VISCOSITY AND DENSITY STUDIES OF LICI SOLUTIONS IN AQUEOUS ACETONE AT DIFFERENT TEMPERATURES

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ABSTRACT

Density and viscosity measurements have been made on LiCl solutions in 0, 20, 40, 80 wt. % acetone at 298.15, 303.15 and 308.15 K. The experimental results of viscosity and density have been analysed by using Jones – Dole and Masson equations, respectively. The values of constants A and B of Jones – Dole equation and those of ϕ^0_V and Sv of Masson equation are interpreted in terms of solute – solute and solute – solvent interactions, respectively.

INTRODUCTION

Measurements of viscosity and density of electrolytes in solutions provide an excellent method of obtaining data on solute – solute and solute – solvent interactions. Such investigations in mixed solvents are reported previously ^{1–6}. Lithium salts are used in absorption cooling cycle. Therefore, their behavior in various solvents need detail study of interaction with a solvent molecule. There are no reports available about solute–solvent interaction in LiCl solutions in aqueous acetone. Therefore, attempts have been made to detect preferential solvation of LiCl molecule in mixed aqueous acetone solvent through their density and viscosity studies.

EXPERIMENTAL

Water was distilled over alkaline $KMnO_4$, followed by successive distillations. The electric conductance of distilled water was $7 \times 10^{-1} \text{ S cm}^{-1}$. Acetone (Merck with purity 99.5%) was directly used without further purification. The purity of acetone was checked by comparing the observed density and viscosity with corresponding literature values. The conductivity water and acetone were mixed to give 0, 20, 40, 60 and 80 mass % acetone mixtures, which served as solvent.

LiCl anhydrous (Qualigens, Glaxo, purity 99%) was dried in vaccum at about 90° C. Known masses of the LiCl were dissolved in a particular solvent to give concentrations varying from 0.0769 to 0.03854 M. Each time fresh solution was used. Densities were measured using 15 cm^3 bicapillary pyknometer as described earlier^{8, 9}. The estimated accuracy of density measurements was $\pm 1 \times 10^{-5}$ g.cm⁻³. The viscosity measurements were made using suspended level Ubbalohde viscometer¹⁰ with an accuracy of ± 0.001 mPaS. Pyknometer and viscometer

were calibrated using conductivity water. The air bubble free experimental liquids were filled in pyknometer and viscometer. All the measurements are carried out by clamping pyknometer and viscometer in a transparent water bath maintained at constant temperatures \pm 0.01 K.

RESULTS AND DISCUSSION

The observed densities (ρ) of solutions, which are the mean of the three or four series of many measurements, at 298.15, 303.15 and 308.15 K. are used to calculate apparent molar volumes (ϕ_v) of the salt using equation (1).

$$\phi_{v} = [1000 (\rho_{0} - \rho) / C \rho_{0}] + \rho_{0} \qquad ...(1)$$

where ρ and ρ_0 are densities of solution and solvent, respectively, C is the molarity of solution and M is the molecular weight of solute.

The ϕ_v values have been found to vary linearly with square root of the concentration in conformity with Masson 11 equation (Fig. 1). The limiting apparent molar volume (ϕ^0_v) at infinite dilution is a measure of solute – solvent interaction and slope Sv is a measure of solute – solute interaction. The values of these parameters are listed in Table 1. The positive ϕ^0_v values in all the systems at all temperatures suggested the presence of solute – solvent interactions. The

Table 1. Limiting apparent molar volumes ϕ^o_v , and experimental slopes, S_v , of LiCl in (Acetone + Water) mixture at 298.15, 303.15 and 308.15 K

Wt.% Acetone	298.15 K		303.15 K		308.15 K	
	ф ⁰ _v / cm ³ .mol ⁻¹	Sv / cm ³ .L ^{1/2} mol ^{-3/2}	$\phi^0_{\rm v}$ / cm ³ .mol ⁻¹	Sv / cm ³ .L ^{1/2} mol ^{-3/2}	$\phi^0_{\rm V}$ / cm ³ .mol ⁻¹	Sv / cm ³ .L ^{1/2} mol ^{-3/2}
0	17.194 $(17.1)^{a}$ $(17.00)^{b}$ ± 0.003	$ \begin{array}{c} 1.536 \\ (1.49)^{a} \\ (1.48)^{b} \\ \pm 0.020 \end{array} $	17.674 ± 0.003	1.669 ± 0.020	18.154 $(18.718)^{c}$ ± 0.002	1.889 ± 0.010
20	15.488 ± 0.005	-1.697 ± 0.030	16.101 ± 0.004	-1.285 ± 0.030	16.718 ± 0.003	-0.887 ± 0.020
40	13.827 ± 0.003	- 6.03 ± 0.020	14.458 ± 0.009	- 6.261 ± 0.050	15.090 ± 0.004	- 6.497 ± 0.020
60	12.212 ± 0.006	-7.322 ± 0.030	12.220 ± 0.010	- 6.886 ± 0.060	12.258 ± 0.005	- 6.578 ± 0.030
80	10.625 + 0.008	-8.760 ± 0.050	10.658 ± 0.009	-8.445 ± 0.050	10.702 ± 0.007	-8.188 ± 0.050

