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Molar volume and conductance studies of Lithium Chloride in different composition of Lactose

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ABSTRACT

Molar volume and conductance of lithium chloride in 2, 4 and 6 wt. % of lactose have been calculated from density and conductance data respectively at temperatures 303.15, 308.15, 313.15 and 318.15K. The solute-solvent interactions for lithium chloride in 2, 4 and 6 wt. % of lactose have been inferred from ϕ_v^o, *and* Λ_m^o *values. The structure making/breaking behavior of lithium chloride is inferred from the sign of* $[\partial^2 \phi_v^o / \partial T^2]_p$ *and temperature coefficient of Walden product i.e.* $d(\Lambda_m^o \eta_o)/dT$. *It has been found that lithium chloride behaves as structure-breaker in 2, 4 and 6 wt. % of lactose from molar volume and conductance studies.*

Keywords: Molar volume, conductance, Lithium Chloride– water – Lactose system.

INTRODUCTION

The study of apparent molar volumes of electrolytes at infinite dilution, molar conductance at infinite dilution and Walden product studies can furnish useful information on the nature of solute – solvent interactions. The behavior of electrolytes in aqueous carbohydrates and carbohydrates containing small quantity of ions which are present in body fluids has recently been subject of interest. Ion-ion and ion-solvent interactions can furnish useful information on structural changes occurring in the solutions. Apparent molar volumes of electrolytes at infinite dilution, molar conductance at infinite dilution and Walden product studies may be used toinvestigate these interactions in the solutions. Multi-component solutions similar to bio-fluids areused extensively these days for better understanding of biological processes[1-8].The study of lithium chloride in 2, 4 and 6 wt. % of lactose at 303.15K, 308.15K, 313.15K and 318.15K temperatures was carried out to understand the nature of solute-solute and solute–solvent interactions by measuring the density and molar conductance of their solutions.

EXPERIMENTAL SECTION

Water used for solutions had specific conductance in range 0.1- 1.0 x $10^{-6}\,\Omega^{-1}cm^{-1}$. Lithium chloride, lactose (Anala R) were dried over anhydrous calcium chloride for more than 48h and used as such. All the solutions were prepared by weight and conversion of molality to molarity was done by using the standard expression [9]. The concentration range of lithium chloride in 2, 4 and 6 wt. % of lactose was 0.01 to 0.12 m. The density was measured with the help of DSA (Density and Sound Analyser) 5000, Anton Paar, GmbH, Garz, Austria. The conductance was measured with the help of calibrated Digital conductivity meter, CM 180, ElicoLimited. All measurements were made in a water bath maintained at 30, 35, 40, 45^{0}C (±0.05).

RESULTS AND DISCUSSION

The apparent molar volume of lithium chloride in 2, 4 and 6 wt. % of lactose have been calculated from density data (Table 1) by using eq.(1)

$$\phi_v = \frac{M_2}{d^o} - \frac{1000\ (d - d^o)}{mdd^o} \tag{1}$$

Where d^0 is the density of solvent, d is the density of solution, m the molality of solution and M_2 the molecular weight of lithium chloride. Errors in ϕ_v were calculated from eq. (2).

$$\Delta\phi_V = \left(\frac{2\Delta d}{d^2}\right)\left(\frac{1000}{m + M_2}\right) \tag{2}$$

Eq. (2) assumes error to be associated with the density of solution (d) and solvent (d^0). Moreover, errors associated with determination of solution concentration are not the limiting factor while calculating the apparent molar volumes. The error in apparent molar volume as derived from eq. (2) was estimated to range from ±0.06 $cm^3\ mol^{-1}$ at 0.01m concentration to ±0.10$cm^3\ mol^{-1}$ at 0.12m concentration.

Table 1: Densities, apparent molar volumes and molar conductance of lithium chloride in different compositions of lactose (2, 4 and 6%) solutions at different temperatures

Molality (m)	ρ x 10^{-3} (Kg m^{-3})	ϕ_v (cm^3mol^{-1})	Λ_m ($\Omega^{-1}cm^2mol^{-1}$)
Lithium chloride in 2% aqueous Lactose			
Temperature = 303.15K			
0.00	1.0030	-	-
0.01	1.0033	9.466	169.51
0.02	1.0036	11.252	163.55
0.04	1.0041	13.877	154.13
0.06	1.0046	15.823	147.37
0.08	1.0050	17.499	142.03
0.10	1.0053	18.978	137.05
0.12	1.0056	20.293	131.93
Temperature = 308.15K			
0.00	1.0013	-	-
0.01	1.0016	12.200	179.79
0.02	1.0019	13.622	173.18
0.04	1.0024	15.608	163.84
0.06	1.0028	17.184	156.86
0.08	1.0032	18.509	151.05
0.10	1.0036	19.609	145.67
0.12	1.0039	20.652	140.93
Temperature = 313.15K			
0.00	0.9994	-	-
0.01	0.9997	13.878	188.13
0.02	1.0000	15.030	182.16
0.04	1.0005	16.665	172.21
0.06	1.0009	17.970	164.94
0.08	1.0013	19.037	158.58
0.10	1.0017	19.974	153.19
0.12	1.0020	20.863	148.12
Temperature = 318.15K			
0.00	0.9973	-	-
0.01	0.9975	14.509	192.55

