

MELTING POINT DEPRESSION OF IONIC SALTS INDUCED BY COMPRESSED CARBON DIOXIDE

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Melting points for several classes of organic solids have previously been found to decrease in the presence of high pressure CO₂. Until recently, only few studies about melting point depression of ionic salts were found. This behaviour is important in the case of ionic salts because there are a myriad of cation-anion combinations, but only a limited number of them actually melt near room temperature. CO₂-induced melting point depression might expand the useful range of ionic liquids. In this work, we used high pressure carbon dioxide to induce melting point depression of ionic salts that contain quaternary ammonium, guanidinium, imidazolium and phosphonium cations, combined with various anions. Melting point depression effect obtained in our laboratory for these groups of ionic salts went as high as 70 °C.

Introduction

Room temperature ionic liquids (ILs) and carbon dioxide are one of the most promising alternative solvents due to their characteristics. ILs have negligible vapour pressure, they are non-flammable, thermally stable and easily recyclable. Therefore, they could reduce, or completely replace the use of hazardous and traditional volatile organic solvents. Carbon dioxide is highly soluble in some ionic liquids, while the solubility of the ionic liquids in carbon dioxide is usually very low. There is a continuing interest in applying this concept to different chemical and enzymatic reactions, in order to achieve easy product separation and catalyst/enzyme reuse [1]-[6].

It has been known that melting point depression of some organic solids can be induced by compressed gases. For example, lipids and polymers are known to melt at temperatures 10-25 °C lower than their normal melting point, when they are exposed to high pressure gases. Hammam et al. tested a series of glycerides that showed a melting point depression of 15-25 °C in the presence of high pressure carbon dioxide [7]. Similar behaviour of solid lipids was noticed by Sampaio de Sousa and co-workers [8], where decrease in the melting points up to 13 °C was observed. The same type of behaviour was found for some polymers [9],[10].

In the case of ionic salts, only two reports about melting point depression in the presence of carbon dioxide could be found [11],[12], until Kazarian et al. observed liquid-crystal transition for an imidazolium salt, [C₁₆mim][PF₆] with carbon dioxide [13]. These authors found that high

pressure carbon dioxide induces melting point depression in the range of what was found for other organic solids – not higher than 25°C. Very recently, Scurto et al. reported that high pressure carbon dioxide can induce surprisingly high melting point depression, up to 120 °C [14].

In this work, quaternary ammonium, guanidinium, imidazolium and phosphonium cations, combined with various anions, were tested. Bulky and asymmetric structures of cations were chosen in order to achieve higher solubility of CO₂ in the ionic salts and, in principle, higher melting point depression effects. This study opens the way to design novel ionic liquids that might contain chiral or biocompatible ions.

Materials and experimental methods

Most of the ionic salts used for these measurements were synthesized in our laboratories, except salts that are commercially available (phosphonium salts – lolitec [15] and tetrabutylammonium salts - Sigma Aldrich [16]).

All samples were dried under vacuum for 24 hours.

Carbon dioxide was supplied by Air Liquid with a purity of 99.99 mol%.

The ionic salts chosen for this work had bulky cations that hold, on one side, shorter alkyl chains, and on the other side longer ones, in order to introduce asymmetry (see Fig.1). The anions studied were: bis(trifluoromethylsulfonyl)imide, hexafluorophosphate, thiocyanate, chloride, iodide, tetrafluoroborate, p-toluenesulfonate, tetraphenylborate, and triflate.

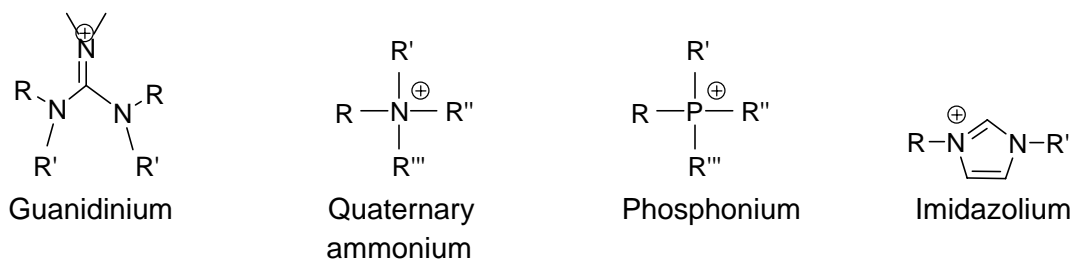


Fig.1 The structures of cations and anions that were studied

The melting temperatures and melting temperature depressions induced by high pressure carbon dioxide on different classes of ionic salts (quaternary ammonium, guanidinium, imidazolium and phosphonium salts, combined with various anions) were measured in the high-pressure apparatus depicted in Fig.2 and Fig.3.

