IJRCE

ISSN 2248-9649

International Journal of
Research in Chemistry and Environment
Available online at: www.ijrce.org

Research Paper

Exploration of Non-Covalent Interactions of Lithium Salts in Acetonitrile-Water Binaries with the Manifestation of Solvation Consequences

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(Received 09th September 2018, Accepted 30th October 2018)

Abstract: *The properties of material like densities and viscosities of some selected lithium salts (namely, lithium nitrate, lithium iodide and lithium acetate) have been studied in acetonitrile-water binary mixed solvent systems at the temperature 298.15K. Apparent molar volumes (ϕ_V) and viscosity B coefficients of these salts are obtained from these data supplemented with their densities and viscosities, respectively. Limiting apparent molar volumes ($\phi_V°$) and experimental slopes (S_V*) derived from density date using Masson equation have been interpreted in terms of ion-solvent and ion-ion interactions, respectively. The viscosity data have been analyzed using Jones-Dole equation, and derived parameters B and A have also been interpreted in terms of ion-solvent, ion-ion interactions, respectively. It has been observed from the both derived parameters the ion-solvent interaction is predominant than interaction of ions (ion-ion) itself in all the studied binaries. Furthermore, the structure making/breaking capacities of salts investigated have been discussed in terms of the rearrangement with symmetrically of the interacting ions. Another two parameters, refractive index and conductivity have been taken into account to give explanation and confirming the same results occurring into the studied solutions system.*

Keywords: Lithium salts, acetonitrile-water binaries, non-covalent interactions, salvation consequences

Introduction

Studies on thermophysical properties namely, viscosities, densities, and refractive index, conductivity of ionic solutions assist in characterizing structures and properties of binary solutions. Various types of interactions exist among the ions in solutions, and of them, ion-ion and ion-solvent interactions are occurring in solutions is plying interesting role in all branches of chemistry. These interactions help in better understanding the nature of solute and solvent, i.e., whether solute modifies or distorts structure of the solvent. A survey of the literature showed that although a lot of studies have been carried out for various electrolytic solutions, few works have been done to discuss the behavior of mineral salts in water as reported earlier[1]. The present mineral salts have been selected for study because they are significant constituents of lithium as bio-fluids, Lithium batteries etc. Main ionic solutes in biofluids in the mixed solvent; are common ions are the small amounts of CN^{-2}, H^+, Li^+, $-OH^-$. The present investigation has been undertaken to endow with better understanding of nature of these mineral salts in polar mixed solvent throw light on ion-solvent interactions[2-5].

Material and Methods

Lithium iodide, lithium nitrate, lithium acetate (all are A.R.) were used as such, only after drying over P_2O_5 in a desiccators for more than 48h. Freshly prepared distilled conductivity water was taken for the experiments. Aqueous mixed solvents of acetonitrile were made by mass; conversion of molality into molarity was done. Figure 1, 2 shows diagram of the sample taken and the dielectric constants.

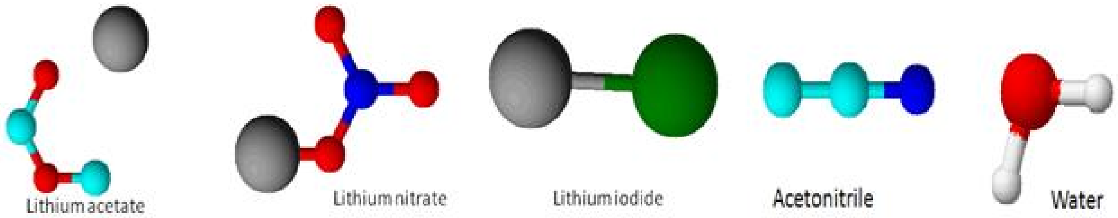
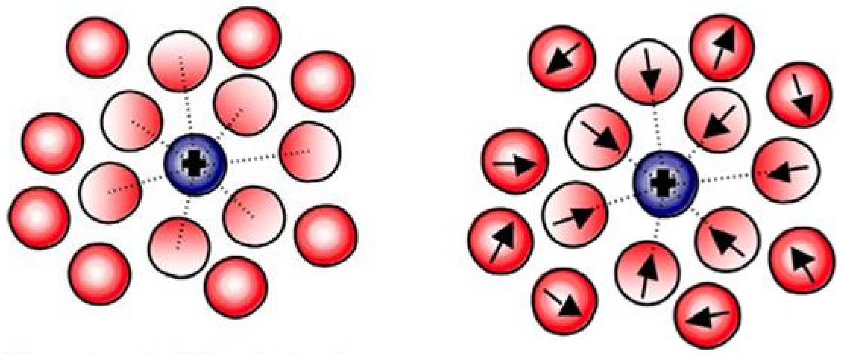


Figure1: Three dimensional representations of the salts and the mixture of binary solvents used in the work



Charge in acetonitrile solvent only (dielectric constant = 36.6)

Charge in acetonitrile + water in the binary mixture (dielectric constant of water = 78 + dielectric constant of acetonitrile = 36.6)

