

# *Characterization of the ionic liquid bmimPF<sub>6</sub> in supercritical conditions*

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## **1. INTRODUCTION**

Ionic liquids are organic salts, which, according to their singular characteristics, are the subject of extensive research. They are considered as potential candidates for the replacement of organic solvents. The ionic liquids have a very good solvent capacity for materials organic and inorganic, polar and non-polar. In addition, the ionic liquids are thermally stable, often non flammable and they have a negligible vapor pressure, which reduces environmental pollution and decreases the risks of exposure compared to conventional organic solvents.

Ionic liquids and supercritical CO<sub>2</sub> are benign environmental solvents, and each one has its clean and single properties. The combination of the advantages of these two types of green solvent is a new and interesting study. Recently, BRENNECKE *and al* [1-3] studied the solubility of CO<sub>2</sub> compressed in the ionic liquids. They found that supercritical CO<sub>2</sub> is largely soluble in most ionic liquids, but the solubility of these ionic liquids in the supercritical CO<sub>2</sub> is negligible. Yet, the studies explaining the behaviour of the phases of the ionic liquids in the presence of the supercritical fluids are rare. In the objective to understand the phenomena arising from putting into contact an ionic liquid with a supercritical fluid, we were based in our study on what the other researchers made to set up new measurement techniques of solubility and density of the mixture CO<sub>2</sub>/ionic liquid. The processes of generation of divided solids by the use of supercritical fluids (FSC) are industrially promising. Among these processes, the SAS technique (Supercritical AntiSolvent), based here on the use of supercritical CO<sub>2</sub> (CO<sub>2</sub>-SC) as anti-solvent and of an ionic liquid as solvent, offers the advantage of being completely clean. However, the phenomena governing this process are badly controlled and many parameters are unknown. Thus, in order to model this process, techniques of characterization of the properties of the binary solvent/antisolvent must be developed.

## **2. MEASURE OF THE SOLUBILITY AND DENSITY**

We present here results concerning reference binary: CO<sub>2</sub>/1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF<sub>6</sub>) (the cheapest one). Various properties of the selected ionic liquid were studied in the presence of supercritical CO<sub>2</sub> or in atmospheric

conditions. An apparatus was used to carry out measurements of the solubility of CO<sub>2</sub> in the bmimPF<sub>6</sub> and the density of the bmimPF<sub>6</sub>/CO<sub>2</sub> mixture. The temperatures considered in the experiments vary from 45°C to 65°C and the selected range of pressure varies from 100 bars to 400 bars. The various results obtained were compared with those of SHARIATI *and al* [4] and BLANCHARD *and al* [5].

## 2.1. THE APPARATUS

An equipment was especially dedicated to the measurement of the phase equilibrium, of a liquid or a gas put into contact with CO<sub>2</sub> in liquid or in supercritical conditions. This equipment allows the measure within broad ranges of pressure being able to reach 500 bars and temperatures up to 200 °C. The design, realization and development were carried out by company “Sitec Sieber Engineering Ag”. The principle of the equilibrium measurement is to put into contact the desired substance with the carbon dioxide. A certain volume of the substance is thus placed in a cell which is controlled in temperature and pressure and into which the carbon dioxide is introduced. The mixture is agitated with magnetic stirrer during all the experiment until reaching the equilibrium characterized by a constant pressure inside the cell, thanks to a piston of regulation. The sampling is made using a syringe pump, keeping a constant pressure in the cell. The sampled ionic liquid is then degassed and the volume of CO<sub>2</sub> is measured by two gasometers to get a better precision. The general diagram of the apparatus is presented on the Figure (1.1).

## 2.2. DESCRIPTION OF THE DIFFERENT ELEMENTS

### 2.2.1. OPTICAL CELL (1)

The 50 ml cell of cylindrical form is equipped with two sapphire windows of 28 mm diameter, the first one being placed in front of the cell and the other behind it, where we light, in order to visualize what occurs inside.

