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Aggregation Behavior of Pyridinium-Based Ionic Liquids in Aqueous Solution

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Abstract Aggregation of the ionic liquids 1-butylpyridinium tetrafluoroborate, 1-butylpyridinium triflate, 1-butyl-2-methylpyridinium tetrafluoroborate, 1-butyl-3-methylpyridinium tetrafluoroborate, 1-butyl-4-methylpyridinium tetrafluoroborate, 1-butyl-3-methylpyridinium dicyanamide, and 1-octyl-3-methylpyridinium tetrafluoroborate in aqueous solution has been characterized at 298.15 K through density, ρ, speed of sound, u, and conductivity, σ, measurements. In addition, apparent molar volumes, V_ϕ, and isentropic compressibilities, κ_s, have been calculated from the experimental data. To characterize the formation of aggregates, the critical aggregation concentration of the ionic liquids, *cac*, the degree of ionization of the aggregates, β, and the standard Gibbs energy of aggregation, $\Delta G^\circ_\mathrm{m}$, have been obtained, with good agreement between results derived from the different methods. The dependence on the structural variation of these ions has been analyzed by comparing the results obtained for this series of ionic liquids.

Keywords Ionic liquids · Aggregation · Conductivity · Density · Speed of sound

1 Introduction

Ionic liquids (ILs) have burst into the scientific panorama, providing new options in research and the development of further applications in different areas. Their unusual properties, related to the electrostatic interactions between their ionic components, give these materials the chance of providing benefits over conventional solvents. Therefore, the interest of several studies is focusing on ILs in order to take advantage of their promising features, including

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negligible vapor pressure at low and moderate temperatures and a broad range of conditions in which they can remain as a liquid.

Consequently, many efforts are directed toward a systematic characterization of pure ILs on the basis of the nature of their ions and their intermolecular interactions, since it is an essential requirement to encourage the use of ILs as solvents [1–6]. Moreover, studies of their thermodynamic properties in binary mixtures with water is also pursued to analyze the influence of solvent on structural and energetic properties [7, 8]. As a result of several investigations, it has been found that some imidazolium and pyridinium based ILs can form aggregates in water at low concentrations. A specific arrangement of hydrophobic and hydrophilic domains similar to that of classical cationic surfactants can be observed in aqueous solutions [8] due to the inherent amphiphilic nature of their cations, not only with long hydrocarbon chains as alkyl groups but also with short chains [8, 9]. This capacity of ILs to aggregate, that is, to show nano-heterogeneity in aqueous solution, has contributed to an increase in the importance of these compounds.

The interest in the aggregation process arises from both practical and fundamental considerations. On one hand, compounds that can be considered surfactants are widely used in industry appearing in diverse products such as detergents, paints, polymers, and cosmetics, since their special properties make them very useful for numerous functions. On the other hand, aggregation in solution is particularly interesting from the theoretical point of view. A closer view of the mechanism of their action provides useful knowledge concerning the interactions that take place in the mixture because this organization results from a balance between interactions in pure ILs and those that can be established with the solvent [10]. Moreover, an analysis of the influence of the ionic structural characteristics, such as the length of the alkyl chain of the cation or the position of the substitutes, on properties is interesting.

Taking into account the importance of a deeper understanding of ILs as a new type of surfactant with special properties from both fundamental and applied viewpoints, a systematic investigation of their aggregation processes would be expected. However, there are few data available about the thermophysical properties of ILs in aqueous solution. This motivated us to pursue a well planned study of aqueous solutions of a series of pyridinium based ILs, with the aim of analyzing the aggregation behavior and the relationship with their molecular features. Specifically, in this paper we report densities, ρ, speeds of sound, u, and conductivities, σ, of aqueous solutions of 1-butylpyridinium tetrafluoroborate ([bpy][BF_4]), 1-butylpyridinium triflate ([bpy][CF_3SO_3]), 1-butyl-2-methylpyridinium tetrafluoroborate ([b2mpy][BF_4]), 1-butyl-3-methylpyridinium tetrafluoroborate ([b3mpy][BF_4]), 1-butyl-4-methylpyridinium tetrafluoroborate ([b4mpy][BF_4]), 1-butyl-3-methylpyridinium dicyanamide ([b3mpy][$N(CN)_2$]), and 1-octyl-3-methylpyridinium tetrafluoroborate ([o3mpy][BF_4]) at 298.15 K. Moreover, apparent molar volume, V_ϕ, and isentropic compressibility, k_s, have been calculated from experimental data. To characterize the aggregation formation, different parameters such as critical aggregation concentration, *cac*, degree of ionization of the aggregates, β, and standard Gibbs energy of aggregation, $\Delta G^\circ_{\mathrm{m}}$, have been obtained. A comparison of results for the ILs has been used to understand the effect of the alkyl chain length of the cation, the dependence on the anion nature and the influence of the position of the substituents on the aggregation behavior of these ILs. This work completes the physicochemical characterization of the pure ILs based on thermal, thermodynamic and transport properties which we have carried out [11–13]. The previous studies provide us useful information about the influence of the ionic structure and intermolecular interactions in the ILs, that leads to a better understanding of their properties in aqueous solution.

