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Thermodynamic Studies on Ion Association of Lithium Chloride and Lithium Nitrate in Acetonitrile + Water Mixed Solvents at Different Temperatures

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The present study reports the ion association of lithium chloride (LiCl) and lithium nitrate ($LiNO_3$) electrolytes in acetonitrile + water (AN+W) mixtures at 283.15 K to 311.15 K. Their limiting molar conductance (Λ_o), the association constant values (K_A) for their different mole fractions, *i.e.* 0.0000, 0.0588, 0.1233, 0.1942, 0.2727, 0.3600, 0.4576, 0.5676, 0.6923, 0.8351 and 1.0000 have been evaluated using Shedlovsky technique. The K_A and Walden products ($\Lambda_o\eta_o$) for LiCl and $LiNO_3$ salts have been calculated in the acetonitrile-water solvent at experimental temperatures. The calculated values qualitatively examined the possible nature of the solvent-solvent, their ion-ion, and ion-solvent and interactions of the two selected compounds mixed solvents of (acetonitrile + water). Then dependence of K_A temperature has also been investigated to obtain the thermodynamic functions of different parameters, such as ΔGº, ΔSº, ΔHº and E_a, as a function of the mixed composition of the composition solvents AN+W (acetonitrile + water).

Keywords: Lithium chloride, Lithium nitrate, Acetonitrile, Thermodynamic parameters, Walden products, Shedlovsky technique.

INTRODUCTION

The electrical conductivity measurement of an electrolyte solution became the primary tool engaged and such measurements are given knowledge of thermodynamics in the form of an association constant (K_A) since there is a direct understanding between the formation of electro-neutral ion pairs and a decreased conductivity of the solution [1,2]. The electrical conductivity measurement of a dilute solution of complexes has become one of the important methods employed for investigating the formation of the association in mixed solvents [3,4]. The significant effect of the dielectric constant based on the ion-association of an electrolyte has also been published [5,6]. Besides, the dictating influence of the short-range or specific ion-solvent interactions over the said process is also increasingly recognized [7].

The experimental studies revealed that lithium has been used extensively for batteries as an anode material in the form of a non-aqueous solution [8,9]. The electrolyte of lithium salts *viz*., $LiPtF_6$, $LiClO_4$, $LiBF_4$ and LiXs were used for lithium ion batteries in the field of binary mixtures in non-polar solvents and organic polar [10]. The batteries of electronic instruments such as smartphones, desktops, laptops, tablets, *etc*., extensively used these electrolytic solutions [11-13]. The conductance studies in the field of binary solvent mixtures also give an idea about ion solvation as well as solvent-solvent interactions and ion-solvent interactions [14]. Ions must be present in the electrolyte cannot completely dissociate in a solution. In order to occur ion-association, there should be sufficiently large electrostatic interaction between the two oppositely charged ions [15,16]. The extent of the ion association depends on different factors, some important factors being the nature of the ions, size of the ions, charges of the ions, the characteristic property of the solvent and temperature of the solvent [17]. Ion association in a solution of alkali metal ions was studied extensively both in aqueous solution and organic solvent mixtures.

EXPERIMENTAL

Lithium chloride (BDH 99% minimum purity) and lithium nitrate (BDH 98% purity) were used after crystallization (>99.9 % purity for LiCl and 99.8% for $LiNO_3$). Purification of acetonitrile (BDH) was done as reported by Vogel [18] with specific conductance < 1.0×10^{-7} Scm. The specific conductance of water (1.0×10^{-6} Scm) was used. The overall accuracy of the measured molar conductance was better than ± 0.07%. The dielectric constant, their viscosity and the density values were obtained from the given values available in the literature [19-21]. The conductivity measurement of model EUTECT- PC-700 was used. The experiment was performed within the temperature ranges 10-40 ºC. For temperature control, a thermostatic bath-Cole-Palmer, Polystat R6L was used. The accuracy of the temperature measurement was ± 0.01 ºC.