The pressure in the cell is maintained during all the experiment and at the time of the sampling (which can be made from the bottom or from the top of the cell) thanks to a piston of regulation (2) placed at the cell upstream. The pressure regulation is performed by equilibrium between the pressure of the cell and a compressed air provided by a bottle connected to the apparatus. The ratio of the two surfaces of the piston (one in contact with the cell, the other in contact with the compressed air) is 10 what makes it possible to have a pressure of cell ten times higher than that of the compressed air. Then, a small change in air pressure can induce a significative change of the piston position. This piston moves towards the bottom reducing volume and thus maintains the pressure. Using PID regulators, the temperature control is done by circulation of a coolant which circulates around the cell in a jacket. A hotplate placed just below the cell also does heating of the cell. The image of the interior of the cell is transmitted by the sapphire windows via a camera to the screen placed on the center of the face of the unit.

### 2.2.2. CIRCULATING PUMP (3)

The circulating pump makes it possible to circulate the lower or higher phase without pulsations. By this way, the contact between the two phases is improved and the time necessary to reach equilibrium is decreased.

The phase to circulate can be chosen by the direction of rotation of the engine. The circulating pump is heated by an electrical heating controlled (just like the cell) by a temperature regulator PID in order to maintain the temperature of the circulating phase.

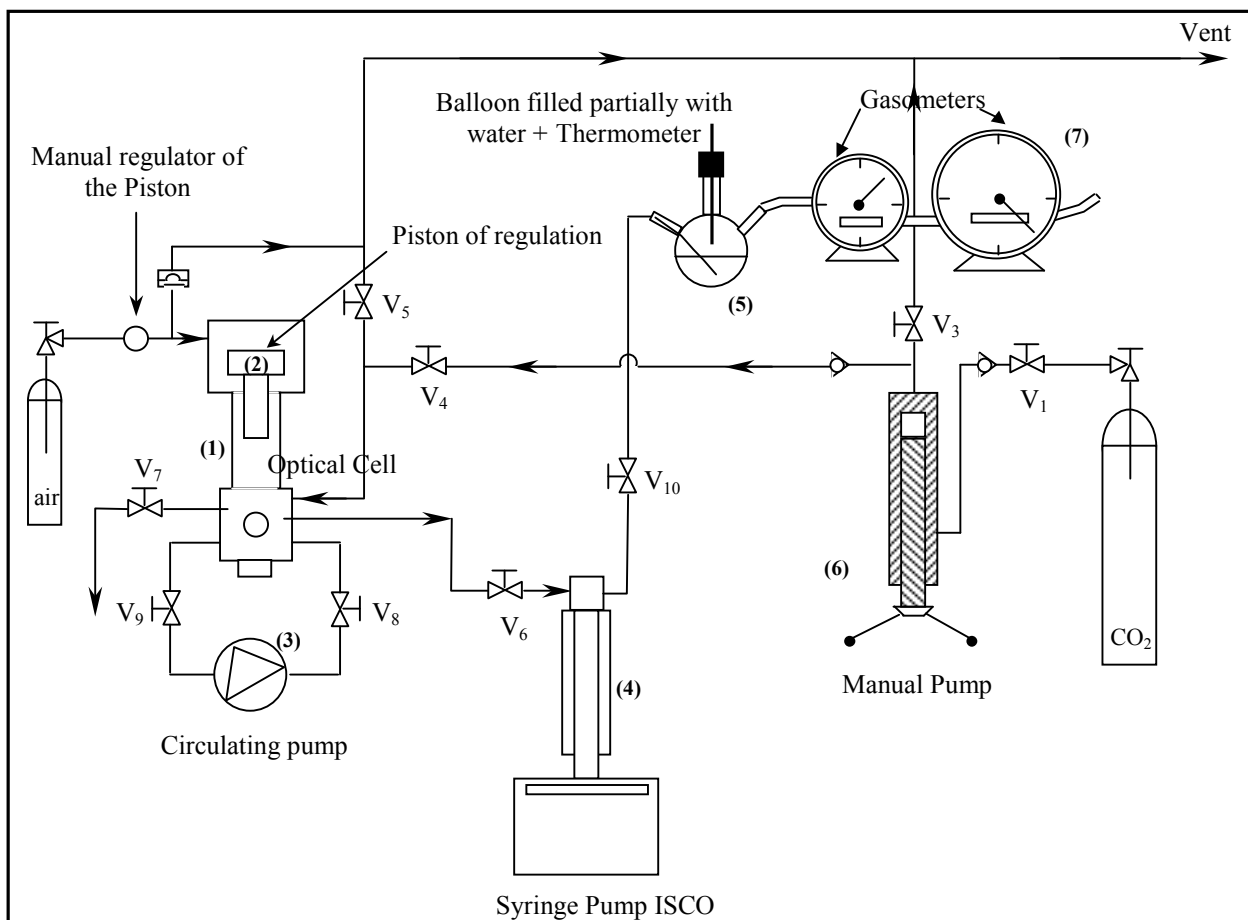


Figure 1.1. Apparatus for measurements of solubility

### 2.2.3. MANUAL PUMP (6)

The increase in the supply pressure of CO<sub>2</sub> to the desired value is reached by a manual pump with very fine fittings. This pump makes it possible to compress CO<sub>2</sub> introduced into a chamber by a no-return valve. This chamber is equipped with a jacket ensuring a water circulation and thus making it possible to cool and to liquefy CO<sub>2</sub>.

