

Full Paper

Effect of L-Arginine on Electrical Conductances of Aqueous Ionic Liquids 1-Alkyl-3-methylimidazolium Bromide Solutions at $T = 298.15$ K

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Abstract- Electrical conductances of aqueous ionic liquids, 1-propyl-3-methylimidazolium bromide, 1-butyl-3-methylimidazolium bromide, 1-pentyl-3-methylimidazolium bromide, 1-hexyl-3-methylimidazolium bromide solutions in dilute region in the presence of amino acid, L-arginine, have been measured at $T = 298.15$ K. The ion association constants, K_A , limiting molar conductivities, Λ_0 , and distance parameters, R were obtained using low concentration Chemical Model (lcCM) conductivity equation for the investigated ionic liquids. The results show that the K_A value and limiting molar conductivity, Λ_0 decrease with increasing L-arginine concentration and lengthening alkyl chain of ionic liquids. Therefore, there is slight ion association effect in [HMIm]Br. This can be attributed to the interaction of [RMIm]Br with the amino acids and increasing viscosity of mixture.

Keywords- Electrical conductance, Ionic liquids, L-arginine, Ion association constant

1. INTRODUCTION

L-Arginine is classified as a conditionally essential amino acid and used in food, beverage, and dietary supplement applications. This amino acid, the natural precursor of NO, is infused in patients to restore endothelial function. However, it also has a number of NO-independent properties, such as the ability to regulate blood and intracellular pH and the effect on the depolarization of endothelial cell membranes. It has antihypertensive and

antioxidant properties, and it influences on blood viscosity and the coagulation / fibrinolysis system. L-Arginine inhibits the development of spontaneous, transplantable solid tumors and chemically induced mammary tumors [1-4].

Interaction of L-arginine with their surrounding environment plays an important role in their conformational characteristics. The study of these interactions provides an important insight into the conformational stability and unfolding behavior of globular proteins. Ionic liquids as a new class of chemical compounds with the unique property such as excellent solvation ability, high thermal stability, broad liquid temperature range and negligible vapor pressure [5-6] are investigated widely. These organic electrolytes played the important role in various fields such as synthesis, biology, catalysis, separation, and electrochemistry. They have large effects on the structural and properties of amino acids including their solubility, denaturation, dissociation into subunits, and the activity of the enzymes. Recently, the effect of ionic liquids as additives on the separation of amino acids in HPLC [7], performance of CO₂ absorption in mixed aqueous solution of amino acid and ionic liquids [8], and as novel solvent additives to separate peptides [9] have been investigated. Therefore, it is necessary to study conductometric properties of amino acids in aqueous ionic liquid solutions which can provide important information about solute-solute and solute-solvent interactions occurring in this type of mixtures. Conductometry is an electrochemical technique, which provides us most precise data and valuable information concerning ion association and ion solvation behavior in solution, and character of the ion-pair [10-12].

In this work, molar conductivities, Λ of aqueous ionic liquids, 1-alkyl-3-methylimidazolium bromide (R = propyl, butyl, pentyl, and hexyl), [RMIm]Br solutions in the presence of amino acid, L-arginine have been measured at 298.15 K. The experimental conductivity data have been analyzed by means of the low concentration Chemical Model (lcCM) conductivity equation [12] and the ion association constant, K_A , limiting molar conductivity, Λ_0 , and distance parameter, R have been obtained for the investigated systems. All these parameters were used to interpretation of solute-solute and solute-solvent interactions occurring between the various components of in these ternary mixtures.

2. EXPERIMENTAL

The chemicals used in this work were N-methylimidazole (>99%), 1-bromopropane (>99%), 1-bromobutane (>99%), 1-bromopentane (>99%), 1-bromohexane (>99%), L-arginine (>99 %), ethyl acetate (GR, >99.8 %) and toluene (>99 %) in mass fraction obtained from Merck. N-methylimidazole was distilled at reduced pressure and L-arginine was dried in vacuum over blue silicagel at room temperature for at least 72 h. The other reagents were used without further purification. The doubly distilled water with specific conductivity less than 0.7 $\mu\text{S}\cdot\text{cm}^{-1}$ was freshly used for preparation of solutions.