The experimental conductance measurement values of LiCl and LiNO$_3$ in water-acetonitrile mixture after solvent modification were examined using Shedlovsky extrapolation technique [22]. Shedlovsky equation is given by:

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2}\right)\left(C\Lambda f_\pm^2 S(z)\right) \tag{1}$$

where Λ is equivalent conductance at concentration c (g mol dm^{-3}), Λ_o the limiting equivalent conductance and K_A the observed association constant. The other symbols involved are [23]:

$$S(z)\left(\frac{z}{2}\sqrt{1+\left(\frac{z}{2}\right)^2}\right)^2 ; Z = \left|\frac{\propto \Lambda_o}{\Lambda_o^{s/z}}\right|(C\Lambda)^{1/2} ; \propto = \frac{17.147\times 105W}{(DT)^{3/2}}$$

$$w = z_+z_-\frac{2q}{1+q^{1/2}} ; q = \frac{z_+z_-}{z_++z_-}\times\frac{\lambda_++\lambda_-}{z_+\lambda_-+z_-\lambda_+} ; \beta = \frac{151.47}{\eta(DT)^{1/2}}$$

where z and λ represent valence and conductance of the ions respectively excluding their signs; D is the dielectric constant of medium, η the viscosity (c.p); τ is the degree of dissociation related to S(z) by eqn. 2 [24]:

$$\tau = \frac{\Lambda S(z)}{\Lambda_o} \tag{2}$$

All the calculations were done by a basic computer programmer, IBM-PC-AT/386.

RESULTS AND DISCUSSION

From the experimental measurements, Λ_o values directly increased as the increased in temperature in all solvents irrespective of the mole fraction of acetonitrile, resulting in less solvation of ions. From Table-1, the determined association constant values (K_As) were found to increase with the increase in X_1 (linear plot). The large values of K_A indicated that the existence of specific short-range interaction between the ions resulting in an exothermic ion pair formation. Solvent-solvent interaction is maximum where η of the solvent mixture is maximum. At a particular temperature, the solvated radius of cation is inversely proportional to $\Lambda_o\eta_o$ [25]. Using the following relation:

$$\Lambda_o\eta_o = \frac{1}{6\pi rT} \tag{3}$$

where r represents the effective radius of the concern ion. As demonstrated from Table-1, the r values decreased with an increased in mole fraction of acetonitrile up to $X_1 = 0.046$ and then increased in acetonitrile rich region. In water-rich medium, due to the highly effectual cation radius, we got smaller $\Lambda_o\eta_o$ values from eqn. 3. The conductivity of ion mainly relies on its ions mobility, it is suitable to manage the conductance data as same as the one that engaged for the rate of operating processes taking place with alteration of temperature [26] (eqn. 4):

$$\Lambda_o = A.e^{E_a/RT} \text{ or } \ln\Lambda_o = \ln A - \frac{E_a}{RT} \tag{4}$$

TABLE-1a
EXPERIMENTAL VALUES OF Λ_o, K_A, $\Lambda_o\eta_o$ AND r OBTAINED FOR LITHIUM CHLORIDE IN ACETONITRILE + WATER MIXTURES AT 288.15-313.15 K

$X_{Acetonitrile}$	Λ_o (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	$\Lambda_o\eta_o$	r	Λ_o (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	$\Lambda_o\eta_o$	r
	T = 288.15 K				T = 293.15 K			
0.0000	97.92	368.39	120.54	1.528	111.75	316.71	117.84	1.537
0.0464	87.32	430.77	131.48	1.401	97.88	376.42	124.32	1.456
0.1582	76.64	487.37	108.59	1.696	83.02	428.16	94.68	1.912
0.3048	68.53	542.13	80.99	2.274	77.18	484.26	75.85	2.387
0.5057	76.13	600.91	67.20	2.741	83.83	537.92	57.62	3.142
0.6369	87.08	688.35	59.41	3.101	96.60	618.07	48.64	3.723
	T = 298.15 K				T = 303.15 K			
0.0000	127.63	262.07	114.60	1.553	141.18	212.19	112.56	1.556
0.0464	105.27	320.31	120.25	1.480	114.44	268.02	116.98	1.497
0.1582	90.68	389.32	96.75	1.840	100.31	322.70	93.56	1.871
0.3048	81.97	434.13	74.68	2.383	90.09	380.84	71.48	2.449
0.5057	88.25	470.79	57.54	3.094	99.16	426.81	54.72	3.200
0.6369	105.83	547.19	46.72	3.180	113.72	483.40	42.31	4.138
	T = 308.15 K				T = 313.15 K			
0.0000	153.77	157.21	109.15	1.578	167.53	106.06	106.23	1.596
0.0464	122.16	202.79	114.21	1.508	135.23	153.73	111.51	1.520
0.1582	111.66	268.62	90.47	1.904	119.40	211.75	87.42	1.939
0.3048	100.22	326.04	67.54	2.550	108.66	265.29	65.45	2.590
0.5057	110.09	370.33	51.29	3.358	118.79	314.13	46.58	3.639
0.6369	122.45	427.50	40.05	4.301	133.76	368.97	37.05	4.575