0.02	0.9978	15.661	185.67
0.04	0.9983	17.143	175.65
0.06	0.9987	18.401	167.98
0.08	0.9991	19.391	161.52
0.10	0.9995	20.290	156.10
0.12	0.9998	21.125	151.09
Lithium chloride in 4% aqueous Lactose			
Temperature = 303.15K			
0.00	1.0106	-	-
0.01	1.0109	9.092	140.53
0.02	1.0112	10.077	135.69
0.04	1.0118	11.424	128.90
0.06	1.0124	12.448	123.75
0.08	1.0129	13.321	119.24
0.10	1.0134	14.108	115.56
0.12	1.0139	14.841	112.05
Temperature = 308.15K			
0.00	1.0089	-	-
0.01	1.0092	10.712	154.64
0.02	1.0095	11.480	148.61
0.04	1.0101	12.592	140.18
0.06	1.0106	13.410	133.82
0.08	1.0112	14.142	128.63
0.10	1.0117	14.774	123.91
0.12	1.0121	15.340	119.56
Temperature = 313.15K			
0.00	1.0070	-	-
0.01	1.0073	11.708	168.84
0.02	1.0076	12.365	162.90
0.04	1.0081	13.319	153.02
0.06	1.0087	14.025	145.44
0.08	1.0092	14.633	138.95
0.10	1.0097	15.172	133.27
0.12	1.0102	15.643	128.51
Temperature = 318.15K			
0.00	1.0043	-	-
0.01	1.0046	12.213	185.23
0.02	1.0048	12.823	177.99
0.04	1.0054	13.671	167.78
0.06	1.0059	14.322	159.89
0.08	1.0065	14.871	153.23
0.10	1.0070	15.368	147.40
0.12	1.0074	15.803	142.20
Lithium chloride in 6% aqueous Lactose			
Temperature = 303.15K			
0.00	1.0183	-	-
0.01	1.0186	9.626	133.58
0.02	1.0189	10.592	129.27
0.04	1.0195	11.934	123.36
0.06	1.0200	12.940	118.76
0.08	1.0206	13.808	115.06
0.10	1.0211	14.579	111.79
0.12	1.0215	15.267	108.72
Temperature = 308.15K			
0.00	1.0165	-	-
0.01	1.0168	10.875	147.58
0.02	1.0172	11.660	142.68
0.04	1.0177	12.743	135.88
0.06	1.0183	13.571	130.65
0.08	1.0188	14.280	126.48
0.10	1.0193	14.912	122.54
0.12	1.0198	15.468	119.03
Temperature = 313.15K			
0.00	1.0146	-	-
0.01	1.0149	11.653	161.66
0.02	1.0152	12.334	156.06

0.04	1.0158	13.263	148.12
0.06	1.0163	13.967	142.34
0.08	1.0168	14.597	137.31
0.10	1.0173	15.103	132.92
0.12	1.0178	15.609	128.73
Temperature = 318.15K			
0.00	1.0124	-	-
0.01	1.0127	12.022	175.64
0.02	1.0130	12.662	169.44
0.04	1.0136	13.510	160.40
0.06	1.0141	14.148	153.53
0.08	1.0146	14.689	147.77
0.10	1.0151	15.185	142.49
0.12	1.0156	15.651	138.28

The densities of various solutions of lithium chloride in 2, 4 and 6 wt. % of lactose obey Root's equation and justify the use of Masson's eq.(3) for the estimation of the limiting apparent molar volume.

$$\phi_v = \phi_v^o + S_v\sqrt{C} \tag{3}$$

Where ϕ_v^o and S_v are calculated from the intercept and slope from the extrapolation of the plots of ϕ_v versus $\sqrt{C}$. The sample plot of ϕ_v versus $\sqrt{C}$ for lithium chloride in 2 wt. % of lactose solutions is shown in fig. (1).