The ionic liquids, 1-alkyl-3-methylimidazolium bromide, [RMIm]Br were synthesized and purified according to standard procedures described in the literature [13,14]. Briefly, these ionic liquids were synthesized by direct alkylation of N-methylimidazole, 0.05 moles (freshly distilled) with an excess of 1-bromoalkane, 0.06 moles was added dropwise over 1 h into vigorously stirring of N-methylimidazole in a two-necked round bottom flask in ice bath. Then mixture, already turbid, was refluxed for 48-72 h under a nitrogen atmosphere. The crude product was decanted from hot solution in a separator funnel, washed twice with 50 ml ethyl acetate. The product was dried in at 343 K using a rotary evaporator for at least 4 h at reduced pressure (0.7 kPa) which was used after high vacuum desiccated (0.1 Pa) for at least 24 h to remove trace amount of moisture. Water contents found by Karl Fischer method in ionic liquids was less than mass fraction 0.1 %. The obtained ionic liquids have purity greater than mass fraction 0.99 % mass fraction. Ionic liquids were analyzed by ^1H NMR (Bruker Av-300) and IR (Buck Scientific) spectra to confirm the absence of any major impurities and they were found to be in good agreement with those reported in the literature [13, 14].

Electrical conductance measurements were carried out on a digital conductivity meter (Metrohm, 712) with a sensitivity of 0.1% and a dipping type conductivity cell with platinized electrodes with a cell constant of 0.95 cm^{-1} under nitrogen atmosphere and at a frequency of 1 MHz. The conductivity meter was calibrated with a 0.01 molar aqueous KCl solution. About 50 ml of pure solvent was placed in the conductivity cell and closed. All solutions were made up by weight and with an analytical balance (Sartorius) with precision $\pm 1 \cdot 10^{-4}$ g. Weighed pure ionic liquid was added with a syringe to the cell containing solvent. Circulating water from a thermostatically regulated bath around the sample holder with double wall to maintain the temperature with an uncertainty 0.02 K. The measured specific conductivities of ionic liquid solutions were always corrected for the contribution of the pure solvent.

3. RESULTS AND DISCUSSION

The measured molar conductivities, Λ of the aqueous solutions of ionic liquids as functions of molar concentration, c of ionic liquids at different concentration of L-arginine are given in Table 1.

Table 1. Molar conductivities (Λ) of aqueous solutions of [RMIm]Br as a function molar concentrations (c) of ionic liquid in different mass of L-arginine at 298.15 K

c $m = 0.0000$	Λ	c $m = 0.5$	Λ	c $m = 1$	Λ	c $m = 1.5$	Λ
[PMIm]Br + water							
1.0734	143.43	0.4683	111.04	0.5804	103.54	0.4623	97.99
2.1264	142.29	1.0950	108.86	1.1538	99.84	0.9840	97.86
4.2459	138.06	1.5426	107.48	1.8050	95.40	1.5784	97.44
6.7551	134.22	2.4035	106.35	2.4491	92.11	2.6021	96.42
8.9840	131.49	3.4021	105.14	3.6241	88.60	3.6060	95.95
12.3069	127.75	5.3303	103.11	4.9549	86.12	5.3694	94.74
16.9083	122.62	7.6925	100.96	7.0500	82.42	7.2582	93.67
21.3115	118.73	10.0615	98.94	9.1240	78.47	9.1339	92.74
27.0068	113.83	13.0297	96.74	11.3112	72.30	11.0293	91.76
32.8868	109.35	15.5433	94.99	13.2861	69.98	12.7861	90.97
40.1684	104.67	18.5598	93.29			14.5428	90.08
48.2294	99.92					16.8280	89.26
[BMIm]Br + water							
0.5200	121.91	0.3875	91.87	0.6074	90.71	0.5810	82.45
1.6540	114.16	0.6282	91.68	1.1648	89.46	1.1152	82.23
2.9384	107.24	0.9864	91.44	1.7158	88.41	1.6694	81.94
4.3794	106.75	1.7497	90.70	3.0184	86.70	2.8914	81.27
6.7163	103.84	2.5247	89.95	4.3084	85.48	4.1936	80.55
9.9554	102.18	3.8517	88.35	6.1495	84.10	5.4089	80.01
12.4113	101.13	5.0847	87.24	8.0719	83.36	6.9715	79.52
15.3434	99.27	6.4292	86.31	9.9443	82.35	8.7077	79.02
18.2881	97.56	8.1849	85.39	11.8918	81.53	10.5774	78.27
21.4645	95.61	10.0638	84.14	13.8331	80.86	12.6475	77.40
26.1259	93.06	12.2186	83.12	15.9309	80.07	14.8311	76.79
30.0604	91.02	13.9155	82.40	18.4922	79.09	15.4922	76.61
[PnMIm]Br + water							
0.4520	118.05	0.3977	99.08	0.5516	96.81	0.6064	93.83
0.8125	116.24	0.898	98.80	0.9727	96.54	1.0496	93.27
1.7396	114.95	1.4822	98.10	1.3878	96.19	1.6269	92.45
2.7811	112.28	2.4643	97.51	2.7698	95.39	2.8281	91.55
4.1431	110.85	3.6693	96.75	3.9144	94.71	4.0818	90.87
5.5794	108.66	5.5732	95.37	5.6581	93.49	6.0177	89.67
8.2175	105.59	8.0254	94.18	8.5050	92.02	7.8486	88.79
11.0673	102.42	10.5378	92.79	11.1739	90.57	10.5310	87.97
13.8256	99.78	13.0563	91.97	13.9378	89.47	13.2020	86.76
17.2992	96.62	16.4726	90.26	17.1167	88.22	15.9539	86.09
21.5739	92.87	19.4730	89.24	20.4025	86.99	18.6070	85.20
24.9616	90.44	23.2026	83.36	23.0358	86.13	22.0123	84.29
						25.3070	83.39

