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

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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-BF_4) 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-BF_4 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.

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 different 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 indefinably 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-BF_4) 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

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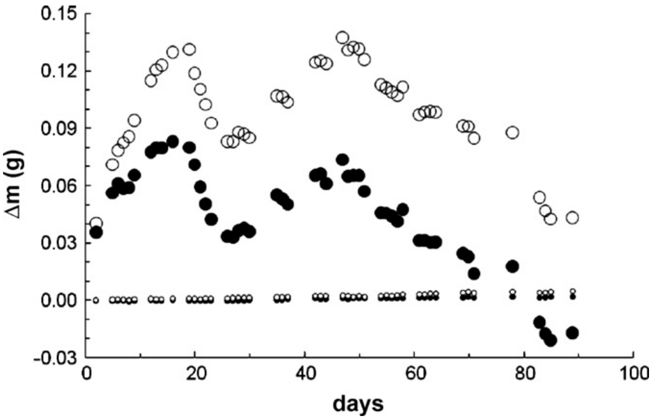

Fig. 1. Variation of mass suffered by EMIM-ES (open dots) and EMIM-BF_4 (solid dots) during 3 months left in the window of our laboratory. The big symbols represent the Eppendorf bins opened to atmosphere, while the small symbols those closed used as targets.

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-BF_4 (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-BF_4 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 (BF_4) is common. This series includes four ILs, with Cn as ethyl (EMIM-BF_4), butyl (BMIM-BF_4), hexyl (HMIM-BF_4) and octyl (MOIM-BF_4). In the second series the cation (EMIM) was common while the anion alkyl sulfate (CnS) changes its size. We have studied the higroscopyc 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-BF_4 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-BF_4) and MOIM-BF_4 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-BF_4 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-BF_4. 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.