

Experimental measurement of the hygroscopic grade on eight imidazolium based ionic liquids

S. Cuadrado-Prado, M. Domínguez-Pérez, E. Rilo, S. García-Garabal, L. Segade, C. Franjo, O. Cabeza*

Dto. de Física, Fac. de Ciencias, Campus da Zapateira s/n, Universidade da Coruña, 15071 A Coruña, Spain

ARTICLE INFO

Article history:

Received 27 October 2008

Received in revised form

23 December 2008

Accepted 29 December 2008

Available online 8 January 2009

Keywords:

Ionic liquids

Imidazolium

Hygroscopicity

Humidity

Anion size and cation size

ABSTRACT

We present measurements of the variation of mass suffered by eight different ionic liquids (ILs) according to the atmosphere humidity grade. The ILs studied belong to two different families, thus four of them belong to the 1-alkyl-3-methyl imidazolium tetrafluoroborate (CnMIM-BF₄) family, and the other four to the 1-ethyl-3-methyl imidazolium alkyl sulfate (EMIM-CnS) one. This allows us to study the influence of the alkyl chain length on the water absorption from atmosphere. The results indicate that the water is physio-adsorbed in the free surface of the sample when the humidity grade increases, and later this is desorbed again when the atmosphere is dry. In the CnMIM-BF₄ family desorption is complete, meanwhile in the EMIM-CnS one some residual adsorbed water remains. In addition, we have studied the influence of the free IL surface size in the adsorption process. Finally, we left two ILs (one of each family) and an equimolar aqueous solution of one of them during more than 70 h to observe adsorbed water saturation.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

As it is well known, water is omnipresent in ionic liquids (ILs). Even the apparently hydrophobic ones saturate with about 1.4% mass of water, which is a significant molar amount. For more hydrophilic ILs, water uptake from air is much greater. Imidazolium based ionic liquids in particular are extremely hygroscopic, i.e., they absorb water from atmosphere [1]. This means that all commercial products contain some greater or lesser amount of water, depending on the production conditions and the logistics, because the ILs can reasonably be expected to come into some contact with traces of water. This water content may be a problem for some applications, but not for others. However, one should in all cases know the approximate amount of water present in the used ionic liquid, because of the presence of water has significant influence on its physicochemical properties. It has been published that a simple 0.1 molar fraction of water content (which means about a 1%wt of water in the sample) decrease viscosity about a 20% [2] and it increases the electrical conductivity about a 30% [3]. So, it is important to remove the small amount of water that the IL contents from suppliers (usually less than 1000 ppm) if we want to obtain exact measurements of their physical properties. Some authors have reported that even only 0.01% water mass content leads to invalid physical magnitude values for the pure compound [4]. There are published two differ-

ent procedures to remove the water content in the ILs, such as a gentle heating in vacuum for tenths of hours [4,5], or to freeze the sample in vacuum to sublimate the water [6]. The dry samples must be preserved and manipulated in an inert wet free atmosphere to avoid water contamination.

Moreover, many of the proposed applications of ionic liquids described in literature have to be made in contact with atmosphere humidity [1,7], because of that the used ionic liquid will be contaminated with water (but the given application usually still works). As noted above, the knowledge of the quantity of water that an ionic liquid can absorb from the atmosphere is very interesting from the practical point of view, because we need to know the different physical magnitude values to design any proposed application. Also, it must be useful to study the ionic liquid surface from the theoretical point of view, because this experiment will give information about the interfacial forces between the IL and water.

In our first experiment we tried to know the maximum water content that some IL samples, previously water contaminated due to humidity, could absorb if they were leaved indefinitely in contact with the atmosphere. To do that we took on 21 November of 2007 four Eppendorf bins with 0.8 cm diameter. We introduced a quantity of 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMIM-BF₄) in two bins and in another two 1-ethyl-3-methyl imidazolium ethyl sulfate (EMIM-ES). Then, we weighed the four Eppendorf bins and left them near to the lab open window. Two of the bins were left open (each with a different IL) and the other two were closed and would be used as target samples. The four bins were weighed every morning when arriving to the laboratory, avoiding stir them, and

* Corresponding author. Tel.: +34 981 167000; fax: +34 981 167065.