Figure 2: Diagrammatic representation of the solvation sphere

The densities (ρ) were calculated with an Ostwald-Sprengel type pycnometer having a bulb volume of 25cm^3 and an internal diameter of the capillary of about (0.1 cm) and pycnometer was calibrated at 298.15K with doubly distilled water. Pycnometer with the test solution was equilibrated in a water bath maintained at (0.01 K of the desired temperature by means of a mercury in glass thermo regulator, and temperature was determined with a calibrated thermometer and a Muller bridge. The pycnometer was then detached from the thermostatic bath, properly dried, and weighed. The evaporation losses remained insignificant throughout the time of actual measurements. Averages of triplicate measurements were taken into description. Density values were reproducible to ($\pm 3\cdot 10^{-5}$ g·cm^{-3}) and details have been described earlier[1].

The viscosities of the test solutions measured by means of a suspended level Ubbelode viscometer at the desired temperature (accuracy ± 0.01 K). The precision of viscosity measurements was 0.05% and details have been described earlier[1-3].

Refractive index was also measured with the aid of a Digital Refractometer Mettler Toledo. The light source was LED, (k = 589.3nm). The refractometer was calibrated twice using distilled water, and calibration was checked after every small amount of measurements. The uncertainty of refractive index measurement was detected to be ±0.0002 units.

The experimental data's of densities (ρ_0), viscosities (η_0) with corresponding concentrations (*c*) of aqueous binary mixture has been recorded in Table 1.

Table 1: Density (ρ_0), Viscosity (η), refractive index (n_D) of aqueous acetonitrile solutions

Solvent mixture	$\rho_0 \cdot 10^{-3}$ (kg m^{-3})	η (mP$_{a}$s)	n_D
T=298.15K			
0.10	0.9808	0.867	1.3974
0.20	0.9612	0.862	1.3835
0.30	0.9387	0.858	1.3696
T=308.15K			
0.10	0.9773	0.707	1.3562
0.20	0.9551	0.705	1.3549
0.30	0.9317	0.697	1.3432
T=318.15K			
0.10	0.9733	0.584	1.3387
0.20	0.9489	0.580	1.3245
0.30	0.9248	0.578	1.3231

The conductance measurement were done in a Systronic-308 conductivity meter (accuracy ± 0.01 %) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately (0.1 ± 0.001) cm^{-1}. Measurements were made in a water bath maintained within *T*=(298.15 ± 0.01) K and the cell were calibrated by technique proposed by Lind et al[15].

The conductance values were reported at a frequency of 1 kHz and the accuracy was ±0.3%.

Results and Discussion

Density

The experimental observed values of the density, viscosity, and refractive index have been tabulated in table 2-4. Volumetric properties, for instance, apparent molar volumes, ϕ_V and limiting apparent molar volumes $\phi_V°$ are regarded as approachable parameter for the understanding of interactions taking place in solutions. The apparent molar volume can be considered to be the summation of the geometric volume of the fundamental solute molecule and changes in the solvent volume due to its interface with the solute around the peripheral/co-sphere. For this principle, ϕ_V has been determined from density of solutions by means of the suitable equation. The apparent molar volumes ϕ_V were determined from solutions densities using the equation

$$\phi_V = \frac{M}{\rho} - \frac{1000\,(\rho-\rho_0)}{m\,\rho\,\rho_0} \qquad (1)$$

and given in Table 5-7. Where M is the molar mass of ionic salts, m is the molality of solution, ρ and ρ_0 is the density of solution and aqueous acetonitrile mixture.

Table 2: Density, Viscosity, Refractive index of [25 %H_2O + 75% CH_3CN] solvent mixture at 25^{0}C

Salt	Conc (m) (mol kg^{-1})	$\rho_0 \cdot 10^{-3}$ (kg m^{-3})	η (mP$_a$s)	n$_D$
CH_3COOLi	0.005	17.3178	0.451	1.3441
	0.02	17.3225	0.453	1.3443
	0.035	17.3245	0.455	1.3442
	0.05	17.3401	0.457	1.3443
	0.065	17.3503	0.458	1.3445
	0.08	17.3744	0.459	1.3446
$LiNO_3$	0.005	17.3009	0.442	1.3438
	0.02	17.3235	0.446	1.3440
	0.035	17.3280	0.448	1.3441
	0.05	17.3009	0.449	1.3443
	0.065	17.3574	0.453	1.3445
	0.08	17.3744	0.457	1.3447
LiI	0.005	17.2721	0.440	1.3429
	0.02	17.2732	0.443	1.3431
	0.035	17.3000	0.446	1.3433
	0.05	17.3211	0.448	1.3438
	0.065	17.3270	0.447	1.3441
	0.08	17.3472	0.449	1.3447

Table 3: Density, Viscosity, Refractive index of [50 %H_2O + 50% CH_3CN] solvent mixture at 25^{0}C