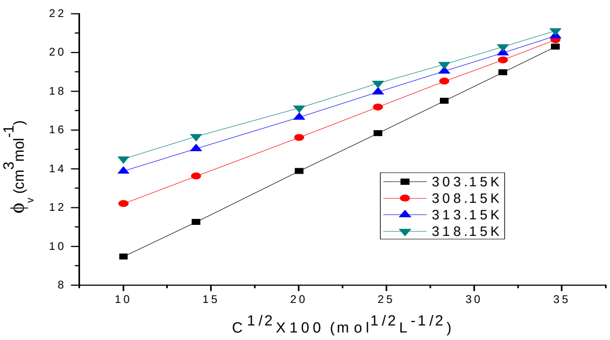

Fig.1: Plots of ϕ_v vs $C^{1/2}$ for LiCl in 2% lactose at different temperatures

The values of limiting apparent molar volume and slopes S_v are recorded in (Table 2).

Table 2: Limiting apparent molar volume ϕ_v^o, S_v and apparent molar expansibility (ϕ_E^o) of lithium chloride in different compositions of lactose (2, 4 and 6%) solutions at different temperatures

Temperature (T) (K)	ϕ_v^o (cm^{3}mol^{-1})	S_v (cm^3 l$^{1/2}$ mol$^{-3/2}$)	ϕ_E^o (cm^3 mol^{-1} K^{-1})
Lithium chloride in 2% aqueous Lactose			
303.15	5.045	0.440	1.032
308.15	8.756	0.344	0.455
313.15	11.019	0.284	-0.125
318.15	11.835	0.268	-0.704
Lithium chloride in 4% aqueous Lactose			
303.15	6.774	0.231	0.550
308.15	8.823	0.187	0.270
313.15	10.107	0.160	-0.010
318.15	10.757	0.145	-0.290
Lithium chloride in 6% aqueous Lactose			
303.15	7.348	0.227	0.448
308.15	9.015	0.185	0.217
313.15	10.059	0.159	-0.013
318.15	10.576	0.145	-0.243

The slope $S_v$in Masson's equation may be attributed to be as a measure of ion-ion or solute-solute interactions [10-12], low and positive values accounts for weak solute-solute interactions in 2, 4 and 6 wt. % of lactose. There is a decrease in inter ionic interactions with increase in temperature for lithium chloride in 2, 4 and 6 wt. % of lactose, which may be due to more solvation of solute ions with rise in temperature.

The ϕ_v^o is a measure of solute-solvent interactions [13]. The ϕ_v^o values for lithium chlorideare generallypositive and increase with a rise in both the temperature and concentration in 2, 4 and 6 wt.% of lactose. This indicates the presence of strong ion–solvent interactions andthese interactions are further strengthened at higher temperatures and higher concentrations suggesting larger electrostriction at highertemperatures.A quantitative comparison of the magnitude of values shows ϕ_v^o values are much greater in magnitude than $S_v$values, for all the solutions. This suggests thation–solvent interactions dominate over ion–ion interactions in all the solutions and atall experimental temperatures [14]. The partial molar volumes (ϕ_V^o) were fitted to a polynomial of the following typein terms of absolute temperature (T):

$$\phi_V^o = a + bT + cT^2 \qquad (4)$$

Values of the coefficients a, b, and c of the above equation for different concentrations of lithium chloride in 2, 4 and 6 wt. % of lactose are reported in (Table 3).

Table 3: Values of a, b, c for lithium chloride in different compositions of lactose (2, 4 and 6%) solutions

Solvent System	a	b	C
LiCl in 2% aq. Lactose	-5629.96	36.1445	-0.0579
LiCl in 4% aq. Lactose	-2734.13	17.5328	-0.0280
LiCl in 6% aq. Lactose	-2242.02	14.3916	-0.0230

The partial molar expansibilities (ϕ_E^o) can be obtained by the following equation:

$$\phi_E^O = \left(\frac{\partial \phi_V^O}{\partial T}\right)_P \qquad (5)$$

The values of ϕ_E^o for different solutions of the studied electrolyte at 303.15, 308.15, 313.15and 318.15K are reported in (Table 2). The values of ϕ_E^o decreases with increase in temperature for lithium chloride in 2, 4 and 6 wt. % of lactose solutions indicates the absence of "caging effect" [15] and its behavior is just like common electrolytes[16-17]. The structure making/ breaking capacity of lithium chloride may be interpreted with the help ofHepler's reasoning [18], i.e. on the basis of sign of $(\partial^2 \phi_v^o / \partial T^2)_p$. It has been shown from general thermodynamic eq. (6)

$$\left(\frac{\partial \bar{C}_P^0}{\partial P}\right)_T = -T\left(\frac{\partial^2 \phi_V^O}{\partial T^2}\right)_P \qquad (6)$$

where$\overline{C_p^o}$ is the partial molar heat capacity at infinite dilution. From eq. (6), it is clear that structure making electrolytes should have a positive value of $(\partial^2 \phi_v^o / \partial T^2)_p$and structure breaking electrolytes should have negative value of $(\partial^2 \phi_v^o / \partial T^2)_p$. For lithium chloride in 2, 4 and 6 wt. % of lactose solutions sign of $(\partial^2 \phi_v^o / \partial T^2)_p$ has been found negative, which suggests that it acts as structure- breaker in 2, 4 and 6 wt. % of lactose solutions.