E-mail address: oscabe@udc.es (O. Cabeza).

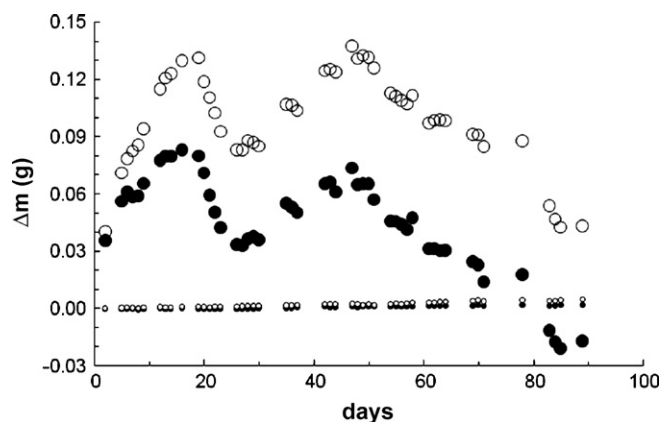


Fig. 1. Variation of mass suffered by EMIM-ES (open dots) and EMIM-BF₄ (solid dots) during 3 months left in the window of our laboratory. The big symbols represent the Eppendorf bins opened to atmosphere, while the small symbols those closed used as targets.

we noted down the increase of mass. The obtained results after three months of experiment appear in Fig. 1, where we plot the data for samples EMIM-BF₄ (solid dots) and EMIM-ES (open dots), also, we plot the respective target weights in small symbols. We observe that the mass of samples increases in the first 16 days, decreases the next 7 days, later it increases again for 20 days and finally it decreases. In spite of the fact that each compound absorbs different quantities of water, the trend was similar for both. Unfortunately, we did not measure the humidity and temperature of the atmosphere around samples. But we really note that the increasing of weigh was related with stormy weather periods, while the decreasing of weigh took place for sunny weather. As observed in Fig. 1, the EMIM-BF₄ sample presents a lower weight at the end of the experiment than his initial one, probably due to the fact that the IL samples had already absorbed water from atmosphere when the experiment began. These results suggested us to perform a similar experience but in a controlled atmosphere. Thus, we present experimental measurements of the water quantity absorbed by eight different hygroscopic imidazolium based ionic liquids according to the ambient humidity at room temperature and pressure. We study the influence of IL cation size, IL anion size and type, surface area exposed, time to be completely saturated of water at 100% humidity, and even the hygroscopicity of an equimolar aqueous solution of one ionic liquid. At our knowledge it is the first time that this kind of measurement is published for any ionic liquid.

2. Experimental procedure

The studied ionic liquids (ILs) belong to two different imidazolium based families. For the first one the organic cation 1-alkyl-3-methyl imidazolium (CnMIM) changes its size while the anion tetrafluoro borate (BF₄) is common. This series includes four ILs, with Cn as ethyl (EMIM-BF₄), butyl (BMIM-BF₄), hexyl (HMIM-BF₄) and octyl (MOIM-BF₄). In the second series the cation (EMIM) was common while the anion alkyl sulfate (CnS) changes its size. We have studied the higriscopyc behavior of four ILs, with Cn equal to ethyl (EMIM-ES), butyl (EMIM-BS), hexyl (EMIM-HS) and octyl (EMIM-OS). The eight ionic liquids were purchased to Solvent Innovation GmbH (recently absorbed by Merck KGaA). Its purity is better than 99% for all except EMIM-BF₄ and EMIM-ES where it is better than 98%. The water content certified by the dealer is lower than 1000 ppm as it is observed in Table 1. From the eight ILs six are miscible with water, one is partially (HMIM-BF₄) and MOIM-BF₄ is not miscible in water at room conditions, as it is indicated in Table 1.