2 Experimental

The ionic liquids: [b3mpy][BF_4], 99%; [b4mpy][BF_4], 99%; [o3mpy][BF_4], 98%; and [b3mpy][$N(CN)_2$], 98% were provided by Solvent Innovation, whereas: [bpy][BF_4], 99%; [bpy][CF_3SO_3], 99%, and [b2mpy][BF_4], 99% were supplied by IoLiTec. Due to their hygroscopic nature, ILs were dried for 48 hours under a vacuum of ca. 0.05 kPa under stirring with the aim of ensuring that these liquids are water free. Chemical structure, formula weight, density and speed of sound of pure ILs are shown in Table 1. Dilutions of the compounds have been made using Milli Pore MilliQ water with resistivity of 18.2 MΩ·cm. The mixtures were prepared using a Sartorious semi-micro balance CP225-D with an uncertainty of $\pm 10^{-5}$ g. The maximum estimated error in the molality is $\pm 1 \times 10^{-4}$ mol·kg^{-1}.

Densities, ρ, and speed of sounds, u, of the pure compounds were determined simultaneously with an Anton Paar DSA 5000, automatically thermostated within ±0.001 K. The calibration was carried out with ultra pure water supplied by SH Calibration service GmbH, and dry air. The final uncertainty of density and speed of sound can be estimated in $\pm 10^{-6}$ g·cm^{-3} and ±0.01 m·s^{-1} respectively.

Conductivity measurements were performed at 298.15 K with an Orion 3-Star Meter conductimeter provided with an epoxy-graphite electrode. The temperature of the sample was kept constant within ±0.01 K by means of a Lauda E-200 thermostat and it was measured with a thermometer F250 form Automatic Systems Laboratories. The cell was calibrated with aqueous NaCl solutions at different concentrations supplied by Orion. The uncertainty of the measurements is estimated in 0.5%.

3 Results

Conductivity, density, speed of sound, apparent molar volume, and isentropic compressibility as a function of molality of ILs in aqueous solution at 298.15 K are gathered in Table 2.

The critical aggregation concentration, *cac*, corresponds to the concentration at which a very small but often clearly detectable concentration of aggregates exists. At a concentration slightly below of this value no aggregates can be detected by present methods. Hence, the *cac* is a good measure of the ease of forming aggregates [10]. This type of organization in the fluid produces changes in the system that lead to variations in physicochemical properties. This effect is signaled by the appearance of an inflection point in plots of the properties of solutions with the concentration of ILs. In our case, the value of the *cac* has been calculated from the intersection of the system behavior before and after the aggregate formation using experimental data of apparent molar volume, isentropic compressibility, and conductivity. In this way, an analysis of the agreement between results obtained from different properties can be performed.

The apparent molar volumes, V_ϕ, of the ILs as a function of molality at 298.15 K were calculated using the following equation:

$$V_\phi = \frac{M}{\rho_0} + \frac{1000(\rho_0 - \rho)}{m\rho_0\rho} \tag{1}$$

where M and m are the formula weight and the molality of the solute and ρ and ρ_0 are the densities of solutions and pure water, respectively. The variation of V_ϕ with the reciprocal of molality (m^{-1}) is illustrated in Fig. 1. The concentration at which the two lines intercept corresponds to the *cac*. The *cac* values are reported in Table 3.

