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Study of Molecular Interactions of Ternary L-Arginine-Water-1-Ethyl-3-Methylimidazolium Chloride Solutions

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The knowledge of thermodynamic properties of amino acids in aqueous medium can provide valuable information about the stability of proteins. In this study we have reported the density of L-arginine in water and aqueous solution of 1-ethyl-3-methylimidazolium chloride [EMIM][Cl] (0.1, 0.2, 0.3) mol kg^{-1} at (298.15, 303.15, 308.15) K. From this data the apparent molar volume, partial molar volume and partial molar volume of transfer were calculated. The results were used to interpret the concentration and temperature dependence of solute-solute and solute-solvent interactions.

Keywords: Density, Apparent molar volume, L-Arginine, [EMIM][Cl].

INTRODUCTION

Thermodynamic study of the complex structure of proteins is quite difficult [1]. Therefore amino acids as basic units of proteins are used to study the interactions of these macromolecules [2]. From the literature survey, it is suggested that there has been extensive studies done on the volumetric properties of amino acids in aqueous [3-9] and in mixed aqueous solutions [10-18] such as aqueous saccharide solutions [19-24] and aqueous salt solutions. But the studies on the aqueous solutions of ionic liquids have been found to be rare. Ionic liquids [ILs] are generally considered as environmentally acceptable media. The green character of ionic liquids has been justified with their air and water stability, their negligible vapour pressure (in normal temperature and pressure conditions) and their non-flammability [25-29]. The successful use of ionic liquids as solvent has been demonstrated for a wide range of chemical reactions [30] and industrial processes [31]. Thus, ionic liquids are considered as potential substitutes to many traditional solvents. To design the processes involving ionic liquids as solvents, it is necessary to know physical properties of pure salts and the related mixtures.

EXPERIMENTAL

L-Arginine, (purity > 99 %), 1-ethyl-3-methylimidazolium chloride [EMIM][Cl] (purity > 99 %) were procured from S.D. Fine Chemicals and Sigma Aldrich respectively. The L-arginine and [EMIM]Cl were used after drying under vacuum over beads in a vacuum desiccators. The triply distilled water obtained by heating it in $KMnO_4$ was used for all density measurements and all the solutions were made by weight. An electronic single pan five digit analytical balance (Mettler; Model AE-240) with a precision of ± 0.00001 g was used for weighing.

Procedure: All the solutions were prepared with care and stored in special airtight bottles to avoid the exposure of solution to air and evaporation. The possible error in the mole fraction is calculated to be less than $\pm 1 \times 10^{-4}$. The density of solutions was measured using vibrating tube density meter (Model: DMA 4500 M, Anton Paar, Austria) with an uncertainty of ±0.00005 g cm^{-3}. Before each series of measurement, it was calibrated using doubly distilled water and dry air at atmospheric pressure. The temperature was automatically kept constant within ± 0.03 K with the help of in-built peltier system.

RESULTS AND DISCUSSION

The experimental densities and apparent molar volumes of L-arginine in water and aqueous [EMIM][Cl] (0.1, 0.2 and 0.3) mol kg^{-1} as a function of molality of L-arginine at T = (298.15, 303.15 and 308.15) K are given in Table-1.

The apparent molal volumes (ϕ_v) for L-arginine in aqueous and mixed aqueous solution of [EMIM][Cl] at different temperatures was calculated from density using eqn. 1.

TABLE-1
MOLAL CONCENTRATION (m), DENSITY (ρ), APPARENT MOLAR VOLUMES (ϕ_v) OF L-ARGININE IN DIFFERENT COMPOSITIONS OF WATER + [EMIM][Cl] AT DIFFERENT TEMPERATURES

