Ion−Solvent Interactions of Some Halides of Common Cations with Organic Solvent Mixtures by Conductometric, Volumetric, Viscometric, and Refractometric Techniques

Mahendra Nath Roy,* Rajani Dewan, and Lovely Sarkar

Department of Chemistry, University of North Bengal, Darjeeling 734013, India

Electrolytic conductivities, densities, viscosities, and refractive indices of some lithium halides (LiCl, LiBr, and LiI) have been studied in mass fraction (0.10, 0.20, and 0.30) of ethylene glycol monomethyl ether + methyl alcohol mixtures at 303.15 K. The limiting molar conductivities (Λ^0), association constants (K_A), and the distance of closest approach of the ion (R) have been evaluated using the Fuoss conductance equation (1978). The Walden product is obtained and discussed. The limiting apparent molar volumes (ϕ_V°), experimental slopes (S_V^*) derived from the Masson equation, and viscosity A and B coefficients using the Jones−Dole equation have been interpreted in terms of ion−ion and ion−solvent interactions, respectively.

Introduction

Conductivities of many electrolytes in various mixed solvent systems are of much interest to chemists. The electrical conductivity of electrolytes in mixed solvent solutions mainly depends upon the concentration of the electrolyte and also upon the viscosity of the solvent. The use of mixed solvents in high energy batteries has also extended the horizon in the field of mixed solvent systems.[1,2] Lithium batteries are widely used in products such as portable consumer electronic devices. Hence, studying the behavior of lithium salts in different solvent systems will help in the production of more useful and cost-effective batteries.

Volumetric, viscometric, and refractometric studies also render an insight into the different molecular interactions prevailing in salt solutions containing mixed solvent systems and helps in the better understanding of the behavior of the salt with different solvents. Studies on the apparent and partial molar volumes of electrolytes and the dependence of viscosity on the concentration of solutes have been employed as a function of studying ion−ion and ion−solvent interactions.[3]

This work is concerned with the thermodynamic and transport properties of lithium halides, LiX (where X = Cl, Br, and I), in ethylene glycol monomethyl ether + methyl alcohol mixtures at 303.15 K. Thermodynamic parameters are evaluated and discussed.

Experimental Section

Materials. Methyl alcohol, ethylene glycol monomethyl ether, and lithium salts (analytical reagent grade) were procured from Merck, India, and were purified by standard methods.[4]

Apparatus and Procedure. Binary solvent mixtures were prepared by mixing the required volume of ethylene glycol monomethyl ether and methyl alcohol using the appropriate conversion of the required mass of each liquid into volume at 303.15 K using experimental densities. A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The uncertainty of molarity of different salt solutions is evaluated to be ± 0.0001 mol·dm⁻³.

* Corresponding author. Tel.: +91 353 2776381. Fax: +91 353 2699001. E-mail: mahendraroy2002@yahoo.co.in.

Table 1. Values of Density (ρ), Viscosity (η), and Dielectric Constant (ε) of Ethylene Glycol Monomethyl Ether + Methyl Alcohol Mixtures at 303.15 K

mass fraction (w_1) (ethylene glycol monomethyl ether)	ρ / g·cm⁻³	η / mPa·s	ε
$w_1 = 0.00$	0.782	0.523	31.90
$w_1 = 0.10$	0.798	0.538	30.37
$w_1 = 0.20$	0.817	0.557	28.84
$w_1 = 0.30$	0.833	0.577	27.31
$w_1 = 1.00$	0.956	1.404	16.59

The values of relative permittivity (ε) of the solvent mixtures was assumed to be an average of those of the pure liquids and calculated using the procedure as described by Rohdewald and Moldner.[5] The physical properties of the binary solvent mixtures at different mass fractions at 303.15 K are listed in Table 1.

Densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of about 25 cm³ and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 303.15 K with doubly distilled water and benzene. The pycnometer with experimental liquid was equilibrated in a glass-walled thermostatted water bath maintained at ± 0.01 K of the desired temperature. The pycnometer was then removed from the thermostat, properly dried, and weighed in an electronic balance with a precision of ± 0.01 mg. Adequate precautions were taken to avoid evaporation losses during the time of measurements. An average of triplicate measurements was taken into account. The uncertainty of density values is within ± 3·10⁻⁴ g·cm⁻³.

Solvent viscosities were measured by means of a suspended Ubbelohde-type viscometer, calibrated at 303.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature.[6−8] A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to ± 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to ± 0.1 s. At least three repetitions of each data reproducible to ± 0.1 s were taken to average the flow times. The uncertainty of viscosity values is ± 0.003 mPa·s. The details of the methods and measurement techniques have been described elsewhere.[9,10]

The conductance measurements were carried out in a systronic 308 conductivity bridge (precision of $\pm$ 0.01 %) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately 0.1 $\pm$ 10 %. Measurements were made in a water bath maintained within $T = (303.15 \pm 0.01)$ K, and the cell was calibrated by the method proposed by Lind et al.[11]

The conductance data were reported at a frequency of 1 kHz and were uncertain to $\pm$ 0.3 %.