Table 1

Some characteristics of the ionic liquids (ILs) used in this study, as its molar weight (MW), its original water content in ppm, the initial mass of IL used for the experiments, m_0 , the molar fraction of water adsorbed after 24 h in a 100% humidity atmosphere, x_{water} , and the miscibility with water at laboratory conditions of each IL.

	MW (g/mol)	Water (ppm)	m_0 (g)	x_{water}	Miscible
EMIM-BF ₄	197.98	220	1.262	0.77	Yes
BMIM-BF ₄	226.03	1040	1.201	0.70	Yes
HMIM-BF ₄	254.09	273	0.942	0.62	Partial
MOIM-BF ₄	282.14	776	0.683	0.57	No
EMIM-ES	236.29	157	2.112	0.91	Yes
EMIM-BS	264.35	165	2.262	0.90	Yes
EMIM-HS	292.40	181	2.162	0.89	Yes
EMIM-OS	320.45	218	2.023	0.87	Yes

The data for m_0 and x_{water} for the CnMIM-BF₄ compounds were taken from Fig. 3 while those for the EMIM-CnS ones from Fig. 4.

The sealed chemical bins were opened into an atmosphere chamber with a humidity grade lower than a 10%, measured with a hygrometer Kestrel 3500, which has an accuracy of 0.1%. To obtain a so tiny humidity grade the chamber was vented with dry air for more than 2 h and with silica gel in its interior. In this atmosphere we took 1 mL of 6 different IL with a pipette (except EMIM-BS and EMIM-OS), they were placed in 6 different Petri plates of 3.9 ± 0.2 cm diameter, covering completely the plate base (also we sealed one sample that was used as target). To begin the experience we weighted each IL with an electronic balance having an accuracy of ± 1 mg, which was placed into the chamber. The molar weight of each IL, MW, are given in Table 1, where also appears the initial mass, m_0 , for the CnMIM-BF₄. After removing the silica gel, we began to increase the chamber humidity grade by introducing controlled quantities of steam water. We left the samples in that environment for at least 1 h and we weighed all six (plus the target sample) trying to not stir them. We continued increasing the humidity grade of the chamber step by step up to 100%, where we left the samples 24 h before weighing them. Later, we began to diminish the humidity of the chamber step by step venting it with dry air and introducing silica gel until we reach the initial humidity (about 10%). We weighed the 6 samples after at least 1 h for each different humidity grade. The temperature was about 20 °C with a maximum variation of ± 1 °C for the experiment. The pressure inside the chamber was the atmospheric and it was not totally constant for the experiment. In any case the comparison among different ILs is valid because the expected variations of temperature and pressure will affect all of them in each weight.

We performed other three different experiments. For the second one, a small quantity of any of the four components of the EMIM-CnS family was left in Petri plates of 3.9 ± 0.2 cm diameter in an atmosphere at less than 15% humidity. The initial mass, m_0 , is included in Table 1. The humidity was increased to 69%, and the four samples weighted after 15 h. We increased the humidity up 100%, and the samples are left near 70 h in this atmosphere before weigh them. The humidity is decreased again at about 70% and samples left there another 70 h before weight them. Later, the chamber is vented with dry air and silica gel to come back the initial conditions (humidity lower than a 10%) and samples were weighed for the last time after being more than 100 h in that dry atmosphere.

For the third experiment the same IL is placed in two different size Petri plates (with 3.9 and 6.7 cm diameter) and left in a 100% humidity atmosphere for about 70 h (with a weekend in the middle). This experiment shows the influence of the free IL surface with the absorption of water. Finally, for the fourth experiment we left over 100 h in a saturated 100% humidity atmosphere a pure sample of EMIM-ES (the IL that absorbs more water as we will observe below) and an equimolar aqueous solution of that IL with water (both in a 6.7 cm diameter Petri plate) to observe saturation.

