

Molecular Features and Transport Properties of DBU Based Protic Ionic Liquids

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High vapor pressure and flammability are some disadvantages of organic solvents currently used in chemical processes. In this scenario, protic ionic liquids (PILs) became a promising alternative to replace conventional solvents due to their interesting physicochemical properties. Understanding the charge transport and molecular features governing PILs is still required to allow their implementation in current and new technologies. Thus, the present work reports the study of PILs based on the 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBU) cation and two anions obtained from strong acids, trifluoromethylsulfonate (TFO⁻) and bis(trifluoromethylsulfonyl)imide (TFSI⁻) using different NMR techniques. ¹H NMR spectra confirm that the high acidity of the PILs constituents is a determinant factor governing their features. Moreover, information on the transport properties of the PILs is obtained by diffusion NMR. The results show a peculiar behavior of the acidic proton, indicative of a different mechanism of charge transport in these systems.

1. Introduction

The environmental consequences caused by the extensive use of fossil fuels is a worldwide concern. In this framework, electrochemical devices, such as lithium batteries, have been extensively explored as a competitive power source. The electrolytes commonly used in lithium batteries consist of lithium salt and organic solvents, which are volatile and highly flammable compounds. Thus, they present risks to the safety of electrochemical devices (Armand et al., 2020).

Protic ionic liquids (PILs) are potential candidates to replace organic solvents in electrochemical applications due to their interesting characteristics such as low flammability, low vapor pressure, high ionic conductivity, and high thermal stability (Macfarlane et al., 2014). These characteristics of PILs are advantageous to overcome the issues associated with the electrochemical devices, further expanding their applications. However, the key factors controlling the properties of the PILs are still unclear, hampering their technical usage.

The most significant parameter claimed to govern the features of PILs is the ΔpK_a resulting from the pK_a difference of the constituent acid and protonated base in water. The ΔpK_a is commonly related to the driving force for the proton transfer from a Brønsted acid to a Brønsted base during the synthesis of a PIL. Equation 1 shows the proton transfer scheme from the Brønsted acid (HA) to the Brønsted base (B) used in the present work and referred to as DBU. For more details on the chemical structure of DBU vide ultra and see Figure 1. In general, thermally stable PILs have sufficiently high ΔpK_a (usually 15 for DBU-based PILs), even if the minimum ΔpK_a value is still under discussion (Miran et al., 2019).



A challenging task in PILs is to tune their physicochemical properties according to the nature of the ionic species. For this purpose, microscopic investigations are needed to provide information on the molecular

interactions present in PILs, consequently providing information about their organization. Besides, studies at the molecular level provide evidence about the ionic transport in PILs, including the protonic conductivity. The proton conduction is expected, at least theoretically, for PILs enabling their application as electrolytes components in electrochemical devices. For instance, fuel cells should operate at temperatures lower than 70 °C with humidification to keep water inside the membranes (Lee et al., 2010). Developing PILs as a non-volatile electrolyte could overcome this issue allowing the cell to operate well above 100 °C. Consequently, the efficiency and performance of these electrochemical devices can be increased. In this context, the description of the protonic conductivity is essential to understand the aspects governing proton mobility. Commonly, the charge transport occurs by the vehicle and/or the Grotthuss mechanisms (Blanchard et al., 2011). In the Grotthuss type mechanism, the proton diffuses hopping through the hydrogen-bonded network using its H-bonding ability. Contrariwise, in the vehicle mechanism, the acidic proton moves attached to a carrier molecule as ionic species. Until now, the aspects governing the mechanism of charge transport in PILs are not well defined.

NMR spectroscopy is a useful technique to provide information on the molecular structure and transport properties of PILs (Judeinstein et al., 2008). Thus, the present work applied different NMR methods to investigate two PILs here reported as paradigmatic examples of a general class of PILs. The PILs were based on the super-strong base 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBU, $pK_a = 13.4$ (Miran et al., 2012)) and the following acids: trifluoromethylsulfonic (HTFO, $pK_a = -7$ (Miran et al., 2012)) and bis(trifluoromethylsulfonyl)imide (HTFSI, $pK_a = -10$ (Miran et al., 2012)). The structures of these PILs are displayed in Figure 1. In the present work, the NMR results revealed a different molecular and dynamic behavior of these systems.