Refractive indices, n_D, were measured with an Abbe refractometer. The values of refractive index were obtained using sodium D light. The temperature was controlled to $\pm$ 0.01 K with circulating thermostat water to a jacketed sample vessel. Calibration was performed periodically using double-distilled water. The sample mixtures were directly injected into the prism assembly of the instrument using an airtight hypodermic syringe, and an average of four measurements was taken for each mixture. The uncertainty of the refractive index measurement was estimated to be $\pm$ 0.0002 units.

Results and Discussion

The equivalent conductances, Λ, of electrolytes measured at the corresponding molar concentrations, c, are given in Table 2. The conductance data have been analyzed using the Fuoss conductance equation.[12,13] For a given set of conductivity values (c_j, Λ_j, $j = 1$, ..., n), three adjustable parameters, the limiting molar conductivity, $\Lambda°$, the association constant, K_A, and the distance of closest approach of ions, R, are derived from the following set of equations.

$$\Lambda = P[\Lambda°(1 + R_X) + E_L] \tag{1}$$

$$P = 1 - \alpha(1 - \gamma) \tag{2}$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \tag{3}$$

$$-\ln f = \beta\kappa/2(1 + \kappa R) \tag{4}$$

$$\beta = e^2/(\varepsilon k_B T) \tag{5}$$

$$K_A = K_R/(1 - \alpha) = K_R/(1 + K_S) \tag{6}$$

where the terms have their usual meaning.

The computations were performed using a program suggested by Fuoss. The initial $\Lambda°$ values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the program is the set (c_j, Λ_j, $j = 1$, ..., n), n, ε, η, T, initial values of $\Lambda°$, and an instruction to cover a preselected range of R values.

In practice, calculations are performed by finding the values of $\Lambda°$ and α which minimize the standard deviation:

$$\delta^2 = \sum [\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2/(n - 2) \tag{7}$$

for a sequence of R values and then plotting δ against R; the best-fit R corresponds to the minimum of the $\delta-R$ versus R curve. So, approximate runs are made over a fairly wide range of R values using 0.1 increments to locate the minimum, but no significant minima were found in the $\delta-R$ curves for all the salts studied here; thus, R values are assumed to be $R = a + d$, where a is the sum of the crystallographic radii of the ions and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance d is given by

$$d(\text{A}°) = 1.183(M/\rho)^{1/3} \tag{8}$$

where M is the molar mass of the solvent and ρ is its density. For mixed solvents, M is replaced by the mole fraction average molar mass (M_{av}) which is given by

$$M_{av} = M_1 M_2/(w_1 M_2 + w_2 M_1) \tag{9}$$

where w_1 is the mass fraction of the first component of molar mass M_1. The values of $\Lambda°$, K_A, and R obtained by this procedure are reported in Table 3.

It has been earlier reported[14] that the conductance of lithium halides in methyl alcohol follow the order LiCl < LiBr < LiI, and in ethylene glycol monomethyl ether the case is reversed.[15] In our paper, the values of $\Lambda°$ (Table 3) of all lithium halides decrease as the concentration of ethylene glycol monomethyl ether in the solvent mixture increases. Figure 1 shows the values of $\Lambda°$ both in pure methyl alcohol and solvent mixture. $\Lambda°$ of lithium halides with common cations follows the sequence $Cl^- > Br^- > I^-$ in the solvent mixture and the reverse trend in pure methyl alcohol. This can be explained in view of the dielectric constant of the solvent mixtures. The dielectric constant of the solvent mixture decreases with increasing concentration of the ethylene glycol monomethyl ether in the mixtures rendering to lesser solvation of Cl^- than that of Br^- and I^-. This can also be interpreted on the basis of

Table 2. Molar Conductance (Λ) and Molar Concentration of Various Lithium Halides in Ethylene Glycol Monomethyl Ether + Methyl Alcohol Mixtures at 303.15 K