CONDUCTANCE STUDIES

The limiting molar conductance Λ_m^o for lithium chloride in 2, 4 and 6 wt. % of lactose solutions were obtained by extrapolating the linear plots of Λ_m (Table 1) versus $\sqrt{C}$ to zero concentration. The limiting molar conductance for lithium chloride in 2, 4 and 6 wt. % of lactose solutions at 303.15, 308.15, 313.15 and 318.15 K temperatures are recorded in (Table 4), shows that limiting molar conductance increases with increase in temperature, which may be due to increase in ionic mobility of ions at infinite dilution.

Table 4: Values of limiting molar conductance (Λ_m^o), Viscosity of solvent (η_o) and Walden Product for lithium chloride in different compositions of lactose (2, 4 and 6%) solutions at different temperatures

Temperature (T) (K)	Λ_m^o ($\Omega^{-1}cm^2mol^{-1}$)	η_o (cp)	$\Lambda_m^o \eta_o$ ($\Omega^{-1}cm^2mol^{-1}$ poise)
Lithium chloride in 2% aqueous Lactose			
303.15	184.79	0.8246	152.37
308.15	195.48	0.7441	145.46
313.15	204.91	0.6703	137.34
318.15	209.47	0.6158	129.00
Lithium chloride in 4% aqueous Lactose			
303.15	152.06	0.8483	128.99
308.15	168.73	0.7631	128.76
313.15	185.95	0.6875	127.84
318.15	202.74	0.6299	127.71
Lithium chloride in 6% aqueous Lactose			
303.15	143.55	0.8867	127.28
308.15	159.07	0.7856	124.96
313.15	174.91	0.7059	123.48
318.15	190.94	0.6459	123.33

The sample plot of Λ_m versus $\sqrt{C}$ for lithium chloride in 2 wt. % of lactose solutions is shown in fig. (2).

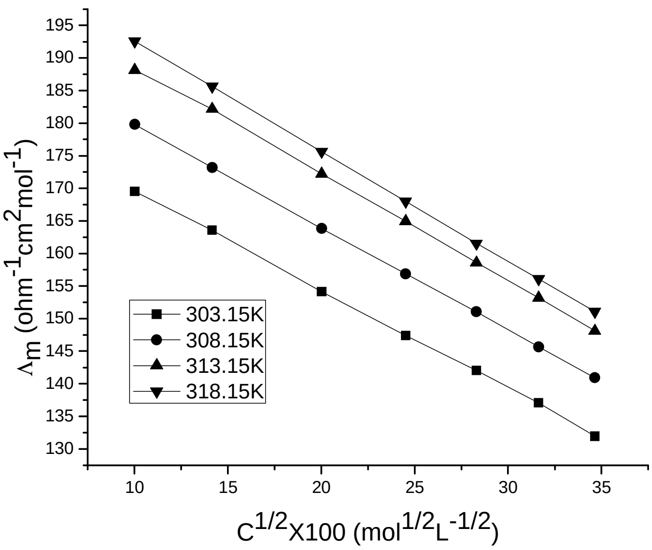

Fig.2: Plots of $\Lambda_m$vs $C^{1/2}$ for LiCl in 2% lactose at different temperatures

The Walden product data ($\Lambda_m^o \eta_0$) have been recorded in (Table 4). The structure making/ breaking nature of solute has been determined from temperature coefficient of Walden product i.e. [d ($\Lambda_m^o \eta_o$)/dT] [19]. The negative temperature coefficient of Walden product for lithium chloride in 2, 4 and 6 wt. % of lactose solutions indicate that lithium chloride behaves as structure-breaker in 2, 4 and 6 wt. % of lactose solutions.

CONCLUSION

Molar volume and conductance studies of molecular interactions in lithium chloride in 2, 4, 6 wt. % lactose have been carried out at wide range of concentrations at different temperatures (i.e.303.15K-318.15K). The experimental parameters such as limiting molar volume and waldenproduct gives valuable information regarding ion-solvent interactions in aqueous solutions. The molar volume and conductance studies provide comprehensive investigations between solute and solvent molecules. The result of the present investigation reveals that there are significant ion-solvent interactions in lithium chloride in 2, 4 and 6 wt. % lactose at different temperatures (i.e.303.15K-318.15K). It has been found that that lithium chloride behaves as structure-breaker in 2, 4 and 6 wt. % of lactose solutions with negative sign of($\partial^2 \phi_v^o / \partial T^2)_p$and the negative temperature coefficient of Walden products supports these results.

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