Regular Article

Conductometric Analysis of some Ionic Liquids, 1-Alkyl-3-methylimidazolium Bromide with Aspirin in Acetonitrile Solutions

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In recent years, ionic liquids have been used in pharmaceutical processes. Therefore, having a deep insight into the ion association behavior of ionic liquids in the presence of a drug is of particular importance. So, in this work, the molar conductivities of the ionic liquids, 1-alkyl-3-methylimidazolium bromide, $[C_nMIm]Br$ (n = 4, 6 and 8) in various concentrations of aspirin (ASA) in acetonitrile (MeCN) solutions are determined in very diluted region of ILs, (molality less than 0.01 mol kg^{-1}) and at 298.15 K. The obtained conductivity data were analyzed by low concentration Chemical Model (lcCM) of conductance equation. Using this model the limiting molar conductivities (Λ_0) and ion association constants (K_A) were calculated. The results show that the Λ_0 and K_A values of ionic liquid are affected by the alkyl chain length of cation and the concentration of ASA. The values of Λ_0 and K_A decrease as the alkyl chain length of cation and ASA concentration increase. The K_A was also used to calculate the standard Gibbs energy (ΔG_A^0) of ion-pairing association. In general, 1-butyl-3-methylimidazolium bromide, [BMIM]Br, has the low values of ion-pair formation and the high negative values of ΔG_A^0 and stronger interaction between [BMIM]Br and ASA.

Keywords: Ionic liquids, ASA, Molar conductivity, Ion associations constant, Low concentration, Chemical model (lcCM)

INTRODUCTION

Aspirin, as an active ingredient in acetylsalicylic acid (ASA), is a medication often used to relieve pain, fever and inflammation [1]. It is one of the water poor soluble drugs (0.33 g in 100 ml at *T* = 298.15) which is feasibly hydrolyzed in the presence of moisture; no wonder that there is no another solvent as important as acetonitrile (MeCN) in the pharmaceutical [2,3]. Poor solubility of ASA in water can dramatically reduce its bioavailability [4]. Various approaches have been employed to improve the oral bioavailability such as size reduction, salt formation, co-solventcy and solid dispersion, though some of these methods are not always applicable [5-8].

Recently to overcome these problems, ionic liquids have been suggested as a new class of organic salts in pharmaceutical with a melting point around or below room

temperature [9-14]. They have many interesting features like, low vapour pressure, high electrical conductivity, non-flammability and favourable solvating properties for a range of polar and non-polar compounds [15-19]. They are also applied in multidisciplinary sciences such as electro-chemistry, separation processes, synthesis and specially in pharmaceutical industrial [20].

Analyzing the interactions between a drug and ionic liquid (IL) would be a prerequisite factor evaluate the drug solubility in it. In this respect, there are some reports concerning the qualitative and quantitative analyses of dominant molecular interactions between ionic liquid and drug probed by electrical conductance [23]. Using the conductometric analysis we can provide the valuable information about the ion association and ion solvation of the electrolytes [24]. For example, addition of ASA strongly affects the value of ion association and molar conductivity of ILs. Interactions between ions and solute cause to increase the distance between cation and anion. Importance

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of molar conductivity and ion association of ionic liquid has been a motivation for the extensive research efforts on the conductometric analysis of the ionic liquids, mostly in water or other molecular solvents for a wide range of IL concentrations. Results show that the cation and anion types of ionic liquids highly affect the ion association and limiting molar conductivities of ILs [25-34]. Despite the applications of ionic liquids in pharmaceutical, the number of studies on the thermophysical properties of ionic liquid in the presence of drug is very limited.

Recently in our laboratory, thermophysical properties including density, speed of sound and molar conductivity of acetaminophen in the aqueous solutions of ionic liquid, 1-hexyl-3-methylimidazolium bromide have been studied. The results show that acetaminophen would be acting as a structure breaker in water and this behavior will be weakened with increasing ionic liquid concentration [35].

In continuation of our systematic thermodynamic investigation of drug in the ionic liquid solutions, in this work, the electrical conductance of some imidazolium based ionic liquid with bromide anion, $[C_nMIm]Br$ (n = 4, 6 and 8), in several molality (0.05, 0.10, 0.15 and 0.2) mol kg^{-1} of aspirin (ASA) in MeCN solutions is investigated in a very diluted region of ILs, (molality less than 0.01 mol kg^{-1}) and at 298.15 K. The obtained data are used to calculate the ion association constant (K_A), limiting molar conductivity (Λ_0), Walden product ($\Lambda_0\eta$) and distance parameter (R) using the low concentration Chemical Model (lcCM). Gibbs free energy of ion pair formation (ΔG_A^0) is also estimated using the K_A values.

EXPERIMENTAL

Chemicals

N-methylimidazole, 1-bromobutane, 1-bromohexane, 1-bromooctane, ethyl acetate, acetyl salicylic acid (ASA) and acetonitrile (MeCN) were purchesed from Merck. A sample description of the used chemicals is provided in Table 1. All of the purities are given in mass percentage.