### 2.2.4. SYRINGE PUMP ISCO (4)

This syringe pump (Isco, models 260D) is connected to the measuring apparatus of phase equilibrium, more exactly, with the lower part of the cell (in the liquid phase) to carry out samples at the pressure of the experiment. This pump can function either with constant

flow or with constant pressure, for flows of  $0.1 \mu\text{l}\cdot\text{min}^{-1}$  to  $100 \text{ ml}\cdot\text{min}^{-1}$  and pressures up to 50 MPa. The pump is heated by a water circulation in a jacket surrounding the higher part of the pump including the piston.

#### 2.2.5. GASOMETERS (7)

The quantity of  $\text{CO}_2$  leaving the syringe pump is measured using two gasometers placed in series at the downstream syringe pump. This double reading allows a checking of the volume measure. As the carbon dioxide is water soluble, we placed a balloon filled with water so that the carbon dioxide passes through it before passing through the gasometers. The temperature of the outgoing  $\text{CO}_2$  from the pump is measured using a thermometer placed in the balloon. Before beginning measurement and regulating the level, water filling the gasometers must be previously saturated with gas while making pass from  $\text{CO}_2$ . During measurement, the modification allows the saturation of  $\text{CO}_2$  by water before its arrival to the gasometers. Thus, water and gas are in equilibrium and concentration of water vapour remains constant throughout all the measurement.

### **2.3. EXPERIMENTAL PROCEDURE**

Ionic liquid [bmim][PF<sub>6</sub>] ( $\text{C}_8\text{H}_{15}\text{F}_6\text{PN}_2$ ) (of a purity higher than 98% mass, provided by Solvionic, France) was dried in vacuum at  $50^\circ\text{C}$  during two days. The water contents is less than 15 ppm for all the samples used. [bmim][PF<sub>6</sub>] used has a density of  $1370\text{kg}/\text{m}^3$  and a molar mass of  $284\text{g}/\text{mol}$ .

The volume of water placed in the balloon connected to the syringe pump is initially saturated with  $\text{CO}_2$  to have a reliable measurement of the volume of  $\text{CO}_2$  dissolved for each handling. In the initial state, the piston of the syringe pump is in the high position, the piston of the cell is also in the high position, the valve  $V_3$  is open and the valves  $V_1$ ,  $V_4$ ,  $V_5$ ,  $V_6$ ,  $V_7$ ,  $V_8$ ,  $V_9$  and  $V_{10}$  are closed.