Table 1 Formula weight, density, and speed of sound of pure ILs at 298.15 K

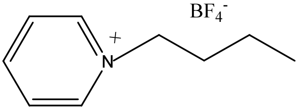
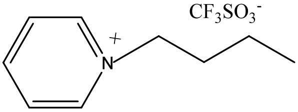
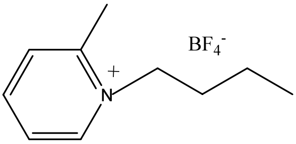
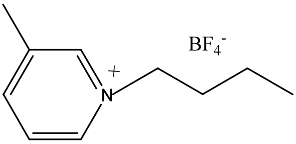
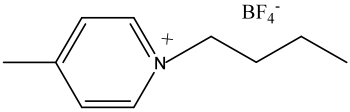
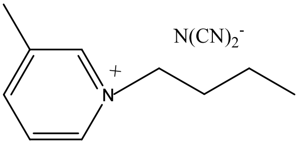
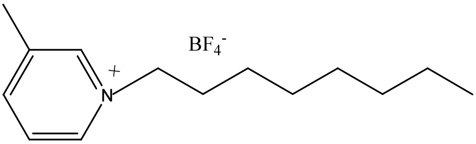
IL	$Fw/\mathrm{g{\cdot}mol^{-1}}$	$\rho/\mathrm{g{\cdot}cm^{-3}}$	$u/\mathrm{m{\cdot}s^{-1}}$
 [bpy][BF_4]	223.022	1.21370	1599.63
 [bpy][CF_3SO_3]	285.283	1.31433	1416.11
 [b2mpy][BF_4]	237.048	1.20138	1644.84
 [b3mpy][BF_4]	237.048	1.1826	1583.8
 [b4mpy][BF_4]	237.048	1.1826	1597.0
 [b3mpy][$N(CN)_2$]	216.282	1.0496	1757.2
 [o3mpy][BF_4]	296.156	1.0945	1511.4

Table 2 Conductivity, density, speed of sound, apparent molar volume and isentropic compressibility of ILs in aqueous solution at 298.15 K

m (mol·kg^{-1})	σ (mS·cm^{-1})	ρ (g·cm^{-3})	u (m·s^{-1})	V_ϕ (cm^3·mol^{-1})	κ_s (TPa^{-1})
[bpy][BF$_4$] + H$_2$O					
0.0106	0.956	0.997487	1497.66		446.96
0.0225	1.913	0.997951	1498.73	182.92	446.11
0.0292	2.474	0.998212	1499.23	183.20	445.70
0.0400	3.30	0.998631	1500.13	183.45	444.98
0.0464	3.65	0.998878	1500.59	183.56	444.59
0.0546	4.40	0.999195	1501.24	183.64	444.07
0.0625	4.86	0.999497	1501.82	183.73	443.59
0.0697	5.42	0.999774	1502.41	183.76	443.12
0.0797	6.00	1.000157	1503.19	183.81	442.49
0.0881	6.59	1.000475	1503.77	183.86	442.01
0.1007	7.43	1.000944	1504.73	183.99	441.24
0.1103	8.19	1.001303	1505.35	184.05	440.72
0.1153	8.46	1.001486	1505.78	184.10	440.38
0.1228	8.89	1.001763	1506.34	184.15	439.94
0.1354	9.62	1.002229	1507.26	184.20	439.19
0.1445	10.18	1.002560	1507.87	184.26	438.69
0.1574	10.91	1.003032	1508.75	184.30	437.98
0.1600	11.07	1.003128	1508.94	184.30	437.82
0.1711	11.68	1.003530	1509.69	184.34	437.21
0.1767	11.97	1.003734	1510.07	184.35	436.91
[bpy][CF$_3$SO$_3$] + H$_2$O					
0.0091	0.706	0.997718	1497.75	211.37	446.8
0.0228	1.559	0.998686	1498.98	213.29	445.64
0.0295	2.077	0.999157	1499.59	213.59	445.06
0.0393	2.772	0.999844	1500.55	213.83	444.19
0.0495	3.23	1.000556	1501.47	213.98	443.33
0.0590	3.95	1.001218	1502.36	214.05	442.51
0.0696	4.60	1.001951	1503.29	214.14	441.64
0.0752	5.01	1.002339	1503.77	214.15	441.19
0.0816	5.30	1.002779	1504.32	214.19	440.67
0.0888	5.86	1.003272	1505.21	214.23	439.93
0.1026	6.51	1.004153	1506.11	214.89	439.02
0.1087	6.74	1.004542	1506.65	215.11	438.54
0.1217	7.32	1.005362	1507.77	215.57	437.53
0.1249	7.46	1.005568	1508.03	215.63	437.29
0.1314	7.77	1.005973	1508.93	215.83	436.59
0.1351	7.85	1.006206	1509.14	215.92	436.37
0.1364	7.95	1.006287	1509.05	215.95	436.39
0.1449	8.36	1.006825	1509.89	216.10	435.67
0.1542	8.69	1.007397	1510.46	216.34	435.09

