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High pressure phase behaviour of methane in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

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ABSTRACT

Solubility data of methane in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide are presented within temperature and pressure ranges of 300–450 K and 1–16 MPa, respectively. Experiments were carried out in a view-cell based on the synthetic method. Results indicated rather low methane solubility in the ionic liquid, ranging from 3 up to 22 mole% at the higher pressure limit of 16 MPa. In comparison to some other gases of concern to ionic liquid gas purification membranes, methane had much lower solubility than carbon dioxide and higher solubility than hydrogen. Isothermal methane solubility was shown to increase with pressure in an almost linear manner. However, temperature effects were more predominant at low temperatures, i.e. increasing the temperature caused a more notable decrease in solubility at lower temperatures than at higher temperatures. Solubility results of methane are also compared to those of ethane, propane and butane in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. Methane is by far less soluble than ethane, propane, and butane.

1. Introduction

Due to a range of attractive properties, ionic liquids (ILs) are receiving exponentially increasing attention in a range of different disciplines. Room temperature ionic liquids are defined as organic salts, consisting of anions and cations, which melt at or below room temperature. They consist of an organic cation such as quaternary ammonium, imidazolium, pyridinium, or pyrrolidinium ions combined with either an organic or an inorganic anion of usually smaller size and more symmetrical shape such as Cl^-, Br^-, I^-, $AlCl_4{}^-$, $BF_4{}^-$, $PF_6{}^-$, or Tf_2N^- (bis(trifluoromethylsulfonyl)imide). It is the Coulombic attraction between these ions that is responsible for the recognized lack of IL vapour pressures even up to their thermal decomposition temperatures [1,2]. In fact, they have been called "liquid solids" because they incorporate some of the most useful physical properties of both phases [3]. In addition to facilitating separations and minimizing expenses resulting from solvent loss, the seemingly insignificant vapour pressures of ILs minimize environmental pollution problems and highly reduce working exposure hazards in comparison with the conventional organic solvents being used in industries today. Aside from this, ILs posses a range of other outstanding characteristics which suggest a promising industrial future for them: most ILs are in the liquid state at room temperature and will remain liquid until high temperatures, so processes such as heterogeneous reactions can instead be performed in a single liquid phase within a wide temperature range. ILs are thermally stable, are non-flammable, and have high ionic conductivity. Unlike conventional organic solvents, it is possible to adjust the properties of ILs to produce task-specific solvents by combining different anions and cations or their functional groups such as the alkyl chain length. Based on these properties, there is an extensive perspective of potential industrial applications for ILs in catalytic reactions, gas drying and separations, liquid–liquid extractions, electrolyte/fuel cells, and as lubricants, heat transfer fluids, plasticizers, and solvents for cleaning operations [4].

The insignificant vapour pressure of ionic liquids is the remarkable ionic liquid property that has recently started attracting attention on the possibility of using ionic liquids as supported

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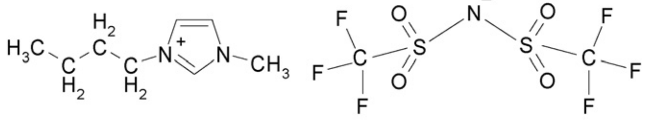

Fig. 1. Molecular structure of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

membranes for selectively separating gases [5–16]. As opposed to liquid absorption techniques commonly used for gas separation, this lack of vapour pressure in ionic liquids minimizes the loss of the “capturing agent” into the gas stream, thus making these materials highly attractive for gas processing. Whether separating acid gases from natural gas or purifying the products from steam reforming or gas-shift reactions using ILs, knowledge of the solubility of methane, among other gases, in the relevant ionic liquids is necessary. Such information could also be useful in other gas + ionic liquid applications such as homogenous reactions or supercritical fluid extractions of solutes from ionic liquids. As part of a more general project investigating the feasibility of separation-enhanced reactors for hydrogen production from fossil fuels such as natural gas, this study focuses on the solubility of methane in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]) over a range of (high) pressures and temperatures. The molecular structure of this IL is presented in Fig. 1. As far as we are aware, no experimental data have yet been published in literature on the binary system of CH_4 in [bmim][Tf_2N].