Continued Table 1

[HMIm]Br + water							
0.4273	110.77	0.4372	88.29	0.4971	78.46	0.6388	73.57
1.0960	109.08	1.0003	83.37	0.9649	77.52	1.2852	73.14
1.7338	107.77	1.4894	81.64	1.4327	76.53	1.8639	72.69
3.1828	105.74	2.7046	80.12	1.9591	75.09	2.5177	72.33
4.6132	104.43	3.9420	78.92	3.0482	73.88	3.2167	71.78
6.91044	102.40	5.6685	77.67	4.1740	73.26	4.4868	70.94
10.1366	100.06	7.4691	76.80	5.9430	72.64	6.6287	69.74
13.2574	98.08	9.4698	75.86	7.7851	72.33	7.9891	69.36
16.5640	96.13	12.0113	74.01	10.2704	71.49	9.9957	68.79
19.8211	94.16	14.5381	72.77	12.8143	70.69	11.9723	68.33
23.0905	92.34	17.0352	71.67				
29.9391	82.01						

Figure 1 shows the dependence of the molar conductivity, Λ on the molar concentration c of aqueous solutions of [PnMIm]Br at $T = 298.15$ K. It is observed that molar conductivity, Λ decreases with the increasing amount of ionic liquid at each concentration of L-arginine. At increasing concentrations of ionic liquid, ion association, relaxation and electrophoretic effects occur between the anion and cation of ionic liquid, thus resulting in more aggregates of the ionic liquid dispersed in water. The plot of molar conductivities, Λ versus square root of ionic liquid concentration, $c^{1/2}$ is not linear at various concentrations of L-arginine (as shown in Figure 1) for aqueous solutions of [PnMIm]Br, which indicating interactions of ions with each other and thus Λ_0 , can not be determined by extrapolation of molar conductivities, Λ versus square root of ionic liquid concentration ($c^{1/2}$) to $c = 0.0 \text{ mol.dm}^{-3}$. Therefore, other equations are needed for determination of Λ_0 values.

