl	7.63	23.30	2.85	-8.41
KCl	16.97	35.75	10.87	-15.30
NH₄Cl	26.12	70.06	11.86	-22.36
NaNO₃	44.91	76.96	4.19	-28.06
KNO₃	58.96	65.88	-11.99	13.78
NH₄NO₃	37.33	46.36	-8.42	21.85
BaCl₂	151.86	175.01	11.16	-17.40
MgCl₂	193.93	197.47	-17.45	-28.38
Ba(NO₃)₂	170.73	213.18	-19.11	-6.99
Mg(NO₃)₂	192.02	194.25	-20.95	-20.43
Temperature 313.15K				
Urea Electrolyte	$V_{\phi}°$ (CM³Mol⁻¹)		S_v(cm³dm^{1/2}mol^{-3/2})	
	0.0	1.0	0.0	1.0
NaCl	9.03	29.69	2.61	-13.32
KCl	22.88	37.75	8.43	-15.53
NH₄Cl	30.19	80.41	11.06	-23.56
NaNO₃	49.53	77.93	4.44	-30.94
KNO₃	61.02	76.70	-10.83	6.11
NH₄NO₃	47.24	49.22	-13.26	15.82
BaCl₂	157.07	188.34	8.79	-23.76
MgCl₂	195.04	200.46	-18.92	-34.81
Ba(NO₃)₂	173.09	215.10	-25.22	-7.43
Mg(NO₃)₂	197.87	204.83	-29.55	-32.36

Table 4: Free energy of ctivation of viscous flow, Δμ0# for water and 0.10 mol dm-3 aqueous urea at different temperatures

	$\Delta\mu_1^{0\#}$ (KJ Mol⁻¹)		
Solvent system	293.15K	303.15K	313.15K
Water	20.54	20.67	20.84
0.10mol dm⁻³ Urea	20.70	20.84	21.13

Table 5: Values of free energy of activation of viscous flow, Δμ20# for uni-univalent and bi-univalent electrolytes in water and in 0.10 mol dm-3 aqueous urea at different temperatures

Electrolyte	Solvents	$\Delta\mu_1^{0\#}$ (KJ Mol-1)		
		293.15K	303.15K	313.76K
NaCl	Water	24.53	27.15	28,91
	0.10 mol dm-3 aq. Urea	66.03	71.03	74.76
KCl	Water	46.69	50.80	53.49
	0.10 mol dm-3 aq. Urea	108.21	112.27	118.72
NH4Cl	Water	45.76	48.81	51.51
	0.10 mol dm-3 aq. Urea	95.88	108.33	113.59
NaNO3	Water	37.03	40.16	45.80
	0.10 mol dm-3 aq. Urea	89.74	100.62	109.31
KNO3	Water	44.65	49.50	57.21
	0.10 mol dm-3 aq. Urea	95.65	100.70	107.02
NH4NO3	Water	49.26	56.60	64.23
	0.10 mol dm-3 aq. Urea	69.34	73.74	77.37
BaCl2	Water	48.77	55.56	62.50
	0.10 mol dm-3 aq. Urea	109.91	113.80	120.60
MgCl2	Water	60.67	69.76	76.07
	0.10 mol dm-3 aq. Urea	110.37	116.13	122.83
Ba(NO3)2	Water	61.36	66.28	69.65
	0.10 mol dm-3 aq. Urea	93.20	99.83	105.85
Mg(NO3)2	Water	63.75	71.71	76.43
	0.10 mol dm-3 aq. Urea	100.75	104.42	115.21

RESULT AND DISCUSSION

Densities (ρ) and viscosities (η) of uni-univalent and di-univalent electrolytes in purely aqueous solutions and in the presence of 0.10 mol dm3 urea have been determined as the function of molar concentration (C) of these electrolytes at 293.15, 303.15 and 313.15 ±0.01K.

Representative data in respect of KCl have been given in Table 1.

