J. Chem. Eng. Data **2001,** *46,* 1327−1329 **1327**

Study of Ion−Solvent Interactions of Some Alkali Metal Chlorides in Tetrahydrofuran + Water Mixture at Different Temperatures

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The apparent molar volumes and viscosities of three alkali metal chlorides, namely, lithium chloride, sodium chloride, and potassium chloride, have been determined in a 40 mass % tetrahydrofuran + water mixture at 303, 308, 313, and 318 K. The limiting apparent molar volumes (V_ϕ^o) and slopes (S_v*) have been interpreted in terms of ion−solvent and ion−ion interactions, respectively. Structure-making/-breaking capacities of various electrolytes have been inferred from the sign of ($d^2V_\phi^o/dT^2$), dB/dT, and the *B* coefficient for all electolytes studied. The viscosity data have been analyzed using the Jones−Dole equation. The results show that the three electrolytes act as structure promoters in this solvent mixture.

Introduction

The volumetric behavior of solutes has been proven to be very useful in elucidating the various interactions occurring in aqueous and nonaqueous solutions.[1] Studies on the apparent and partial molar volumes of electrolytes and the dependence of viscosity on concentration of solutes and temperature of solutions have been employed as a function of studying ion−ion and ion−solvent interactions.[2] It has been found by a number of workers[3−5] that the addition of electrolyte could either break or make the structure of a liquid. Because a liquid's viscosity depends on the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at different concentrations and temperatures.

In this paper, we report the limiting apparent molar volumes (V_ϕ^o), experimental slopes (S_v*), limiting apparent molar expansibilities (ϕ_E^o), and viscosity *B* coefficients for three alkali metal chlorides, namely, lithium chloride, sodium chloride, and potassium chloride, in a 40 mass % tetrahydrofuran (THF) + water solvent mixture at different temperatures.

Experimental Section

Tetrahydrofuran (Merck, India) was kept for several days over KOH, refluxed for 24 h, and distilled over $LiAlH_4$.[6] The boiling point (66 °C), density (0.8807 g·cm^3), and viscosity (η_0 = 0.0046 P) compared well with the literature values.[7] The specific conductance of THF was $\sim 0.81 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ at 25 °C.

Alkali metal chlorides (Fluka) were of purum or puriss grade and purified by us as described earlier.[8,9]

A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The conversion of molality to molarity was done using density values.

The densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of ~0.1 cm. The pycnometer was calibrated at 298, 308, and 318 K with doubly distilled water and benzene. The 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 thermoregulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge. The pycnometer was then removed from the thermostatic bath, properly dried, and weighed. The evaporation losses remained insignificant during the time of actual measurements. An average of triplicate measurements was taken into account. The density values are reproducible to $\pm 3 \times 10^{-5}$ g·cm^{-3}. Details were given earlier in a publication from our laboratory (Das and Roy, 1994).[10]

Table 1. Properties of Pure Tetrahydrofuran (THF) and a 40 Mass % THF + H_2O Solvent Mixture at Different Temperatures

		ρ_0/g·cm^{-3}		η_0/cP	
T/K	mass %	this work	lit.	this work	lit.
298	100 (pure THF)	0.88072	0.88072[a] 0.88070[c]	0.46300	0.46300[b] 0.46000[c]
303	100	0.87595		0.44536	
308	100	0.87116	0.87116[a]	0.42770	0.42770[b]
313	100	0.86627		0.40893	
318	100	0.86140	0.86140[a]	0.39017	0.39017[b]
298	40	0.96640	0.96640[a]	1.73210	1.73210[b]
303	40	0.96381		1.52760	
308	40	0.96120	0.96120[a]	1.32310	1.32310[b]
313	40	0.95359		1.18412	
318	40	0.94598	0.94598[a]	1.04516	1.04516[b]

[a] ρ_0.[9,10,22] [b] η_0.[9,10] [c] ρ_0, η_0.[7]

The viscosities were measured by means of a suspended-level Ubbelohde[23] viscometer at the desired temperature (accuracy of ±0.01 °C). The precision of the viscosity measurement was 0.05%. We have previously given the details.[10]

The experimental values of densities (ρ_0) and viscosities (η_0) of pure THF and 40 mass % THF + water at 298, 303, 308, 313, and 318 K are given in Table 1.