Table 2 (*continued*)

m (mol·kg^{-1})	σ (mS·cm^{-1})	ρ (g·cm^{-3})	u (m·s^{-1})	V_ϕ (cm^3·mol^{-1})	κ_s (TPa^{-1})
0.1603	9.09	1.007778	1510.91	216.43	434.67
0.1714	9.60	1.008462	1511.78	216.63	433.87
[b2mpy][BF$_4$] + H$_2$O					
0.0150	1.303	0.997635	1498.33	197.93	446.49
0.0231	1.882	0.99794	1499.07	198.51	445.91
0.0283	2.33	0.998136	1499.64	198.68	445.49
0.0407	3.19	0.998601	1500.70	198.93	444.65
0.0497	3.68	0.998937	1501.54	199.04	444.01
0.0602	4.63	0.999328	1502.32	199.11	443.37
0.0691	5.16	0.999658	1503.09	199.16	442.77
0.0793	5.88	1.000034	1504.03	199.21	442.05
0.0879	6.34	1.00035	1504.80	199.24	441.46
0.0983	7.07	1.000725	1505.70	199.34	440.77
0.1069	7.60	1.001032	1506.45	199.42	440.19
0.1139	7.87	1.001283	1506.99	199.46	439.77
0.1218	8.41	1.001562	1507.63	199.52	439.27
0.1276	8.78	1.001769	1508.11	199.55	438.90
0.1348	9.17	1.002023	1508.63	199.59	438.49
0.1362	9.20	1.002071	1508.90	199.61	438.31
0.1415	9.60	1.002258	1509.26	199.63	438.02
0.1507	10.05	1.002579	1510.10	199.69	437.39
0.1553	10.30	1.002740	1510.34	199.71	437.18
[b3mpy][BF$_4$] + H$_2$O					
0.0119	1.071	0.997501	1497.92	198.94	446.80
0.0232	2.000	0.997906	1498.96	200.16	446.00
0.0269	2.321	0.998039	1499.40	37.17	445.67
0.0418	3.31	0.998569	1500.76	23.92	444.63
0.0556	4.48	0.999058	1502.03	17.99	443.66
0.0644	5.00	0.999368	1502.83	15.53	443.05
0.0717	5.49	0.999625	1503.38	13.95	442.61
0.0859	6.42	1.000118	1504.66	11.64	441.64
0.0953	7.09	1.000442	1505.41	10.49	441.06
0.1043	7.63	1.000752	1506.26	9.59	440.43
0.1184	8.37	1.00123	1507.37	8.45	439.57
0.1278	8.86	1.001544	1508.20	7.82	438.95
0.1427	9.77	1.002046	1509.40	7.01	438.03
0.1534	10.32	1.002405	1510.31	6.52	437.35
0.1593	10.76	1.002598	1510.87	6.28	436.94
0.1763	11.52	1.003160	1512.03	5.67	436.02
0.1851	12.00	1.003450	1512.75	5.40	435.48
[b4mpy][BF$_4$] + H$_2$O					
0.0122	1.314	0.997506	1497.89	199.48	446.81
0.0233	2.065	0.997900	1498.90	200.58	446.03

Table 2 (*continued*)

m (mol·kg^{-1})	σ (mS·cm^{-1})	ρ (g·cm^{-3})	u (m·s^{-1})	V_{ϕ} (cm^3·mol^{-1})	κ_S (TPa^{-1})
0.0429	3.57	0.998595	1500.71	201.05	444.65
0.0624	4.86	0.999277	1502.49	201.29	443.29
0.0704	5.54	0.999555	1503.20	201.35	442.75
0.0823	6.38	0.999968	1504.25	201.41	441.95
0.1012	7.57	1.000616	1505.81	201.51	440.75
0.1207	8.71	1.001274	1507.31	201.63	439.58
0.1394	9.79	1.001897	1508.83	201.74	438.43
0.1514	10.12	1.002296	1509.87	201.79	437.65
0.1607	10.72	1.002601	1510.55	201.83	437.12
0.1775	11.85	1.003156	1511.78	201.87	436.17
0.1942	12.69	1.003697	1513.07	201.94	435.19
0.2141	13.60	1.004344	1514.56	201.97	434.05
0.2309	14.42	1.004880	1515.74	202.02	433.15
0.2498	15.24	1.005472	1517.09	202.10	432.12
[b3mpy][N(CN)$_2$] + H_2O					
0.0093	0.723	0.997194	1497.89	200.56	446.95
0.0185	1.317	0.997302	1499.01	202.79	446.24
0.0276	1.798	0.997409	1500.07	203.51	445.56
0.0400	2.65	0.997554	1501.55	203.97	444.61
0.0550	3.47	0.997731	1503.21	204.20	443.55
0.0692	4.20	0.997891	1504.73	204.42	442.59
0.0841	5.02	0.998062	1506.41	204.53	441.53
0.0977	5.58	0.998210	1507.86	204.67	440.61
0.1120	6.29	0.998363	1509.30	204.80	439.70
0.1176	6.55	0.998423	1509.90	204.84	439.33
0.1304	6.98	0.998559	1511.13	204.92	438.55
0.1356	7.25	0.998614	1511.74	204.95	438.18
0.1506	7.85	0.998766	1513.13	205.06	437.30
0.1637	8.24	0.998898	1514.39	205.14	436.52
0.1642	8.30	0.998906	1514.60	205.13	436.39
0.1832	8.89	0.999099	1516.32	205.21	435.32
0.1973	9.44	0.999236	1517.65	205.29	434.50
[o3mpy][BF$_4$] + H_2O					
0.0026	0.2415	0.997124	1497.24		447.37
0.0071	0.633	0.997257	1497.89		446.92
0.0151	1.273	0.997492	1499.07	263.99	446.11
0.0169	1.417	0.997545	1499.39	264.01	445.90
0.0233	1.901	0.997732	1500.35	264.10	445.25
0.0312	2.479	0.997962	1501.54	264.15	444.44
0.0390	3.08	0.998189	1502.59	264.16	443.72
0.0440	3.30	0.998333	1503.35	264.19	443.20