Synthesis of the Ionic Liquids

1-Alkyl-3-methylimidazolium bromide ([C_nMIm]Br, n = 4, 6, 8) was synthesized according to the procedure described in literatures [36-37], by direct alkylation of *N*-methylimidazole with an excess amount of 1-haloalkane in a round bottom flask mixed by a magnetic stirrer under a nitrogen atmosphere. The mixing of the chemicals was performed at first under ice-cooling, and then after rising the temperature to room temperature. The temperature was gradually increased over a period of time (several hours) to a final reaction temperature of about 50 °C and kept constant until the end of the reaction. The reaction mixture was stirred for one week. Finally, the crude product was separated from reagents and then washed three times with fresh ethylacetate. The removal of residual volatile compounds from the ionic liquid was carried out in high vacuum at 75 °C using a rotary evaporator for at least 4 h at the reduced pressure. The obtained ionic liquid was verified by ^{1}H NMR spectroscopy. ^{1}H NMR spectra of [BMIm]Br, [HMIm]Br and [OMIm]Br are provided in the supporting information as Figs. S1, S2 and S3, respectively. The details of NMR chemical shifts along with the assigned protons are as follows: [BMIm]Br: ^{1}H NMR (400 MHz, CDCl$_3$): δppm = 0.91 (3H, t, but-CH$_3$), 1.34 (2H, m, CH$_2$), 1.86 (2H, m, CH$_2$), 4.08 (3H, s, NCH$_3$), 4.29 (2H, t, NCH$_2$), 7.46 (1H, s, NCH), 7.58 (1H, s, NCH), 10.30 (1H, s, NCHN). [HMIm]Br: ^{1}H NMR (400 MHz, CDCl$_3$): δppm 0.804 (t, 3H; CH$_3$), 1.250 (m, 6H, CH$_2$CH$_2$CH$_2$), 1.837 (m, 2H; CH$_2$), 4.074 (s, 3H, N-CH$_3$), 4.243 (t, 2H, NCH$_2$), 7.464 (t, 1H; N-CH=C), 7.633 (t, 1H, NCH= C), 10.288 (s, 1H, N-CH=N). [OMIm]Br: ^{1}H NMR (400 MHz, CDCl$_3$): δppm = 0.853 (t, 3H, CH$_3$), 1.251 (m, 10H, CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 1.905 (m, 2H, CH$_2$), 4.145 (s, 3H, N-CH$_3$), 4.311 (m, 2H, N-CH$_2$), 7.465 (t, 1H, N-CH=C), 7.642 (t, 1H, N-CH=C), 10.408 (s, 1H, N-CH=N). The ionic liquids were used after vacuum desiccated for at least 48 h to remove trace amount of moisture. Water content found by Karl Fischer method in the ionic liquids was less than 0.3%.

Apparatus and Procedure

Density and viscosity measurements. The sample densities were measured with a vibrating tube densimeter (Anton Paar, DSA 5000 densimeter and speed of sound analyzer), calibrated with dried air and doubly distilled water at atmospheric pressure. Density is extremely sensitive to temperature, so it was kept constant within ±1.0 × 10^{-3} K using the Peltier technique built in densimeter.

Table1. Sample Description Table of the Chemicals Used

Chemical name	CAS No.	Provenance	Mass fraction purity
Aspirin	56-40-6	Merck	>0.998
N-methylimidazole	210-484-7	Merck	≥0.99
Bromobutane	109-65-9	Merck	≥0.980
Bromohexane	111-25-1	Merck	≥0.980
Bromooctae	111-83-1	Merck	≥0.980
Ethyl acetate	141-78-6	Merck	≥0.998
[BMIm]Br	-	Synthesized	0.980
[HMIm]Br	-	Synthesized	0.980
[OMIm]Br	-	Synthesized	0.980

Table 2. Densities (*d*) and Viscosities (*η*) ASA in MeCN Solutions at *T* = 298.15 K

m (mol kg^{-1})	$10^3 d$ (kg m^{-3})	η (mPa s)
0.0523	0.790608	0.395
0.1014	0.793338	0.401
0.1031	0.793432	0.401
0.1506	0.796073	0.406
0.1536	0.796240	0.406
0.2039	0.799037	0.412
0.2031	0.798992	0.412

[a]Standard uncertainties for u (*d*) = 5 × 10^{-2} kg m^{-3} and u (*η*) = 0.005 mPa s.

The uncertainty of density measurements for ASA in MeCN solutions was better than ±5 × 10^{-2} kg m^{-3}. The analytical balance was analytical balance (AND, GR202, Japan) with the precision of ±1 × 10^{-8} kg. The viscosities were measured using an Ubbelohde-type viscometer, calibrated with doubly distilled water. Viscosity of the solutions (*η*) was obtained by the following equation:

$$\frac{\eta}{d} = Lt - \frac{K}{t} \tag{1}$$

where *d* is the density, *t* is the flow time of the solution, *L*, and *K* are the viscometer constants. A digital stopwatch with a resolution 0.01 s was used to measure the flow time. The estimated uncertainty of the experimental viscosity was

±0.005 mPa s. Viscosities and densities of (ASA + MeCN) mixtures at different concentrations are listed in Table 2.