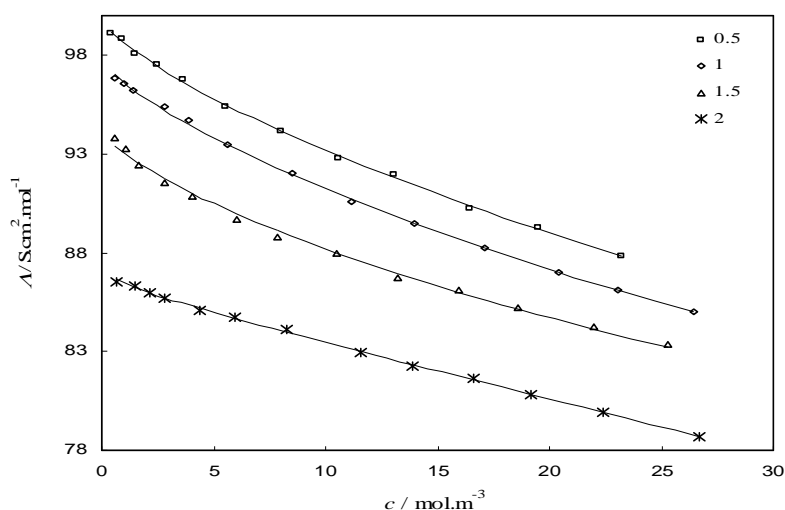


Fig. 1. Molar conductivity of [PnMIm]Br in different mass of aqueous L-arginine solutions; □, 0.5 g ; ◇, 1.0 g ; △, 1.5 g ; *, 2.0 g at 298.15 K

There are many different equations for the analysis of the conductance data depending on the precision required, which are preferred by authors for the treatment of conductance data. The low concentration chemical model (lcCM) of conductivity equation is widely recently applied for the correlation of conductance data in aqueous and nonaqueous electrolyte solution [12]. The conductivity equation of the lcCM is the Fuoss–Onsager type equation for a given set of conductivity values, three adjustable parameter, the limiting molar conductivity, Λ_0 , the ion association constant, K_A , and the distance parameter, R , are defined from the analysis of conductivity data based on this model as the following set of equations.

$$\Lambda = \alpha[\Lambda_0 - S(c\alpha)^{1/2} + Ec\alpha \ln(c\alpha) + J_1c\alpha + J_2(c\alpha)^{3/2}] \quad (1)$$

$$K_A = \frac{1-\alpha}{\alpha^2 c \gamma_{\pm}^2} \quad (2)$$

$$\ln \gamma_{\pm} = -\frac{\kappa q}{1 + \kappa R} \quad (3)$$

where

$$\kappa^2 = \frac{16 \times 10^3 N_A z^2 e^2 \alpha c}{\varepsilon_0 \varepsilon k_B T} \quad (4)$$

$$q = \frac{z^2 e^2}{8\pi \varepsilon_0 \varepsilon k_B T} \quad (5)$$

where Λ and Λ_0 are the molar conductivities at molarity, c and infinite dilution, α is the fraction of oppositely charged ions acting as ion pairs, K_A , R and γ_{\pm} are the ion association constant of ionic liquids, distance parameter, and the corresponding mean activity coefficient of the free ions, respectively. The coefficients of equation (1) reflect the relaxation and electrophoretic effects. In equation (1), S the coefficient of the Debye-Hückel-Onsager, and E depends only on the properties of the solvent and the charge on the ions, while J_1 and J_2 depend on the same parameters but also on the distance parameter, R . The rest quantities have the usual meaning [12]. Three-parameter fits of molar conductivity data yield the ion-association constant K_A , the limiting molar conductivity Λ_0 , and distance parameter R , by non-linear least-squares iteration. The calculation are made by finding the values Λ_0 , K_A , and R that minimized the standard deviation $\sigma(\Lambda)$. The standard deviation of the measured molar conductivities Λ_{exp} and the calculated one Λ_{calc} was computed as follows:

$$\sigma(\Lambda) = \left(\sum [\Lambda_{exp} - \Lambda_{calc}]^2 / (n - p) \right)^{1/2} \quad (6)$$

where n and p show the number of the experimental data and parameters, respectively. The values of K_A , Λ_0 and R obtained by this procedure are summarized in Table 2.

