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Purification of ionic liquids by supercritical CO_2 monitored by infrared spectroscopy

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ABSTRACT

Transmission infrared and Attenuated Total Reflection (ATR) *in situ* infrared spectroscopies were combined for the time-resolved monitoring of both liquid and supercritical phases during extraction of water and other impurities from ionic liquids with supercritical carbon dioxide ($scCO_2$). Cleaning and drying by $scCO_2$ at 100 bar and 40 °C proved to be efficient for all ionic liquids tested, including 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), and 1-butyl-3-methylimidazolium trifluoromethansulfonate ([bmim][TfO] or [bmim] triflate). Despite the moderate solubility of water in $scCO_2$ compared to other classical solvents, the amount of water decreased continuously during the drying. The extraction could be followed by simple transmission IR spectroscopy of the supercritical phase. During the extraction, organic impurities and water were removed rapidly from the ionic liquid phase as $scCO_2$ improved the transport properties in the ionic liquids.

1. Introduction

Ionic liquids (ILs) are defined as salts with a melting point below the boiling point of water. With their peculiar properties, such as negligible vapor pressure, ILs have gained considerable attention in research and application, as for example in catalysis [1,2]. Especially interesting is the combination of ILs with carbon dioxide, because ILs are practically insoluble in supercritical carbon dioxide ($scCO_2$), whereas $scCO_2$ is fairly soluble in ILs. CO_2 is commonly used as it is inexpensive, nontoxic, nonpolluting, and easily removable by simple depressurization. One of the most common utilizations of $scCO_2$ is supercritical fluid (scf) extraction [3]. Using ILs and $scCO_2$ together offers interesting opportunities for new chemical processes; as a first example, in 1999, Blanchard et al. demonstrated the extraction of naphthalene from IL using $scCO_2$ [4]. After that, the extraction of various organic compounds from ILs using $scCO_2$ has been developed [5,6]. Some of the applications of binary IL/$scCO_2$ systems, e.g. for extractions or chemical reactions, were recently reviewed by Roth [7]. Exposure of $scCO_2$ to IL induces a decrease of the viscosity of the IL, which can substantially improve the transport properties in the liquid phase, a fact beneficial for any extraction process [8]. One of the limitations of using ILs is their often strong hygroscopicity and the sensitivity of several physical-chemical properties of the ILs towards the amount of water dissolved in them [9–11]. Thus, for many applications ILs have to be dried prior to use and generally water is extracted under vacuum (or even high vacuum) for hours and often days [12]. Despite their potential importance, IL/water/CO_2 ternary systems have so far only barely been investigated [13,14].

Infrared (IR) spectroscopy techniques have previously been successfully applied to analyze the partition of a model solute (benzil, (1,2-diphenylethane-1,2-dione)) between 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and $scCO_2$ [15]. Besides its usability for the quantification of chemicals even under high pressure without any perturbation of the experiment, IR spectroscopy is also able to provide information about molecular interactions of fluids and solutes. As an example of a quantification study, the solubility of CO_2 in [bmim][PF_6] at 40 °C under high pressure was published recently [16]. In the particular case of ILs containing water, the early work of Cammarata et al. nicely showed that the IR spectra of wet ILs (with 8 different anions) can be used to describe the hydrogen bond network as anion···H–O–H···anion [17]. More recently, the molecular organization of a small concentration of water in ILs was also meticulously analyzed using IR and Raman spectroscopy and compared to density functional theory (DFT) calculations to validate the proposed structure of wet ILs [18,19]. IR studies have also been performed on IL/CO_2 systems. Kazarian et al. explained the organization of

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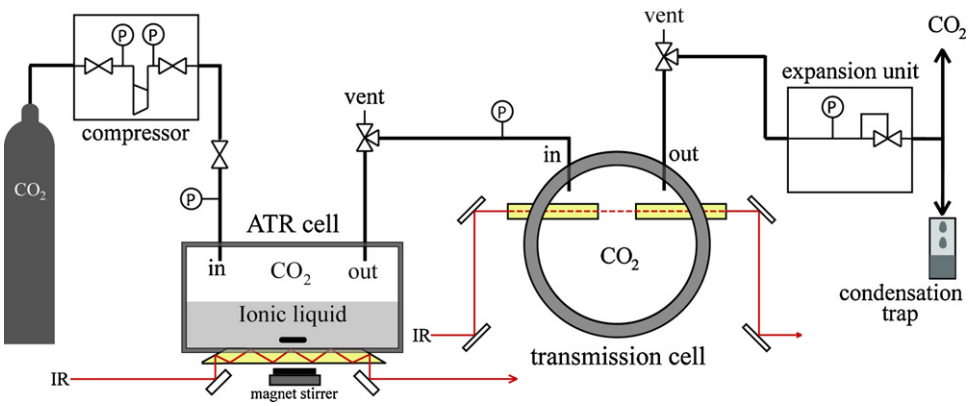

Fig. 1. Schematic view of the experimental setup with the two spectroscopic cells employed to analyze simultaneously the two phase of the biphasic system.

carbon dioxide in 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) under high pressure using the bending mode vibration of the CO_2 molecule [20].

