

HIGH-PRESSURE CO₂-INDUCED SWELLING OF IONIC LIQUIDS.

Sakellarios N. I., Kazarian S. G.*

Department of Chemical Engineering and Chemical Technology,

Imperial College, London, SW7 2AZ, United Kingdom

E-mail: s.kazarian@imperial.ac.uk

Fax: 44-207-594-5604

In situ IR spectroscopic method was used to measure swelling of the expanded ionic liquids subjected to high-pressure CO₂. The CO₂ sorption and the consequent swelling of ionic liquid have been measured simultaneously at high-pressure. Swelling of [bmim][PF₆] was ca.18% under the 72 bar of CO₂ at 25 °C.

INTRODUCTION

Currently, ionic liquid media (IL) are receiving a great deal of attention as they present great potential for the development of new “green” technologies. Examples of technologies that could benefit from the utilization of ionic liquids include organic synthesis [1], separations [2] and electrochemistry [3] to mention a few. The reason for ionic liquids being such a promising medium for the development of new environmentally friendly technologies can be identified to their highly solvating, yet non-coordinating nature, which allows for the solvation of many organic and inorganic substances. Recent work has also demonstrated that CO₂ is highly soluble in certain ionic liquids [4-8], an observation extending the potential applications of IL in separating CO₂-soluble reaction products from IL by the use of SCF/liquid extraction [9]. Recently it has also been reported that the liquid phase volume expansion of ionic liquids with the introduction of even large amounts of CO₂, is negligible [10]. *In situ* spectroscopic techniques developed by us provide effective means to investigate these phenomena.

RESULTS AND DISCUSSION

The advantages of *in situ* FT-IR spectroscopy has been used in this work to study the interactions between CO₂ and [bmim][PF₆] ionic liquid (kindly supplied by SACHEM, Austin, TX, USA) and the phase behavior of IL/CO₂ system. Figures 1 and 2 show the trend followed by the IR absorption bands of ionic liquid and the CO₂ correspondingly as the pressure of the CO₂ increases. As observed from Figure 1, the absorbance of the band assigned to the [bmim][PF₆] decreases with increasing CO₂ pressure; a phenomenon attributed to the fact that as the concentration of CO₂ dissolved in the IL increases (denoted by the increase in the band absorbance in Figure 2), the density of the IL drops, hence leading to smaller amounts of ionic liquid absorbing the IR light passing through the sample. Consequently, by analysis of these absorbance bands we conclude that ionic liquid does swell under the high pressure CO₂. Assuming that the molar absorptivity, ϵ , does not change with the concentration of the absorbed CO₂, the absorbance of the band of the ionic liquid (at ca. 6205 cm⁻¹) before (A^0) and after (A) exposure to CO₂ follows the Beer-Lambert equations:

$$A^0 = \epsilon \cdot c^0 \cdot d \quad (1)$$

$$A = \epsilon \cdot c \cdot d \quad (2)$$

where c^0 and c are the concentrations of the ionic liquid before and during exposure to gas.

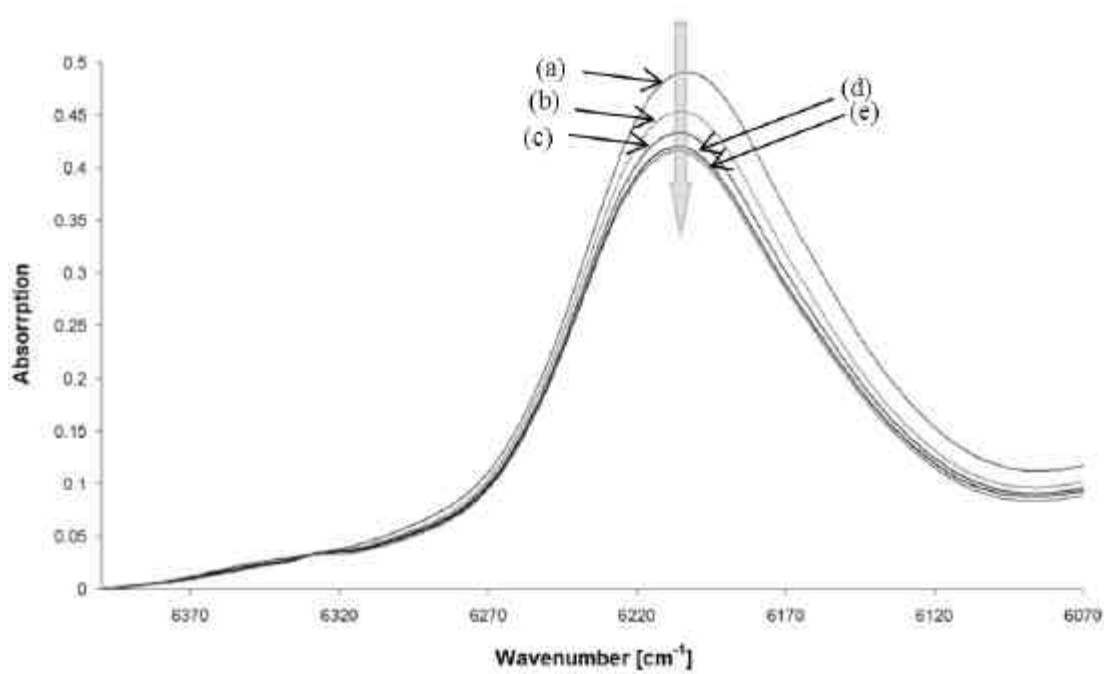


Figure 1: The IR spectra of the combination band of [bmim][PF₆] at 25°C and CO₂ pressure of (a) ambient pressure, (b) 24 bar, (c) 42 bar, (d) 60 bar, and (e) 72 bar.