Table 2. Ion association constant (K_A), limiting molar conductivity (Λ_0), distance parameters (R), and standard deviations ($\sigma(\Lambda)$) of [RMIm]Br in aqueous L-arginine solutions at 298.15 K

$^a m$	K_A	Λ_0	$10^{10} \cdot R$	$\sigma(\Lambda)$
[PMIm]Br + water				
0.0000	13.36	146.76	10.85	0.25
0.0431	12.95	111.10	2.77	0.52
0.0882	11.23	101.74	25.58	2.79
0.1230	6.35	98.99	9.27	0.13
[BMIm]Br + water				
0.0000	13.36	132.76	9.23	0.29
0.0429	9.59	92.81	1.34	0.22
0.0845	9.03	90.57	2.31	0.63
0.1196	4.94	83.21	8.97	0.09
[PnMIm]Br + water				
0.0000	15.33	118.56	11.94	0.33
0.0467	6.44	99.90	7.40	0.12
0.0876	7.99	94.76	7.76	0.25
0.1789	2.74	87.31	10.53	0.82
[HMIm]Br + water				
0.0000	17.09	112.78	8.96	0.55
0.0430	15.35	109.40	15.14	2.42
0.0844	7.39	77.69	0.22	0.87
0.1295	5.96	74.15	0.70	0.29

^a m = molality of L-arginine

Some features can be concluded from the ion association constant K_A values listed in Table 2. Effect of alkyl chain length on conductivity data ionic liquids [RMIm]Br (R= Propyl, Butyl, Pentyl and Hexyl). The results in Table 2 show that decrease the molar conductivity values with increasing alkyl chain of [RMIm]⁺ cation. This can be ascribed to the facts that (i) with the increasing concentration of amino acids, the dielectric constant of mixture decrease and electrostatic attraction between the ions increases, and hence the ions in the free state decrease; (ii) the increased size of ions caused by possible association of [HMIm]Cl and amino acid reduces the ionic mobility; (iii) with the increase in microscopic viscosity of mixtures, the mobility of ions decrease.

The calculated interaction energy for 1-alkyl-3-methylimidazolium based ionic liquids (alkyl = ethyl, propyl, and butyl) using ab initio calculation decreases with increasing alkyl chain of cation, and anion size in the order [BF₄]⁻ > [PF₆]⁻ = [NTf₂]⁻. These results are in agreement from those observed for this study. Therefore, the ion pair formation of 1-alkyl-3-methylimidazolium cation with small anion are remarkable and other hand, there is low

sensitivity to alkyl chain length of ionic liquid. This conclusion has been also observed in our earlier papers using other technique [15,16].

As can be seen in Table 2, K_A values decrease at higher concentration of L-arginine. This shows that ion association in ionic liquid solutions decreases with increasing amino acid content and thus ion-solvent interactions decreases. The limiting molar conductivity values Λ_0 , are recorded in Table 2. The Λ_0 values decrease in the order [HMIm]Br < [PnMIm]Br < [BMIm]Br < [PMIm]Br at experimental temperature, indicating that the size effect of cation on the Λ_0 values are in reverse and the Λ_0 values of studied ionic liquids increase as the L-arginine content increases since the mobility of free ions is increased. R values reflect the most probable separation between the ions in the ion-pair and are not very close to the sum of the ionic radii in the crystal. The distance parameter, R values for all of ionic liquids solutions under study are also reported in Table 2. As seen from this table, no systematic trend in R values for the ionic liquids solution has been observed.

4. CONCLUSION

Molar conductivities of aqueous solutions of ionic liquids, 1-propyl-3-methylimidazolium bromide, [PMIm]Br, 1-butyl-3-methylimidazolium bromide, [BMIm]Br, 1-pentyl-3-methylimidazolium bromide, [PnMIm]Br, and 1-hexyl-3-methylimidazolium bromide, [HMIm]Br in the presence of L-arginine have been reported at $T = 298.15$ K. The ion-association constants, K_A , limiting molar conductivities, Λ_0 and distance parameters, R were calculated from low concentration Chemical Model (lcCM) conductivity equation. The evaluation of the results has been discussed in terms of the ion-association and ion-solvation between the ions of the ionic liquids and L-arginine. The conductometric studies show that the values of Λ_0 and K_a of these ionic liquids in aqueous amino acid solutions decrease with increasing amino acid content in solutions. This is due to increasing medium viscosity with increasing amino acid concentration and attraction between ionic liquid and amino acid, and hence presolvation of ions by amino acid molecule, causing an increase of hydrodynamic radii of ions and a decrease of their mobility.

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