Table 2 (*continued*)

m (mol·kg^{-1})	σ (mS·cm^{-1})	ρ (g·cm^{-3})	u (m·s^{-1})	V_ϕ (cm^3·mol^{-1})	κ_s (TPa^{-1})
0.0497	3.77	0.998498	1504.06	264.19	442.71
0.0553	4.02	0.998658	1504.57	264.22	442.34
0.0572	4.08	0.998693	1504.72	264.57	442.24
0.0615	4.19	0.998747	1505.09	265.70	442.00
0.0703	4.20	0.998803	1505.05	268.37	442.00
0.0711	4.20	0.998801	1505.08	268.68	441.98
0.0762	4.21	0.998837	1505.09	269.86	441.96
0.0811	4.21	0.998894	1505.04	270.56	441.96
0.0894	4.22	0.998972	1505.12	271.79	441.88
0.0984	4.22	0.999023	1505.02	273.24	441.92
0.1067	4.22	0.999088	1505.04	274.18	441.88
0.1149	4.23	0.999156	1505.07	274.94	441.83
0.1470	4.25	0.999402	1505.13	277.23	441.68

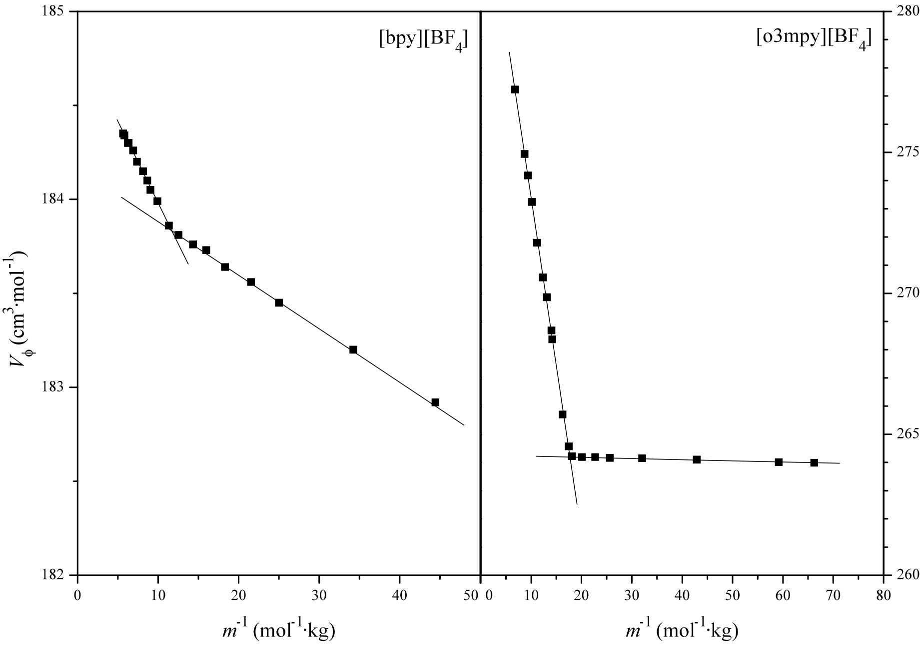


Fig. 1 Variation of V_ϕ with the inverse of molality for [bpy][BF$_4$] and [o3mpy][BF$_4$] at 298.15 K

