

SYNTHESIS AND PROPERTIES OF A NEW IONIC LIQUID WHICH JELLYFIES AT ROOM CONDITIONS

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ABSTRACT

In this communication the synthesis and physical properties of the new ionic liquid 1-ethyl-3-methyl imidazolium decyl sulfate, are shown. The interest of this new salt lies in its tendency to jellify when it is exposed to the atmosphere by absorbing water from moisture up to about a 10% of its own mass; then it keeps the mass $\pm 2\%$ stable depending on the atmospheric humidity grade. The rigid-gel state appears from 15 °C to 60 °C. Below 15 °C it crystallizes and above 60 °C it liquefies. According to TGA measurements the compound is stable up to 300°C. The compound 1-ethyl-3-methyl imidazolium decyl sulfate was prepared in two steps. First the alkylation of 1-methylimidazole with diethyl sulfate afforded 1-ethyl-3-methylimidazolium ethyl sulfate. Then a later transesterification reaction allowed to obtain the desired 1-ethyl-3-methyl imidazolium decyl sulfate with high yield and purity. Its structure was confirmed by ¹H, ¹³C NMR. Also we performed IR spectroscopy as well as Mass Spectrometry. The FTIR spectrum of this new compound, and the temperature behavior of some physical properties such as electrical conductivity, viscosity, density and refractive index, will be presented.

INTRODUCTION

Ionic Liquids are a new group of chemical compounds formed solely by ions that are liquid below 100°C (by definition) but usually they are liquid at room temperature. These compounds are so molten salts with a very low melting temperature. This is because they are formed by a big organic cation and an anion (usually inorganic but in some cases also organic), that can be a halogen (Cl, Br or I), a fluorinated ion (BF₄, PF₆), a sulfate, a nitrate, a phosphate; or other more complex anion (as tosylate, bis(trifluoromethylsulfonyl) imide, acetate...). Among the common characteristics of all ILs are: non flammability, very low vapor pressure, high stability both thermal and chemical, ionic conductivity (usually higher than 0.1 mS/cm) and wide electrochemical window (> 1 V). Also, each particular IL has its

own properties, thus some of them are completely soluble in water while others are hydrophobic. There is an appropriate IL to dissolve nearly each chemical compound and so they can be tailored specifically for every application [1].

In this communication we present a new IL, not described before in literature and obviously not commercial, the 1-ethyl-3-methyl imidazolium decyl sulfate [EMIm][DSO₄]. It has the ability to gel when it is mixed with a tiny quantity of water (around a 10 % of its own weight) that the compound can absorb directly from the atmosphere moisture. Once in gel state the compound is stable at room conditions conserving its properties unaltered. Thus we have a stable electrically conductor gel in the range of temperatures from 15°C to 60°C. Below that the compound crystallizes and above that range it liquefies. At our knowledge, it is the first hydrated compound that is in rigid gel state at room temperature without need of any gelator [2,3]. The applications of this compound go from electrolytes to lubricants. Here we present the synthesis and some physical properties of this new material (ionic conductivity, density, viscosity), as well as the X-ray diffraction of the crystal-gel transition, their FTIR spectra and thermal characterization.

SYNTHESIS

The new Ionic liquid [EMIm][DSO₄] was prepared in two steps (Figure 1). First 1-ethyl-3-methyl imidazolium ethyl sulfate ([EMIm][ESO₄]) was obtained by direct alkylation of 1-methylimidazole with diethyl sulfate in toluene to give the desired compound as a colourless liquid with high purity (99%) and high yield (92%). Its structure was confirmed by ¹H-NMR and ¹³C-NMR spectroscopy and by comparison with literature data.

Then [EMIm][DSO₄] was prepared from [EMIm][ESO₄] by a trans-esterification reaction that was carried out by treatment of a mixture of 1-decanol and [EMIm][ESO₄] with methane sulfonic acid. [EMIm][DSO₄] was obtained as a colourless liquid with high purity (99%) and high yield (92%). Its structure was confirmed by ¹H-NMR and ¹³C-NMR spectroscopy as well as low and high MS spectrometry.