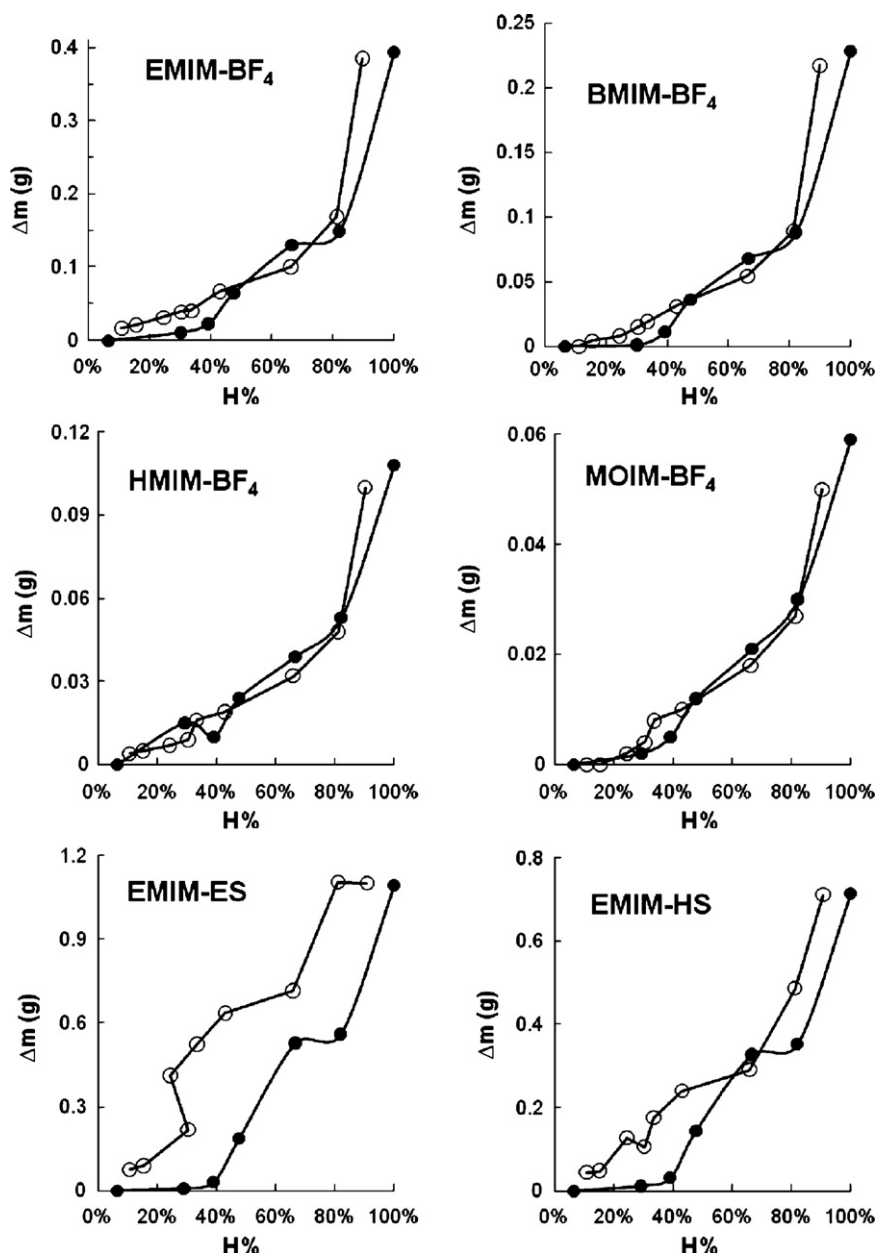


Fig. 2. Increase (solid symbols) and decrease (open symbols) of mass suffered by the six ionic liquids studied according to the humidity grade of the chamber where they were left.