TABLE-1b
EXPERIMENTAL VALUES OF Λ_o, K_A, $\Lambda_o\eta_o$ AND r OBTAINED FOR LITHIUM NITRATE IN ACETONITRILE + WATER MIXTURES AT 288.15-313.15 K

$X_{Acetonitrile}$	Λ_o (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	$\Lambda_o\eta_o$	r	Λ_o (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	$\Lambda_o\eta_o$	r
	T = 288.15 K				T = 293.15 K			
0.0000	105.34	315.88	129.67	1.421	118.73	252.62	123.18	1.600
0.0464	94.93	378.08	140.58	1.310	105.81	319.74	132.88	1.363
0.1582	82.93	421.22	121.57	1.515	94.39	363.71	114.25	1.584
0.3048	72.58	485.34	105.89	1.740	83.55	419.79	96.56	1.875
0.5057	81.74	538.21	87.67	2.101	91.84	467.37	80.47	2.250
0.6369	92.88	594.67	68.41	2.666	101.56	519.92	63.43	2.855
	T = 298.15 K				T = 303.15 K			
0.0000	131.38	201.47	119.55	1.489	144.79	156.38	115.62	1.514
0.0464	117.42	255.96	125.49	1.419	129.07	207.52	120.57	1.452
0.1582	106.08	307.05	107.52	1.656	115.91	254.46	102.05	1.716
0.3048	93.93	356.29	91.27	1.951	104.09	304.73	87.27	2.006
0.5057	102.27	402.52	75.41	3.920	113.55	350.29	72.51	2.415
0.6369	113.77	461.25	58.46	3.045	125.06	408.86	56.94	3.075
	T = 30815 K				T = 313.15 K			
0.0000	156.27	104.34	112.73	1.528	167.58	62.45	107.91	1.571
0.0464	138.65	147.71	116.98	1.473	147.44	103.82	112.66	1.505
0.1582	125.73	198.79	100.06	1.721	134.78	142.58	96.59	1.755
0.3048	116.37	252.05	85.61	2.012	126.06	198.71	82.36	2.058
0.5057	124.52	297.71	70.61	2.439	135.38	241.62	67.24	2.521
0.6369	135.91	353.28	53.61	3.213	144.28	301.72	48.55	3.491

where, the frequency factor is given by A, the ideal gas constant R and the Arrhenius activation energy is E_a of transport processes. E_a values can be determined from the slope of the plot of log Λ_o *versus* 1/T (Fig. 1).

Arrhenius activation energy (E_a) values increase with the increase in X_1 up to $X_1 = 0.07$ and then decrease rapidly. This result shows that when the water in the rich region is up to $X_1 = 0.07$, the higher activation energy for the operation of the transport process has been reliable for both the chosen salts, as the acetonitrile in the mixed solvents increases, but the case is reverse after $X_1 = 0.07$ (Table-2). At normal temperature, a reaction with higher activation energy is slow, which shows the lower Λ_o values.

The free energy change (ΔG^o) for association was obtained from the given relation $\Delta G^o = - RT InK_A$ [27]. The enthalpy of association (ΔH^o) calculated from the slopes of the linear plot of log K_A *vs.* 1/T (Fig. 2). The determined ΔH^o values were established to systematically increase with the mixed solvent composition. The change of entropy ((ΔS^o) was found out from the Gibbs-Helmholtz equation [$\Delta G^o = \Delta H^o - T\Delta S^o$]. The experimentally determined thermodynamics parameters are given in Table-2. The ion association processes are exothermic indicated by the negative values of ΔH^o at all experimental temperatures. The values of Arrhenius activation energy (E_a) increased with an increase in X_1 up to $X_1 = 0.07$ and beyond this, it decreases abruptly [28]. Mole fraction of methanol, *i.e.*