Results

The apparent molar volumes, V_ϕ, of the solutes were calculated from the densities of the solutions by using the equation

$$V_\phi = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0 \qquad (1)$$

10.1021/je010009w CCC: $20.00 © 2001 American Chemical Society
Published on Web 08/21/2001

Table 2. Limiting Apparent Molar Volumes (V_ϕ^o) and Experimental Slopes (S_v*) of Different Salts in 40 Mass % THF + Water at Different Temperatures

	V_ϕ^o at various temps ($cm^3\ mol^{-1}$)				S_v* at various temps ($cm^3\ L^{1/2}\ mol^{-3/2}$)			
salt	303 K	308 K	313 K	318 K	303 K	308 K	313 K	318 K
LiCl	−191.75	−240.502	−443.849	−633.905	388.194	525.746	971.602	1355.919
NaCl	−224.461	−285.361	−502.611	−719.110	466.507	650.985	1039.870	1620.59
KCl	−464.253	−541.196	−770.164	−982.70	1024.510	1234.66	1753.641	2243.321

Table 3. Limiting Apparent Molar Expansibilities (ϕ_E^o) for Various Salts in 40 Mass % THF + Water at Different Temperatures

	limiting apparent molar expansibilities ϕ_E^o ($cm^3\ mol^{-1}\ K^{-1}$)			
electrolyte	303 K	308 K	313 K	318 K
LiCl	−44.656	−41.998	−39.340	−36.682
NaCl	−43.675	−43.525	−43.375	−43.225
KCl	−50.722	−47.436	−44.149	−40.863

where M is the molecular weight of the solute, ρ_0 and ρ are the densities of the solvent mixture and the solution, respectively, and c is the concentration in molarity. The correction to V_ϕ due to hydrolysis of salts may be negligible, because the strong H^- bonding[11] between THF and water will reduce the hydrolysis of these salts by free water molecules considerably.

Because the data concerning the pressure dependence of the dielectric constant of the THF + water mixture are not available, the limiting apparent molar volume (V_ϕ^o) was calculated by using the equation[12]

$$V_\phi = V_\phi^{\ o} + S_v{}^* c^{1/2} \tag{2}$$

where S_v* is a constant dependent on charge and salt type and can be related to ion−ion interactions and V_ϕ^o is the limiting apparent molar volumes. These values were estimated by Microsoft Excel, which is a computerized least-squares method. Values of V_ϕ^o and S_v* are given in Table 2.

The temperature dependence of V_ϕ^o for various electrolytes studied here in the above solvent mixture can be expressed by the equation

$$V_\phi^{\ o} = a_0 + a_1 T + a_2 T^2 \tag{3}$$

where T is the temperature in degrees kelvin.

The limiting apparent molar expansibilities (ϕ_E^o) can be obtained by differentiating eq 3 with respect to temperature.

$$\phi_E^{\ o} = (dV\phi^o/dT)p = a_1 + 2a_2 T \tag{4}$$

The ϕ_E^o values of the electrolytes at 303, 308, 313, and 318 K are given in Table 3.

The relative viscosities of solutions for various electrolytes, namely, LiCl, NaCl, and KCl, in a 40 mass % THF + H_2O mixture at different temperatures were also determined. The data were analyzed by using the Jones−Dole[13] equation

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc$$

$$(\eta/\eta_0 - 1)/c^{1/2} = A + Bc^{1/2} \tag{5}$$

where $\eta = (Kt - L/t) \times \rho$, η_0 and η are the viscosities of the solvent mixture and solution, respectively, A and B are constants, ρ is the density of the particular solvent mixture or solution, and K and L are constants for a particular viscometer.

The values of A and B were calculated by a computerized least-squares method. Molar concentrations, densities, viscosities, apparent molar volumes, and values of the B coefficient and A are recorded in Table 4.

Discussion

The values of S_v* shown in Table 2 are large and positive for the alkali metal chlorides studied here in a 40 mass % THF + H_2O mixture at all of the temperatures investigated. This is an indication of strong ion−ion interactions in this solvent mixture medium.[14,15] This type of behavior of alkali metal chlorides and some common salts has been also observed in propylene glycol−water mixtures.[16] A possible explanation for the positive slopes in the 40 mass % THF + H_2O mixture may be that the ionic association would become quite appreciable in this medium as the concentration of the electrolyte is increased, thereby weakening the ion−solvent interactions.

As a consequence, contraction of the solvent mixture would be gradually lowered with the increase in concentration of the added solute. The S_v* values (ion−ion interactions) increase as the size of the cation increases as well as with increase in temperature. Exactly the same conclusion regarding the ion association behavior of these electrolytes in THF and DME has been drawn from our conductometric studies.[6] The limiting apparent molar volumes V_ϕ^o shown in Table 2 are large and negative, and these values decrease as the size of the alkali metal ion increases (from Li^+ to K^+) as well as with increase in temperature (from 303 to 318 K). This indicates that there is a large amount of electrostriction occurring in these solutions, and this electrostrictive solvation is greater at higher tempearture and with larger metal ion. Similar results are reported for some metal sulfates in different DMF + H_2O mixtures at different temperatures.[15] It is evident from Table 3 that the ϕ_E^o values of all the salts in this solvent mixture increase with increase of temperature. The increase in magnitude per degree of temperature is positive, indicating that the behavior of all of these salts is similar to that of symmetrical quaternary ammonium alkyl salts.[1,17]

It is also found that [$d^2V_\phi^o/dT^2$] values for solutions of all studied salts here are positive, showing that these studied electrolytes (LiCl, NaCl, and KCl) behave as structure promoters[15,16,18] in this medium.