The measurement of specific conductivity. Specific conductivities were measured using a conductivity meter (Metrohm model 712, Switzerland) with accuracy ±0.5%. The cell constant was calculated by the repeated measurements of KCl solution in 0.01 mol kg^{-1}. About 50 ml of solvent was filled into the conductivity cell and the cell was closed. Weighting was performed by an analytical balance (AND, GR202, Japan) with the precision of ±1 × 10^{-8} kg. After the measurement of the solvent conductivity, a weighted amount of pure ionic liquid was added with a syringe to the cell containing solvent and the measurement was repeated. To minimize the risk of the presence of concentration gradients in the cell, the solution was continuously stirred with a magnetic stirrer. The water from a thermostatically regulated bath was circled around the cell with double wall to maintain the temperature with an uncertainty ±0.02 K. Specific conductivity (κ) is related to the ion mobility and the number of charge carriers, which can be expressed by; $\kappa = \sum n_i q_i \mu_i$ where n_i is the number of charge carriers of species i, q_i is the charge, and μ_i is the mobility. An increase in concentration of the ionic liquid in MeCN results in an increase in the number of the charge carriers and charge [38]. For this region in above equation the effect of mobility of the ions is lower than those of other two parameters. Moreover, the specific conductivity of the alkyl side chain increases at the same concentration due to the decrease in the ions mobility. On the other hand the specific conductivity decreases with addition of ASA to the ionic liquid solution. This indicates the low mobility of the ions due to the increase of the interaction between ion-ASA.

Model Detail

The values of obtained molar conductivity (Λ) for the ionic liquids in the studied solutions (ASA + MeCN) have been calculated by the relation $\Lambda = 1000\kappa/c$, where κ is the specific conductivity of the ionic liquid solutions. The conductivity data were analyzed with low concentration Chemical Model (lcCM) conductivity equation using the following set of equations [39] which is the Fuoss-Onsager type equation.

$$\Lambda = \alpha\left[\Lambda_0 - S(c\alpha)^{1/2} + Ec\alpha\ln(c\alpha) + J_1 c\alpha + J_2(c\alpha)^{3/2}\right] \quad (2)$$

$$K_A = \frac{1-\alpha}{\alpha^2 c\gamma^2_\pm} \quad (3)$$

$$\ln\gamma_\pm = -\frac{\lambda_D q}{1 + \lambda_D R} \quad (4)$$

$$\lambda_D^2 = \frac{16000 N_A z^2 e^2 \alpha c}{\varepsilon_0 \varepsilon k_B T} \quad (5)$$

$$q = \frac{z^2 e^2}{8\pi\varepsilon_0 \varepsilon k_B T} \quad (6)$$

In above equations, Λ and Λ_0 are molar conductivities at molarity c and at infinite dilution, (1-α) is the fraction of oppositely charged ions acting as ion pairs, $\gamma_\pm$ is the corresponding mean activity coefficient of the free ions, λ_D is the Debye parameter, e is the electronic charge, z is the ionic charge, ε_0 is the permittivity of vacuum, ε is the dielectric constant of the solvent, and the other symbols have their usual meanings. The coefficients E, J_1 and J_2 required for calculations were taken from Ref. [40]. The initial guess of limiting molar conductivity and ion association constant were obtained from Debye-Hückel-Onsager extrapolation of the data [41]. Due to the lack of association constant for the studied solutions, K_A was first estimated from the Arrhenius-Ostwald relation [41] and then the other parameters were determined using Eq. (2). The parameter R represents the center-to-center distance between the ions in the ion pairs.

RESULTS AND DISCUSSION

The values of the molar conductivity (Λ) for the ionic liquids, [BMIm]Br, [HMIm]Br and [OMIm]Br in the several concentrations (0.0, 0.10, 0.15, 0.20) of aspirin (ASA) in acetonitrile (MeCN) solutions are listed in Table 3. The results show that the molar conductivity decreases with increasing the concentration of ionic liquids due to the increase in the ion pair formation. These values for [OMIm]Br in several molality of ASA in MeCN solutions are plotted in Fig. 1. This trend can be interpreted in terms of strengthening interactions between the ionic liquid and ASA which may reduce the ion pair

Table 3. The Molar Conductivities (Λ) of the Ionic Liquids [BMIm]Br, [HMIm]Br and [OMIm]Br in the Several Molality of ASA in MeCN Solutions as a Function of IL Concentration at 298.15 K