Experimental densities and speeds of sound of the aqueous solution of ILs at 298.15 K were used to calculate isentropic compressibility, κ_s, by means of the Newton-Laplace equation:

$$\kappa_s = \frac{1}{\rho \cdot u^2}. \tag{2}$$

Table 3 Critical aggregation concentration, ionization degree of aggregates, and standard Gibbs energies of aggregation for the ILs in aqueous solutions at 298.15 K

IL	*cac*/mol·kg^{-1}			β	$\Delta G^\circ_\mathrm{m}$/kJ·mol^{-1}
	V_ϕ	κ_s	σ		
[bpy][BF_4]	0.085	0.091	0.108	0.81	−18.48
[bpy][CF_3SO_3]	0.089	0.091	0.090	0.70	−20.75
[b2mpy][BF_4]	0.091	0.096	0.090	0.82	−18.83
[b3mpy][BF_4]	0.091	0.087	0.090	0.76	−19.79
[b4mpy][BF_4]	0.096	0.097	0.106	0.72	−19.88
[b3mpy][$N(CN)_2$]	0.100	0.100	0.101	0.65	−21.15
[o3mpy][BF_4]	0.056	0.057	0.056	0.01	−34.07

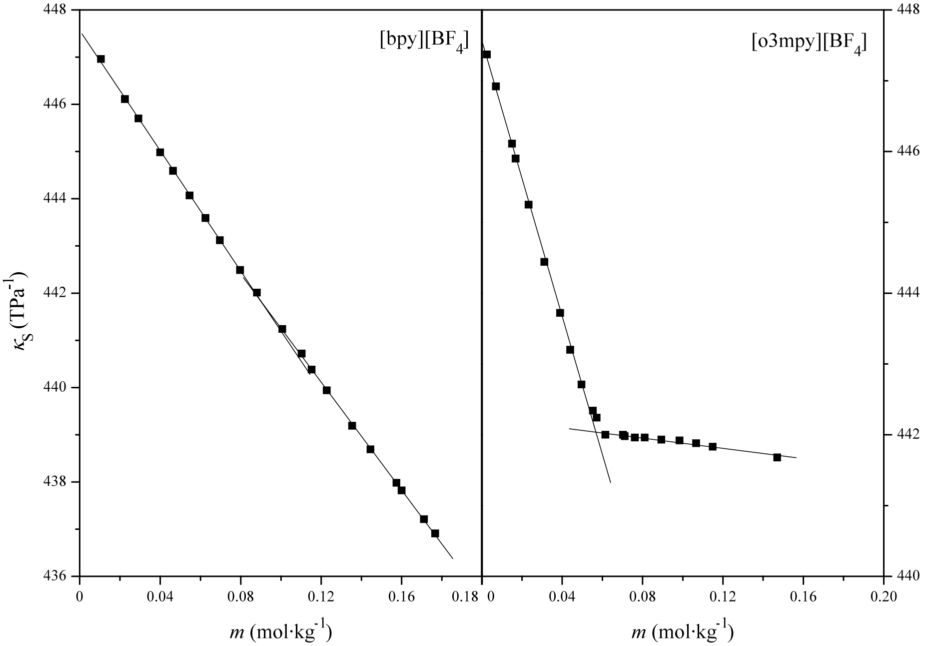


Fig. 2 Variation of κ_s with molality for [bpy][BF_4] and [o3mpy][BF_4] at 298.15 K

Plots of the isentropic compressibility, κ_s, against the molality for pyridinium based ILs are visualized in Fig. 2. The *cac* values calculated form these data are gathered in Table 3.

Experimental conductivities, σ, for aqueous solutions of pyridinium based ILs as a function of molality at 298.15 K are shown in Fig. 3. They exhibit typical behavior with two linear fragments in which the point of intersection of the two conductivity lines was taken as the *cac*. Moreover, the ratio of the slopes of the linear fragments above and below the *cac* gives an estimation of the degree of ionization of the aggregates, β. Ionic surfactants are generally considered fully dissociated below the *cac* whereas strong interactions occur between the charged aggregates and the counterions above this point, mainly due to the high charge density of surface of the aggregates [14]. For this reason, β is one of the key para-