3. Results and discussion

In Fig. 2 we present the increase of mass suffered for each of the six different ILs according to the humidity grade. We include two different series of points in Fig. 2, one for increasing humidity (solid dots) and the other when it decreases (open dots). We can observe that all samples absorb water according to the humidity grade, and they desorb it to atmosphere when it gets dryer (about a 10% of humidity). The desorption process is not complete for the two EMIM-CnS ILs. Although the MOIM-BF₄ is not miscible with water at the used temperature and pressure, it increases its mass too. The observed behavior suggests that the water is really adsorbed (and not absorbed) from atmosphere, generating a water film on the IL surface. So, there is not mixture of the water with the IL, even for the most miscible ones. The quantity of water adsorbed for each sample for the different humidity values depends on the kind of IL. We explain the data as physic-adsorption phenomena, where the water

molecules are fixed in the surface of the IL due to physical attractive forces such as Van der Waals or hydrogen bonds. The weakness of the adhesion forces would explain why the water is desorbed to atmosphere nearly completely. The EMIM-CnS family does not desorb water completely, maybe some mixture between water and IL happens, or it could have pores in the surface at molecular level where the water would be trapped permanently. To remove the water completely in those ILs it is necessary to use one of the drying techniques described in Section 1 [4–6]. On the other hand the number of anchorage points for water molecules would depend on the nature of the IL. In Fig. 3 we show the increase of mass suffered by the six IL samples used in the first experiment in function of the number of carbon atoms of their alkyl chain, *n*. The Fig. 3(a) shows the family of CnMIM-BF₄, and Fig. 3(b) part of the EMIM-CnS family. The black symbols in both figures represent the water adsorption of the samples at 100% humidity over 24 h, the white symbols are for 15 h at 67% humidity (increasing) and the grey symbols over 15 h at

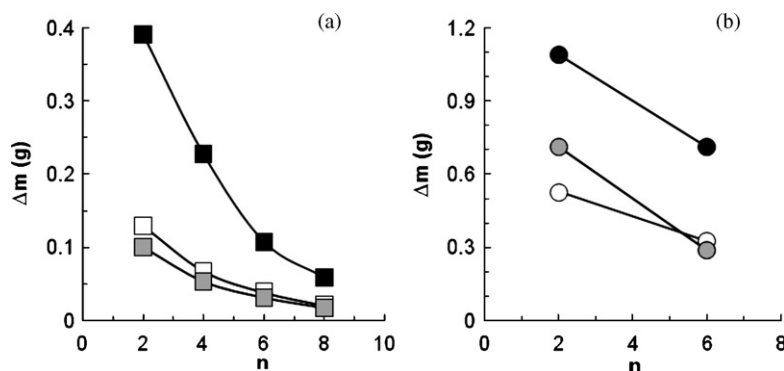


Fig. 3. Increase of mass suffered by CnMIM-BF₄ (a) and EMIM-CnS (b) vs. the number of carbon atoms of the alkyl chain, n . Black symbols represent the increase of mass after 22 h at 100% humidity, white symbols after 15 h at 67% humidity when it was increasing and grey symbols after 15 h at 66% humidity when it was decreasing. Data was taken from Fig. 2.

66% humidity (decreasing). Both IL families show a decrease water adsorption with the alkyl length, but this effect is not due to the increase of the molecular weight because the water adsorption is maximum for EMIM-ES. Also, the increase of mass at about 66% of humidity grade is lower for decreasing humidity than for increasing (except for EMIM-ES). From the data at 100% of humidity we deduce that the adsorbed water represents an increase of mass over 60% for EMIM-ES. In any case, this value is not important because we guess that the adsorption strongly depends on the exposed surface of the IL. That quantity of adsorbed water in molar fraction will be about 0.9 for EMIM-ES and EMIM-HS. For the other four ILs the resulting molar fraction of water would be lower but still important, and the quantities are given in Table 1. From Fig. 3 we conclude that the adsorption process depends on the chemical nature of the IL anion and cation and for both families of ILs studied it decreases with the alkyl chain length. Following our discussion, if the alkyl chain length diminishes, the anchorage sites for water molecules to be adsorbed will increase, and so the quantity of mass would be proportional to the number of those sites. In this sense, if we divided the mass adsorbed for each IL by the mass adsorbed for the IL with two carbons more of the same family, the result would be about 1.85 ± 0.03 for all of them. This suggests that the decrease of the alkyl length in two carbon atoms increases the anchorage sites for water molecules over 85%. To complete those results, we performed the second experiment with four ILs of the EMIM-CnS family. The results are presented in Fig. 4, where we show the increase of mass