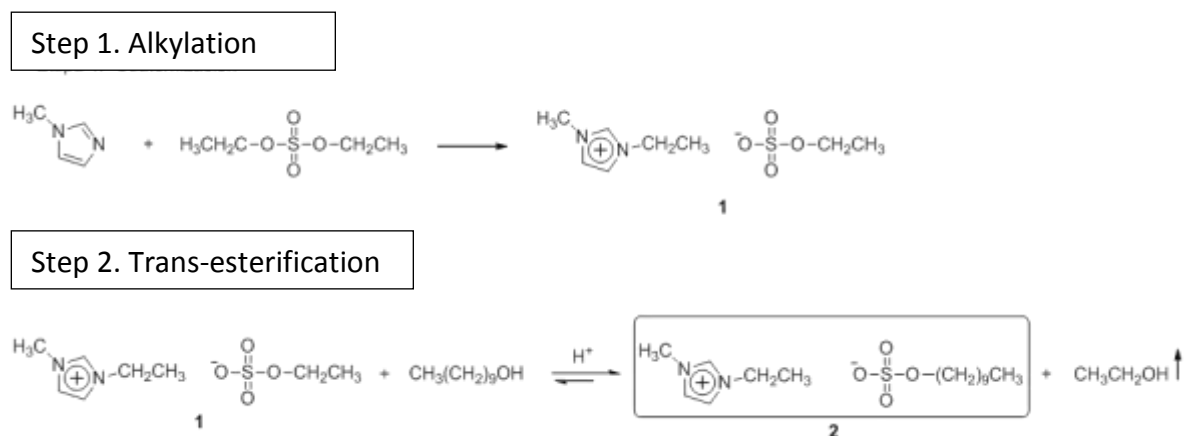


Figure 1. Scheme of the two steps followed to synthesize [EMIm][DSO₄]

Finally, the pure $[\text{EMIm}][\text{DSO}_4]$ was naturally hydrated by leaving it in contact with the ambient moisture. About one hour later it was observed that the liquid hydrates and so it transforms in a rigid gel due to the absorption of the atmospheric water. Once the compound is in the new rigid gel state its weight stays stable for months, as it was observed by leaving it opened to the atmosphere for 5 months. Figure 2 shows the evolution of the weight of the sample located on a petri plate with the time, being the first point (at $t = 0$), the weight of the pure compound. The quantity of absorbed water changes between 8% and 12% of the pure $[\text{EMIm}][\text{DSO}_4]$ weight, depending on the humidity grade of the atmosphere, being the relationship between both percentages roughly linear (Figure 3). The Fourier Transformed Infrared (FTIR) spectrum of the hydrated sample is shown in Figure 4, where the peaks corresponding to the water content are marked.

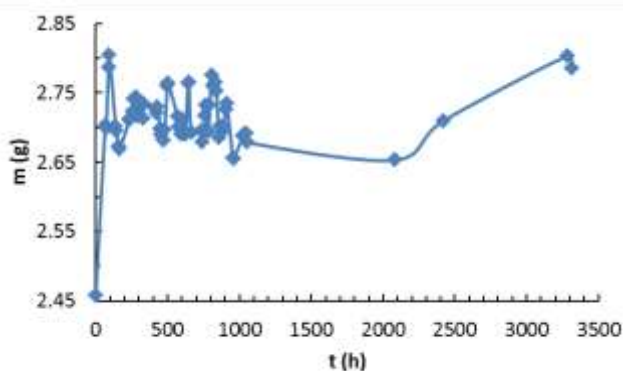


Figure 2. Weight variation of the sample open to atmosphere with time

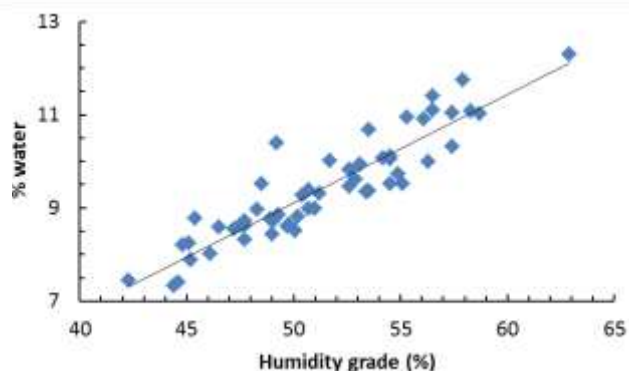


Figure 3. Percentage of water absorbed vs. the atmospheric humidity grade

MICROSTRUCTURE

In Figure 5 two Debye circles obtained from X-ray diffraction pattern for a sample of hydrated $[\text{EMIm}][\text{DSO}_4]$ can be observed; one of them corresponds to the crystal solid ($T = 0^\circ\text{C}$, at left side) and the other one to the rigid gel state ($T = 50^\circ\text{C}$, at right side), which demonstrates the crystallinity of the compound when it is in solid state and the amorphous character when it is in rigid gel state. The microstructure of the rigid gel at room temperature resembles a liquid crystal as it is observed in Figure 6, where two micrographs obtained with white polarized light are shown: a cone structure on the right and a striped pattern on the left, both characteristic of a smectic A phase [4].