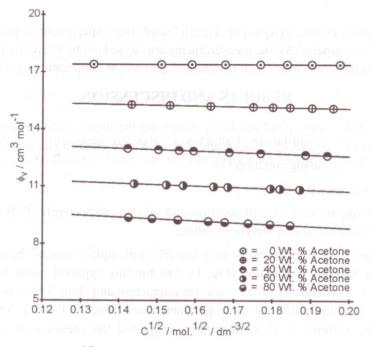


Fig. 1. Plots of ϕ_v versus $C^{1/2}$ of LiCl in different (Acetone + Water) mixtures at 298.15 K

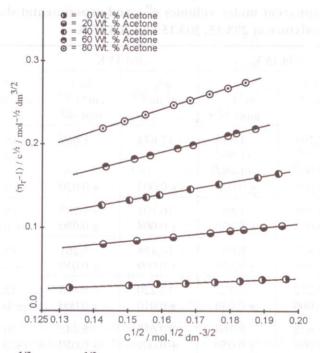


Fig. 2. Plots of (η_r-1) $C^{1/2}$ versus $C^{1/2}$ of LiCl in different (Acetone + Water) mixtures at 298.15 K

change of ϕ^0_v values with change in composition of solvent mixtures has been attributed to variable and preferential solvation of LiCl ions by different species present in the solvent systems. The negative Sv values (except 0% acetone) suggested the absence of solute – solute interaction in aqueous acetone.

The data on viscosity were analysed with the help of well known Jones–Dole equation 12.

$$\eta r = /o = 1 + A C^{1/2} + BC$$
 ...(2)

Where A and B are constants and C is the solute concentration in moles per liter.

The values of A and B constants in this equation have been determined from intercepts and the slopes of the linear plots of η_r –1/C^{1/2} versus C^{1/2} (Fig. 2). These values are presented in Table 2. As expected, all A coefficients are positive indicating solute – solute interaction. The positive B values and negative dB/dT values^{2,13,14} in solutions in aqueous acetone indicate that LiCl acts as solvent structure promoter resulting in strong solute – solvent interaction.

Table 2. Parameters of Jones – Dole equation of LiCl, in (Acetone + Water) mixtures at 298.15, 303.15 and 308.15 K

Wt.% Acetone	298.15 K		303.15 K		308.15 K	
	A	В	A	В	Α	В
	dm ^{3/2} . mol ^{-1/2}	dm ³ mol ⁻¹	dm ^{3/2} . mol ^{-1/2}	dm^3 mol^{-1}	dm ^{3/2} . mol ^{-1/2}	dm ³ mol ⁻¹
0	0.00950	0.13901 (0.143) ^a (0.143) ^b	0.00951	0.14497 (0.1427) ^c	0.00922	0.14298 (0.143) ^a (0.143) ^b
	±0.00400	±0.02000	±0.00300	±0.01000	±0.00300	(0.1431) ±0.02000
20	0.02000 ±0.00001	0.42390 ±0.00007	0.01750 ±0.00003	0.40996 ±0.0020	0.15560 ±0.00002	0.38190 ±0.00010
40	0.02612 ±0.00040	0.71290 ±0.0300	0.02663 ±0.00008	0.69920 ±0.00050	0.02723 ±0.00020	0.68870 ±0.00090
60	0.03087 ±0.00090	0.99480 ±0.00500	0.03156 ±0.00010	0.98020 ±0.00060	0.03270 ±0.00060	0.96760 ±0.00300
80	0.03614 +0.00010	1.28320 ±0.00090	0.03637 ±0.00030	1.26240 ±0.00200	0.03597 ±0.02000	1.24810 ±0.10000

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