Determination of the Viscosity of the Ionic Liquids [bmim][PF_6] and [bmim][TF_2N] Under High CO_2 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][PF_6] and [bmim][TF_2N] (bmim = 1-methyl-3-butylimidazolium, TF_2N = bis(trifluoromethylsulfonyl)imide) have been determined under CO_2 pressure at 298 K. The viscosity decreases from 381 to 23 cP for [bmim][PF_6] without CO_2 and for 2.17 molal CO_2 solutions (mole fraction X_{CO_2} = 0.381, 55 bar CO_2), respectively. For [bmim][TF_2N] the viscosity decreases from 54 cP for the ionic liquid to 21 cP for a 1.61 molal solution of CO_2 (mole fraction X_{CO_2} = 0.403, 55 bar CO_2).

Key words: Ionic Liquids, CO_2 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.* H_2, CO) [2]. Subsequently, this method has been used to determine the solubility of H_2 in the ionic liquid [emim][TF_2N] (emim = 1-ethyl-3-methylimidazolium, TF_2N = bis(trifluoromethylsulfonyl)imide) in the presence of CO_2, the presence of CO_2 helping to increase the H_2 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 CO_2 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 CO_2 dissolved in [bmim][PF_6] interacts with the anion [5], and molecular modelling has provided further insights [6]. The difference between the ^{19}F NMR spectra of [bmim][PF_6] and [bmim][PF_6] under 55 bar of CO_2 (Fig. 1) shows a strong anion interaction with CO_2; the chemical shift of the characteristic doublet of the hexafluorophosphate anion in the ^{19}F NMR spectrum changes by $\Delta\delta \sim 0.5$ ppm.

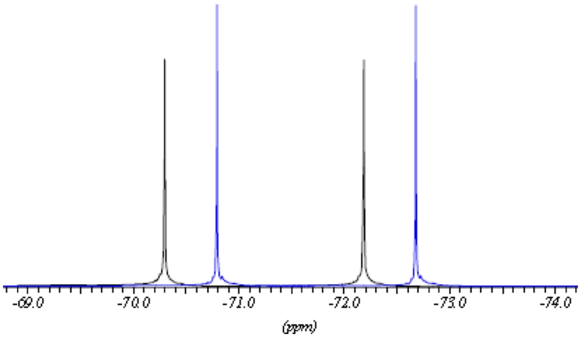

Fig. 1. ^{19}F NMR spectra of [bmim][PF_6] (black) and under 55 bar CO_2 pressure (blue) (color online).

In the ^{13}C, ^{31}P (Figs. 2, 3) and ^{1}H 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 CO_2 solubilization (Fig. 4). The ^{13}C NMR spectrum was also used to quantify the concentration of dissolved CO_2 in [bmim][PF_6] under 55 bar CO_2 at 298 K, which was

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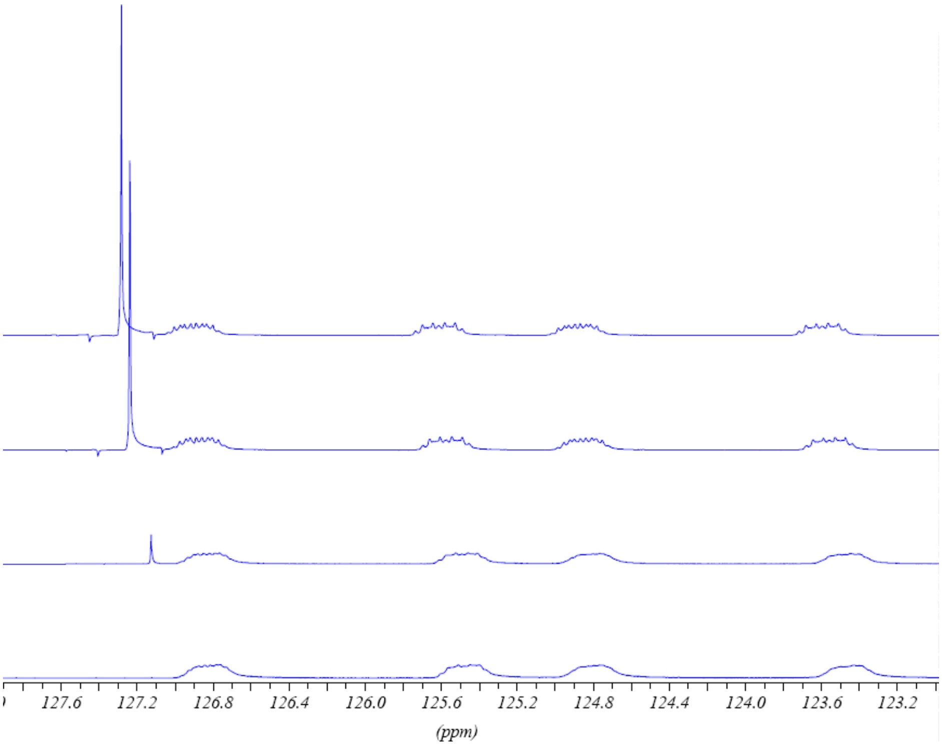

Fig. 2. ^{13}C NMR spectra of [bmim][PF$_6$] at the CO$_2$ region under 0, 5, 55 and 98 bar CO$_2$ pressure (from bottom).