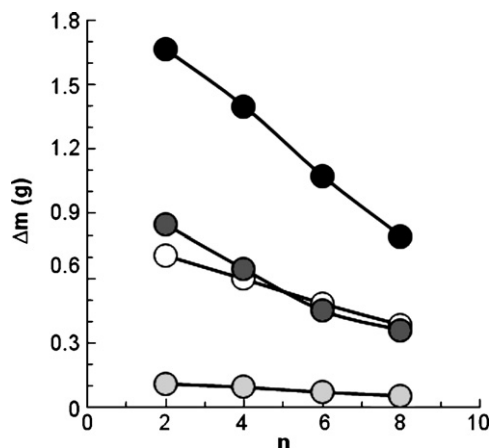


Fig. 4. Increase of mass suffered by EMIM-CnS vs. the number of carbon atoms of the alkyl chain, n . Black symbols represent the increase of mass after 70 h at 100% humidity, white symbols after 15 h at 69% humidity when it was increasing, dark grey symbols after 70 h at 66% humidity when it was decreasing and light grey symbols after more than 100 h at 13% humidity.

suffered by each compound, thus black symbols represent the water adsorption of the samples at 96% humidity over 70 h, white symbols are for 15 h at 69% humidity (increasing), dark grey symbols are for 70 h at 67% humidity (decreasing) and light grey symbols after more than 100 h at 13% humidity. As observed the water adsorption decrease linearly with the carbon atoms number, and the desorbed water process is not complete at a dry atmosphere even after a great number of hours, as we had observed previously for this ILs family. The data shown in this Fig. 4 cannot be directly compared with that of Fig. 3, because the humidity grade is not exactly the same and also the samples have not been left the same time at the different atmosphere conditions. In any case, although the values do not agree, the relative behavior among the two common ILs for both figures is the same.

In Fig. 5 we present the increase of mass suffered by 4 samples left into an atmosphere with 100% humidity during several days. Cross symbols represent BMIM-BF₄ in a 3.8 cm diameter Petri plate and triangle symbols the same compound but in a Petri plate of 6.7 cm diameter. These two sets of data are referred to right axis. As it is expected, the quantity of water adsorbed depends on the size of the opened surface to atmosphere, but it is not proportional. The smallest surface adsorbs more water per unit surface than the biggest one. In fact, after nearly 10 h the sample in the small plate adsorbed approximately 30 mg/cm², while that in the big plate is less than 14 mg/cm². After 75 h the proportion is still worse because the small plate increased its mass about 50 mg/cm² while big plate only 18 mg/cm². This difference in mass adsorption per surface unit

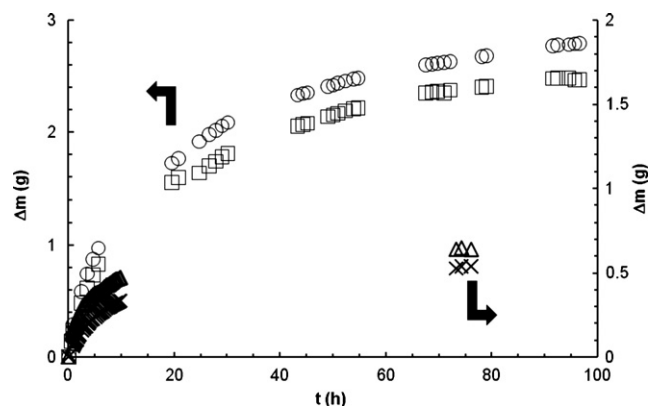


Fig. 5. Increase of mass in function of time in a 100% humidity atmosphere. Cross symbols are for a BMIM-BF₄ sample in a 3.6 cm diameter Petri plate, triangle symbols represents the same IL in a 6.7 cm diameter Petri plate (both referred to right axis), dot symbols are for EMIM-ES sample in the big plate and square symbols for an equimolar mixture of EMIM-ES + water also in the big plate (both referred to left axis).