$10^3\,c_{IL}$ (mol m⁻³)	Λ (S cm² mol⁻¹)	$10^3\,c_{IL}$ (mol m⁻³)	Λ (S cm² mol⁻¹)	$10^3\,c_{IL}$ (mol m⁻³)	Λ (S cm² mol⁻¹)	$10^3\,c_{IL}$ (mol m⁻³)	Λ (S cm² mol⁻¹)	$10^3\,c_{IL}$ (mol m⁻³)	Λ (S cm² mol⁻¹)
[BMIm]Br									
m_{ASA}= 0.0000 mol kg⁻¹		m_{ASA} = 0.0523 mol kg⁻¹		m_{ASA} = 0.1031 mol kg⁻¹		m_{ASA} = 0.1506 mol kg⁻¹		m_{ASA} = 0.2039 mol kg⁻¹	
0.1586	170.69	0.1598	150.69	0.2107	139.69	0.1840	128.45	0.1244	124.03
0.3250	160.33	0.3399	148.50	0.3876	137.55	0.3619	126.52	0.2592	122.46
0.4764	154.32	0.5323	146.49	0.5672	135.44	0.5516	124.94	0.5176	120.42
0.6391	147.46	0.7106	144.65	0.7129	134.24	0.7602	122.78	0.6858	118.52
0.8081	141.94	0.8871	142.58	0.8853	133.17	1.0055	121.46	0.8394	116.55
1.0034	137.15	1.0677	141.41	1.0591	132.28	1.2040	120.13	0.9830	115.55
1.1797	133.53	1.2307	140.72	1.2515	131.20	1.3692	119.51	1.1381	114.29
1.3853	129.08	1.4194	140.05	1.4289	130.31	1.5309	118.91	1.2775	113.88
1.5666	125.64	1.5999	139.12	1.6017	129.73	1.7263	117.85	1.4215	112.97
1.7117	123.81	1.7706	138.98	1.8036	128.63			1.5428	112.00
1.8482	121.38							1.6849	111.32
[HMIm]Br									
m_{ASA} = 0.0000 mol kg⁻¹		m_{ASA} = 0.0522 mol kg⁻¹		m_{ASA} = 0.1014 mol kg⁻¹		m_{ASA} = 0.1536 mol kg⁻¹		m_{ASA} = 0.2031 mol kg⁻¹	
0.1511	170.56	0.1842	145.28	0.1854	132.03	0.1423	125.78	0.1103	124.70
0.2877	167.93	0.3360	143.37	0.3388	130.02	0.2851	124.05	0.2312	122.73
0.3987	165.90	0.4702	141.58	0.4321	129.09	0.4105	123.16	0.4604	121.19
0.5672	164.26	0.6039	139.91	0.5590	128.33	0.5327	122.22	0.6096	120.29
0.7380	162.58	0.7501	138.51	0.6874	127.22	0.6786	120.98	0.7458	119.49
0.8923	160.78	0.9039	137.76	0.7838	126.22	0.8146	120.18	0.8732	118.76
1.0683	160.04	1.0316	136.88	0.9286	125.06	0.9491	119.28	1.0108	118.13
1.2553	158.59	1.1774	135.73	1.0648	124.18	1.0898	118.55	1.1344	117.59
1.4103	157.53	1.3108	134.67	1.1987	123.07	1.2109	118.18	1.2621	117.11
1.5686	156.17	1.4713	133.42	1.4025	122.24			1.3697	116.67
1.7634	155.14	1.6167	132.62	1.5336	121.76			1.4957	115.93
[OMIm]Br									
m_{ASA} = 0.0000 mol kg⁻¹		m_{ASA} = 0.0520 mol kg⁻¹		m_{ASA} = 0.1012 mol kg⁻¹		m_{ASA} = 0.1530 mol kg⁻¹		m_{ASA} = 0.2030 mol kg⁻¹	
0.1829	164.62	0.1663	130.64	0.1093	128.76	0.0862	122.80	0.1148	110.09
0.3091	163.15	0.3081	128.54	0.1773	127.90	0.1667	121.92	0.2513	109.10
0.4417	161.58	0.4708	126.59	0.2983	126.80	0.3177	120.68	0.3889	108.29
0.5462	160.12	0.6511	125.37	0.4143	125.75	0.4125	119.82	0.5140	107.80
0.6562	159.15	0.8094	124.52	0.5193	124.61	0.5162	118.93	0.6467	107.11
0.8125	158.14	0.9624	123.52	0.6478	123.67	0.6198	118.24	0.7780	106.74
0.9297	157.73	1.1126	122.85	0.7610	122.96	0.8578	117.05	0.8935	106.26
1.0540	157.06	1.3566	121.32	0.8432	122.18	0.9646	116.71	1.0207	105.95
1.1694	156.62	1.5250	120.05	0.9379	121.88	1.0883	115.95	1.1566	105.53
1.2441	156.13	1.6583	119.45	0.1093	128.76	1.2233	115.09	1.2727	105.40
1.4238	155.60								
1.6337	155.11								