In a first step, we introduce a volume of ionic liquid in the cell by dismounting the piston of regulation to be able to make the filling. Then, we open the valve  $V_1$  and  $V_4$  to be at the pressure of the  $\text{CO}_2$  bottle (approximately 50 bars) and we close again  $V_4$ .

After having started agitation and heating to the desired temperature, we increase the pressure using the manual pump and we fill the cell with  $\text{CO}_2$  until reaching the desired operational pressure by opening and closing again the valve  $V_4$ . The valve  $V_6$  is always maintained open so that the pump and the cell are at the same pressure.

In a second step, we move the piston of the cell by applying a small air pressure so that it deviates slightly from the previous the top position. We keep the sample under agitation approximately 36 h until reaching the equilibrium characterized by an unchanged pressure of cell in function of time. Then, we note the temperature, the pressure and the position of the piston. We can take a sample by filling the syringe pump (heated at the same temperature of cell). This sampling is stopped when the regulation piston arrive at a few millimetres from the bottom position. We isolate the syringe pump by closing the valve  $V_6$  and we note the new position of the regulation piston. We then decrease the pressure inside the syringe pump by lowering the piston. We open the valve  $V_{10}$  and we recover  $\text{CO}_2$  in the

balloon filled with water. We note the temperature of CO<sub>2</sub> as well as its volume on the gasometers. The mixture remaining in the syringe pump is slowly degassed for a long length of time until reaching 1 bar. Then we push the liquid until seeing it in the pipe. Endly, we weigh the volume of liquid obtained.

## 2.4. RESULTS:

We gathered in the following graph, the results carried out at 45 °C and from 100 to 400 bar and compared to those from literature. In the Figure (1.2a), the molar fraction of CO<sub>2</sub> dissolved into the bmimPF<sub>6</sub> at various temperatures, is represented. Among all the studies made on the solubility of CO<sub>2</sub> in the bmimPF<sub>6</sub> (already quoted in the first paragraphs), only SHARIATI *and al* [4] carried out experiments at high pressures (up to 800 bars). We can notice that our results fit rather well with these data meanwhile their experimental procedure is completely different from our.