2. Experimental

2.1. Apparatus

Experiments were carried out in a Cailletet apparatus, schematically shown in Fig. 2. This apparatus allows the measurement of phase equilibrium according to the synthetic method. At any desired temperature, the pressure is varied for a sample of constant overall composition until a phase change is observed visually. A sample of fixed known composition is confined over mercury in the sealed end of a thick-walled Pyrex glass tube, called the Cailletet tube. The open end of this tube is placed in an autoclave, immersed in mercury. Thus, mercury is used for both sealing and transmitting pressure to the sample. The sample is stirred by a stainless steel ball, whose movement is activated by reciprocating magnets. The autoclave is connected to a hydraulic oil system, generating the pressure by means of a screw type hand pump. A dead weight pressure gauge is used to measure the pressure inside the autoclave. The temperature of the sample is kept constant by circulating thermostat liquid through a glass thermostat jacket surrounding the glass tube. The thermostat bath is capable to maintain the thermostat liquid at the desired temperature with a constancy better than ±0.01 K. A platinum resistance thermometer, located close to the sample-containing part of the Cailletet tube, records the temperature of the thermostat liquid with a maximum error of 0.02 K [17]. The accuracies of measurements were within 0.02 K for temperature, 0.03% of the reading for pressure, and 0.001 for molar fraction of methane. Further explanations of the Cailletet equipment are given elsewhere [18].

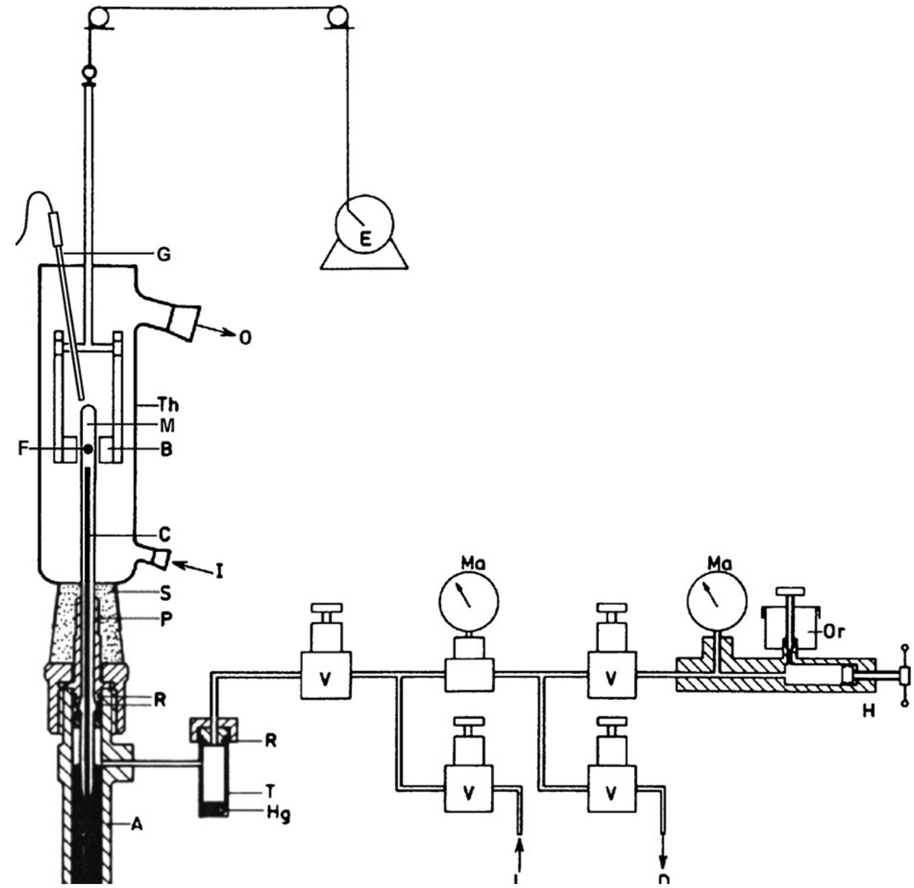

Fig. 2. Schematic representation of the Cailletet apparatus: A: autoclave, B: magnets, C: capillary glass tube, D: drain, E: motor, F: metal stirrer, G: platinum resistance thermometer, H: rotating hand pump, Hg: mercury, I: thermostat liquid in, L: line to dead weight pressure gauge, M: mixture being investigated, Ma: manometers, O: thermostat liquid out, Or: hydraulic oil reservoir, P: closing plug, R: Viton-O-rings, S: silicone rubber stopper, T: mercury trap, Th: glass thermostat, and V: valve.