c_{IL} is molarity of ionic liquid in (ASA +MeCN) solutions and m_{ASA} is the molarity of the solution of aspirin in MeCN.
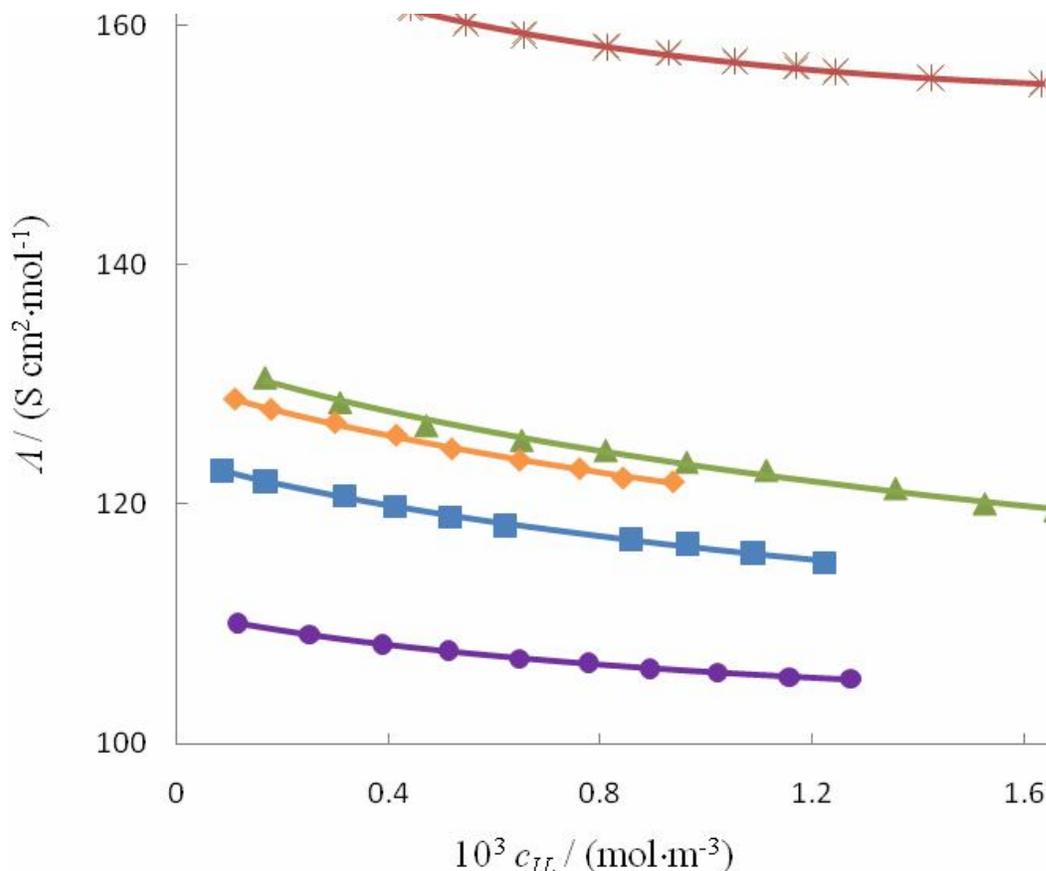
Fig. 1. Molar conductivities (Λ) of [OMIm]Br in several molality of ASA in MeCN solutions at 298.15 K; (∗, 0.0000; ▲, 0.0523; ♦, 0.1031; ■, 0.1506; ●, 0.2039 mol kg^{-1}).

formation of the ionic liquid. The limiting molar conductivity values Λ_0 for ionic liquids in MeCN in this work are respectively 181.19, 173.73 and 168.50 for [BMIM]Br, [HMIM]Br and [OMIM]Br while these values in reference [42] are 185.3, 178.1 and 169.1. The comparison shows a good agreement between the Λ_0 values of the ionic liquids in MeCN with those reported in the literatures [42].

The values of Λ_0 for ionic liquids with different alkyl chains are in this order: octyl < hexyl < butyl. This sequence agrees with the order of the interaction energies calculated experimentally and theoretically for the ILs [42]. Based on

the relative abundances of fragment ions originating from the MS/MS decompositions of mixed complexes ([C^1......Br......C^2]$^+$) it was possible to infer a qualitative order of intrinsic bond strength to Br$^-$:[emim]$^+$ > [bmim]$^+$ > [hmim]$^+$ > [omim]$^+$ [43]. The values of the limiting molar conductivity of cations for the ionic liquids, [BMIm]Br, [HMIm]Br and [OMIm]Br are 84.6, 77.4 and 68.4 S cm^2 mol^{-1}, respectively and for anion Br$^-$ is 100.7 S cm^2 mol^{-1} [42]. These values show that the contribution of anion in molar conductivity is more than cations. In pure acetonitrile, the [OMIm]Br is more solvated than two other ionic liquids, so has the low values of molar conductivity. The values of

Table 4. The Limiting Molar Conductivities (Λ_0), Walden Products ($\Lambda_0\eta$), Ion Association Constants (K_A), Standard Gibbs Energies of Ion-pairing Formation (ΔG_A^0) and Distance Parameters (R) of the Ionic Liquids in the Several Concentration of ASA in MeCN Solutions at 298.15 K

m_{ASA} (mol kg^{-1})	K_A (dm^3 mol^{-1})	Λ_0 (S cm^2 mol^{-1})	$10^9 R$ (m)	$\Lambda_0\eta$ (S cm^2 mPa s mol^{-1})	ΔG_A^0 (KJ mol^{-1})
[BMIm]Br					
0.0000	158.20	181.19	2.65	78.79	-12.52
	152 [42]	185.3 [42]			
0.0523	141.85	154.57	3.64	54.10	-12.28
0.1031	131.16	143.41	3.28	51.05	-12.09
0.1506	125.14	131.16	2.85	47.49	-11.97
0.2039	106.87	126.29	1.22	46.22	-11.57
[HMIm]Br					
0.0000	128.25	173.73	2.93	75.57	-12.03
	130 [42]	178.1 [42]			
0.0522	118.63	148.60	2.27	55.07	-11.84
0.1014	114.80	134.98	2.32	52.01	-11.76
0.1536	109.83	127.92	2.70	47.79	-11.65
0.2039	98.59	125.40	1.87	46.66	-11.39
[OMIm]Br					
0.0000	122.99	168.50	3.83	73.30	-11.93
	120 [42]	169.1 [42]			
0.0520	110.25	132.90	2.33	46.51	-11.66
0.1011	100.74	130.52	2.11	45.16	-11.42
0.1537	95.05	124.09	2.40	44.18	-11.29
0.2000	80.55	111.35	2.81	40.75	-10.88