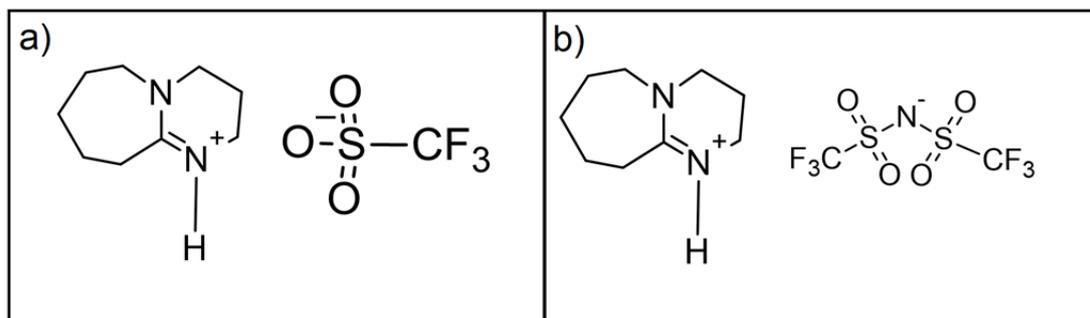


Figure 1: Structure of the PILs studied DBUH-TFO (a) and DBUH-TFSI (b)

2. Experimental

2.1 Synthesis of the PILs

1,7-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%), trifluoromethylsulfonic acid (HTFO, 99%), and nitric acid (HNO_3 , 65 wt.% solution in water) were purchased from Sigma-Aldrich. Lithium bis(trifluoromethylsulfonyl)imide salt (LiTFSI , > 99.9 wt.%) was provided by 3M. The synthesis of DBUH-TFO consisted of a standard neutralization reaction. For the synthesis, the acid:base mole ratio was equal to 1:1. The acid was added in 3 wt.% excess to assure the full protonation of the DBU. The acid was added dropwise to the base under stirring, kept in a cooling water/ice bath to avoid sudden temperature increase and unexpected oxidation. The DBUH-TFSI was synthesized reacting DBU with nitric acid for neutralization yielding DBUH- NO_3 . Then, DBUH-TFSI was formed by a metathesis reaction using LiTFSI dissolved in water. Upon synthesis, the DBUH-based ILs were rinsed several times with deionized water to remove water-soluble impurities, acid excess (DBUH-TFO) and, for DBUH-TFSI, water-soluble LiNO_3 and the excess of LiTFSI . Finally, all PILs were vacuum dried at 50 °C for at least 1 hour and, then, at 100 °C for at least 18 h and stored in an Ar atmosphere glove box ($[\text{O}_2] < 1$ ppm, $[\text{H}_2\text{O}] < 1$ ppm). The samples were placed in 5 mm NMR tubes and flame-sealed in a controlled environment (dry-room, relative humidity < 0.1% at 20 °C) to prevent any contamination and air contact. All the NMR tubes contained a flame-sealed capillary tube of deuterated DMSO (DMSO-d_6) as a reference/lock solution.

2.2 NMR measurements

^1H and ^{19}F NMR experiments of the pure PILs were performed at 11.74 T with a Bruker NEO 500 console equipped with a direct observe 5 mm pulsed-field z-gradient BBFO iProbe. For each sample, the probe was carefully tuned, and the 90° pulses were evaluated. The sample temperature was set and controlled using a

variable temperature control unit using air gas flow. Standard Bruker library programs were used for the measurements. Spectra were acquired over a temperature range from 298 to 373 K for DBUH-TFO, and from 308 K to 373 K for the DBUH-TFSI, with a temperature step of 5 K and a minimum of 30 min allowed for thermal equilibration.