$c \cdot 10^4$	Λ	$c \cdot 10^4$	Λ	$c \cdot 10^4$	Λ
mol·dm^{-3}	S·cm^2·mol^{-1}	mol·dm^{-3}	S·cm^2·mol^{-1}	mol·dm^{-3}	S·cm^2·mol^{-1}
LiCl		LiBr		LiI	
		($w_1 = 0.00$)			
9.7344	86.51	10.5625	99.16	10.4976	107.47
24.8004	82.17	13.0321	98.35	12.8881	106.35
30.6916	80.68	18.0625	96.78	17.9776	104.78
35.7604	79.66	22.3729	95.60	22.4676	103.60
40.3225	78.93	25.0000	94.80	25.3009	102.80
44.2225	78.28	29.2681	93.64	29.3764	101.64
47.7481	77.53	32.1489	93.02	32.2624	101.02
50.8369	77.07	34.6921	92.45	34.5744	100.45
53.7289	76.40	40.9600	91.11	40.8321	099.11
LiCl		LiBr		LiI	
		($w_1 = 0.10$)			
12.7487	102.13	12.9870	83.93	11.5613	53.38
17.6521	101.15	16.8349	82.40	16.0080	52.29
21.8550	100.16	20.1522	81.38	19.8194	51.47
25.4975	99.33	26.7378	79.66	23.1227	51.03
28.6847	98.66	30.7586	79.33	26.0130	50.74
31.4969	97.73	34.0134	78.50	28.5633	50.18
38.2462	96.52	40.8848	77.53	32.8585	49.64
41.7232	95.46	43.9881	77.07	36.3356	49.26
45.8955	94.67	47.3848	76.40	42.6880	48.49
50.1158	94.10	50.1769	75.73	46.2453	48.32
LiCl		LiBr		LiI	
		($w_1 = 0.20$)			
10.5624	99.41	10.6467	79.93	11.5600	44.67
14.6248	98.46	12.2847	79.43	18.3095	43.25
18.1069	97.56	15.2096	78.40	20.5982	43.01
21.1247	96.10	17.7445	77.64	22.6176	42.58
26.0953	95.04	19.9626	76.80	24.4127	42.19
29.1179	94.10	26.6167	75.52	26.0188	41.89
35.2079	93.16	38.8461	72.85	27.4642	41.69
37.5072	92.25	41.4038	72.46	29.9610	41.40
43.8745	91.40	43.3754	72.16	33.8021	40.91
50.5714	90.37	44.9158	71.69	35.9876	40.50
LiCl		LiBr		LiI	
		($w_1 = 0.30$)			
9.3396	86.52	11.5580	72.11	10.4709	44.36
13.3423	85.33	12.7374	71.60	15.1246	43.40
15.5660	84.76	14.8603	70.66	18.6833	42.32
18.3962	83.96	19.8137	69.36	21.4929	41.79
23.9185	82.48	22.8341	68.76	24.7494	41.28
27.6377	81.36	27.0982	67.90	27.9223	40.82
30.3128	80.7	29.9642	67.08	30.2492	40.66
33.1624	80.03	32.3670	66.73	32.7700	40.28
36.4348	79.60	34.5627	66.55	34.8218	39.92
37.4510	79.37	36.2480	66.18	37.2713	39.75

Table 3. Derived Conductivity Parameters for Lithium Salts in Ethylene Glycol Monomethyl Ether (1) + Methyl Alcohol (2) Mixtures at 303.15 K
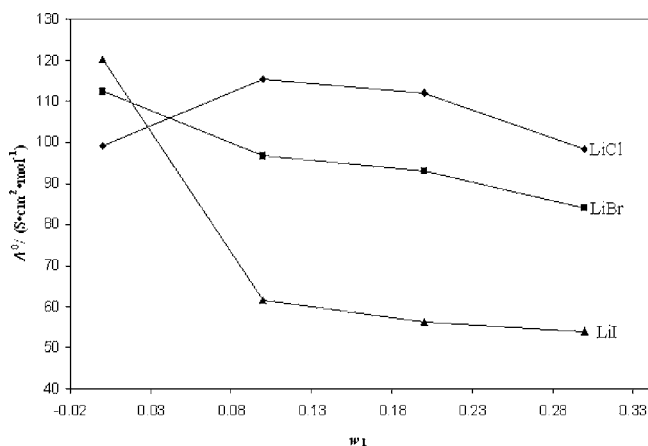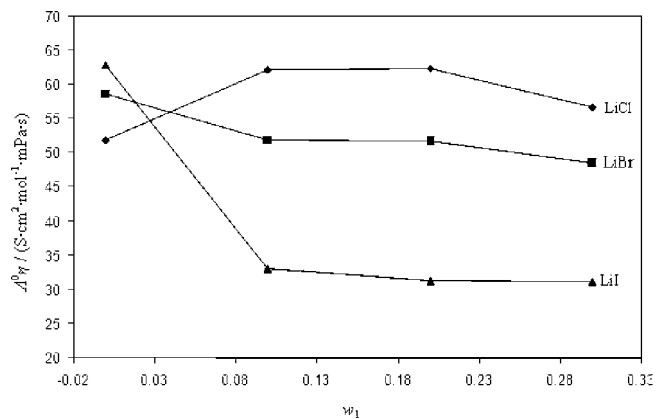
mass fraction (w_1) (ethylene glycol monomethyl ether)	$\Lambda°$ $S \cdot cm^2 \cdot mol^{-1}$	$K_A \cdot 10^{-4}$ $dm^3 \cdot mol^{-1}$	$R/A°$	δ
	LiCl			
$w_1 = 0.00$	099.23	5.22	5.79	0.31
$w_1 = 0.10$	115.54	3.90	6.89	0.40
$w_1 = 0.20$	112.07	4.20	6.61	0.29
$w_1 = 0.30$	098.26	4.81	6.04	0.25
	LiBr			
$w_1 = 0.00$	112.28	4.46	5.93	0.24
$w_1 = 0.10$	096.57	4.89	7.05	0.20
$w_1 = 0.20$	092.89	5.67	6.75	0.17
$w_1 = 0.30$	084.01	5.74	6.18	0.21
	LiI			
$w_1 = 0.00$	120.23	4.03	6.15	0.21
$w_1 = 0.10$	061.55	5.22	7.27	0.09
$w_1 = 0.20$	056.18	7.46	6.97	0.12
$w_1 = 0.30$	053.92	8.05	6.40	0.11

preferential solvation. These halides prefer ethylene glycol monomethyl ether to methyl alcohol. As a result, the solvation in the case of ethylene glycol monomethyl ether is higher than that of methyl alcohol resulting in decreasing conductance with increasing mass percent of ether to the mixtures.