Despite the rather poor solubility of water in scCO_2 (mole fraction of 0.42% at 40 °C and 100 bar) [21] compared to other usual solvents, drying ILs using scCO_2 extraction can be efficient when the task consists of removing only some water and other impurities at a time or in continuous mode. ScCO_2 as a drying agent was employed because of the low surface tension and the high diffusivity of supercritical fluids which allow CO_2 to easily penetrate various materials. For instance, this technology has been used to dry highly porous structures such as aerogels [22]. Drying of polymers has also been tested and monitored *in situ* by IR spectroscopy and exhibited the advantage of being faster than vacuum drying (which takes several days) [23]. Recently, our group studied some ternary systems of IL/H_2O/CO_2 and showed that even with the limited solubility of water in supercritical CO_2, the concentration of water decreased rapidly when scCO_2 was added to the IL (with a volume of the scCO_2 phase an order of magnitude larger than the IL phase) [16].

The detection of a small concentration of water in the IL phase using the ATR mode is limited. Transmission mode measurements of the IL phase would have a better sensitivity, but due to the highly absorbing medium, the optimal path length would be in the range of some hundred micrometers. In such a setup the stirring of the IL is ineffective, which would lead to a particularly slow diffusion of molecules in the IL phase [16,24], and the supercritical CO_2 extraction would not be efficient when performed in a transmission IR cell with such a small inner diameter. To overcome this problem, the analysis of the water concentration can be done in the supercritical phase, since the IR spectra are not saturated even with some centimeters of path length. Thus, much smaller concentrations of water can be detected. Many groups have utilized transmission IR spectroscopy for monitoring in real time dynamic concentration changes occurring during scCO_2 extraction of other biphasic systems [25–27].

Here we aim at the elucidation of the molecular exchange (partitioning behavior) occurring between IL and the supercritical phase during extraction in a time-resolved manner. For this purpose we used an experimental strategy which combined the favorable features of *in situ* ATR and transmission infrared spectroscopy. ATR-IR was employed to follow the concentration and some interactions of water and CO_2 in the IL phase, while transmission IR was used for tracking traces of water and other impurities in the supercritical phase. With this combination the advantages of both techniques could be used beneficially for analyzing the two phases of the binary system simultaneously and for investigating the efficiency of scCO_2 extraction of water (and other impurities) from several hydrophilic ILs.

2. Experimental details

For monitoring *in situ* both phases two specially constructed spectroscopic high pressure IR cells were connected via a high pressure line and were positioned in two spectrometers. Fig. 1 presents the general setup used for the experiments. The first high pressure IR cell equipped with a magnetic stirrer contained an ATR-IR ZnSe (or Ge) crystal (size 50 mm × 20 mm × 2 mm, angle of incidence 60°; 6 active reflections) placed on the bottom to study the liquid phase of the binary system. A Ge crystal was used to decrease the IR absorption for the strongest bands in ATR mode since the refractive index of Ge is much higher than the one of ZnSe. For consistency, only spectra obtained by a ZnSe crystal are presented in this paper. The internal volume of this first cell was 10 mL and the cell could be used up to 120 °C and was tested up to 150 bar. The second high pressure IR cell was used to analyze the supercritical phase and had a variable volume (between 20 and 68 cm^3) and several optical probing paths, including two sapphire windows to observe directly the phase behavior, two ZnSe windows for transmission infrared measurements in the gas (or supercritical) phase (path length up to 38 mm), and an ATR crystal. The ATR mode of the second cell was not used during this study. The second cell used in this work has been described in detail elsewhere [28]. The first cell (ATR) was placed in an EQUINOX-55 Fourier transform infrared (FT-IR) spectrometer (Bruker Optics) while the second cell (transmission) was positioned in an IFS-66 spectrometer (Bruker Optics). Spectra were recorded with a resolution of 2 cm^{-1}, using a liquid N_2-cooled MCT detector in the range of 4000–600 cm^{-1} in ATR mode, while in transmission mode the range of the spectra was 7500–600 cm^{-1}. High pressure CO_2 was fed into the cell using a PM-101 compressor (NWA). After the second cell, the CO_2 was expanded down to ambient pressure in an expansion unit (NWA PE-103) where the flow was measured and adjusted. In a typical extraction experiment, 5 g of IL were used; the temperature of the fluid was 40 ± 2 °C during and between the extraction cycles at a pressure of 100 ± 5 bar, and the CO_2 flow was in the range of 1–10 Nl/min.

After an experiment, it was not possible to reopen the high pressure cell without completely avoiding fast readsorption of atmospheric water in the hygroscopic IL. To diminish this effect, only the bottom part of the liquid phase was taken out quickly with a syringe and analyzed by Karl Fischer titration at Simec AG (Zofingen, Switzerland). ^{1}H NMR (nuclear magnetic resonance (Bruker Avance 500, 500 MHz)) was used to quantify the amount of possible organic impurities in the IL before and after scf extraction.

Hygroscopic ILs ([bmim][BF_4], [bmim][PF_6], and 1-butyl-3-methylimidazolium trifluoromethansulfonate ([bmim][TfO])) purchased from Acros Organics were used and employed without further purification. [bmim][BF_4] and [bmim][TfO] were chosen as examples of ILs difficult to dry. At the beginning of an experiment,