Pulsed-Field-Gradient (PFG) NMR was applied to determine the self-diffusion coefficients (D_i) of the ionic species in the selected PILs. Cation (including acidic protons) and anion self-diffusion coefficients were measured independently by carrying out PFG experiments in the ^1H and ^{19}F frequency domains, respectively. The self-diffusion coefficients were determined using the bipolar pulse longitudinal eddy current delay (BPP-LED) pulse sequence. All experiments were carried out over a spectral width of 11.76 ppm or 78.71 ppm for ^1H and ^{19}F , respectively, with a total of 8 transients per increment. The relaxation delay was set to at least five times T_1 , and 8 dummy scans were programmed prior to acquisition. The pulse gradients were incremented from 2 to 95% of the maximum gradient strength in a linear ramp with 32 steps. For each DOSY experiment, the duration of the magnetic field pulse gradients (δ) and the diffusion times (Δ) were optimized to obtain, where possible, 95% signal attenuation for the slowest diffusion species at the last step experiment. For ^1H diffusion experiments, δ values were in the 3–6 ms range, while Δ values were 0.5–0.8 s long. For ^{19}F diffusion experiments, δ values were in the 3.4–6 ms range, while Δ values were 0.5–0.8 s long. The raw spectra acquired were subjected to manual phasing and automatic baseline correction. Data were processed using an exponential filter in F_2 dimension (LB = 0.3 Hz). Integrals were employed in the Bruker T_1/T_2 module of TopSpin to fit the Stejskal–Tanner relation (Stejskal & Tanner, 1965):

$$\frac{I}{I_0} = e^{-\gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right)} \quad (2)$$

where I is the signal intensity with the gradient applied, I_0 is the initial signal intensity, γ is the gyromagnetic ratio of the investigated nucleus, g is the gradient strength applied.

3. Results

3.1 1D ^1H NMR measurements

The ΔpK_a between the acid and the base used as PILs constituents is stated as a key factor governing their physicochemical properties. ^1H -NMR affords structural information about the protonation of the base, which is strictly related to the acidity strength. According to Miran et al. (2012), the ^1H chemical shift decreases linearly with the acid strength.

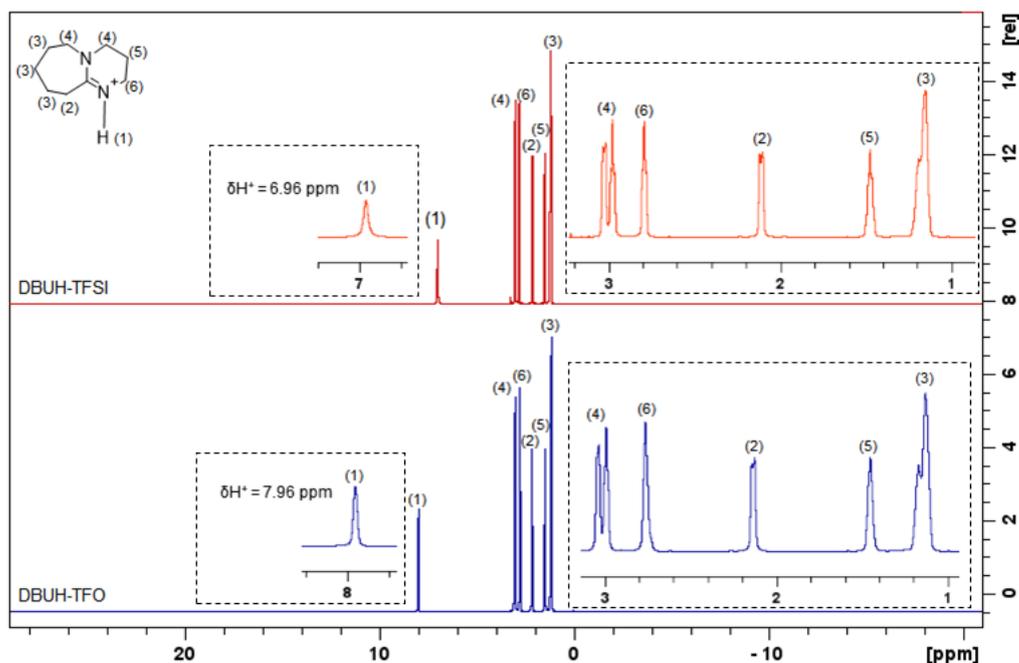


Figure 2: ^1H NMR spectra and the chemical shift assignments of the PILs investigated at 328 K.