Salt	Conc (m) (mol kg^{-1})	$\rho_0 \cdot 10^{-3}$ (kg m^{-3})	η (mP$_a$s)	n$_D$
CH_3COOLi	0.005	18.4016	0.717	1.3428
	0.02	18.3569	0.720	1.3436
	0.035	18.3473	0.725	1.3442
	0.05	18.3185	0.729	1.3448
	0.065	18.2935	0.733	1.3354
	0.08	18.2888	0.740	1.3357
$LiNO_3$	0.005	17.6383	0.405	1.3432
	0.02	17.5211	0.428	1.3438
	0.035	17.4297	0.445	1.3441
	0.05	17.3391	0.458	1.3446
	0.065	17.3119	0.514	1.3450
	0.08	17.1822	0.529	1.3429
LiI	0.005	18.2758	0.719	1.3431
	0.02	18.2709	0.718	1.3433
	0.035	18.2688	0.722	1.3441
	0.05	18.2685	0.719	1.3447
	0.065	18.2683	0.726	1.3448
	0.08	18.2681	0.727	1.3449

Table 4: Density, Viscosity, Refractive index of [75 %H_2O + 25% CH_3CN] solvent mixture at 25^{0}C

Salt	Conc (m) (mol kg^{-1})	$\rho_0 \cdot 10^{-3}$ (kg m^{-3})	η (mP$_a$s)	n$_D$
CH_3COOLi	0.005	18.2702	0.738	1.3449
	0.02	18.3027	0.743	1.3403
	0.035	18.3300	0.745	1.3406
	0.05	18.3595	0.746	1.3420
	0.065	18.4002	0.747	1.3426
	0.08	18.4403	0.749	1.3395
$LiNO_3$	0.005	18.5946	0.733	1.3424
	0.02	18.7078	0.731	1.3432
	0.035	18.7129	0.728	1.3435
	0.05	18.7134	0.726	1.3435
	0.065	18.7152	0.724	1.3438
	0.08	18.7385	0.722	1.3440
LiI	0.005	18.2788	0.726	1.3421
	0.02	18.2918	0.727	1.3419
	0.035	18.3193	0.729	1.3416
	0.05	18.3956	0.735	1.3413
	0.065	18.4472	0.737	1.3410
	0.08	18.4361	0.733	1.3407

The limiting apparent molar volumes $\phi_V°$ were obtain by a least-square treatment to the plots of ϕ_V versus $\sqrt{m}$ using Masson equation and shown in Table 8.

$$\phi_V = \phi_V^o + S_V^* \sqrt{m} \qquad (2)$$

The extent of ϕ_V (Table 5-7) is found to be large and positive for all the considered systems, suggesting strong solute-solvent interactions. The ϕ_V values are decreased with increasing molality (*m*) of ionic salts in the aqueous acetonitrile solution (Figure 3).

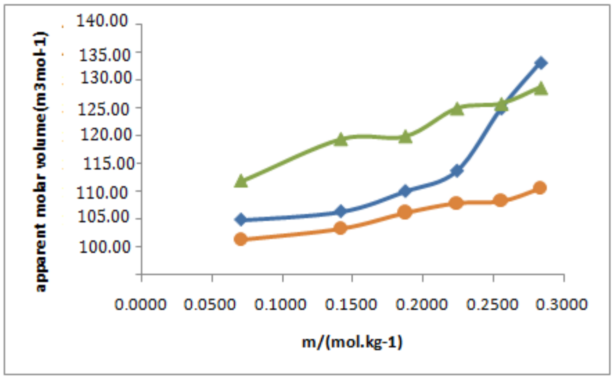


Figure 3: Plot of apparent molar volume with respect to concentrations at 298.15K [yellow line for LiI, blue line for LiNO₃, green line for CH₃COOLi]

ϕ_V, varied linearly with *c* and could be least-squares fitted to Masson equation from where limiting molar volume $\phi_V°$ (infinite dilution partial molar volume) have been projected. If variation of ϕ_V with *c* show significant scatter, $\phi_V°$ has been determine either graphically or has been taken as the average of the ϕ_V values when slope tends to zero. The values of $\phi_V°$ and S_V^* are reported in Table 8. Owing to a quantitative comparison, magnitude of $\phi_V°$ are much greater than S_V*, in every solutions. This suggests that ion-solvent interactions dominate over ion-ion interactions in all solutions. The drift of variation of $\phi_V°$ for particular systems is in order

LiI < $LiNO_3$ < CH_3COOLi

The increase of $\phi_V°$ for ionic salts with increasing mass fraction of aq. acetonitrile and the increasing positive shift volumes suggest that the ion-ion and ion-hydrophilic group interactions are stronger (Figure 4). In the present ternary system (ionic salts + aq. acetonitrile), the interaction is well-built (Scheme 1)

It noted that $\phi_V°$ of LiI is less than that of $LiNO_3$ and CH_3COOLi owing to greater electrostriction. This is because acetate anion of lithium acetate provides an increasing structure enforcing tendency in aqueous acetonitrile solution due to greater resonance effect, and as a result, the water in the overlapping spheres is more structured due to ion-solvent interaction. In the ionic salts, the interactions increase with the addition of excess of the acetonitrile in solvent mixture shown in Figure 4.

