

Determination of the Viscosity of the Ionic Liquids [bmim][PF₆] and [bmim][TF₂N] Under High CO₂ Gas Pressure Using Sapphire NMR Tubes

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Dedicated to Professor Gérard Demazeau on the occasion of his 65th birthday

The viscosities of the ionic liquids [bmim][PF₆] and [bmim][TF₂N] (bmim = 1-methyl-3-butylimidazolium, TF₂N = bis(trifluoromethylsulfonyl)imide) have been determined under CO₂ pressure at 298 K. The viscosity decreases from 381 to 23 cP for [bmim][PF₆] without CO₂ and for 2.17 molal CO₂ solutions (mole fraction $X_{\text{CO}_2} = 0.381$, 55 bar CO₂), respectively. For [bmim][TF₂N] the viscosity decreases from 54 cP for the ionic liquid to 21 cP for a 1.61 molal solution of CO₂ (mole fraction $X_{\text{CO}_2} = 0.403$, 55 bar CO₂).

Key words: Ionic Liquids, CO₂ Pressure, Viscosity, High Pressure, Sapphire NMR Tube

Introduction

Solubility of gases in ionic liquids is an area of intense research activity [1]. Recently, we showed that high (gas) pressure NMR spectroscopy is an excellent method for the determination of gas solubilities in ionic liquids, especially suited to gases with low solubilities (*e.g.* H₂, CO) [2]. Subsequently, this method has been used to determine the solubility of H₂ in the ionic liquid [emim][TF₂N] (emim = 1-ethyl-3-methylimidazolium, TF₂N = bis(trifluoromethylsulfonyl)imide) in the presence of CO₂, the presence of CO₂ helping to increase the H₂ gas solubility and reduce the overall viscosity of the system [3]. The latter was quantified using a special home built equipment [4]. In this paper we extend our original work using high-pressure NMR tubes (sapphire) to determine the viscosity of ionic liquids under high gas pressures.

Results and Discussion

Prior to the viscosity determinations the quantity of dissolved CO₂ was established by NMR spectroscopy, also providing insights into the interactions between the ionic liquid and the gas solute. It has already been shown by IR spectroscopy that CO₂ dissolved in [bmim][PF₆] interacts with the anion [5], and molecular modelling has provided further insights [6]. The dif-

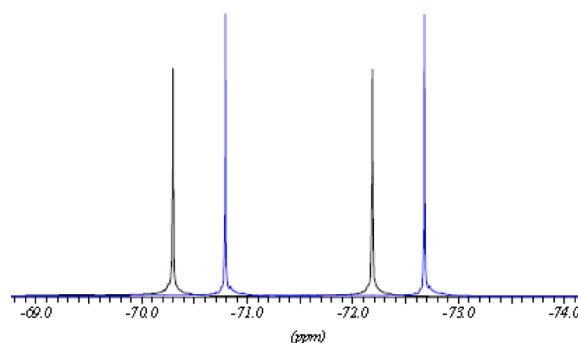


Fig. 1. ¹⁹F NMR spectra of [bmim][PF₆] (black) and under 55 bar CO₂ pressure (blue) (color online).

ference between the ¹⁹F NMR spectra of [bmim][PF₆] and [bmim][PF₆] under 55 bar of CO₂ (Fig. 1) shows a strong anion interaction with CO₂; the chemical shift of the characteristic doublet of the hexafluorophosphate anion in the ¹⁹F NMR spectrum changes by $\Delta\delta \sim 0.5$ ppm.

In the ¹³C, ³¹P (Figs. 2, 3) and ¹H NMR spectra all peaks undergo a slight modification.

The most notable changes in frequency are observed for the alkyl-group protons indicating that the cation is not innocent with respect to the CO₂ solubilization (Fig. 4). The ¹³C NMR spectrum was also used to quantify the concentration of dissolved CO₂ in [bmim][PF₆] under 55 bar CO₂ at 298 K, which was