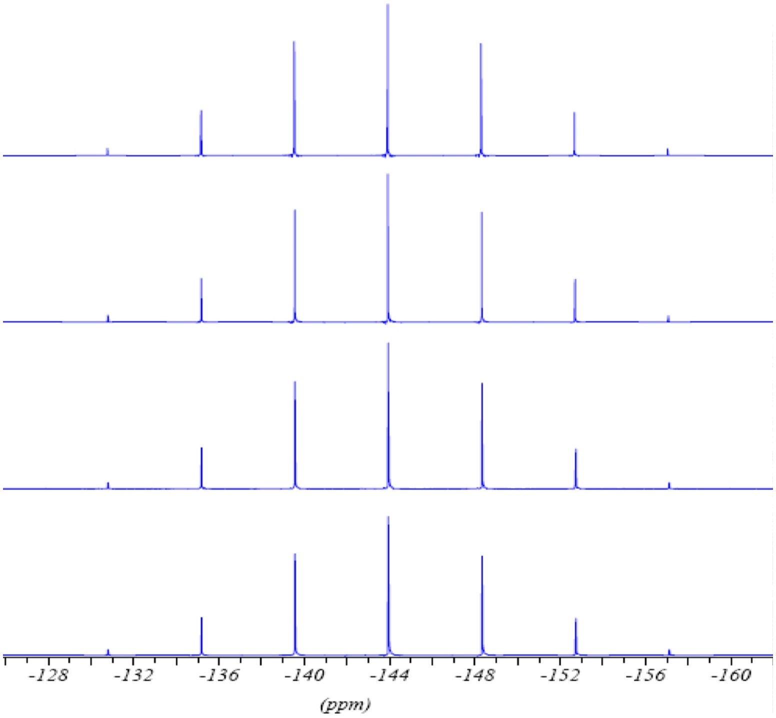

Fig. 3. Chemical shifts (– 143.94, – 143.96, – 143.98, and – 143.99 ppm) in the ^{31}P NMR spectra of [bmim][PF$_6$] under 0, 5, 55 and 98 bar CO$_2$ pressure (from bottom).

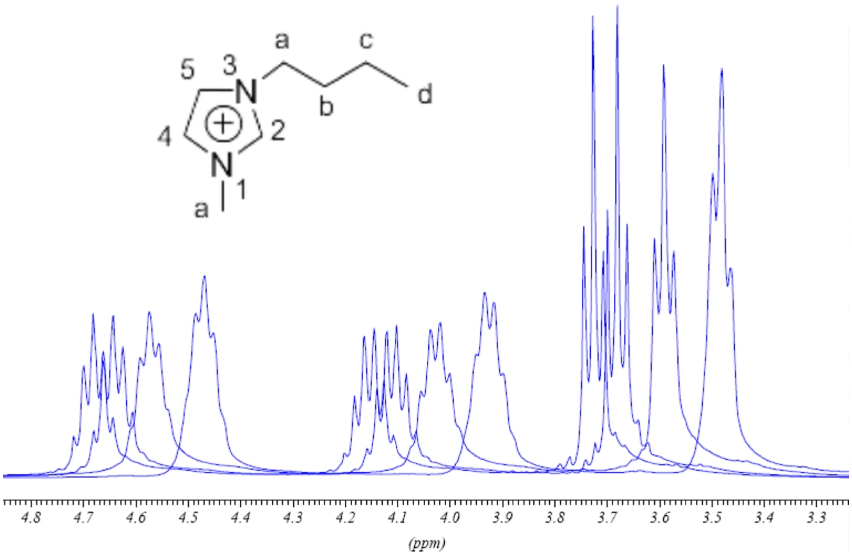

Fig. 4. Chemical shifts of the methyl (3d) and neighboring CH_2 (3c and 3b) protons of the butyl group in the ^1H NMR spectra of [bmim][PF_6] under 0, 5, 55 and 98 bar CO_2 pressure (from right to left).

Table 1. Viscosity of ionic liquids at 298 K[a].

	[bmim][PF_6]	[bmim][Tf_2N]
η, cP (P_{CO_2} = 0 bar)	381 ± 9	54 ± 5
η, cP (P_{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 CO_2 X_{CO_2} = 0.381). Under analogous conditions the solubility of CO_2 in [bmim][Tf_2N] was estimated to be 1.61 molal (mole fraction of CO_2 X_{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][PF_6] by a factor of 17 and for [bmim][Tf_2N] by a factor of 2.5. Although the decrease in viscosity for [bmim][Tf_2N] is smaller than that observed for [bmim][PF_6], the final viscosities under the same pressure of CO_2 gas are essentially the same.

Brennecke first described the remarkable ability of the ionic liquid [bmim][PF_6] to dissolve high concentrations of CO_2 gas [7], and subsequently gas solubilities in ionic liquids have attracted much attention. The solubilities of other important gases have also been reported, including H_2 [2a], CO [2b], CH_4 [8], C_2H_4 [9], H_2S [2c], and O_2 [9], yet CO_2 remains the most widely studied due to some unusual features [3, 9]: (1) CO_2 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 CO_2 can increase the solubility of other gases, *e. g.* hydrogen, which is very low, and therefore could facilitate hydrogenation reactions; (4) the presence of CO_2 decreases the viscosity of ionic liquids.

Conclusions

Ionic liquid-CO_2 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 CO_2.

Experimental Section

Ionic liquids were synthezised 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 CO_2 gas to 55 bar, and shaken vigorously. The concentration of dissolved CO_2 was determined after equilibration by ^{13}C NMR spectroscopy by integrating the ^{13}C NMR signal of the dissolved CO_2 against various ^{13}C 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 D_2O) were used as external references for ^{1}H, ^{13}C, ^{31}P, and ^{19}F 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 mm^3) was placed, and the solution was re-equilibrated with CO_2 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:

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

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][PF_6] and [bmim][Tf_2N], 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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