Temp. (K)	Molal conc. (mol Kg^{-1})	Density of solvent (kg m^{-3})	Density of sample (kg m^{-3})	Apparent molar volume × 10^{-6} (m^3 mol^{-1})	Molal conc. (mol Kg^{-1})	Density of solvent (kg m^{-3})	Density of sample (kg m^{-3})	Apparent molar volume × 10^{-6} (m^3 mol^{-1})
	Water				0.1 [EMIM][Cl] + water			
298.15 K	0.025	0.99707	0.99835	159.57	0.025	1.00426	1.0055	160.39
	0.050	0.99707	0.99963	159.37	0.050	1.00426	1.00674	160.19
	0.075	0.99707	1.00091	159.16	0.075	1.00426	1.00798	160.00
	0.100	0.99707	1.00219	158.96	0.100	1.00426	1.00922	159.80
	0.125	0.99707	1.00347	158.76	0.125	1.00426	1.01046	159.60
	0.150	0.99707	1.00475	158.55	0.150	1.00426	1.01171	159.34
	0.175	0.99707	1.00603	158.35	0.175	1.00426	1.01294	159.21
	0.200	0.99707	1.00730	158.20	0.200	1.00426	1.01419	158.97
303.15 K	0.025	0.99568	0.99696	159.72	0.025	1.00345	1.00469	160.48
	0.050	0.99568	0.99824	159.52	0.050	1.00345	1.00593	160.28
	0.075	0.99568	0.99952	159.31	0.075	1.00345	1.00717	160.08
	0.100	0.99568	1.00080	159.11	0.100	1.00345	1.00842	159.79
	0.125	0.99568	1.00208	158.90	0.125	1.00345	1.00966	159.61
	0.150	0.99568	1.00336	158.70	0.150	1.00345	1.01089	159.50
	0.175	0.99568	1.00464	158.50	0.175	1.00345	1.01214	159.24
	0.200	0.99568	1.00592	158.30	0.200	1.00345	1.01339	159.00
308.15	0.025	0.99407	0.99535	159.90	0.025	1.00247	1.00371	160.59
	0.050	0.99407	0.99663	159.69	0.050	1.00247	1.00495	160.39
	0.075	0.99407	0.99791	159.48	0.075	1.00247	1.00619	160.19
	0.100	0.99407	0.99919	159.28	0.100	1.00247	1.00743	160.00
	0.125	0.99407	1.00047	159.08	0.125	1.00247	1.00867	159.80
	0.150	0.99407	1.00175	158.87	0.150	1.00247	1.00991	159.60
	0.175	0.99407	1.00303	158.67	0.175	1.00247	1.01116	159.35
	0.200	0.99407	1.00431	158.47	0.200	1.00247	1.01242	159.06
	0.2 [EMIM][Cl] + water				0.3 [EMIM][Cl] + water			
298.15	0.025	1.01164	1.01284	161.15	0.025	1.02059	1.02175	161.68
	0.050	1.01164	1.01407	160.36	0.050	1.02059	1.02295	160.73
	0.075	1.01164	1.0153	159.98	0.075	1.02059	1.02414	160.41
	0.100	1.01164	1.01652	159.78	0.100	1.02059	1.02535	159.97
	0.125	1.01164	1.01774	159.59	0.125	1.02059	1.02653	159.86
	0.150	1.01164	1.01896	159.40	0.150	1.02059	1.02774	159.53
	0.175	1.01164	1.02018	159.21	0.175	1.02059	1.02897	159.13
	0.200	1.01164	1.0214	159.02	0.200	1.02059	1.03019	158.84
303.15	0.025	1.01059	1.01179	161.26	0.025	1.01932	1.02048	161.83
	0.050	1.01059	1.01302	160.48	0.050	1.01932	1.02166	161.26
	0.075	1.01059	1.01425	160.09	0.075	1.01932	1.02287	160.55
	0.100	1.01059	1.01548	159.80	0.100	1.01932	1.02409	160.01
	0.125	1.01059	1.01671	159.55	0.125	1.01932	1.0253	159.69
	0.150	1.01059	1.01793	159.38	0.150	1.01932	1.02648	159.61
	0.175	1.01059	1.01915	159.21	0.175	1.01932	1.02769	159.33
	0.200	1.01059	1.02036	159.08	0.200	1.01932	1.02888	159.17
308.15	0.025	1.00941	1.01061	161.40	0.025	1.01791	1.01906	162.38
	0.050	1.00941	1.01184	160.61	0.050	1.01791	1.02025	161.42
	0.075	1.00941	1.01307	160.22	0.075	1.01791	1.02145	160.84
	0.100	1.00941	1.0143	159.93	0.100	1.01791	1.02265	160.46
	0.125	1.00941	1.01554	159.60	0.125	1.01791	1.02384	160.24
	0.150	1.00941	1.01676	159.45	0.150	1.01791	1.02505	159.89
	0.175	1.00941	1.01797	159.34	0.175	1.01791	1.02624	159.71
	0.200	1.00941	1.01919	159.16	0.200	1.01791	1.02743	159.52

$$\phi_v = \frac{M}{\rho_0} + \frac{1000(\rho - \rho_0)}{m\rho\rho_0} \quad (1)$$

where M is the molecular weight of solute, ρ_0 and ρ refer to the densities of solvent and solution, respectively and m is the concentration of L-arginine expressed usually as molality. The data has been used to study the effect of temperature and [EMIM][Cl] concentration on solute-solvent interactions occurring in the ternary mixture of present study. The following linear regression was carried out using the following equation:

$$\phi_v = \phi_v^0 + S_v m \quad (2)$$

where ϕ_v^0 is the partial molal volume at infinite dilution or limiting apparent molal volume which is a measure of solute-solvent interactions, S_v is the experimental slope, also known as volumetric pair wise interaction coefficient [32,33], represents

TABLE-2
PARTIAL MOLAR VOLUMES (ϕ^0_v), EXPERIMENTAL SLOPES (S_v) AND TRANSFER VOLUMES (ΔV^0_{tr}) OF L-ARGININE IN WATER AND [EMIM][Cl] + WATER MIXTURES AT DIFFERENT TEMPERATURES