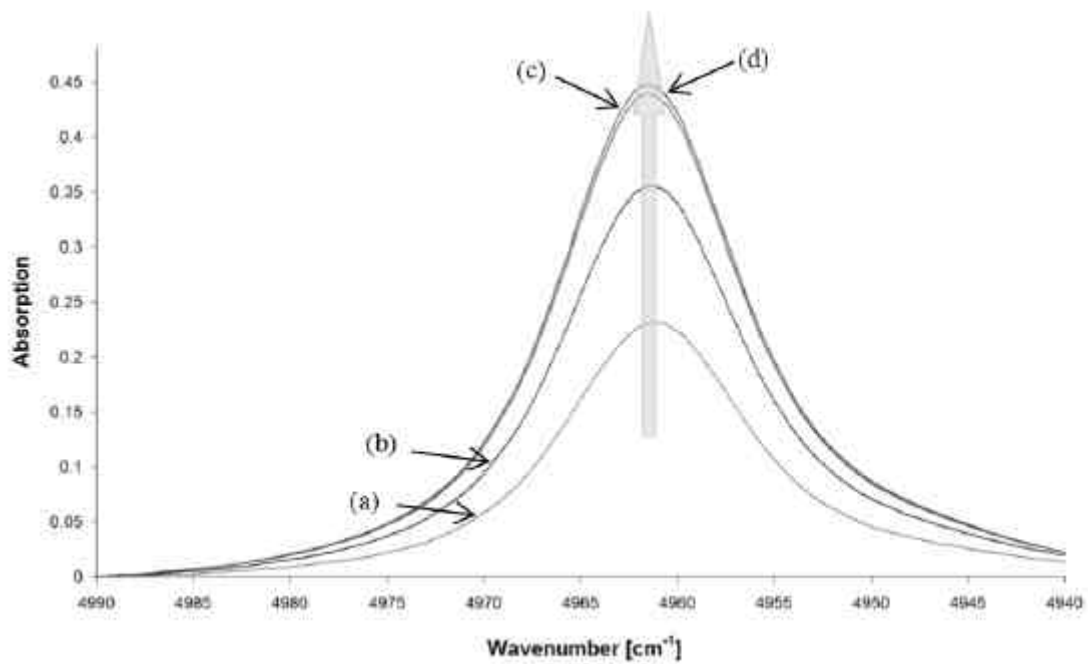


Figure 2: The IR spectra of the combination band of CO₂ dissolved in the ionic liquid medium at 25°C and at CO₂ pressure of (a) 24 bar, (b) 42 bar, (c) 60 bar, (d) 72 bar.

If we consider that the ionic liquid sample occupies a volume V before exposure and a volume $V + \Delta V$ during exposure, the following equation defines the swelling S .

$$\frac{c^0}{c} = \frac{V + \Delta V}{V} = 1 + \frac{\Delta V}{V} = 1 + S \quad (3)$$

by combining equations (1), (2) and (3), the degree of swelling is given by:

$$S = \frac{A^0}{A} - 1 \quad (4)$$

Utilizing equation (4) along with the spectroscopic data acquired for the absorbance of the combination band of the ionic liquid the following graph can be plotted showing the extent of swelling at various pressures of CO_2 .