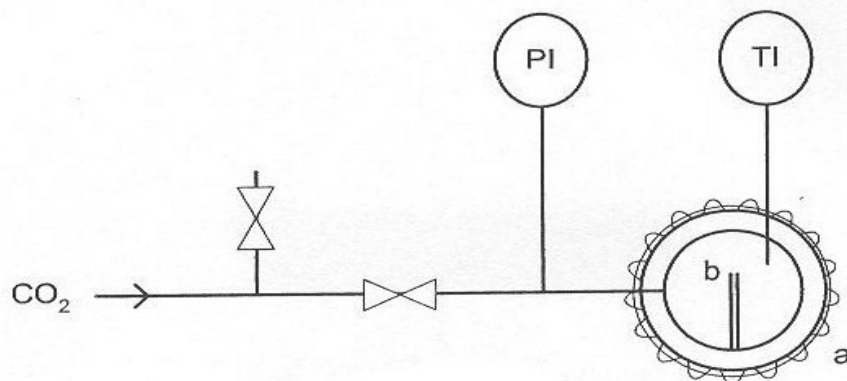


Fig.2 High-pressure apparatus for melting point measurements: (a) sapphire-window cell and (b) capillary tube

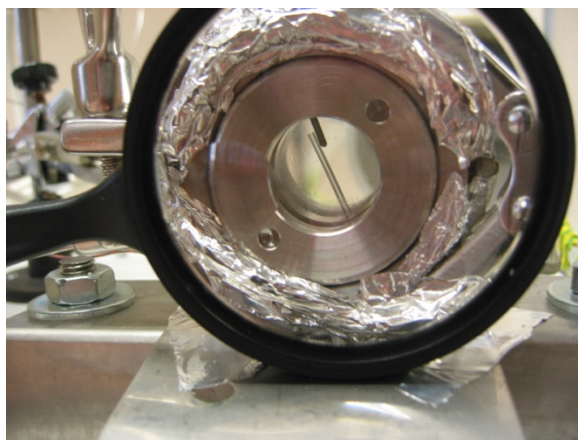


Fig.3 High-pressure stainless steel cell

The procedure for determination of the melting point of the salts in the presence of carbon dioxide was based on the capillary method. A sample was placed inside a capillary tube that was inserted in the stainless steel high-pressure cell with sapphire windows. First, the cell was purged with CO₂, in order to remove air and volatile impurities. Then, the desired amount of CO₂ was pumped into the cell. At fixed pressure, and after an equilibration time of about 20 min, temperature was increased continuously at a rate of app. 0.5 °C/min, until the last solid particle melted. The first measurement on each given sample usually yielded melting points about 1° C higher than for the second and subsequent measurements. The temperature was measured by thermocouple with an accuracy of 0.1°C. Pressure up to 150 bar were used. The maximum working temperature for the apparatus used in this work was 100 °C. Wherever possible, the same apparatus was used for the determination of the melting point of the salts at atmospheric

pressure. For salts with melting points above 100 °C, measurements at atmospheric pressure were performed with a DSC.

Results and discussion

The experiments were performed in the pressure range from 50 bar to 150bar, since that was found to be the area where the solubility effect of CO₂ induced most significant melting point depression. It is reported that pressures higher than 150 bar can induce the opposite trend, due to the effect of the hydrostatic.

In the case of phosphonium and imidazolium salts, melting point depressions in the range of lipids and polymers were obtained, except for two cases of imidazolium salts that exhibited melting point depression around 35 °C.

Among different quaternary ammonium salts, the ones coupled with p-toluenesulfonate anion exhibited larger melting point depression. This behaviour was also noticed for the salts that contain longer alkyl chains in cations. Melting point depression for this group of salts went as high as 56 °C.

The largest effect of compressed CO₂ was found for guanidinium salts. In the case where the cation was coupled with PF₆⁻, a melting point depression of 73.4 °C was obtained. Guanidinium salts that contain bromated alkyl chains were also tested; lower melting point depression was noticed when the guanidinium cation was more bromated.

The results obtained in this study are not sufficient to explain differences of melting point of ionic salts in absence and presence of compressed carbon dioxide. Carbon dioxide could interact with some ions and lead to higher melting point depression. Therefore, solubility measurements of high pressure carbon dioxide in ionic salts have to be performed.

The lower melting points of ionic salts in the presence of high pressure CO₂ can be used to design new classes of ionic liquids that might contain chiral or biocompatible ions. These solvents could find application as chiral media in organic synthesis and biocatalysis.

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