The greater interaction between the charge on the ion and the dipoles of the adjacent solvent molecules leads to a reduction in mobility. The structure forming effect increases with decreasing dimension and consequently mobility in the reverse order. The trend in $\Lambda°$ can be discussed through another characteristic function called the Walden product, $\Lambda°\eta$, as shown in Figure 2. From Tables 3 and 4, it is seen that both $\Lambda°$ and $\Lambda°\eta$ (in most cases) respectively decrease as the concentration of ethylene glycol monomethyl ether increases, although the viscosity, η, of the solvent mixture increases with increasing concentration of ethylene glycol monomethyl ether which suggests the predominance of $\Lambda°$ over η. Changes in the Walden product with concentration are common, and they can be attributed to changes in ion solvation, that is, ion−solvent interactions.

The order of halide ion conductance in the solvent mixture is consistent with the measurement in pure ethylene glycol monomethyl ether,[15] acetone,[16] and glycerol[17] reported earlier.

There are marked characteristic behaviors in the K_A values. However, K_A of all salts increases with an increase in the concentration of ethylene glycol monomethyl ether in the mixture and also with the increase in the anionic size. Such behavior in

Figure 1. Plots of limiting molar conductances, $\Lambda°$, of Li halides in methyl alcohol and in the solvent mixtures with different mass fractions, w_1, of ethylene glycol monomethyl ether at 303.15 K.

Figure 2. Plots of values of Walden products, $\Lambda°\eta$, of Li halides in methyl alcohol and in the solvent mixture with different mass fractions, w_1, of ethylene glycol monomethyl ether at 303.15 K.

Table 4. Values of Walden Products ($\Lambda°\eta$) of Lithium Salts in Ethylene Glycol Monomethyl Ether (1) + Methyl Alcohol (2) Mixtures at 303.15 K

mass fraction (w_1) (ethylene glycol monomethyl ether)	$\Lambda°\eta$ $S \cdot cm^2 \cdot mol^{-1} \cdot mPa \cdot s$			$-\Delta G° \cdot 10^{-4}$ $kJ \cdot mol^{-1}$		
	LiCl	LiBr	LiI	LiCl	LiBr	LiI
$w_1 = 0.00$	51.89	58.72	62.88	2.73	2.70	2.67
$w_1 = 0.10$	62.16	51.95	33.11	2.66	2.72	2.74
$w_1 = 0.20$	62.42	51.74	31.29	2.68	2.76	2.83
$w_1 = 0.30$	56.70	48.47	31.11	2.72	2.76	2.85

the solvent mixture is observed in alcohols[18] where K_A increases with the increasing size of the anion.

The free energy change, $\Delta G°$ for association is calculated from the relation[19]

$$\Delta G° = -RT \ln K_A \qquad (11)$$

and is reported in Table 4.

The measured values of densities and viscosities of lithium salts in the solvent mixture of ethylene glycol monomethyl ether and methyl alcohol as a function of concentration at 303.15 K are listed in Table 5. The densities and viscosities of lithium salts in solvent mixtures increase linearly at the experimental temperature (Figures 3 and 4). For the analysis of interaction of lithium halides in binary mixtures of ethylene glycol monomethyl ether and methyl alcohol, partial molar volumes are important. For this purpose, the apparent molar volumes ϕ_V (Table 5) were determined from the solution densities using the following equation[10]

$$\phi_V = M/\rho_0 - 1000(\rho - \rho_0)/(c\rho_0) \qquad (10)$$

where M is the molar mass of the solute, c is the molarity of the solution, and ρ and ρ_0 are the densities of the solution and solvent, respectively. The limiting apparent molar volumes $\phi°_V$ were calculated using a least-squares treatment to the plots of ϕ_V versus $c^{1/2}$ using the following Masson equation[20]
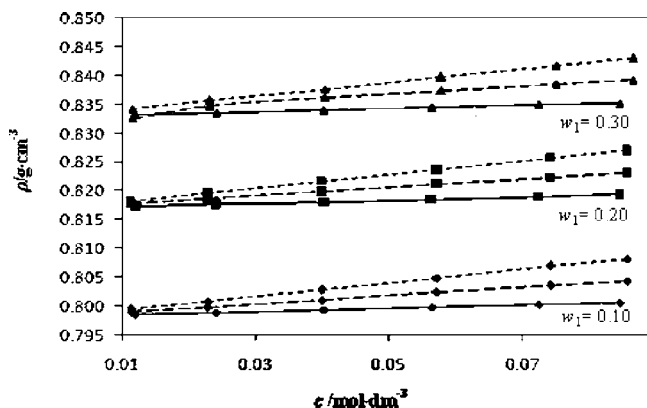
$$\phi_V = \phi°_V + S^*_V c^{1/2} \qquad (11)$$