Temp. (K)	[EMIM][Cl] + Water	$\phi^0_v \times 10^6$ (m^3 mol^{-1})	$S_v \times 10^6$ (m^3 Kg^{-1} mol^{-1})	ΔV^0_{tr} (m^3 mol^{-1})
298.15	0 (water)	160.4552 (± 0.085)	-0.04977 (± 0.002)	–
	0.1	161.3005 (± 0.109)	-0.05046 (± 0.003)	0.8453
	0.2	162.0411 (± 0.162)	-0.06949 (± 0.004)	1.5859
	0.3	163.0009 (± 0.171)	-0.09258 (± 0.005)	2.5457
303.15	0 (water)	160.6316 (± 0.097)	-0.05087 (± 0.002)	–
	0.1	161.4084 (± 0.107)	-0.05195 (± 0.003)	0.7768
	0.2	162.2350 (± 0.165)	-0.07412 (± 0.004)	1.6034
	0.3	163.2743 (± 0.204)	-0.09608 (± 0.006)	2.6427
308.15	0 (water)	160.8087 (± 0.098)	-0.05105 (± 0.002)	–
	0.1	161.5550 (± 0.145)	-0.05270 (± 0.004)	0.7463
	0.2	162.4077 (± 0.170)	-0.07625 (± 0.005)	1.5990
	0.3	163.6814 (± 0.201)	-0.09708 (± 0.006)	2.8727

a measure of solute-solute interaction. The observed values of partial molar volume (ϕ^0_v) and the experimental slopes are given in Table-2.

It is generally observed that the partial molar volume increases with increase in temperature and also with increase in [EMIM][Cl] concentration. As ϕ^0_v reflects the presence of solute-solvent interactions and it can be seen from the Table-2 that ϕ^0_v values are positive for the reported amino acid indicating strong solute-solvent interactions and these interactions further increases with the increase in temperature and concentration of [EMIM][Cl] indicating that the solute-solvent interactions are strengthened with temperature and increase in concentration of [EMIM][Cl]. This may be caused by the reduced electrostriction of water due to (NH_3^+) and (COO^-) groups of the amino acid. The same observations have been shown by other authors [34,35] for amino acids in aqueous electrolyte solutions.

On the other hand S_v values for the reported amino acid is showing negative behaviour indicating weak solute-solute interactions and these interactions are further weakened with increase in concentration of [EMIM][Cl] as well as temperature, thereby showing a regular trend in S_v values. The partial molar volume of transfer from water to aqueous [EMIM][Cl] were calculated by using the following equation:

$$\Delta V^0_{tr} = \phi^0_{v\,(\text{mixed solvent})} - \phi^0_{v\,(\text{in water})} \quad (3)$$

The calculated values of partial molar volume of transfer at infinite dilution are given in Table-2.

The partial molar volume at infinite dilution of a non-electrolyte is a combination of two factors:

$$V^0_{2,m} = V_{int} + V_s \quad (4)$$

where V_{int} is the intrinsic molar volume of the non-hydrated solute and V_s is the contribution due to the interaction of the solute with water. V_{int} is made up of following type of contribution [36,37].

$$V_{int} = V_{vw} + V_{void} \quad (5)$$

where V_{vw} is the vander Waals volume [38] and V_{void} is the volume associated with the voids and empty space present therein [39]. This equation was later modified to evaluate the contribution of a solute molecule to its partial molar volume at infinite dilution as:

$$V^0_{2,m} = V_{vw} + V_{void} - n\sigma_s \quad (6)$$

where σ_s is the shrinkage in the volume caused by the interaction of hydrogen bonding sites present in the solute with water molecules and n is the number of hydrogen bonding sites in molecule. The $V^0_{2,m}$ of amino acids can be written as:

$$V^0_{2,m} = V_{vw} + V_{void} - V_{shrinkage} \quad (7)$$

By assuming that V_{vw} and V_{void} having same magnitude in water and aqueous [EMIM][Cl] the positive values of ΔV^0_{tr} are due to the increase in $V_{shrinkage}$ values.

Further ΔV^0_{tr} values can be explained on the basis of cosphere overlap model [40,41] in terms of solute-cosolute interactions. According to this model, ionic-hydrophilic and hydrophilic-hydrophilic group interactions contribute positively, whereas hydrophilic-hydrophobic and hydrophobic-hydrophobic interactions contribute negatively to ΔV^0_{tr} values. The positive values of ΔV^0_{tr} of L-arginine in aqueous [EMIM][Cl] solution indicate that the former types of interactions are predominant over the latter.

Conclusion

Partial molar volumes of L-arginine have been determined in water and [EMIM][Cl]-water solutions at different temperatures and concentrations of [EMIM][Cl]. From this study it is observed that partial molar volumes increase with increase in temperature and also with increase in [EMIM][Cl] concentrations. All these parameters support strong solute-solvent interactions in the ternary mixture of present study.

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