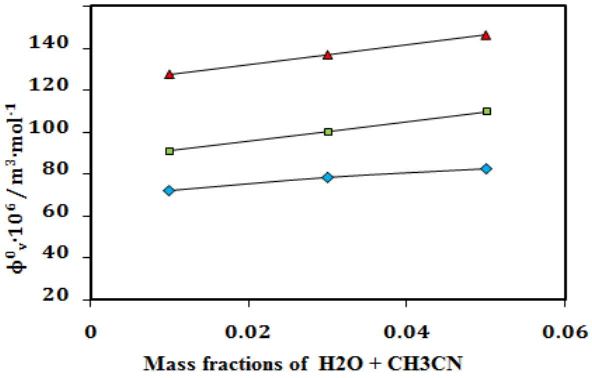


Figure 4: Plot of limiting apparent molar volume with respect to mass fractions of the binary solvent mixture at 298.15K [red symbol for CH₃COOLi, green symbol for LiNO₃, sky symbol for LiI]

If we consider individual acetonitrile, initially in aqueous mixture it would interact with the water molecules present in the solution bulk and give the product of methanol and a bronsted Lowry base which is quite stable in nature. After addition of chosen Lithium ion, they become fascinated to bind with (–OCH_3^-) ion by replacing the water molecules with the proper phase of interaction as a result net increase in the solvation. With increasing conc. of acetonitrile, $\phi_V°$ value increases indicating the ion-solvent interaction increases. S_V* values showed in Table 15 indicates that ion-ion interaction decreases from CH_3COOLi to LiI and ion-ion interaction increases with increases the conc. of water [5-8].

Table 5: Experimental value of apparent molar volume ϕ_V for CH_3COOLi in binary solvent mixtures of H_2O (w_1) + CH_3CN (w_2) at 298.15 K

Molality (mol kg^{-1})	$\phi_V \times 10^6$ (m^3 mol^{-1})	Molality (mol kg^{-1})	$\phi_V \times 10^6$ (m^3 mol^{-1})	Molality (mol kg^{-1})	$\phi_V \times 10^6$ (m^3 mol^{-1})
[25 %H_2O + 75% CH_3CN]		[50 %H_2O + 50% CH_3CN]		[75 %H_2O + 25% CH_3CN]	
0.0158	118.153	0.0172	109.035	0.0177	103.396
0.0309	112.481	0.0345	104.726	0.0347	100.086
0.0467	108.567	0.0489	102.273	0.0545	95.761
0.0614	103.468	0.0668	97.536	0.0726	93.873
0.0776	102.879	0.0848	95.873	0.0885	92.257
0.0925	97.573	0.0999	93.678	0.1086	89.072

Table 6: Experimental value of apparent molar volume ϕ_V for $LiNO_3$ in binary solvent mixtures of H_2O (w_1) + CH_3CN (w_2) at 298.15 K

Molality (mol kg^{-1})	**$\phi_V \times 10^6$ (m^3 mol^{-1})**	**Molality (mol kg^{-1})**	**$\phi_V \times 10^6$ (m^3 mol^{-1})**	**Molality (mol kg^{-1})**	**$\phi_V \times 10^6$ (m^3 mol^{-1})**
[25 %H_2O + 75% CH_3CN]		[50 %H_2O + 50% CH_3CN]		[75 %H_2O + 25% CH_3CN]	
0.0120	104.456	0.0131	103.996	0.1218	86.128
0.0605	104.049	0.0616	100.457	0.0618	81.899
0.1087	100.686	0.1079	94.466	0.1083	76.126
0.1689	92.257	0.1698	83.716	0.1717	70.089
0.2298	85.567	0.2321	84.957	0.2431	65.884
0.2438	83.788	0.2437	83.887	0.2567	64.662

Table 7: Experimental value of apparent molar volume ϕ_V for LiI in binary solvent mixtures of H_2O (w_1) + CH_3CN (w_2) at 298.15 K

Molality (mol kg^{-1})	**$\phi_V \times 10^6$ (m^3 mol^{-1})**	**Molality (mol kg^{-1})**	**$\phi_V \times 10^6$ (m^3 mol^{-1})**	**Molality (mol kg^{-1})**	**$\phi_V \times 10^6$ (m^3 mol^{-1})**
[25 %H_2O + 75% CH_3CN]		[50 %H_2O + 50% CH_3CN]		[75 %H_2O + 25% CH_3CN]	
0.0118	104.153	0.0175	102.035	0.0279	83.396
0.0307	103.781	0.0340	98.726	0.0357	80.086
0.0457	99.567	0.0469	92.273	0.0585	72.761
0.0609	91.468	0.0649	81.536	0.0766	69.873
0.0788	82.879	0.0839	80.873	0.0889	63.257
0.0929	79.573	0.0989	77.678	0.1096	60.072

Table 8: Limiting apparent molar volumes ϕ^0_V, experimental slopes S_V^*, A, B-coefficients for lithium salts in binary solvent mixtures of H_2O (w_1) + CH_3CN (w_2) at 298.15 K