where $\phi°_V$ is the partial molar volume at infinite dilution and S^*_V is the experimental slope. The plots of ϕ_V against the square root of the molar concentration $c^{1/2}$ were found to be linear with positive slopes. The values of $\phi°_V$ and S^*_V are reported in Table 6. The variation of $\phi°_V$ with the increase in the mass fraction of ethylene glycol monomethyl ether in the solvent mixture is shown in Figure 5.

Table 5. Concentration, Density, Viscosity, Apparent Molar Volume, ϕ_V, and $(\eta_r - 1)/c^{1/2}$ for Lithium Halides in Ethylene Glycol Monomethyl Ether (1) + Methyl Alcohol (2) Mixtures at 303.15 K

c $\overline{\text{mol·dm}^{-3}}$	ρ $\overline{\text{g·cm}^{-3}}$	η $\overline{\text{mPa·s}}$	ϕ_V $\overline{\text{cm}^3\text{·mol}^{-1}}$	$(\eta_r - 1)/c^{1/2}$	n_D	c $\overline{\text{mol·dm}^{-3}}$	ρ $\overline{\text{g·cm}^{-3}}$	η $\overline{\text{mPa·s}}$	ϕ_V $\overline{\text{cm}^3\text{·mol}^{-1}}$	$(\eta_r - 1)/c^{1/2}$	n_D
					LiCl						
					$w_1 = 0.10$						
0.0121	0.799	0.538	18.220	0.006	1.3337	0.0565	0.800	0.545	17.900	0.053	1.3348
0.0242	0.799	0.540	18.100	0.025	1.3340	0.0726	0.800	0.547	17.830	0.064	1.3352
0.0403	0.799	0.542	17.990	0.040	1.3344	0.0847	0.801	0.550	17.775	0.073	1.3356
					LiCl						
					$w_1 = 0.20$						
0.0121	0.817	0.558	18.247	0.017	1.3407	0.0564	0.819	0.569	17.924	0.089	1.3427
0.0242	0.818	0.560	18.129	0.040	1.3412	0.0726	0.819	0.573	17.835	0.107	1.3432
0.0403	0.818	0.565	18.014	0.069	1.3420	0.0847	0.819	0.577	17.790	0.120	1.3437
					LiCl						
					$w_1 = 0.30$						
0.0121	0.833	0.580	18.272	0.056	1.3467	0.0565	0.835	0.602	17.933	0.180	1.3491
0.0242	0.834	0.585	18.138	0.092	1.3473	0.0726	0.835	0.610	17.851	0.207	1.3499
0.0403	0.834	0.593	18.020	0.137	1.3482	0.0847	0.835	0.618	17.797	0.236	1.3505
					LiBr						
					$w_1 = 0.10$						
0.0114	0.799	0.539	18.760	0.014	1.3344	0.0572	0.802	0.546	17.990	0.066	1.3357
0.0229	0.800	0.541	18.487	0.032	1.3348	0.0743	0.804	0.550	17.830	0.080	1.3362
0.0400	0.801	0.543	18.207	0.049	1.3352	0.0858	0.804	0.552	17.747	0.091	1.3366
					LiBr						
					$w_1 = 0.20$						
0.0114	0.818	0.559	18.830	0.027	1.3418	0.0572	0.821	0.572	18.060	0.109	1.3436
0.0229	0.819	0.561	18.570	0.052	1.3422	0.0743	0.822	0.577	17.860	0.133	1.3444
0.0400	0.820	0.566	18.300	0.083	1.3430	0.0858	0.823	0.581	17.770	0.149	1.3448
					LiBr						
					$w_1 = 0.30$						
0.0116	0.833	0.581	18.890	0.073	1.3478	0.0579	0.837	0.606	18.100	0.213	1.3504
0.0231	0.835	0.587	18.620	0.116	1.3483	0.0752	0.839	0.617	17.900	0.253	1.3513
0.0405	0.836	0.596	18.330	0.168	1.3493	0.0867	0.839	0.624	17.800	0.279	1.3521
					LiI						
					$w_1 = 0.10$						
0.0114	0.800	0.540	22.670	0.031	1.3366	0.0572	0.805	0.551	21.230	0.100	1.3383
0.0229	0.801	0.543	22.240	0.053	1.3370	0.0743	0.807	0.555	20.900	0.119	1.3389
0.0400	0.803	0.546	21.650	0.077	1.3377	0.0858	0.808	0.559	20.670	0.133	1.3393
					LiI						
					$w_1 = 0.20$						
0.0114	0.818	0.560	22.830	0.045	1.3441	0.0572	0.824	0.577	21.310	0.152	1.3461
0.0229	0.820	0.564	22.330	0.078	1.3446	0.0743	0.826	0.586	20.980	0.187	1.3468
0.0400	0.822	0.571	21.810	0.122	1.3453	0.0858	0.827	0.590	20.760	0.204	1.3474
					LiI						
					$w_1 = 0.30$						
0.0116	0.834	0.583	23.090	0.100	1.3503	0.0579	0.840	0.618	21.460	0.296	1.3533
0.0231	0.836	0.591	22.530	0.163	1.3510	0.0752	0.842	0.631	21.100	0.340	1.3545
0.0405	0.838	0.604	21.950	0.235	1.3522	0.0867	0.843	0.641	20.900	0.374	1.3553