Λ_0 and Λ for ionic liquids in several concentrations and 0.1 molality of ASA in MeCN solutions are presented in Table 4 and Fig. 2. It is clear that the values of Λ and Λ_0 for ionic liquids decrease with addition of ASA to the solutions. These lower values are due to the low mobility of the solvated ions with large radii and increase in the viscosity of medium with addition of ASA. The variation of the limiting molar conductivities (Λ_0) with alkyl chain length of [C$_n$MIm]Br (n = 4, 6 and 8) in several concentration of ASA in MeCN solutions are presented in Fig. 3. The volumetric properties of ASA in the presence of [C$_n$MIm]Br (n = 4, 6 and 8) in MeCN solutions have been studied in our previous papers which confirm the conductometric trend [44,45]. The results show that dominant interaction between ionic liquids
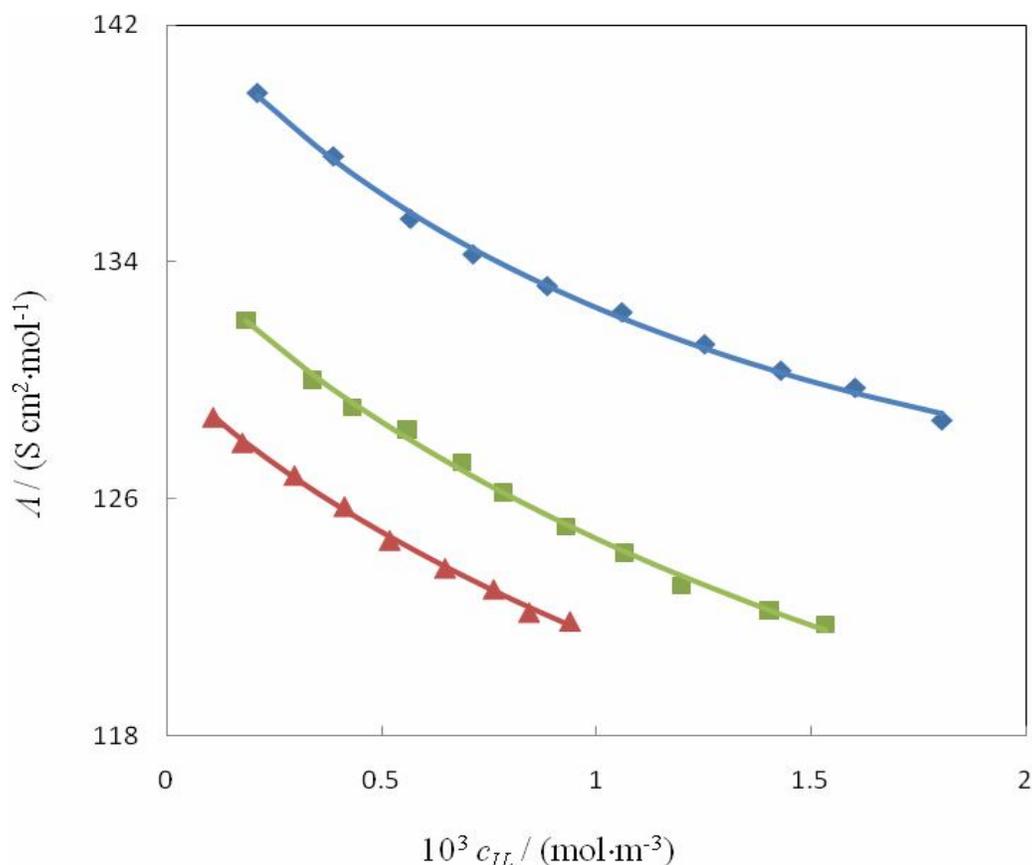
Fig. 2. Comparison of molar conductivities (Λ) of ionic liquids in 0.1 mol kg^{-1} molality of ASA in MeCN solutions at 298.15 K; ($\blacktriangle$, [OMIm]Br; $\blacksquare$, [HMIm]Br; and $\blacklozenge$, [BMIm]Br).

and ASA are ion-polar and polar-polar and stronger interactions are related to [BMIM]Br [44,45]. In this ionic liquid, ions are less solvated by the solvent molecules and have greater ionic mobility so has the large value of limiting molar conductivity. To eliminate the effect of viscosity on the ionic mobility, Walden product which is a useful tool to discuss ion-solvent interactions was calculated. The conductivity of the ions at infinite dilution depends only on their mobility and is inversely proportional to the viscosity of the solvent. It is expected that the product of ion conductivity by the viscosity of the medium is independent of the composition of solvent. Hence, the Walden products ($\Lambda_0\eta$) are expected to be constant for a given electrolyte in a series of solvent mixtures in which the ion-solvent interactions are uniform [46-48]. The calculated values of

Walden product ($\Lambda_0\eta$) are presented in Table 4. These values are plotted against the several molality of ASA in MeCN solutions in Fig. 4. It is clear that the absolute values of Walden product for ionic liquids decrease slowly with increasing the concentration of ASA. This suggests that the ions do not have the same effective radius in different solvent compositions and consequently provides evidence for desolvation of the ions in the solutions. This behaviour seems to be caused by the preferential solvation of the ions of the ionic liquid by the molecules of ASA.