Salts	**$\phi^0_V \times 10^6$ (m^3 mol^{-1})**	**$S_V^* \times 10^6$ (m^3 mol$^{-3/2}$L$^{1/2}$)**	**A (L mol^{-1})**	**B (L$^{1/2}$mol$^{-1/2}$)**
[25 %H_2O + 75% CH_3CN]				
CH_3COOLi	126.532	−94.651	0.559	0.781
$LiNO_3$	117.405	-65.982	0.176	0.756
LiI	107.511	-58.796	0.054	0.552
[50 %H_2O + 50% CH_3CN]				
CH_3COOLi	119.467	−87.443	0.278	0.894
$LiNO_3$	112.316	-59.597	0.165	0.721
LiI	98.452	-55.776	0.041	0.531
[75 %H_2O + 25% CH_3CN]				
CH_3COOLi	115.754	−77.459	0.110	0.947
$LiNO_3$	93.754	-56.163	0.142	0.687
LiI	94.962	-52.219	0.011	0.509

Table 9: Experimental value of apparent molar volume $(\eta_r - 1)/\sqrt{c}$ for CH_3COOLi in binary solvent mixtures of H_2O (w_1) + CH_3CN (w_2) at 298.15 K

Molality (mol kg^{-1})	**$(\eta_r - 1)/\sqrt{c}$ (mol$^{-1/2}$ kg$^{1/2}$)**	**Molality (mol kg^{-1})**	**$(\eta_r - 1)/\sqrt{c}$ (mol$^{-1/2}$ kg$^{1/2}$)**	**Molality (mol kg^{-1})**	**$(\eta_r - 1)/\sqrt{c}$ (mol$^{-1/2}$kg$^{1/2}$)**
[25 %H_2O + 75% CH_3CN]		[50 %H_2O + 50% CH_3CN]		[75 %H_2O + 25% CH_3CN]	
0.0158	0.0715	0.0172	0.1085	0.0177	0.0892
0.0309	0.1196	0.0345	0.1614	0.0347	0.1398
0.0467	0.1563	0.0489	0.2026	0.0545	0.1767
0.0614	0.1852	0.0668	0.2303	0.0726	0.2073
0.0776	0.2133	0.0848	0.2588	0.0885	0.2342
0.0925	0.2395	0.0999	0.2832	0.1086	0.2605

Table 10: Experimental value of apparent molar volume (η_r −1)/√c for $LiNO_3$ in binary solvent mixtures of H_2O (w_1) + CH_3CN (w_2) at 298.15 K

Molality (mol kg−1)	(η_r −1)/√c ($mol^{-1/2}\ kg^{1/2}$)	Molality (mol kg−1)	(η_r −1)/√c ($mol^{-1/2}\ kg^{1/2}$)	Molality (mol kg−1)	(η_r −1)/√c ($mol^{-1/2}kg^{1/2}$)
[25 %H_2O + 75% CH_3CN]		[50 %H_2O + 50% CH_3CN]		[75 %H_2O + 25% CH_3CN]	
0.0120	0.0547	0.0133	0.0895	0.1215	0.0982
0.0605	0.1564	0.0615	0.1393	0.0615	0.1212
0.1087	0.1593	0.1077	0.1762	0.1089	0.1721
0.1689	0.1651	0.1697	0.2073	0.1713	0.2008
0.2298	0.1705	0.2322	0.2344	0.2432	0.2313
0.2438	0.1756	0.2438	0.2604	0.2564	0.2517

Viscosity

The viscosity data has been analyzed by means of Jones-Dole equation

$$\frac{\eta}{\eta_o} = \eta_r = 1 + A\sqrt{m} + B(\sqrt{m})^2 \qquad (3)$$

$$\eta_r - 1 = A + B\sqrt{m} \qquad (4)$$

where *A* and *B* are viscosity coefficient point toward ion–ion and ion–solvent interaction, respectively. The values of *A* and *B* coefficient are obtained by plotting (η_r −1)/√m against √m and reported in Table 9, 10, 11. A perusal of Figure 5 shows that the values of the viscosity *B*-coefficient for lithium salts in the studied mixed solvent systems are positive and higher than *A*-coefficient, thereby suggesting the presence of strong ion–solvent interactions and these type of interactions are strengthened from acetate to iodide but weakened with increasing amount of water in (acetonitrile + water) mixture[9-15].

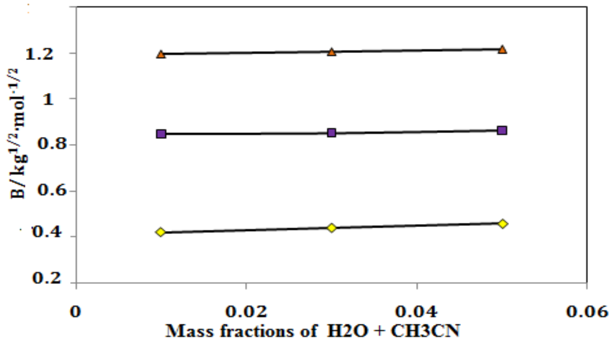


Figure 5: Plot of Viscosity B-coefficient of Lithium salts verses the mass fractions of the solvent mixture at 298.15K [orange symbol points CH_3COOLi, purple symbol points $LiNO_3$, yellow symbol points LiI].

