

Synthesis and Characterization of a New Ionic Liquid Soluble in Supercritical CO₂

Ligia P. Maia¹, Fernanda F. C. Bazito², Roberto M. Torresi¹ and Reinaldo C. Bazito*¹

¹*Instituto de Química, Universidade de São Paulo, C.P. 26077, CEP 05513-970, São Paulo, SP, Brazil*

²*Departamento de Ciências Exatas e da Terra, Universidade Federal de São Paulo - Campus Diadema, Diadema, SP, Brazil*

e-mail: bazito@iq.usp.br, Fax: 55-11-3091-1517

INTRODUCTION

Supercritical fluids (SCF) are very interesting solvents with unique properties, such as high solute diffusivities, low viscosity and density values similar to liquids. All these features can be tuned with modifications in the pressure or temperature or the addition of modifiers [1]. Supercritical CO₂ (sc-CO₂) is one of the most promising alternative solvents because it is cheap, abundant, non-toxic, odorless, non-flammable, easily recycled, can be removed without difficulty from the product and has a low critical point ($P_c=73,8$ bar e $T_c=31,1^\circ\text{C}$) [1]. However, its major limitation is the low dielectric constant and polarizability (in spite of the high quadrupolar moment), making only low molar mass and apolar molecules soluble in it. Polar or ionic compounds, common surfactants and polymers are usually not soluble in this supercritical fluid.

Polysiloxanes and perfluorinated compounds, on the other hand, show good solubility even at low pressures and temperatures [1-4]. Groups that increase the solubility of a molecule in sc-CO₂ (CO₂-philic groups) are usually electron-rich groups, and perfluorinated chains are among the best alternatives for this [5-7].

The solubilization capability of sc-CO₂ can be improved using a surfactant that is effective in this medium. These surfactants are molecules that contain both CO₂-philic and CO₂-phobic groups, leading to aggregation and micelle formation in sc-CO₂, that allows the solubilization of substances that would be insoluble otherwise. The research on the development of such surfactants has been very active in the last few years [8-13].

Ionic liquids (IL) are ionic compounds that have melting points lower than 100°C. They are also alternative solvent due to its negligible vapor pressure, good thermal stability, easy preparation and excellent solubilizing capacity [14,15]. Its addition to sc-CO₂ could be very useful to increase the solubilization capacity of this supercritical solvent. It is worth to note that although some groups are studying the behaviour of ionic liquids in supercritical CO₂, there is no report, to our knowledge of a ionic liquid soluble in this system [16-19].

In this work we will show the preparation and characterization of a new ionic liquid containing a perfluorinated group (Figure 1– IL1) and its solubility in sc-CO₂. In order to compare the effect of such substituent in the solubilization process a similar ionic compound

(IL2) was also studied. The choice of TFSI as the counter-ion was due to the low viscosity of the resulting ionic liquids and the presence of fluoride in its composition.