The values of ion association constant (K_A) of the ionic liquids in the several concentrations of ASA in MeCN solutions are given in Table 4. As shown in Table 4, the values of (K_A) for the ionic liquid decrease with the increase of ASA concentration . This can be ascribed to the facts that
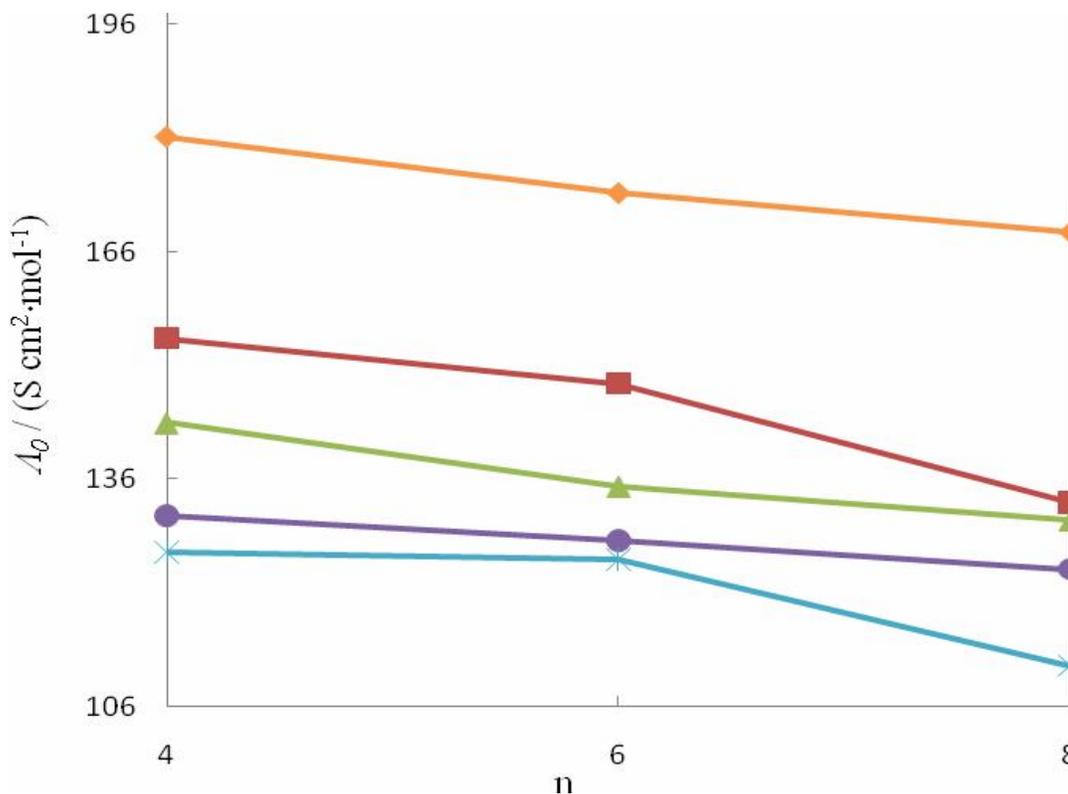
Fig. 3. Variation of limiting molar conductivities (Λ_0) with carbon atom number, n of [$C_n$mim] Br (n = 4, 6 and 8) in several molalities of ASA in MeCN solutions at 298.15 K; ($\blacklozenge$, 0.0; $\blacksquare$, 0.05; $\blacktriangle$, 0.1; $\bullet$, 0.15; $*$, 0.2).

the increased size of ions caused by the possible interactions between ionic liquid and ASA reduces the ion pair formation. At a fixed molality of ASA, the values of ion association constant increase with the alkyl chain length of the cations in this sequence octyl < hexyl < butyl. The high surface electrical charge density of the [BMIM]$^+$ indicates its high ionic association. Clearly, the K_A values of each ionic liquid decrease at higher concentrations of ASA. This is due to the strong ion-ASA interactions in the concentrated solutions which reduce the ion-pair formation.

The calculated values of distance parameters (R) are given in Table 4. The R values decrease as the concentrations of (ASA + MeCN) solutions increase. Because of the stronger interactions between ASA and ionic liquid, addition of ASA to the ionic liquid solutions leads to the decrease of the acetonitrile molecules releasing to the bulk and solvation of the ions, so the distance between ions is reduced. The low values of (R) for [BMIm]Br is related to the strong ionic association.

The association constants were used to calculate the standard Gibbs energy (ΔG_A^0) of ion-association process using the following equation:

$$\Delta G_A^0 = -RT \ln K_A \tag{8}$$
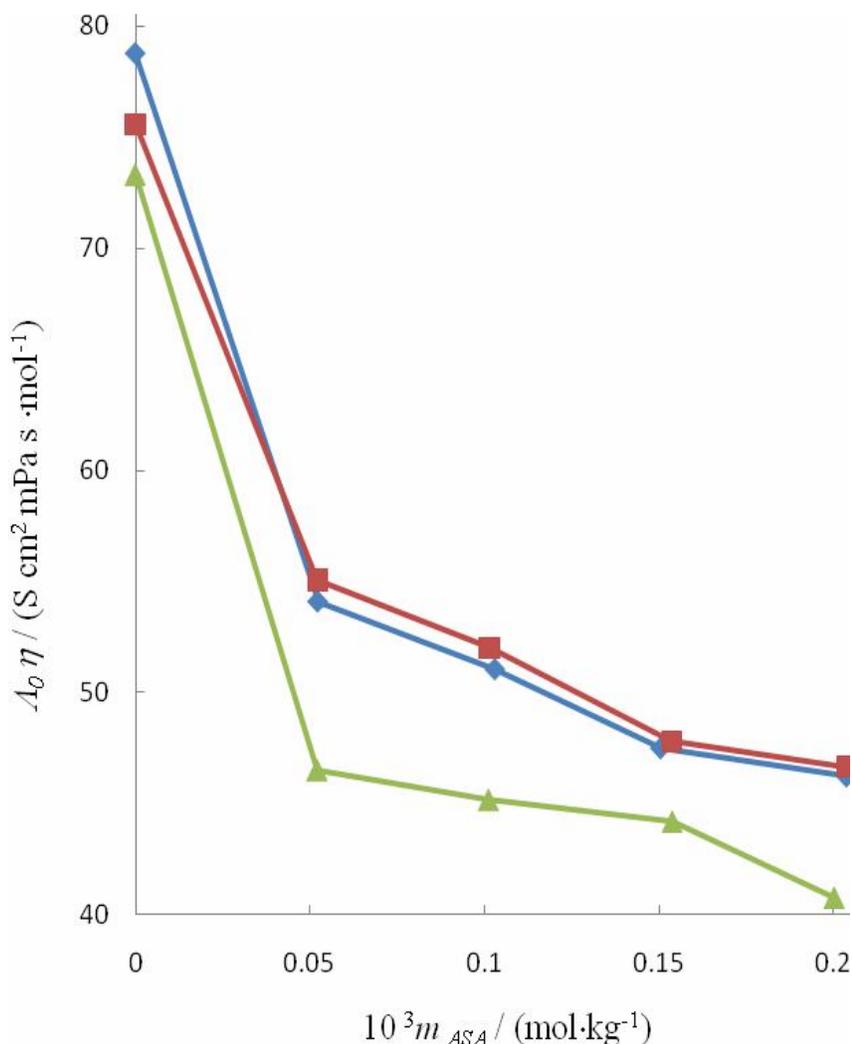
Fig. 4. Walden product ($\Lambda_0\eta$) of the ionic liquids against the several molaity of ASA in MeCN solutions at 298.15 K; (▲, [OMIm]Br; ■, [HMIm]Br, and ♦, [BMIm]Br).

The obtained values of the standard Gibbs energy are given in Table 4. These values are plotted against the several molality of ASA in MeCN solutions in Fig. 5. As seen in this figure, the negative values of ΔG_A^0 become more negative at the low molality of ASA in MeCN solutions. The observed results can be explained by the ion-association phenomena. This means that ion-pair formation decreases with addition of ASA due to the increase in the preferential solvation of ions by the molecules of ASA. In general, it is concluded that addition of ionic liquid to the solutions of ASA leads to the strengthening of the solute-cosolute interactions between ASA and ionic liquid. The values of ΔG_A^0 become more negative as the cation size of the ionic liquid decreases. Therefor, more spontaneity and feasibility of the association process is observed in the ionic liquid [BMIm]Br.

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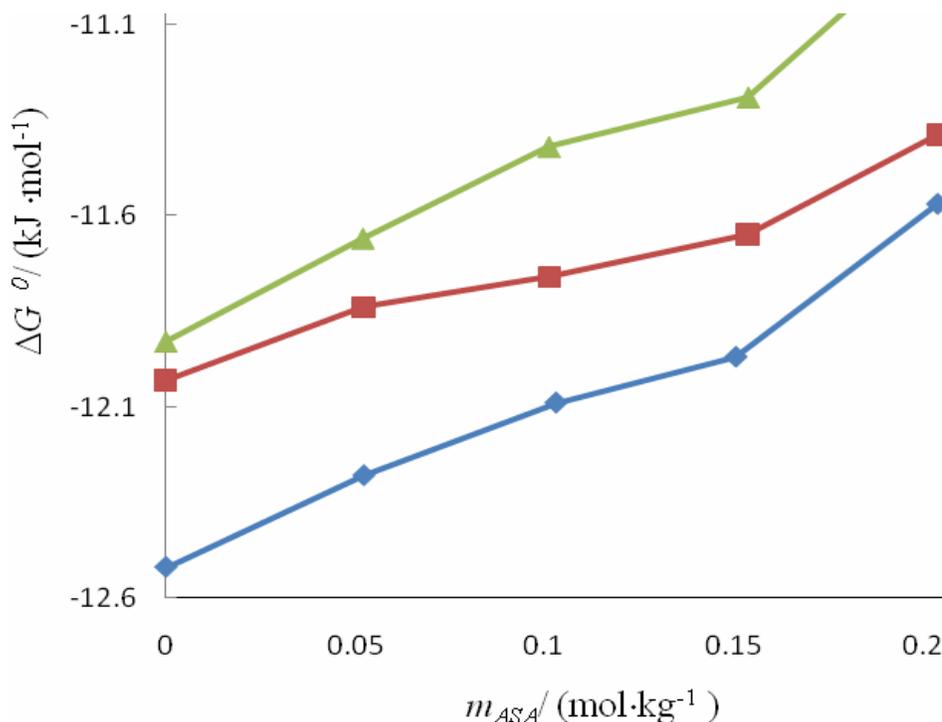
Fig. 5. The standard Gibbs energy (ΔG_A^0) of the ionic liquids against the molality of ASA in MeCN solutions at 298.15 K; ($\blacklozenge$, [OMIm]Br; $\blacksquare$, [HMIm]Br and $\blacktriangle$, [BMIm]Br).

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