Refractive index

The refractive index measurement is also a convenient process for investigating the ion–solvent interaction of electrolyte in solution. The values of refractive index of the chosen mineral salts in binary mixed solution are reported in Table 2, 3, 4. As stated by Deetlefs et al [14-16]. The refractive index of a material is higher when its molecules are more tightly packed or when the compound is denser. The refractive index is directly proportional to molecular polarizability; Figure 6 discloses that limiting molar refraction (R_M^0) values increases linearly with an increasing concentration of the solution of lithium salts but decreases as increasing content of water in (acetonitrile + water) solvent mixtures. Accordingly, we found that higher refractive index value indicating the fact that the salts are more tightly packed and more solvated in solution, leading to low conductance value as obtained by the conductometric study. This is also in superior agreement with the results obtained from density and viscosity parameters discussed above[16].

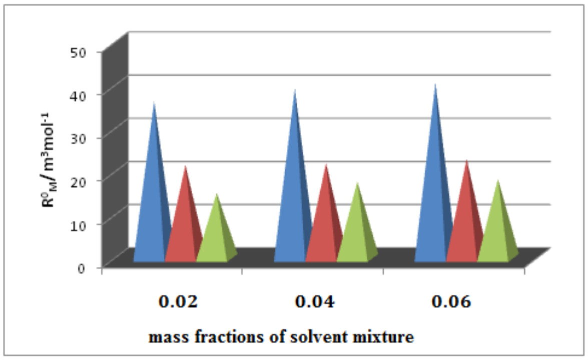


Figure 6: Plot of limiting molar refraction (R_M^0) vs mass fraction for Lithium salts CH_3COOLi (blue), $LiNO_3$ (brown), LiI (green) in aqueous acetonitrile

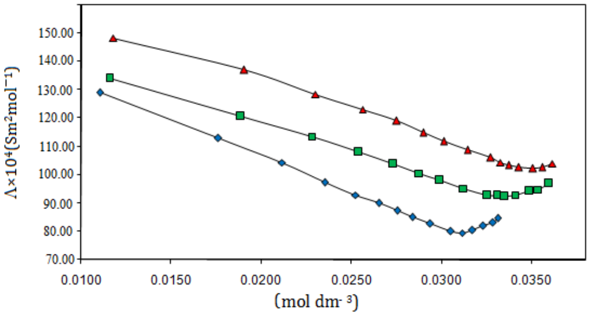


Figure 7: Plot of equivalent conductance verses concentration of lithium salts at 298.15K [red triangles for CH_3COOLi, green squares for $LiNO_3$, and blue small squares for LiI]

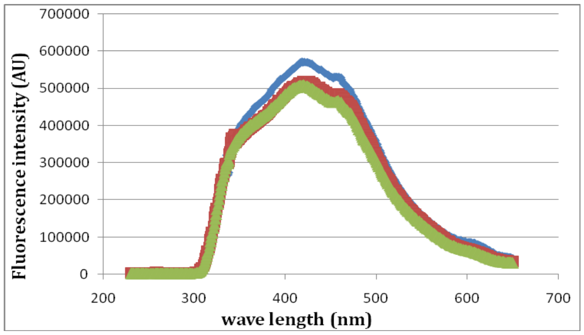


Figure 8: Plot of Fluorescence intensity against wave length of lithium salts at 298.15K [green squares for LiI, red triangles for $LiNO_3$, and blue small squares for CH_3COOLi]

Table 11: Experimental value of apparent molar volume $(\eta_r - 1)/\sqrt{c}$ for LiI in binary solvent mixtures of H_2O (w_1) + CH_3CN (w_2) at 298.15 K

Molality (mol kg−1)	**$(\eta_r - 1)/\sqrt{c}$ ($mol^{-1/2}$ $kg^{1/2}$)**	**Molality (mol kg−1)**	**$(\eta_r - 1)/\sqrt{c}$ ($mol^{-1/2}$ $kg^{1/2}$)**	**Molality (mol kg−1)**	**$(\eta_r - 1)/\sqrt{c}$ ($mol^{-1/2}kg^{1/2}$)**
[25 %H_2O + 75% CH_3CN]		[50 %H_2O + 50% CH_3CN]		[75 %H_2O + 25% CH_3CN]	
0.0118	0.0549	0.0176	0.0895	0.0274	0.0982
0.0307	0.1566	0.0342	0.1398	0.0352	0.1213
0.0457	0.1593	0.0467	0.1763	0.0586	0.1723
0.0609	0.1651	0.0641	0.2076	0.0768	0.2002
0.0788	0.1707	0.0838	0.2345	0.0882	0.2311
0.0929	0.1759	0.0988	0.2608	0.1091	0.2517

Table 12: The equivalent conductance (Λ), the corresponding concentration (c), for lithium salts in binary solvent mixture at 298.15 K