ϕ_V° values are generally positive and increase with the amount of ethylene glycol monomethyl ether in the mixtures. This indicates the presence of strong ion−solvent interactions, and these interactions increase with an increase in the amount of ethylene glycol

Figure 3. Density, ρ, of LiCl (solid line), LiBr (dashed line), and LiI (dotted line) at different concentration of salts in the solvent mixture with various mass fractions, w_1, of ethylene glycol monomethyl ether.
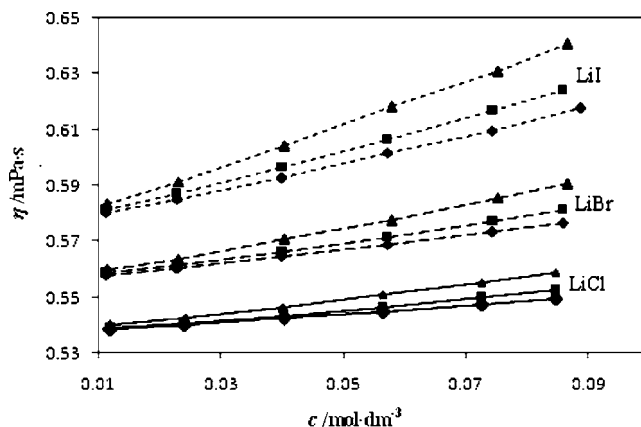
Figure 4. Viscosity, η, of at different concentration of salts in the solvent mixture with 0.10 (◆), 0.20 (■), and 0.30 (▲) mass fractions of ethylene glycol monomethyl ether.

Table 6. Limiting Partial Molar Volume (ϕ_V°) and Experimental Slope (S_V^*) for Lithium Halides in Ethylene Glycol Monomethyl Ether (1) + Methyl Alcohol (2) Mixtures at 303.15 K
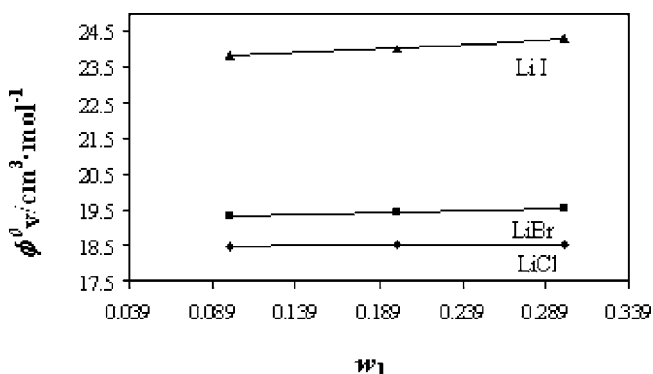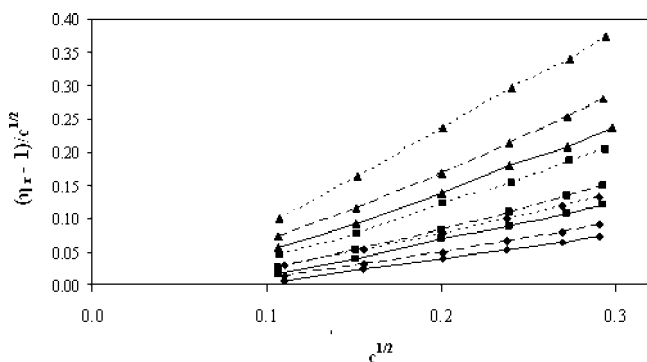
solute	mass fraction (w_1) (ethylene glycol monomethyl ether)	ϕ_V° cm$^3\cdot$mol^{-1}	S_V^* cm$^2\cdot$dm$^{1/2}\cdot$mol$^{-3/2}$
LiCl	$w_1 = 0.10$	18.48	−2.44
	$w_1 = 0.20$	18.53	−2.54
	$w_1 = 0.30$	18.55	−2.60
LiBr	$w_1 = 0.10$	19.32	−5.47
	$w_1 = 0.20$	19.44	−5.76
	$w_1 = 0.30$	19.52	−5.87
LiI	$w_1 = 0.10$	23.84	−10.84
	$w_1 = 0.20$	24.02	−11.19
	$w_1 = 0.30$	24.33	−11.79

monomethyl ether in the mixed solvent under investigation, suggesting a larger electrostriction at higher amounts of ethylene glycol monomethyl ether in the mixture.