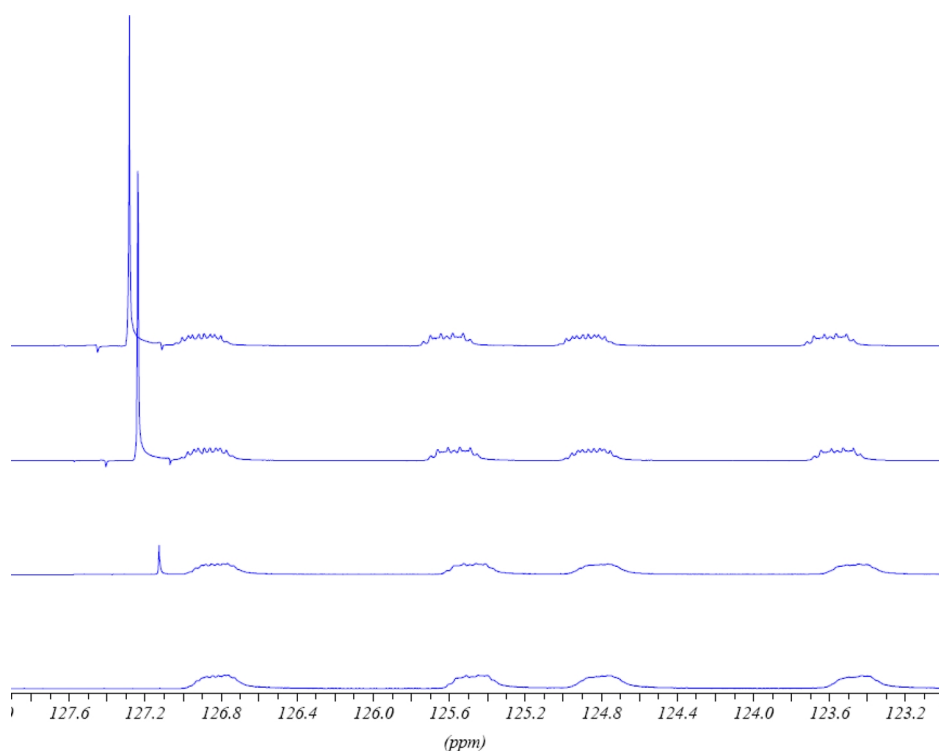


Fig. 2. ¹³C NMR spectra of [bmim][PF₆] at the CO₂ region under 0, 5, 55 and 98 bar CO₂ pressure (from bottom).

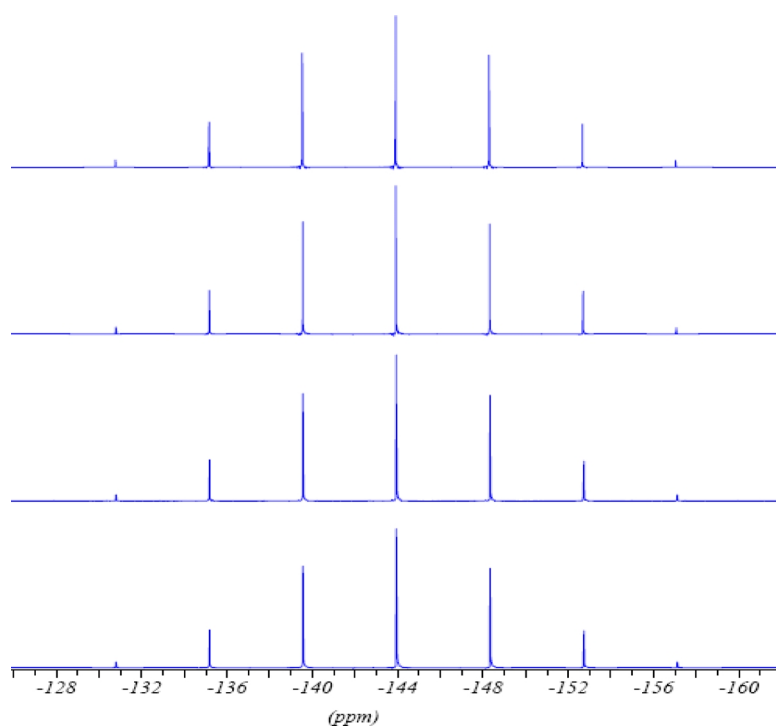


Fig. 3. Chemical shifts (–143.94, –143.96, –143.98, and –143.99 ppm) in the ³¹P NMR spectra of [bmim][PF₆] under 0, 5, 55 and 98 bar CO₂ pressure (from bottom).

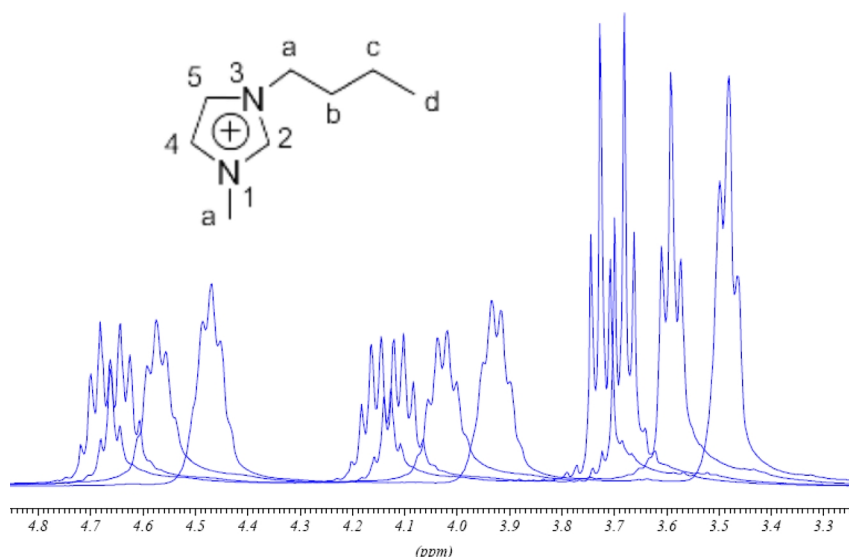


Fig. 4. Chemical shifts of the methyl (3d) and neighboring CH₂ (3c and 3b) protons of the butyl group in the ¹H NMR spectra of [bmim][PF₆] under 0, 5, 55 and 98 bar CO₂ pressure (from right to left).