Conc.	**[25%H_2O + 75% CH_3CN]**		**[50%H_2O + 50% CH_3CN]**		**[75%H_2O + 25% CH_3CN]**	
Salts	**$c\times10^4$ ($mol\ dm^{-3}$)**	**$\Lambda\times10^4$ (Sm^2mol^{-1})**	**$c\times10^4$ ($mol\ dm^{-3}$)**	**$\Lambda\times10^4$ (Sm^2mol^{-1})**	**$c\times10^4$ ($mol\ dm^{-3}$)**	**$\Lambda\times10^4$ (Sm^2mol^{-1})**
CH_3COOLi	1.3382	148.12	1.4926	96.55	4.3682	74.73
	3.5515	104.23	2.7259	93.78	6.8123	71.71
	5.1941	89.28	3.7883	88.55	10.1751	67.67
	6.4553	79.31	5.4728	86.69	14.0635	62.07
	7.4541	67.89	6.7594	83.56	16.9726	59.68
	8.2637	61.36	7.7758	81.23	20.1856	56.75
	8.9336	56.34	8.2277	80.07	22.6308	54.96
	9.7456	50.49	8.9538	79.19	24.6883	52.78
	10.5759	45.25	9.5758	76.93	27.1562	51.37
	10.9136	45.29	10.108	76.97	28.4973	50.55
	11.2117	44.56	10.9426	75.93	29.1957	49.83
	11.5982	45.95	12.0956	73.55	29.6535	49.16
	12.1522	48.43	12.4117	73.28	30.1736	49.17
	12.5034	49.65	13.0654	72.58	30.6608	48.77
	12.9169	54.16				
$LiNO_3$	3.6273	131.22	1.4680	123.41	4.1542	100.86
	5.2857	115.00	2.6720	117.50	7.5326	93.41
	6.5577	103.40	3.7013	114.30	10.4426	88.97
	7.5639	96.20	4.5828	116.59	12.9312	86.26
	8.3793	89.06	5.3560	107.42	15.1853	84.24
	9.0531	83.54	6.0243	105.11	16.9739	81.37
	9.8707	77.72	6.6030	104.97	18.6348	78.47

	10.7066	71.00	7.5949	104.07	20.1132	78.52
	11.0475	68.72	8.0192	101.94	21.4372	75.36
	11.3459	67.18	8.4002	101.87	22.6273	74.28
	11.7549	65.80	9.6221	100.85	23.7154	74.75
	12.2965	64.70	10.5073	98.46	24.6852	73.79
	12.6453	65.54	11.4555	98.57	26.3993	72.54
	13.0613	68.30	11.8171	97.43	29.1930	69.87
LiI	1.1539	120.41	2.5615	95.56	3.9227	68.57
	2.9876	86.93	2.6530	88.34	4.3682	64.74
	4.3412	66.89	3.7111	85.36	8.9401	57.17
	5.3781	53.75	4.5813	83.29	12.9412	52.28
	6.1976	47.87	5.3462	80.97	16.8922	48.44
	6.8616	42.12	6.1143	79.29	18.6346	46.96
	7.4106	33.47	7.1281	78.27	21.4372	44.48
	7.8715	27.91	8.3190	76.69	22.6280	43.68
	8.4397	26.50	8.7380	74.36	25.2064	42.59
	9.0419	21.00	9.1650	74.56	27.5627	39.56
	9.4927	15.10	9.3556	73.68	28.1962	39.38
	9.8615	23.00	10.3100	72.89	30.8125	36.53
	10.2302	25.00	10.6930	71.45	33.6402	34.93
	10.5771	27.10	11.5831	70.59	35.5226	32.87
	10.7585	28.30	12.8303	69.54	38.1923	31.31

Conductometric study

The concentrations and equivalent conductances of Lithium salts in acetonitrile and water at 298.15 K are given in Table 12. Linear conductance curves were obtained for the electrolyte in aqueous acetonitrile solution by extrapolation of $\sqrt{c}$ to zero concentration, evaluated the starting limiting ionic conductance for the electrolyte. Figure 7 concludes at as concentration is raised in the solute-solvent system then the conductance also decreases steeply. The limiting ionic conductance for CH_3COOLi, $LiNO_3$ and LiI in varying mass fractions aqueous acetonitrile solutions were recorded in Table 13. In the state of infinite dilution, the movement of an ion is limited solely by its interaction with surrounding solvent molecules; there are no other ions within a finite distance. Therefore evaluation of limiting ionic conductance should provide equally reliable information regarding ion–solvent interactions. Greater value of limiting ionic conductance may therefore be interpreted as a measure of greater ion–solvent interactions (Table 13), Figure 7.