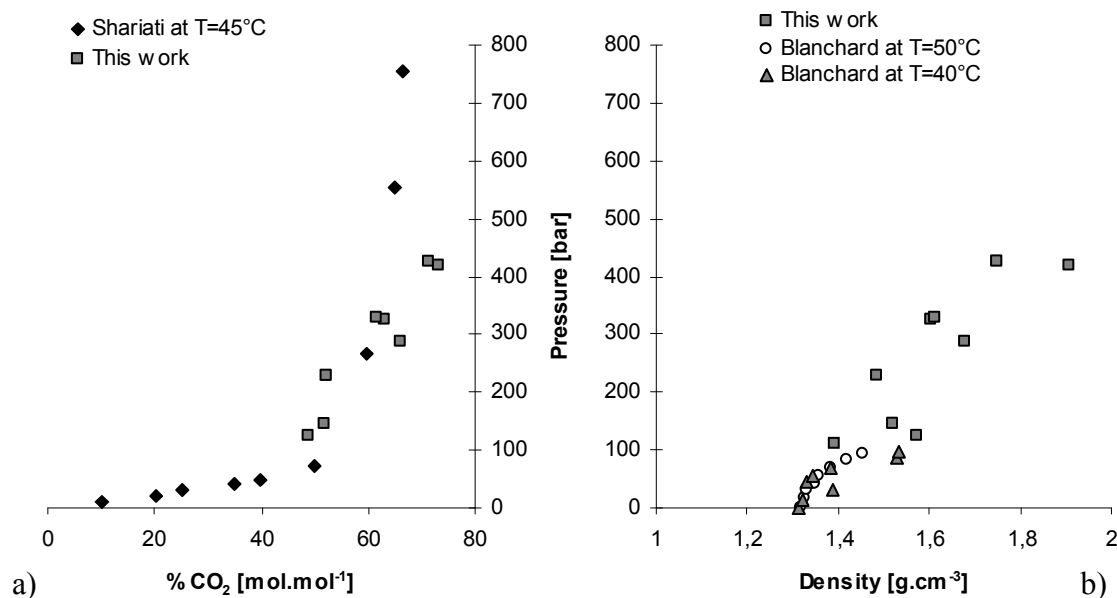


Figure 1.2. **a)** Comparative graph of the solubility of CO<sub>2</sub> in the bmimPF<sub>6</sub> at T=45°C against pressure. **b)** The density of the mixture (bmimPF<sub>6</sub>/CO<sub>2</sub>) against pressure

## 2.5. MEASUREMENTS OF THE DENSITY OF THE MIXTURE BMIMPF<sub>6</sub>/SUPERCRITICAL CO<sub>2</sub>

The data we used to estimate the density of the bmimPF<sub>6</sub>/CO<sub>2</sub> mixture are the respective masses of the ionic liquid and the carbon dioxide and the volume of the sample. From the experiments of CO<sub>2</sub> solubility in the bmimPF<sub>6</sub> already described in the previous paragraph. The density is calculated by the following formula:  $\rho_{mixture} = \frac{m_{CO_2} + m_{LI}}{V_{mixture}}$ .

The Figure (1.2b) presents the evolution of the density at 45°C as a function of pressure. These results are compared to those deduced from the results obtained by BLANCHARD *and al* [5] at 40, 50 and 60 °C. BLANCHARD *and al* [5] presented results concerning to the molar volume of the bmimPF<sub>6</sub>/CO<sub>2</sub> mixture in function of the pressure. The density was then calculated according to the following relation:

$$\rho = M_{mixture} \times V_m^{-1} \text{ and } M_{mixture} = x_{CO_2} M_{CO_2} + (1 - x_{CO_2}) M_{LI}$$

With:  $M_{mixture}$  : Molar mass of the mixture,  $V_m$  : Molar volume and  $x_{CO_2}$  : molar fraction.

Our results are in the continuity of those of BLANCHARD *and al* [5] what can be regarded as a validation of our experiments.

Our technique should be improved in order to minimize errors of measurement seen in Figure 1.2b. However, it is clear that the density as the solubility of the binary mixture bmimPF<sub>6</sub>/CO<sub>2</sub> increases with pressure.

From the obtained results and considering that we deal with the SAS technique, an important question can be asked: does a drop of the ionic liquid undergo an expansion considering the great quantity of CO<sub>2</sub> which dissolves in it? The answer is not. In fact, for example, for T = 45°C and P = 287 bars, the expansion of the volume is just 6%. So, the dissolution of the CO<sub>2</sub> in the ionic liquid increases its density and very little its volume.

### 3. CONCLUSION

We have characterized the mixture bmimPF<sub>6</sub>/CO<sub>2</sub>. Among the properties necessary for the modelling of SAS technique purpose, the solubility of supercritical CO<sub>2</sub> in the ionic liquid and the density of the mixture bmimPF<sub>6</sub>/supercritical CO<sub>2</sub> have been measured. Measurements of solubility were carried out in a new apparatus "Sitec", an apparatus which allows measurement at high pressures and temperatures. Solubility has been compared to those of SHARIATI *and al* [4]. By exploiting the results of the solubility measurement, we could derive the density of the mixture bmimPF<sub>6</sub>/CO<sub>2</sub>. We noticed that our results are coherent with measurements of BLANCHARD *and al* [5]. At high pressures, the variation of density is less important than at low pressures. The surface tension and the diffusivity of the reference binary are the properties that we intend to study next using other apparatus and techniques.

### 4. REFERENCES

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