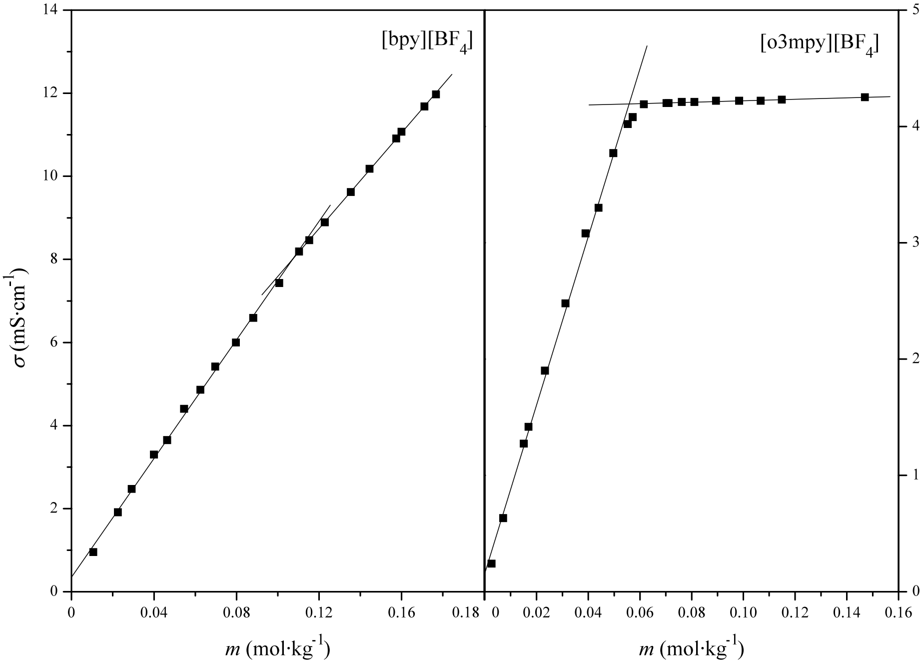


Fig. 3 Dependence of conductivity of [bpy][BF$_4$] and [o3mpy][BF$_4$] on molality at 298.15 K

meters to characterize ionic aggregates. There is no an unambiguous method of measuring this degree of freedom or of binding of the counterions, depending to some extent on the investigated property [10]. In this case the experimental measurements used to calculate β are conductivity slopes. The values of the *cac* and β obtained by least-squares analysis are presented in Table 3.

Furthermore, according to the charged phase separation model of micellization [15], the standard Gibbs energy of aggregation, $\Delta G^\circ_{\mathrm{m}}$, can be calculated from the following relation:

$$\Delta G^\circ_{\mathrm{m}} = (2-\beta)RT\ln x_{cac} \tag{3}$$

where x_{cac} is the critical aggregation concentration obtained from conductivity measurements, expressed in mole fraction. The values for the ILs are included in Table 3.

4 Discussion

Aggregate formation is due to the balance between intermolecular interactions in pure ILs, that includes electrostatic and dispersive forces, π–π interaction as well as hydrogen bonding, and interactions with water. The strength and importance of these depend, among others factors, on the properties of the particular ions involved such as the aromatic ring, the alkyl chain or the counterions. This is why a revision of the physicochemical properties of the present pure ILs is needed. Moreover, the study of the properties of mixtures, such as excess volumes also must be taken into account to evaluate the results since they provide an idea about the interactions between the unlike components. Excess volumes for mixtures of [bpy][BF_4], [b2mpy][BF_4], [b3mpy][BF_4], and [b4mpy][BF_4] with water have been reported before [16–19]. These studies suggest that several effects are involved in determining the mixing properties, including the breaking of hydrogen bonds between the water molecules, the weakening of Coulombic forces and the formation of new interactions between the -OH group and both the anions and the pyridinium cations.

We have performed a comprehensive study of a series of ILs based on the pyridine ring [11–13]. In relation to the analysis of the interactions of these compounds, some general peculiarities associated with them must be pointed out. Firstly, the aromatic protons in the pyridinium cation are less acidic than the hydrogen atoms of other ILs such as those derived from imidazolium, due to the bigger size of the ring and the presence of only one electronegative atom [8]. Moreover, a high cohesive energy has been found for the pyridinium cations which is associated with the cation-cation van der Waals attraction. Hence, NMR-measurements have shown that pyridinium rings are positioned at the aggregate surface in a configuration favorable for ring stacking through π–π interactions [8]. Electrostatic and dispersive forces also influence the behavior of these liquids to a different degree as a function of the structural characteristics of their ions [11–13]. Thus, as it is known, an increase of the alkyl length chain implies an enhancement of the van der Waals interactions between the chains whereas it also causes a decrease of the attractions between the π-clouds on the aromatic rings in the cationic structures and the Coulombic interactions between anions and cations due to steric hindrance [20].