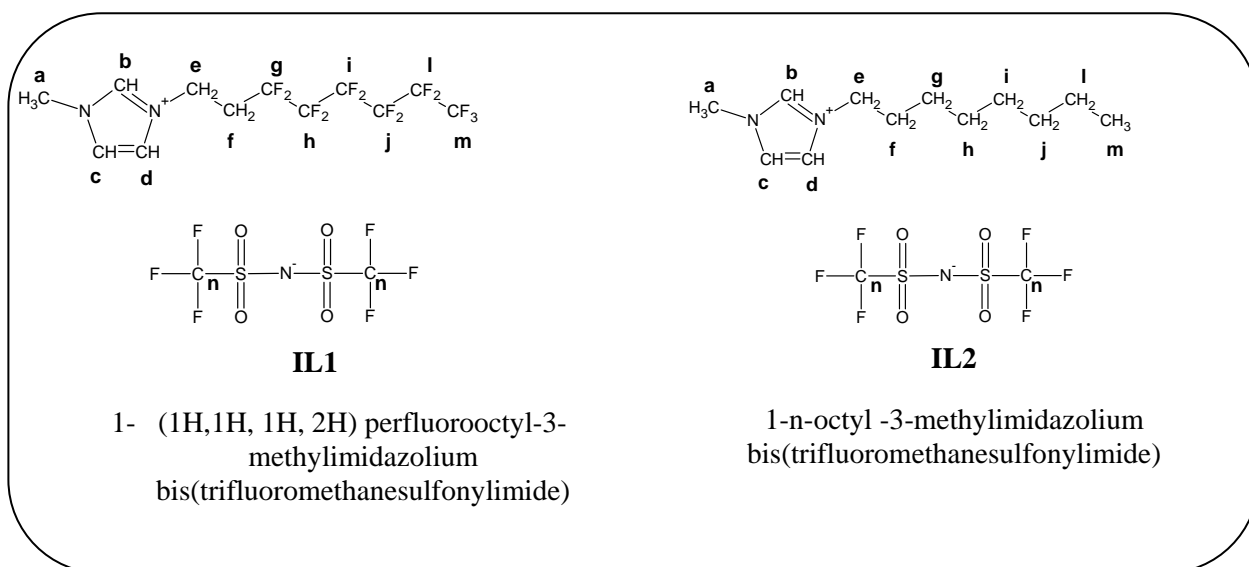


Figure 1: Ionic Liquids Synthesized in This Work

MATERIALS AND METHODS

N-methylimidazole and 1-bromooctane were distilled under reduced pressure before use. The other chemicals were used as received. Solvents were dried by conventional methods and freshly distilled under argon.

Representative synthesis of 1- (1H, 1H, 2H, 2H) perfluorooctyl -3-methylimidazolium bis(trifluoromethanesulfonylimide): In a flask fitted with a reflux condenser were added 0.87 g (11 mmol) of 1 -methylimidazole and 5.00 g (11 mmol) of 1-iodo 1H, 1H, 2H, 2H perfluorooctane. After addition, the mixture was stirred at 80°C for 24 hours to give an yellow oil. The crude product was washed several times with anhydrous toluene and then recrystallized from an acetonitrile/toluene mixture and dried under reduced pressure to give 2.71g (46 % yield) of 1-(1H, 1H, 2H, 2H) perfluorooctyl -3-methylimidazolium iodide as white crystals. In another flask, it was placed 2.71g (5 mmol) of the iodide compound dissolved in 5.0 mL of water followed by an aqueous solution of LiTFSI (1.42 g; 5 mmol) in 5.0 mL of water. The reaction mixture was stirred overnight at room temperature and two phases were formed and separated. The phase containing the ionic liquid was washed several times with water, treated with activated carbon and subjected to column chromatography (alumina, dichloromethane). The ionic liquid was dried under reduced pressure for three days at 100 °C to give 1- (1H, 1H, 2H, 2H) perfluorooctyl -3-methylimidazolium bis(trifluoromethanesulfonylimide) (IL1) as a colorless liquid (1.42g, 41 % yield).

The IL2 was synthesized following the same procedure. The quaternization and ionic exchange steps were performed with 42 % and 58 % yields, respectively obtaining a colorless oil.

All ionic liquids were stored in an argon atmosphere glovebox. The structures of the halide derivatives and of the ionic liquids were identified by ^1H and ^{13}C NMR, and elemental analysis. The results for both ionic liquids are summarized below.

IL1 data: Found: %C: 23.66; %H: 1.51. Calc: %C: 23.71; %H: 1.42; ^1H -NMR (DMSO- d^6 , δ in ppm): 9.19 (s, $-\text{C}_b\text{H}$, 1H), 7.87 and 7.72 (s, $-\text{C}_c\text{H}$ e $-\text{C}_d\text{H}$ 1H e 1H), 4.57 (t, $-\text{C}_f\text{H}_2$, 2H), 3.87 (s, $-\text{C}_a\text{H}_3$, 3H), 3.01 (m, $-\text{C}_e\text{H}_2$, 2H). ^{13}C -NMR (DMSO- d^6 , δ in ppm): 137.14 (s, C_b), 123.6 and 122.6 (s, $-\text{C}_c$ e C_d), 125.8, 121.5, 117.3 and 113.1 (s, C_n), 41.10 (t, C_e e C_f), 35.77 (s, C_a). Peaks between 29.70 and 30.60 are related to the perfluorinated chain (C_g to C_m). Thermal decomposition temperature (T_d): 405°C