Table 1. Viscosity of ionic liquids at 298 K^a.

	[bmim][PF ₆]	[bmim][Tf ₂ N]
η , cP ($P_{\text{CO}_2} = 0$ bar)	381 ± 9	54 ± 5
η , cP ($P_{\text{CO}_2} = 55$ bar)	23 ± 4	21 ± 4

^a Errors are estimated from the reproducibility of the measurements.

found to be 2.17 molal (mole fraction of CO₂ $X_{\text{CO}_2} = 0.381$). Under analogous conditions the solubility of CO₂ in [bmim][Tf₂N] was estimated to be 1.61 molal (mole fraction of CO₂ $X_{\text{CO}_2} = 0.403$). Next, the viscosity of these ionic liquids was determined directly in the sapphire NMR tube (see Experimental Section) and the values obtained are listed in Table 1.

The viscosity of both ionic liquids decreases significantly, for [bmim][PF₆] by a factor of 17 and for [bmim][Tf₂N] by a factor of 2.5. Although the decrease in viscosity for [bmim][Tf₂N] is smaller than that observed for [bmim][PF₆], the final viscosities under the same pressure of CO₂ gas are essentially the same.

Brennecke first described the remarkable ability of the ionic liquid [bmim][PF₆] to dissolve high concentrations of CO₂ gas [7], and subsequently gas solubilities in ionic liquids have attracted much attention. The solubilities of other important gases have also been reported, including H₂ [2a], CO [2b], CH₄ [8], C₂H₄ [9], H₂S [2c], and O₂ [9], yet CO₂ remains the most widely studied due to some unusual features [3,9]: (1) CO₂ solubility is extremely high; (2) only a small change in volume is observed despite of the larger volume of dissolved gas; (the phenomenon has recently been

rationalized using molecular dynamics simulations); (3) dissolved CO₂ can increase the solubility of other gases, *e. g.* hydrogen, which is very low, and therefore could facilitate hydrogenation reactions; (4) the presence of CO₂ decreases the viscosity of ionic liquids.

Conclusions

Ionic liquid-CO₂ interactions appear to offer considerable potential, not only in completely negating the need for organic solvents, but inducing higher reactivity and allowing catalyst immobilization combined with efficient product extraction [3,9]. Apart from applications in catalysis using gases as substrates [10], ionic liquids have found applications in gas storage [11], and there is much current interest in the potential of ionic liquids to selectively extract gases in a variety of processes [12]. The decrease in viscosity quantified herein suggests that ionic liquids of high viscosity could be easily handled in processes involving CO₂.

Experimental Section

Ionic liquids were synthesized according to published procedures [13]. Carbon dioxide (> 99.97%) was supplied by Carbagas and used as received. The method required a high-pressure (sapphire) NMR tube (length 13 cm, internal diameter 0.80 cm), which was built in-house according to a literature protocol [14]. The tube was charged with the ionic liquid to 11 cm, pressurized with CO₂ gas to 55 bar, and shaken vigorously. The concentration of dissolved CO₂ was determined after equilibration by ¹³C NMR spectroscopy by

integrating the ¹³C NMR signal of the dissolved CO₂ against various ¹³C NMR signals of the ionic liquid, as described previously for CO. NMR spectra were recorded on a Bruker DRX 400 MHz NMR spectrometer. TMS, phosphoric acid (50 %) and KF (1 M solution in D₂O) were used as external references for ¹H, ¹³C, ³¹P, and ¹⁹F NMR measurements, respectively. Spectra were fitted using the NMRICMA 2.8 software (non-linear least-squares iterative fitting application for the MatLab program).

Into the high-pressure (sapphire) NMR tube containing the ionic liquid a stainless-steel ball (mass 63.5 mg, volume 8.18 mm³) was placed, and the solution was re-equilibrated with CO₂ gas under 55 bar pressure. The ball was then moved to a point just below the surface of the ionic liquid using a magnet and then released. The time taken for the ball to descend to a point near the bottom (total distance 9.7 cm)

was determined using a high-resolution digital camcorder. All measurements were made at 298 K. The viscosity was subsequently determined using the equation:

$$\eta = \frac{2g(\rho_b - \rho_{il})r^2t}{9l}$$

where η is the viscosity, g is the gravity (9.81 cm s⁻²), ρ_b is the density of the ball (7.8 g cm⁻³), ρ_{il} is the density of the IL (1.36 g cm⁻³ and 1.43 g cm⁻³ for [bmim][PF₆] and [bmim][TF₂N], respectively), r is the radius of the ball (0.125 cm), l is the distance (9.7 cm), and t is the time (s).

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