Two features are clear from the experimental data for ILs. Thus, compounds with a butyl chain on the pyridinium cation exhibit similar behavior in aqueous solution and differ clearly from those with octyl chains. That is, the increase in the alkyl chain length on polar head group lowers the *cac*, for example, of [o3mpy][BF_4], probably due to an increase in the hydrophobic character of the cation [21]. Results are relativity similar for the others ILs, suggesting that alkyl chain length is the main factor in the aggregation for the liquids considered. Nevertheless, it is not possible to neglect the contribution of other structural characteristics. Singh and Kumar [7, 8] have studied the aggregation process in aqueous solutions of 1-butyl-3-methylpyridinium chloride ([b3mpy][Cl]) through several experimental measurements at 298.15 K, and found *cac* values between 0.505 to 0.609 $\text{mol}\cdot\text{L}^{-1}$. The behavior in aqueous solution can be compared with those of [b3mpy][BF_4] and [b3mpy][$N(CN)_2$] to define the role of the anion in the formation of aggregates. After converting the concentration values from molality to molarity scales, the results can be directly compared. It is noted that changing the anion in the IL, the *cac* decreases in the following order: [b3mpy][Cl] > [b3mpy][$N(CN)_2$] $\approx$ [b3mpy][BF_4]. The clear differences between the chloride system and those with tetrafluoroborate or dicyanamide anions may be related with the size of the counterion [10, 21]. The greater the anion size, the weaker the hydration. In this way, it is suggested that large anions as tetrafluoroborate or dicyanamide make aggregation easier since they decrease the charge repulsion between the cations when they are absorbed in the aggregate's surface. On the other hand, strongly hydrated ions as chloride are partially screened by the surrounding polar water molecules and therefore, they are less effective at reducing this repulsion. This shows that anions also can influence aggregation strongly. In this case, the position of the alkyl substituent in the pyridinium cation, or its absence, and comparison of the anions of [bpy][BF_4] and [bpy][CF_3SO_3], do not produce substantial changes in the *cac* values. It is noticeable that *cac* values for all the ILs obtained from apparent molar volume, isentropic compressibility and conductivity data are in relatively good agreement.

Within the analysis of each one of the properties, differences are reflected in several characteristics. Thus, the representation of apparent molar volume for the solution of [o3mpy][BF_4] is different from those for the others ILs. According to the pseudo-phase separation model, it is assumed that the apparent molar volumes should be constant in the concentration range below the *cac* whereas a linear decrease of the V_ϕ versus m^{-1} plot can be expected in the concentration range above *cac* [22]. The result for [o3mpy][BF_4] can be seen to agree approximately with this behavior. That is, the model can be considered as an acceptable approximation and, consequently, it suggests that [o3mpy][BF_4] forms micelles in aqueous solution. In contrast, volumetric data for the ILs with a butyl group as the alkyl chain cannot be described by this model of micellization. It seems to indicate that these compounds form aggregates due to their shorter alkyl chains. Plots of isentropic compressibility against molality also show different behavior for each IL. Thus, κ_s decreases rapidly at lower concentrations and then becomes almost constant in the concentration range above the *cac* for the system formed by [o3mpy][BF_4]. On the other hand, it clearly decreases across the whole range of solvent composition for the rest of ILs, although with slopes slightly different depending on whether or not aggregation has occurred. In the conductivity data, there is an abrupt change of slope after aggregation in [o3mpy][BF_4] before those of the rest of the compounds. This suggests that the added IL forms part of the aggregates above the *cac*, leading to a lower degree of ionization of the aggregates. Contribution of the bulky aggregate ion to the overall conductivity is small in comparison with ions and can be neglected [23]. In the other cases, conductivity grows with concentration after the *cac*. This indicates that the degree of ionization decreases with increasing alkyl chain length of the ILs, showing that the counterion binds with aggregates more easily when its alkyl chain length becomes longer [9]. Moreover, negative values of the standard Gibbs energy of aggregation are found for all the ILs, indicative of spontaneous aggregation [8]. $\Delta G^\circ_\mathrm{m}$ is clearly different for the mixture formed by [o3mpy][BF_4], its value being the most negative. As is known, this indicates that the formation of aggregates is easier as the alkyl chain length of ILs increases.

5 Conclusions

A systematic study of the aggregation behavior of a series of pyridinium based ionic liquids in aqueous solution has been performed at 298.15 K through experimental measurements of density, speed of sound and conductivity. Critical aggregation concentrations, degrees of ionization of the aggregates, and standard Gibbs energies of aggregation have been obtained for all the liquids. A comparison of the results for these ILs has been used to understand the influence of the structural characteristics of ions on the aggregation process. Two types of behaviors are found in aqueous solution of the ILs studied, depending on the alkyl chain length. Thus, compounds with a butyl chain on the pyridinium cation exhibit similar features in aqueous solution and differ clearly from those with an octyl chain. In spite of this fact, other structural effects cannot be neglected. It is noticeable that a relatively good agreement has been obtained for the calculated *cac* from the different properties.

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