IL2 data: Found: %C: 35.38; %H: 4.77. Calc: %C: 35.37; %H: 4.88; ^1H -NMR (CDCl $_3$ - d^1 , δ in ppm): 8.76 (s, $-\text{C}_b\text{H}$, 1H), 7.29 (m, $-\text{C}_c\text{H}$, $-\text{C}_d\text{H}$, 2H), 4.16 (t, $-\text{C}_e\text{H}_2$, 2H), 3.94 (s, $-\text{C}_a\text{H}_3$, 3H), 1.86 (m, $-\text{C}_f\text{H}_2$, 2H), 1.28 (m, $-\text{C}_{g-i}\text{H}_2$, 10H), 0.89 (t, $-\text{C}_m\text{H}_3$, 3H). ^{13}C -NMR (CDCl $_3$ - d^1 , δ in ppm): 136.14 (s, C_b), 123.68 and 122.18 (s, $-\text{C}_c$ and C_d), 126.19, 121.94, 117.68 and 113.43 (s, C_n), 50.27 (s, C_a), 36.38 (s, C_e), 31.62 (s, C_f), 30.07 (s, C_g), 28.92 (s, C_h), 28.80 (s, C_i), 26.11 (s, C_j), 22.55 (s, C_l), 14.01 (s, C_m). Thermal decomposition temperature (T_d): 438 °C

Solubility Tests in Supercritical CO $_2$

The experiments were performed in a Thartech SPM20 Supercritical Phase Monitor, coupled to a Isco 260D syringe pump. In a typical experiment, 100 mg of the ionic liquid where added to the high pressure viewcell of the phase monitor, and 5 mg of methylene blue were added to increase the visibility of the ionic liquid phase. The system was pressurized to 60 bar with liquid CO $_2$, the desired temperature were set and the pressure were increased to 340 bar and then decreased slowly to detect any phase transitions. The temperature and pressure where varied in the range 60-320 bar, 25 to 50°C.

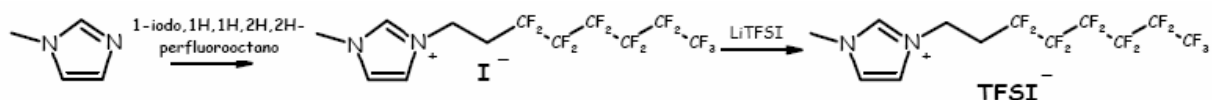
Thermal properties

Differential scanning calorimetry (DSC) was carried out using a T. A. Instruments Q.10 DSC coupled with T. A. refrigerated cooling system (RCS) interfaced to the Thermal Analyst 2000 software under nitrogen atmosphere. The samples for DSC measurements were sealed on aluminum pans. First, the samples were cooled to -80 °C and then heated at a rate of 20 °C min $^{-1}$ up to 100 °C. Thermogravimetric measurements were conducted on a T. A. Instruments Hi-ResTM TGA 2950 interfaced to Thermal Analyst 2000 software from room temperature to 800 °C at a heating rate 20 °C min $^{-1}$, resolution 3 and sensitivity 1, under nitrogen atmosphere on Pt made crucible.

RESULTS

The proposed ionic liquids were prepared in two steps, following similar procedures already described in the literature [20] (Scheme 1). Succinctly, commercial amines were

quaternized with alkyl halides in reasonable yield after prolonged heating, resulting in white crystals or colorless oil after purification processes. These purified salts were submitted to ionic exchange with LiTFSI in aqueous media. These salts were purified by successive washings with water, treatment with activated carbon, liquid chromatography and finally drying. These liquids are colorless and hydrophobic and their structures were confirmed by ^1H and ^{13}C NMR and elemental analysis.



Scheme 1. Preparation of the IL2

The thermal characterization was performed by thermogravimetry (TG) and differential scanning calorimetry (DSC). The RTILs under study have no distinguishable vapor pressure and, as a result, the first thermal event on heating of these ionic liquids is the thermal decomposition. The decomposition temperatures (T_d) for both ionic liquids were higher than $400\text{ }^\circ\text{C}$, IL2 being slightly more stable than IL1. The similarity of the thermal stabilities was expected, since this property is related to the anionic species. For example, the pyrolysis of salts based on imidazolium cations proceeds via a $\text{S}_{\text{N}}2$ process and thereby the basicity or/and nucleophilicity of the counter ion changes the thermal stability of the ionic liquid [21].

The fluorinated ionic liquid is moderately soluble in sc-CO_2 , presenting a cloud pressure of 300 bar at $32\text{ }^\circ\text{C}$. Its phase separation at this pressure occurs as big droplets that rapidly coalesce. The non-fluorinated ionic liquid was not soluble at the pressures reachable with our equipment. Experiments are underway to determine whether the ionic liquid just solubilize or if it forms aggregates in the sc-CO_2 .

CONCLUSION

In summary, the preparation of a new ionic liquid with excellent thermal stability based on imidazolium for potential use as additive in supercritical CO_2 , aiming the improvement of the solubilization capacity of this fluid was shown. The presence of the perfluorinated chain in this ionic liquid seemed to be crucial for the solubilization of this salt in $\text{CO}_2\text{-sc}$.