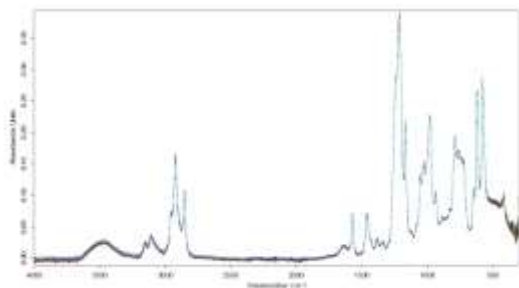


Figure 4. FTIR spectra of the hydrated [EMIm][DSO₄] at room temperature

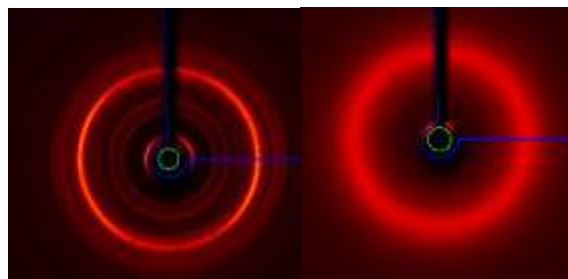


Figure 5. Debye circles of the compound at 0°C (left) and 50°C (right).

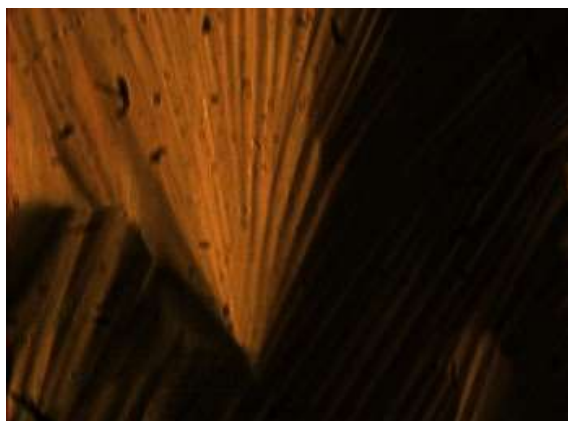


Figure 6. White polarized micrographs of the hydrated [EMIm][DSO₄] at room temperature

PROPERTIES

The most interesting properties of the hydrated compound were also measured. Figure 7 shows the temperature behavior of the electrical conductivity measured with a CRISON GLP conductivimeter. Two interesting points must be underlined: In the crystalline solid-rigid gel transition the typical hysteresis loop can be observed as it has been described for many other ionic liquids [5]. That loop marks the melting point (35°C) and the solidification temperature (15°C) obtained when increasing and decreasing temperature respectively. On the other hand, this figure also shows that electrical conductivity does not change for liquid-rigid gel state transition (60°C for both increasing and decreasing temperature). This behavior has been previously observed in other liquid to rigid gel transitions published by us [6].

In Figure 8 we show the temperature behavior viscosity and density of the hydrated [EMIm][DSO₄] measured with a Stabinger Anton Paar viscodensimeter about the rigid-gel transition. As observed, while the viscosity abruptly changes in that transition while

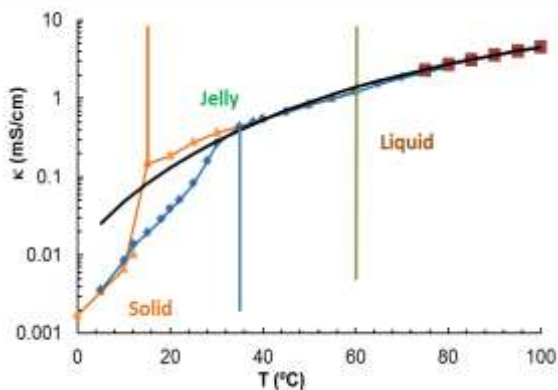


Figure 7. Electrical conductivity of the hydrated [EMIm][DSO₄] vs. temperature

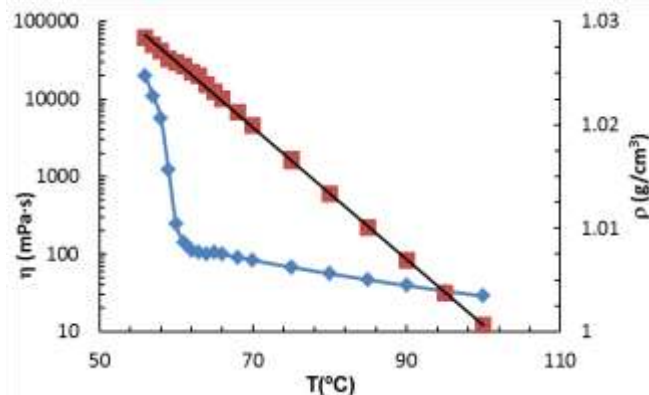


Figure 8. Viscosity (blue rhombus) and density (brown squares) vs. temperature

density does not appreciably change its temperature behavior at the same point. If we compare the viscosity with the electrical conductivity curves we can observe that for this system the charge mobility is completely independent of the viscosity, which contradicts the Walden rule observed usually for the ILs, which relates those two magnitudes [7].

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