The results can be justified in that I$^-$ associates more than either Cl$^-$ or Br$^-$ with ethylene glycol monomethyl ether + methyl alcohol mixtures with an increasing amount of ethylene glycol monomethyl ether in the mixtures. This is in excellent agreement with the results drawn from the conductance data discussed earlier. Similar results were also observed in some 1:1 electrolytes in glycerol.[21]

As a consequence, the S_V^* values (ion−ion interactions) decrease as the size of the anion increases as well as with increasing amount of ethylene glycol monomethyl ether to the mixtures which may be attributed to the increase in the solvation of ions.

The relative viscosities η_r are expressed by $\eta_r = \eta/\eta_0$, where η and η_0 signify the viscosities of the solution and solvent mixture, respectively. The values of $(\eta_r - 1)/c^{1/2}$ are listed in Table 5. These

Figure 5. Limiting apparent molar volumes, ϕ_V°, of Li halides at different mass fractions, w_1, of ethylene glycol monomethyl ether.

Figure 6. Plot of $(\eta_r - 1)/c^{1/2}$ versus $c^{1/2}$ of LiCl (solid line), LiBr (dashed line), and LiI (dotted line) at different concentration of salts in the solvent mixture with 0.10 (◆), 0.20 (■), and 0.30 (▲) mass fractions of ethylene glycol monomethyl ether.

Table 7. Values of Viscosity A and B Coefficients for Lithium Halides in Ethylene Glycol Monomethyl Ether (1) + Methyl Alcohol (2) Mixtures at 303.15 K

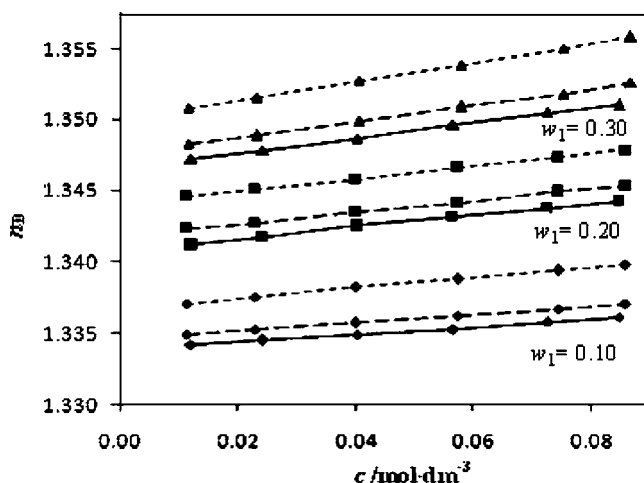| solute	mass fraction (w_1) (ethylene glycol monomethyl ether)	A cm$^{3/2}\cdot$mol$^{-1/2}$	B cm$^3\cdot$mol^{-1}
LiCl	$w_1 = 0.10$	−0.0331	0.3634
	$w_1 = 0.20$	−0.0429	0.5536
	$w_1 = 0.30$	−0.0484	0.9452
LiBr	$w_1 = 0.10$	−0.0331	0.3634
	$w_1 = 0.20$	−0.0462	0.6572
	$w_1 = 0.30$	−0.0497	1.1088
LiI	$w_1 = 0.10$	−0.0342	0.5675
	$w_1 = 0.20$	−0.0501	0.8571
	$w_1 = 0.30$	−0.0585	1.4637

η_r values have been utilized to calculate the viscosity B coefficient analyzed by the Jones−Dole equation[22]

$$\eta_r = 1 + Bc + Ac^{1/2} \qquad (12)$$

$$(\eta_r - 1)/c^{1/2} = A + Bc^{1/2} \qquad (13)$$

where the symbols have their usual meaning. The values of A and B are obtained from the straight line by plotting $(\eta_r - 1)/c^{1/2}$ against $c^{1/2}$ as depicted in Figure 6 and reported in Table 7. A perusal of Table 7 shows that the values of the A coefficient are generally negative for all of the solutions under investigation at all composition ranges and indicate the presence of weak ion−ion interactions, and these interactions further decrease with an increasing amount of ethylene glycol monomethyl ether and size of halides in the mixtures. The viscosity B coefficient[23] reflects the effects of ion−solvent interactions on the solution viscosity. Table 7 illustrates that the values of the viscosity B coefficient for lithium halides in the studied solvent systems are positive, thereby suggesting the presence of strong ion−solvent interactions, and these types of interactions are strengthened with the size of halides in the mixtures.

The values of n_D are included in Table 5, and the plots of n_D versus concentration are found to increase linearly with an increasing amount of solute and also ethylene glycol monomethyl ether in all of the solvent mixtures. As n_D is directly proportional to molecular polarizability, Figure 7 reveals that overall polarizabilty of all of the systems under study increases linearly with the increase in concentration and size of lithium halides and also with the amount of ethylene glycol monomethyl ether in all the solvent mixtures. This is in good agreement with the results obtained from conductance, density, and viscosity parameters.