The viscosity data of the electrolyte solutions were analysed by using Jones-Dole equation

$$\eta/\eta_0 = \eta rel = 1 + AC^{-1/2} + BC$$
$$\text{or } (\eta rel-1)/\sqrt{C} = A + B\sqrt{C}$$

Where η_0 and η are the dynamic viscosities of solvent and solution respectively η_{rel} is the relative viscosity of the solution.

The values of coefficient A and B have been obtained from the linear plots of $(\eta_{rel}-1)/\sqrt{C}$ v/s $\sqrt{C}$ by the least square method and values are listed in Table-2. A perusal of this table reveals that in purely aqueous solutions of NaCl, KCl, NH4Cl, NaNO3 and BaCl2 the values of A are positive which indicate the presence of strong ion-ion interaction in the aqueous solutions of these electrolytes. Further, in these solutions the value of A decreses with the rise in temperature thereby showing that ion-ion interactions are weakened at elevated temperatures. This may be attributed to the increased solvation of ions with the rise temperature.

The apparent molar volume (V_ϕ) for the solutions of uni-univalent and bi-univalent electrolytes in purely aqueous medium as well as in o.10 mol dm-3 aqueous urea has been determined as a function of molar concentration (C) at different temperatures and representative data in respect of KCl are represented in Table-1.

The V_ϕ -C data have been analysed in the light of Masson's Equation

$$V_\phi = V_\phi^0 + Sv\sqrt{C}$$

Where V_ϕ^o is the limiting apparent molar volume and is equal to partial molar volume V_2^0 at infinite dilution, and Sv is the experimental slope. The values of V^{20} and Sv have been obtained from these plots by the method of least squares and presented in Table 3. It is seen that the values of Sv are positive for NaCl, KCl, NH4Cl, NaNO3 and BaCl2 in purely

aqueous solutions at different temperatures, which suggest the presence of strong ion-ion interactions in these solutions. On the other hand, the values of Sv are negative in case of purely aqueous solution of KNO_3, NH_4NO_3, $BaNO_3$, $Mg(NO_3)_2$, $Mg(NO_3)_2$ and $MgCl_2$ thereby showing the presence of 0.10 mol dm3 aqueous urea solution, the values of Sv for NaCl, KCl, NH_4Cl, $NaNO_3$, $BaCl_2$, $MgCl_2$, $Mg(NO_3)_2$ and $Ba(NO_3)_2$ are negative thereby indicating the presence of weak ion-ion interactions in these solutions.

Free energies of activation of viscous flow, $\Delta\mu_1^{0\#}$ and $\Delta\mu_2^{0\#}$, permole of solvent and solute respectively has been calculated as below:

$$B= \bar{\upsilon}_1^0 - \bar{\upsilon}_2^0$$

Where V_1^0 and V_2^0 are the partial molar volumes of the solvent and solute respectively. $\Delta\mu_1^{0\#}$ is the free energy of activation per mole of pure solvent and $\Delta\mu_2^{0\#}$ is the the free energy of activation per mole of solute. These were

$$\Delta\mu_1^{0\#} = RT \ln (\eta \bar{\upsilon}_1^0/hN)$$

$$\Delta\mu_2^{0\#} = \Delta\mu_1^{0\#} + RT[1000B - (\bar{\upsilon}_1^0 - \bar{\upsilon}_2^0)]$$

Where R, h and N are gas constant, Plank's constant and Avogadro's number respectively; and T is the absolute temperature.

The values of $\Delta\mu_1^{0\#}$ and $\Delta\mu_2^{0\#}$ have been presented in Table 4 and Table 5 respectively. It is seen that the values of $\Delta\mu_2^{0\#}$ for all the uni-univalent and bi-usnivalent electrolytes are larger both in purely aqueous solutions as well as in 0.10 mol dm^{-3} aqueous urea solutions as compared to those of $\Delta\mu_1^{0\#}$ and that in each case, $(\Delta\mu_2^{0\#} - \Delta\mu_1^{0\#}) > 0$. This shows [43] that all the uni-univalent and bi-univalent electrolytes used in present study are structure makers in water as well as in (urea+ water) mixed solvent system.

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