Figure 2 displays the ^1H NMR spectra and the chemical shift assignments of the PILs investigated. The regions containing signals of aliphatic protons from the one side and the acidic proton from the other are zoomed and shown in the insets. The ^1H signals appearing in the upfield region (in the range 1 - 3 ppm) correspond to the carbon-bound H nuclei of the protonated DBU. The signal appearing at the highest frequency corresponds to the acidic proton. As shown in Figure 2, the chemical shift of the exchangeable proton moves upfield as the ΔpKa of the PIL increases (see Table 1). This upfield shift is indicative of protonation attributable to the increase in the magnetic shielding experienced by the exchangeable proton interacting with imine nitrogen. Based on this, the chemical shift difference between the acidic proton and the CH_2 (3) group of the DBU is a marker of protonation and an indicator of the acid strength (Judeinstein et al., 2008). No signal is appearing in the range 10–15 ppm, indicating that free acid is not present in the system, as observed by Wiench et al. (1999). The PILs studied are based on super strong constituents, having similar ΔpKa . Consequently, their molecular properties, evidenced by the ^1H NMR, were notably comparable.

Table 1: Correlation between the ^1H with ΔpKa of the PILs studied.

PIL	Anion	$\Delta\delta(^1\text{H})$ ^(a) ppm	ΔpKa	T_m ^(c)
DBUH-TFO	CF_3SO_3^-	6.7	20.4 ^(d)	298.15 K ^(d)
DBUH-TFSI	$(\text{CF}_3\text{SO}_2)_2\text{N}^-$	5.8	23.4 ^(d)	296.15 K ^(d)

^(a) $\Delta\delta(^1\text{H}) = \delta\text{H}^+ - \delta\text{CH}_2(3)$; ^(c) T_m is the melting point; ^(d) Data from Miran et al. (2012)

3.2 Self-diffusion coefficients measurement

Figure 3 displays the self-diffusion coefficient (D_i) of the ionic species, cation, anion, and acidic proton, in DBUH-TFO and DBUH-TFSI measured as a function of the temperature. High diffusion is expected for PILs with low viscosity (high fluidity). Here, this statement agrees with the higher self-diffusion coefficients obtained for the cations and the anions, as they are higher in the DBUH-TFSI, which is the less viscous system (0.1 Pa.s at 308 K).

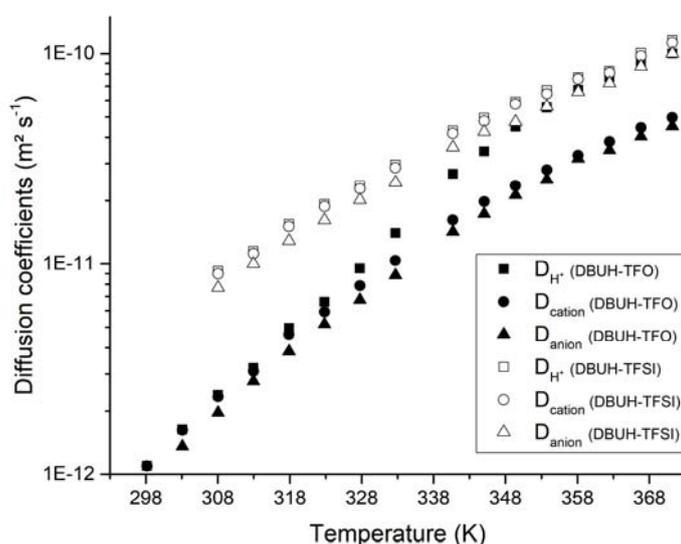


Figure 3. Self-diffusion coefficients of the ionic species in the PILs studied in this work as a function of the temperature.

Studying the ratios of the conducting species reveals more detailed information about their transport properties (Figure 4). As expected in all the systems investigated, the cation and the anion are not diffusing as ion pairs since their diffusivities are not equal (Figure 4c). In both systems, the cation diffuses faster than the anion ($D_{\text{cation}}/D_{\text{anion}} > 1$). Particularly noteworthy are the self-diffusivities measured for the acidic protons (Figure 4a). The diffusion constants measured for the acidic proton D_{H^+} (DBUH-TFSI) are similar to those relative to the cation D_{cation} (DBUH-TFSI), in the DBUH-TFSI, indicating a charge transport mainly based on the vehicular mechanism ($D_{\text{H}^+}/D_{\text{cation}} = 1$). Contrarily, in the DBUH-TFO, D_{H^+} (DBUH-TFO) values strongly deviate

from those relative to the cation (Figure 4a) and the anion (Figure 4b), and the discrepancy increases with the temperature ($D_{H^+}/D_{cation} > 1$). This would mean that the charge transport in DBUH-TFO occurs through a contribution of both Grotthuss and vehicle mechanism. Besides, in both PILs the diffusion of the acidic proton is faster than the anion diffusion ($D_{H^+}/D_{anion} > 1$), indicating that these ionic species are moving separately (Figure 4b).