Figure 7. Refractive index, n_D, of LiCl (solid line), LiBr (dashed line), and LiI (dotted line) at a different concentration of salts in the solvent mixture with various mass fractions of ethylene glycol monomethyl ether.

The plausible diagram of solvation of ions in the solvent mixtures studied here in view of various derived parameters is given below:

Conclusion

The extensive study of lithium halides in the binary mixture of ethylene glycol monomethyl ether and methyl alcohol
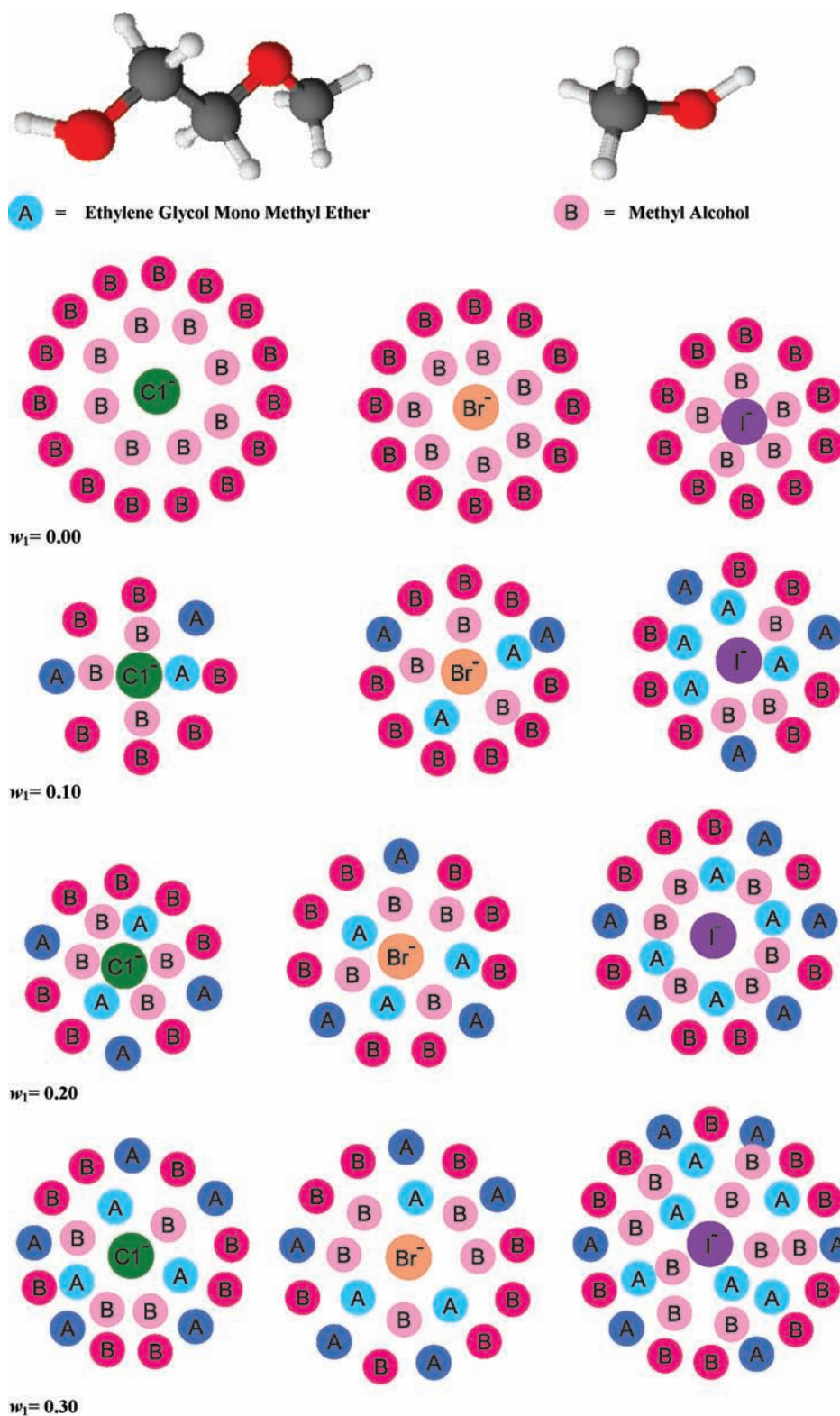
Diagram 1.

Solvation of halides in pure methyl alcohol is shown in the top row, and solvation of those ions with increasing mass fraction of ethylene glycol monomethyl ether in the binary mixtures is shown in the columns.

suggests the fact that these electrolytes remain largely associated in the mixture, and conductance values are consistent with the values of the salts in pure ethylene glycol monomethyl ether. ϕ_V° and viscosity B coefficient values for lithium halides in a

binary mixture of ethylene glycol monomethyl ether and methyl alcohol indicate the presence of strong ion–solvent interactions, and these interactions are further strengthened at higher molarity and size of lithium halides in the solutions. Accordingly, refractive index values were also found to increase linearly with molecular polarizability.

Note Added after ASAP Publication: This paper was published ASAP on October 28, 2009. Diagram 1 was updated. The revised paper was reposted on November 18, 2009.

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