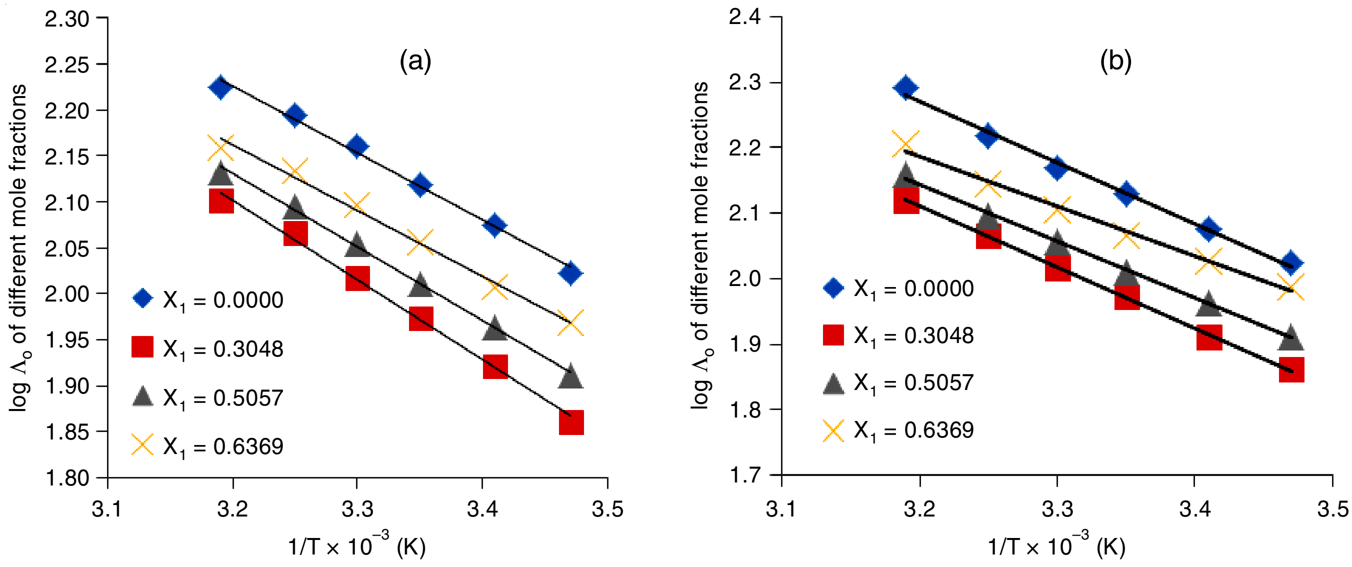

Fig. 1. Plot of log Λ_o *vs.* 1/T for (a) LiCl and (b) $LiNO_3$ in different mole fractions at 288.15-313.15 K

TABLE-2
THERMODYNAMIC PARAMETERS ΔG° (kJ mol^{-1}), ΔH° (kJ mol^{-1}), ΔS° (kJ K^{-1} mol^{-1}), E_a (kJ mol^{-1}) AND 10^{-3} A OF SHEDLOVSKY TECHNIQUES FOR LiCl AND LiNO$_3$ HAVE BEEN MEASURED IN VARIOUS ACETONITRILE + WATER MIXTURES AT DIFFERENT TEMPERATURES

	LiCl						LiNO$_3$					
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
	X_1 = 0.0000						X_1 = 0.0000					
ΔG°	-14.16	-14.04	-13.80	-13.52	-12.96	-12.15	-13.79	-13.48	-13.15	-12.73	-11.91	-11.03
ΔH°	-36.81						-43.66					
10^3 ΔS°	-76.35	-77.67	-77.18	-76.83	-77.40	-78.75	-103.66	-102.29	-102.33	-102.03	-103.03	-104.20
E_a	9.726						9.501					
10^{-3} A	6.789						6.626					
	X_1 = 0.0465						X_1 = 0.0465					
ΔG°	-14.53	-14.46	--14.31	-14.10	-13.61	-13.11	-14.22	-14.06	-13.75	-13.45	-12.80	-12.09
ΔH°	-32.81						-39.79					
10^3 ΔS°	-63.43	-63.77	-63.34	-63.12	-63.82	-66.52	-88.74	-87.67	-87.64	-87.43	-87.45	-87.37
E_a	10.927						10.679					
10^{-3} A	9.516						9.217					
	X_1 = 0.1518						X_1 = 0.1518					
ΔG°	-14.83	-14.80	-14.78	-14.57	-14.50	-13.95	-14.48	-14.37	-14.20	-13.97	-13.56	-12.92
ΔH°	-29.57						-35.71					
10^3 ΔS°	-51.15	-51.78	-51.32	-51.51	-51.25	-52.52	-60.39	-59.92	-60.07	-60.11	-60.38	-59.89
E_a	9.882						9.671					
10^{-3} A	7.361						7.013					
	X_1 = 0.3048						X_1 = 0.3048					
ΔG°	-15.13	-15.09	-15.05	-14.99	-14.83	-14.53	-14.82	-14.72	-14.57	-14.42	-14.17	-13.78
ΔH°	-27.06						-30.95					
10^3 ΔS°	-41.40	-41.72	-41.47	-41.30	-41.46	-42.06	-55.98	-55.36	-55.41	-54.52	-55.13	-55.19
E_a	9.327						9.111					
10^{-3} A	5.919						5.726					
	X_1 = 0.5057						X_1 = 0.5057					
ΔG°	-15.43	-15.33	-15.26	-15.16	-15.09	-14.97	-15.07	-14.99	-14.87	-14.77	-14.60	-14.25
ΔH°	-24.53						-25.83					
10^3 ΔS°	-31.58	-31.62	-31.79	-31.82	-31.63	-31.94	-37.34	-37.49	-37.69	-37.72	-37.63	-37.94
E_a	8.536						8.154					
10^{-3} A	4.096						3.899					
	X_1 = 0.6369						X_1 = 0.6369					
ΔG°	-15.66	-15.57	-15.63	-15.59	-15.52	-15.39	-15.30	-15.24	-15.21	-15.16	-15.03	-14.87
ΔH°	-21.47						-23.31					
10^3 ΔS°	-20.16	-2033	-20.35	-20.24	-20.18	-20.28	-27.80	-27.91	-27.96	-27.82	-27.77	-27.86
E_a	7.947						7.721					
10^{-3} A	3.662						3.420					