Such a difference in the ionic mobility in DBUH-TFO and DBUH-TFSI is counterintuitive. Indeed, the same mechanism of charge transport is expected for the PILs studied because there are both formed mixing very strong precursors, having relatively close ΔpK_a values (20.4 in DBUH-TFO vs 23.4 in DBUH-TFSI). It should be noted that, as shown elsewhere (Blanchard et al., 2011), even very low amounts of water, such as 0.1% (wt. %), can markedly influence the diffusion of the acidic proton in the PILs. Further investigations are hence in progress in our laboratory to verify whether the apparent Grotthuss mechanism observed in the DBUH-TFO is due to traces of water or other impurities in the system (not detected in their 1H NMR spectra) or is related to a real difference in the charge transport.

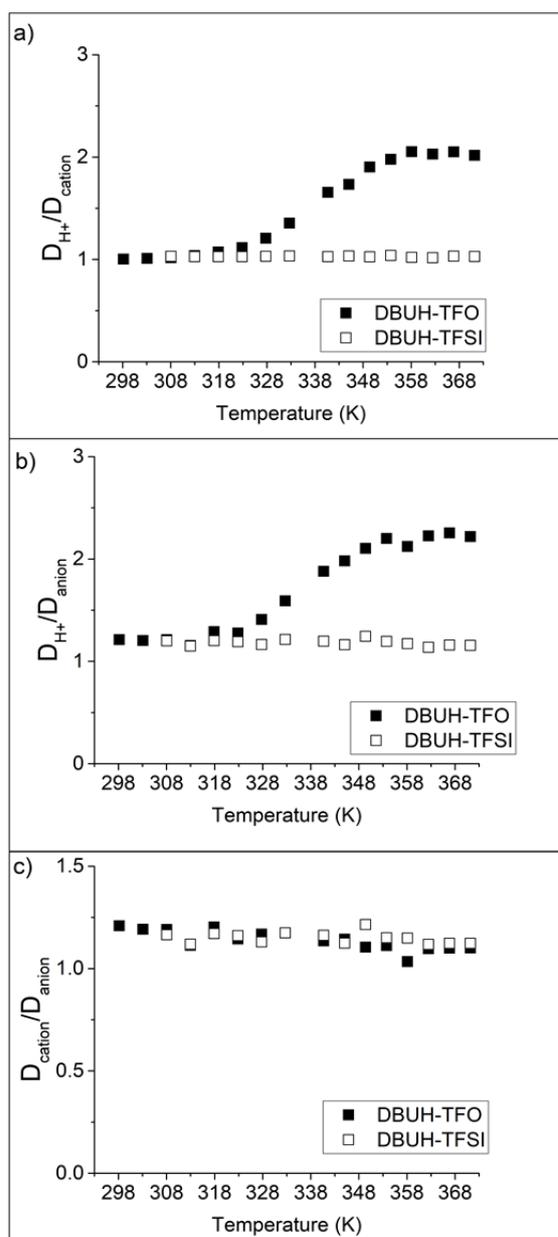


Figure 4. Diffusion ratios of the ionic species.

4. Conclusions

Protic ionic liquids (PILs) are potential candidates to replace organic solvents improving the safety of the electrochemical devices. Understanding the proton diffusion mechanism and molecular interactions of PILs is crucial to promote their future applications in the electrochemical industry. The mechanism of charge conduction inside the protic ionic liquids is still unclear, and this lack of information hampers their possible use as an electrolyte component. To this end, thermally stable PILs formed by a super strong base (DBU) and two different acids (HTFSI and HTFO) were investigated. According to the ^1H NMR spectra, the ΔpK_a of DBUH-TFO is lower than that of DBUH-TFSI. The self-diffusion coefficients of the ionic species in these PILs were determined to characterize their transport properties. Accordingly, the charge transport in DBUH-TFSI occurs as a vehicular mechanism, while in DBUH-TFO both vehicular and Grotthuss-type mechanisms would contribute to the charge transport. The latter occurs predominantly at high temperatures and can be promoted due to traces of water present in the system. Such difference in terms of transport properties is currently under further investigation in our laboratories.

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