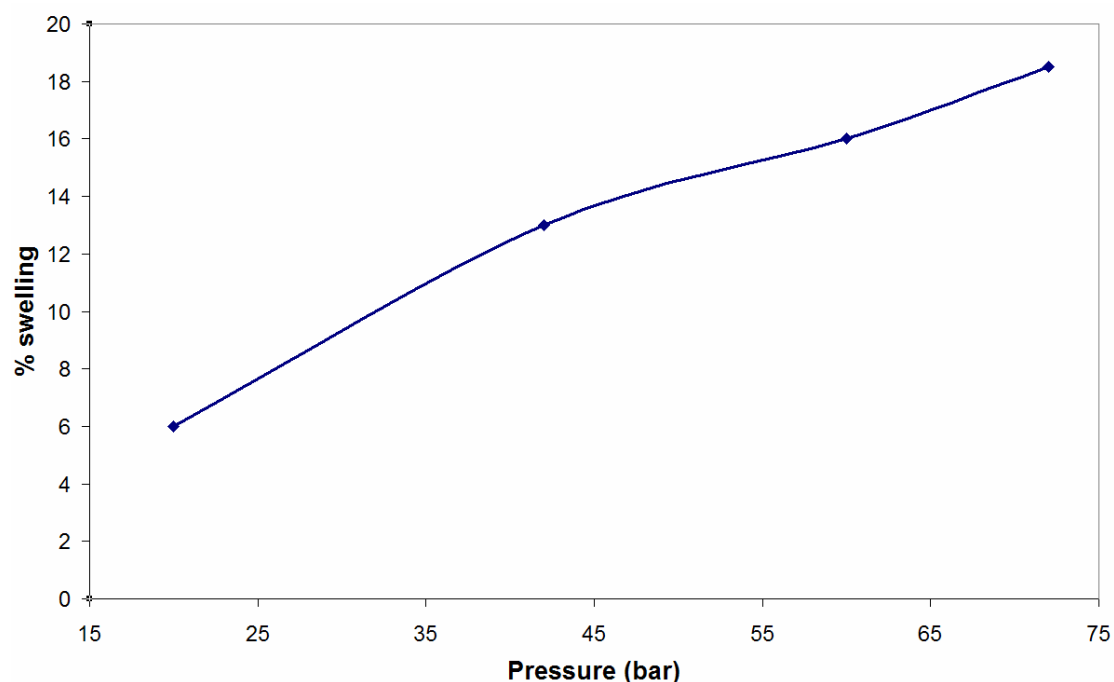


Figure 3: Swelling of [bmim][PF₆] as a function of CO_2 pressure at 25°C

Close inspection of Figures 1 and 2 shows that as CO_2 pressure increases, the extent of change in the absorbance of ionic liquid and CO_2 band diminishes.

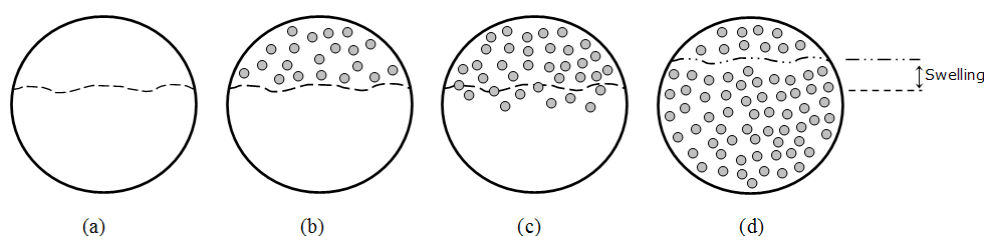


Figure 4: Schematic representation of the mechanism of CO_2 diffusion in ionic liquids and of the consequent swelling of the ionic liquid medium. (a) IL in the high pressure cell, (b) CO_2 is introduced in the cell and is in contact with the IL, (c) CO_2 begins to dissolve into the IL, and (d) swollen IL is saturated with CO_2 .

Figure 4 provides a schematic representation of the ionic liquid swelling phenomena induced by dissolved CO₂, leading to the equilibration of the gaseous CO₂ phase and the mixed CO₂/IL phase co-existing in the high pressure cell.

Thus, the *in situ* IR spectra of [bmim][PF₆] provide direct indication that high-pressure CO₂ induces detectable swelling of this IL, an observation that does not concur with other reports in the literature. The data presented here indicate that [bmim][PF₆] swells approximately by 18% under the 72 bar of CO₂. A detailed study is underway in our laboratory to assess how the structure of ionic liquid (i.e. different combination of anions and cations) affects the swelling phenomena of ionic liquids and will be reported elsewhere. The presented *in situ* IR spectroscopic approach allows simultaneous measurement of CO₂ sorption and swelling of IL which offers advantage over other gravimetric methods of studying phase behavior of such systems. The study of CO₂-expanded ionic liquids opens a possibility to enhance reaction rates due to the reduced viscosity of these solvents.

REFERENCES

- [1] WASSERSCHEILD, P., KEIM, W. *Angew. Chem. Int. Ed.*, Vol. 39, **2000**, p.3773
- [2] VISSER, E., SWATLOSKI, R.P. ROGERS, R.D. *Green Chemistry*, Vol. 2, **2000**, p.1
- [3] HUSSEY, C.L., *Chemistry of Non-aqueous Solutions*, Eds. G. Mamontov and A. I. Popov, Weinheim, **1994**.
- [4] NIEHAUS, D., PHILIPS M., MICHAEL A., WIGHTMAN, R. M. *J. Phys. Chem.*, Vol. 93, **1989**, p.6232
- [5] NIEHAUS, D., WIGHTMAN, R. M., FLOWERS P. A. *Anal. Chem.*, Vol. 63, **1991**, p.1728
- [6] BLANCHARD, L.A., HANCU, D., BECKMAN, E.J., BRENNECKE J. F., *Nature*, Vol. 399, **1999**, p.28
- [7] KAZARIAN, S. G., WELTON, T., BRISCOE B. J., *Chem. Commun.* **2000**, 2047.
- [8] KAZARIAN, S. G., SAKELLARIOS, N, GORDON, C. M. *Chem. Commun.* **2002**, 1314.
- [9] GORDON, C.M., *Applied Catalysis A*, Vol. 222, **2001**, p.101.
- [10] BRENNECKE, J.F., BLANCHARD, L. A., Z. GU, *J. Phys. Chem. B*, Vol. 105, **2001**, p.2437.