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REFERENCES

- [1] JOHNSTON, K. P.; PENNINGER, J. M. L. *Supercritical fluid science and technology*; American Chemical Society: Washington, DC, **1989**.
- [2] MCHUGH, M. A.; KRUKONIS, V. J. *Supercritical fluid extraction : principles and practice*; 2nd ed.; Butterworth-Heinemann: Boston, **1994**.
- [3] DESIMONE, J. M.; GUAN, Z.; ELSBERND, C. S. *Science*, Vol. 257, **1992**, p. 945-947.
- [4] HEITZ, M. P.; CARLIER, C.; DEGRAZIA, J.; HARRISON, K. L.; JOHNSTON, K. P.; RANDOLPH, T. W.; BRIGHT, F. V. *Journal of Physical Chemistry B*, Vol. 101, **1997**, p. 6707-6714.
- [5] KAJIMOTO, O. *Chemical Reviews*, Vol. 99, **1999**, p. 355-389.
- [6] KAZARIAN, S. G.; VINCENT, M. F.; BRIGHT, F. V.; LIOTTA, C. L.; ECKERT, C. A. *Journal of the American Chemical Society*, Vol. 118, **1996**, p. 1729-36.
- [7] DARDIN, A.; DESIMONE, J. M.; SAMULSKI, E. T. *Journal of Physical Chemistry B*, Vol. 102, **1998**, p. 1775-1780.
- [8] MCCLAIN, J. B.; BETTS, D. E.; CANELAS, D. A.; SAMULSKI, E. T.; DESIMONE, J. M.; LONDONO, J. D.; COCHRAN, H. D.; WIGNALL, G. D.; CHILLURA-MARTINO, D.; TRIOLO, R. *Science*, Vol. 274, **1996**, p. 2049-2051.
- [9] PARK, J.-Y.; LIM, J. S.; YOON, C. H.; LEE, C. H.; PARK, K. P. *Journal of Chemical and Engineering Data*, Vol. 50, **2005**, p. 299-308.
- [10] LI, J.; ZHANG, J.; HAN, B.; GAO, Y.; SHEN, D.; WU, Z. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects*, Vol. 279, **2006**, p. 208-212.
- [11] HOEFLING, T. A.; NEWMAN, D. A.; ENICK, R. M.; BECKMAN, E. J. *Journal of Supercritical Fluids*, Vol. 6, **1993**, p. 165-71.
- [12] HARRISON, K. L.; JOHNSTON, K. P.; SANCHEZ, I. C. *Langmuir*, Vol. 12, **1996**, p. 2637-2644.
- [13] SAGISAKA, M.; YODA, S.; TAKEBAYASHI, Y.; OTAKE, K.; KONDO, Y.; YOSHINO, N.; SAKAI, H.; ABE, M. *Langmuir*, Vol. 19, **2003**, p. 8161-8167.
- [14] WELTON, T. *Chemical Reviews*, Vol. 99, **1999**, p. 2071-2083.
- [15] DUPONT, J.; CONSORTI, C. S.; SPENCER, J. *Journal Of The Brazilian Chemical Society*, Vol. 11, **2000**, p. 337-344.
- [16] SHARIATI, A.; RAEISSI, S.; PETERS, C. J. *Developments and Applications in Solubility*, **2007**, p. 131-149.
- [17] LI, J. C.; ZHANG, J. L.; HAN, B. X.; WANG, Y.; GAO, L. *Journal of Chemical Physics*, Vol. 121, **2004**, p. 7408-7412.
- [18] AKI, S. N. V. K.; MELLEIN, B. R.; SAURER, E. M.; BRENNECKE, J. F. *Journal of Physical Chemistry B*, Vol. 108, **2004**, p. 20355-20365.
- [19] WU, W.; ZHANG, J.; HAN, B.; CHEN, J.; LIU, Z.; JIANG, T.; HE, J.; LI, W. *Chemical Communications (Cambridge, United Kingdom)*, **2003**, p. 1412-1413.
- [20] P. BONHOTE, A.-P. DIAS, N. PAPAGEORGIOU, K. KALYANASUNDARAM, M. GRAETZEL, *Inorganic Chemistry*, **1996**, Vol. 35, p. 1168-1171.
- [21] FOX, D. M.; AWAD, W. H.; GILMAN, J. W.; MAUPIN, P. H.; DE LONG, H. C.; TRULOVE, P. C. *Green Chemistry*, Vol. 5, **2003**, p. 724-727.