Perusal of Table 4 shows that the values of B for all of the electrolytes are positive and large, indicating that all of these alkali metal chlorides (LiCl, NaCl, and KCl) act as structure makers in this mixed solvent system. The structure-making tendencies of the salts are in the order lithium salt > sodium salt > potassium salt. A similar trend was reported by other workers.[19,20]

It has been reported by a number of workers that the (dB/dT) value is a better criterion[21,24] for determining the structure-making/-breaking nature of any electrolyte rather than simply the B coefficients. It is found that B values are positive and decrease with a rise in temperature

Table 4. Molar Concentrations, Densities, Viscosities, Apparent Molar Volumes, and Values of the *B* Coefficient and *A* in 40 Mass % THF + Water Mixture at Different Temperatures

c	ρ	η	V_ϕ	B	A
mol dm^{-3}	g·cm^{-3}	cP	dm^3 mol^{-1}	dm^3 mol^{-1}	dm$^{3/2}$ mol$^{-1/2}$
303 K, LiCl					
0.01313	0.96575	0.99243	−145.56		
0.04595	0.97219	1.00110	−110.11		
0.08535	0.97404	1.02710	−80.58	7.205	−3.512
0.13131	0.97482	1.03799	43,13		
0.18383	0.97670	1.06218	- 28.82		
303 K, NaCl					
0.01398	0.96677	1.06336	−160.05		
0.04896	0.97332	1.03639	−141.22		
0.08393	0.97579	1.05111	−87.62	6.281	−3.108
0.12589	0.97756	1.05706	−52.82		
0.174858	0.97876	1.07656	−28.19		
303 K, KCl					
0.04821	0.98263	1.05443	−240.01		
0.07231	0.98290	1.06487	−196.84		
0.09642	0.98330	1.08155	−132.52	4.665	−2.411
0.12052	0.98517	1.09379	−106.70		
0.14462	0.98592		−81.37		
308 K, LiCl					
0.01305	0.96394	0.90829	−175.11		
0.04569	0.96786	0.91471	−107.52		
0.08505	0.97067	0.92137	−71.78	6.419	−3.119
0.13087	0.97157	0.92823	−38.33		
0.18318	0.97325	0.93587	−24.37		
308 K, NaCl					
0.01395	0.96477	0.96952	−205.02		
0.04886	0.97142	0.94613	−156.94		
0.08369	0.97303	0.95573	−86.29	6.261	−2.957
0.12543	0.97393	0.96265	−44.85		
0.17420	0.97512		−22.36		
308 K, KCl					
0.04800	0.97846	0.89552	−293.53		
0.07208	0.97990	0.91118	−195.14		
0.09610	0.98013	0.92732	−128.86	4.434	−2.314
0.12028	0.98322	0.93389	−113.54		
0.14445	0.98480		−92.67		
313 K, LiCl					
0.01300	0.95838	0.81882	−340.51		
0.04563	0.96646	0.83169	−251.30		
0.08479	0.96770	0.84274	−130.12	6.376	−3.067
0.13040	0.96813	0.86306	−72.52		
0.18281	0.97131	0.89269	−57.19		
313 K, NaCl					
0.01394	0.96390	0.84957	−375.55		
0.04884	0.97103	0.85564	−313.25		
0.08357	0.971585	0.89418	−164.52	6.223	−2.669
0.12536	0.973463	0.90996	−104.95		
0.17394	0.973660	0.94027	−59.71		
313 K, KCl					
0.04791	0.97666	0.83841	−426.72		
0.07186	0.97690	0.85276	−262.02		
0.09597	0.97881	0.87157	−198.50	4.364	−2.184
0.11990	0.98019	0.88391	−155.00		
0.14423	0.98331		−137.96		
318 K, LiCl					
0.01299	0.95230	0.73823	−475.66		
0.04555	0.96472	0.74545	−390.28		
0.08454	0.96489	0.76479	−191.72	6.170	−2.964
0.13005	0.96547	0.76495	−113.61		
0.18248	0.96957	0.79444	−91.86		
318 K, NaCl					
0.01380	0.95396	0.76986	−540.561		
0.04862	0.96669	0.79606	−388.62		
0.08316	0.96692	0.79824	−204.62	5.308	−2.523
0.12477	0.96883	0.80578	−131.84		
0.17318	0.96942	0.82426	−81.34		
318 K, KCl					
0.04779	0.97417	0.73289	−544.48		
0.07167	0.97424	0.75281	−338.04		
0.09559	0.97490	0.79315	−241.05	4.299	−2.105
0.11963	0.97794	0.82595	−203.61		
0.14382	0.98051		−175.02		

(negative dB/dT), suggesting a structure-promoting tendency of alkali metal chlorides. The same conclusion is obtained by determining [d$^2V_\phi^{o}$/dT^2] values as mentioned above. Besides, the positive B values and negative dB/dT values show the absence of a firm layer of solvent mixture around the ion in their cosphere.

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Received for review January 17, 2001. Accepted June 14, 2001.

JE010009W