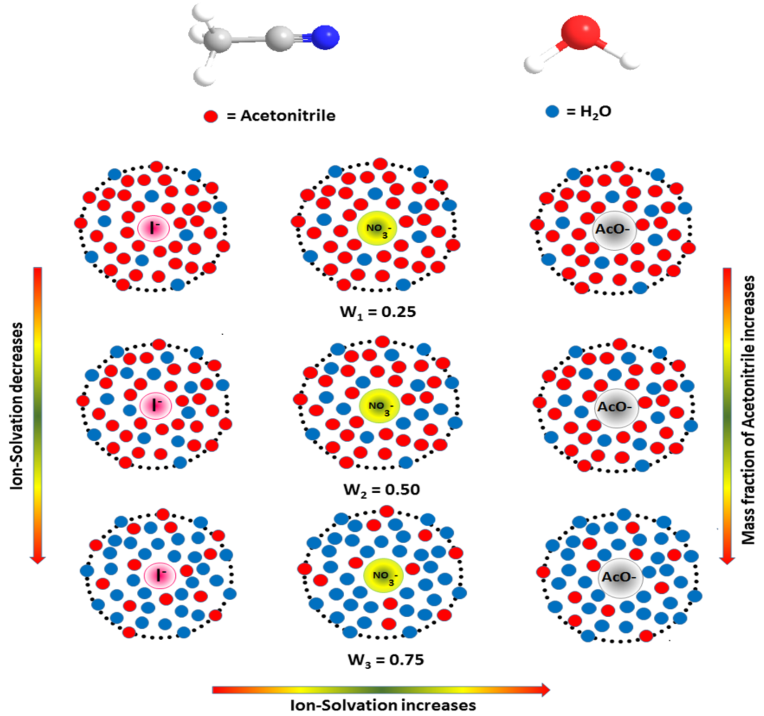
The order of Solute–Solvent interactions for CH_3COOLi, $LiNO_3$, LiI in varying mass fractions of aqueous acetonitrile solutions follow as:

$CH_3COOLi > LiNO_3 > LiI$

We know that the effect of anions upon conductivity is constantly observed. Bulky anions face difficulty to move in a viscous liquid, which affects the mobility of an anion, so that there seem to be no merit to use heavy anions. Conversely the electronic effect of anionic groups upon conductivity is clearly observed and it is positive, which compensates the negative effect derived from the bulkiness of an anion. This evidently indicates the electronic structures of Lithium salts are important in developing advanced organic lithium batteries. Again ion – solvent interaction is inversely associated to the extent of hydration. So, ion – solvent interaction is highest in case of acetate ion (Scheme 1) [15, 16].

Table 13: Calculated limiting ionic conductance at different concentrations of the solvent mixture at 298.15K

Salts	**$\Lambda^0_\pm$/S .cm^2. mol^{-1}**		
	[25%H_2O+ 75%CH_3CN]	**[50%H_2O+ 50%CH_3CN]**	**[75%H_2O+ 25%CH_3CN]**
CH_3COOLi	58.77	72.64	78.52
$LiNO_3$	64.11	69.78	76.25
LiI	67.10	70.32	79.29



Scheme 1: Diagrammatic representation of the ion-solvent interaction

Fluorescence Spectroscopy

Fluorescence spectroscopy is the fundamental tool for analyzing the interaction occurring in the solution systems. The fluorescence data have observed from fluorimeter has been plotted corresponding to the wave length in figure 8. From the figure we can see that the max intensity in fluorescence data have been found at the same range of the wave length 221nm, 220nm, 220nm for LiI, $LiNO_3$, $LiOOCCH_3$, respectively. The figure also signifying that the more intense at lower wave length is due to the more interactions. The interaction (ion-solvent or solute-solvent) is only greater if they are largely coupled to each other, tightly bound, become denser and as a result more reflected or emitted the fluorescence light and thus the intensity become higher. This observation also dealing that good agreement with the results came out from density, viscosity, refractive index, and conductance.

Conclusion

All-embracing study of conductance of lithium salts (CH_3COOLi, $LiNO_3$, and LiI) in the binary mixtures of acetonitrile and water leads to the conclusion that, electrolytes associated more in the mixture. Therefore it can also be seen that in the conductometric studies in the binary mixture of different mass fraction of acetonitrile they probably remains as ion-pairs. The reliable significance of volumetric, viscometric and refractometric studies also suggest that in solution there strong ion–solvent interaction than the ion–ion interaction and these interactions are promote strength at higher molality and with increasing size of lithium salts of homologues series in the solution media.

Acknowledgement

The authors are grateful to the Departmental Special Assistance Scheme, Department of Chemistry, Uviversity of North Bengal under UGC, New Delhi (No. 540/27/DRS/2007, SAP-1) for financial support and instrumental facilities to continue this research work. Miss Koyeli Das is thankful to “RGNF Ref. No. F./2014-15/RGNF-2014- 15D-GEN-WES-80317” for sanctioning research fellowship and financial assistance. Prof. M. N. Roy is thankful to UGC, New Delhi, and Government of India for being awarded one time Grant under Basic Scientific Research via the Grant-in-Aid No. F.4-10/2010 (BSR) regarding his active service for augmenting of research facilities. The special contribution of Dr. Deepak Ekka, Assistant Professor, Department of Chemistry, Cooch Behar Panchanan Barma University, is greatly involved to construct the work in more convenient.

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