can be due to border effects, because the meniscus that water forms with the Petri plate wall can store more water molecules than the plane surface. In any case more research in this direction is necessary. In Fig. 5, we also present the increase of mass suffered by EMIM-ES (dot symbols) and an equimolar aqueous solution of this same IL (square symbols) in function of time, both placed in Petri plates of 6.7 cm diameter into a 100% humidity atmosphere. As we can observe, it takes about 100 h to saturate both samples. If we were stirring the samples it would absorb more water from atmosphere and it would take more time to be saturated as recently published [8]. The most interesting fact is that equimolar solution adsorbs about the same quantity of water than the pure sample with a similar speed rate, which explains why if we stir the sample it will continue adsorbing water. The equimolar aqueous solution adsorption can be easily explained knowing that the surface of that mixture is composed mainly by IL molecules, since if we compare the value of the surface tension of equimolar solutions of these IL with the pure ones, we observe both values are very similar [2,8]. It is necessary to perform new measurements to observe the dependence of the mass adsorption with temperature and pressure, but we guess that for small changes of temperature and pressure the water adsorption will not be greatly affected.

4. Conclusions

We have measured the quantity of mass adsorbed by six ionic liquids according to the humidity grade of the atmosphere. The results show that the water is adsorbed in the surface of the IL, generating a film on it. The quantity of adsorbed water depends on the chemical nature of the ionic liquid, but for the same family of

compounds the increase in the length of the alkyl chain decreases the quantity of water adsorbed. This happens independently so that the alkyl chain corresponds to the organic cation or the anion. When the sample is exposed to a 100% humidity grade it takes up to 100 h to be completely saturated of adsorbed water without stirring. The mass of water adsorbed can be even higher to the weight of the initial pure IL. Another interesting result is that aqueous mixtures of ILs at equimolar composition adsorb water from atmosphere at the same rate, and about the same quantity, than the pure compound.

Acknowledgements

This work is under Research Project from the Spanish M.E.C. with reference FIS2007-66823-C02-01, which is partially supported by FEDER funds.

References

- [1] P. Wasserscheid, T. Welton (Eds.), *Ionic Liquids in Synthesis*, Wiley-Verlag, Weinheim, 2003.
- [2] W. Liu, L. Cheng, Y. Zhang, H. Wang, M. Yu, *J. Mol. Liq.* 140 (2008) 68–72.
- [3] J. Vila, P. Ginés, E. Rilo, O. Cabeza, L.M. Varela, *Fluid Phase Equil.* 247 (2006) 32–39.
- [4] J.A. Widegren, E.M. Saurer, K.N. Marsh, J.W. Magee, *J. Chem. Thermodyn.* 37 (2005) 569–575.
- [5] M.G. Freire, L.M.N.B.F. Santos, A.M. Fernandes, J.A.P. Coutinho, I.M. Marrucho, *Fluid Phase Equil.* 261 (2007) 449–454.
- [6] I.B. Malham, P. Letellier, E. Mayaffree, M. Turmine, *J. Chem. Thermodyn.* 39 (2007) 1132–1143.
- [7] R.K. Rogers, K.R. Seddon (Eds.), *Ionic Liquids, Industrial Applications to Green Chemistry*, ACS, Washington, DC, 2002, ACS Symposium Series 818.
- [8] L.A.S. Ries, F.A. do Amaral, K. Matos, E.M.A. Martini, M.O. de Souza, R.F. de Souza, *Polyhedron* 27 (2008) 3287–3293.