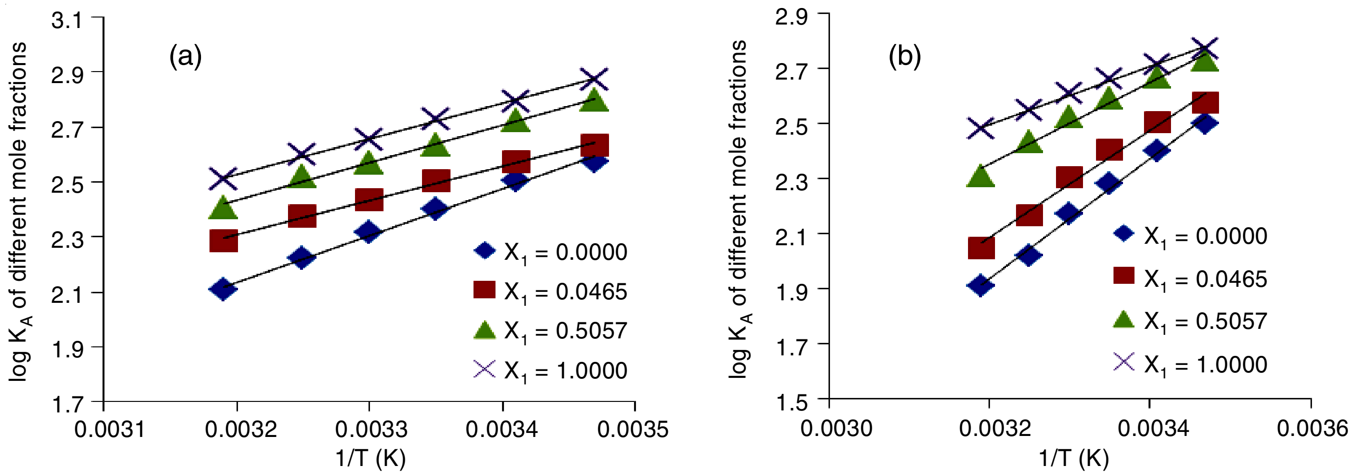

Fig. 2. Plot of log K_A *vs.* 1/T for (a) LiCl and (b) LiNO$_3$ in different mole fractions of acetonitrile and water at 288.15-313.15 K

up to X_1 = 0.3600, the given complex ion preferred higher activation energy for transport processes as the methanol content in the mixed solvent increases but the case was reversed after X_1 = 0.07.

Conclusion

The experimentally determined association constant values (K_A) values increased systematically with an increase in mole fraction of acetonitrile that indicates the association process becomes increases as acetonitrile is added to water. The calculated molar conductance of limitation (Λ_o) values increased straightly with the rise in temperatures. In the water-rich region, the effective radius (r) of the cation became larger, the Walden product ($\Lambda_o\eta_o$) values decreased. The maximum value of $\Lambda_o\eta_o$ indicates the minimum value of effective cation radius. The experimental determination of ΔHº the negative values, which confirmed ion association process is exothermic in nature. The variation of ΔGº with temperature reveals that the ion association process is favored at low temperatures. The (Λ_o) which is the limiting equivalent conductance values increased directly with the rise in temperature irrespective of the nature of the solvent. The Λ_o values of the solute decreased up to X_1 = 0.07. In water-rich region (< $X_{methanol}$ = 0.07). Low energy is required by the ion association processes to became more stable than in water-rich regions. The activation energy (E_a) values rise with an increase in X_1 up to about X_1 = 0.07, and it decreased rapidly. It is concluded that whenever acetonitrile is at a high percentage, the ΔGº values become more negative which reveals that when the dielectric constant of the medium is lowered, the ion-association processes are mostly favoured.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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