Fluid Phase Equilibria 372 (2014) 26–33

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Solubility of carbon dioxide, nitrous oxide and methane in ionic liquids at pressures close to atmospheric

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ARTICLE INFO

Article history:
Received 6 January 2014
Received in revised form 12 March 2014
Accepted 15 March 2014
Available online 24 March 2014

Keywords:
Ionic liquids
Greenhouse gas
Solubility
Henry's law constant

ABSTRACT

The purpose of this work is to determine the solubility of greenhouse gases in different ionic liquids (ILs). Experimental values for the solubility of carbon dioxide, methane and nitrous oxide in ionic liquids are measured at different temperatures and at pressures close to atmospheric. Carbon dioxide is the most soluble gas studied with mole fraction solubility of the order of 10^{-2}. Nitrous oxide is one order of magnitude less soluble than carbon dioxide, whereas methane is the least soluble gas. Finally, a group contribution method aimed at estimating the Henry's law constant of CO_2 in ILs as a function of temperature was developed. Such a method makes it possible to predict the solubility of CO_2 in ionic liquids when experimental data are unavailable.

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1. Introduction

Greenhouse gases like CO_2, CH_4 or N_2O are acknowledged as the major source responsible for global warming which is considered as the greatest environmental challenge the world is facing. Currently, a number of technologies have been developed in order to reduce and capture these gases.

Since CO_2 is one of the most abundant greenhouse gases, the research and development in the CO_2 emission reduction have long been the focus of many academic and industrial studies. Among a number of separation technologies that can be applied to CO_2 capture, one approach being considered for capturing CO_2 is the use of liquid absorbents designed to selectively solvate CO_2 [1]. The alkanolamines such as monoethanolamine (MEA) are the most generally accepted and widely used liquid absorbents for removal of CO_2 from natural gas stream due to their reactivity and availability at low cost. Although these aqueous alkanolamine solutions are industrially effective on CO_2 removal, this family of solvents presents several drawbacks such as an intensive energy consumption, cost increases, and corrosion problems [2,3]. In this regard, it is necessary to find new alternatives for absorption solvents.

Another class of solvents, namely the ionic liquids (ILs) [4] seem to be good candidates for capturing greenhouse gases due to their high thermal stability and their negligible vapor pressure. Moreover, physical properties of ILs can be modified and adjusted by using different cation–anion combinations [5–9]. For all these reasons, a wide range of studies on the solubility of CO_2 in ILs have been performed [10–16]. Recently, a few research groups have published measurements of solubility of other gases in ILs like CH_4 [17], H_2S [18] and SO_2 [19]. To our knowledge only one study presented the solubility of N_2O in ILs [13]. Nevertheless, N_2O is a potent greenhouse gas with a global warming potential approximately 310 times greater than CO_2 when normalized over 100 years [20]. Moreover, N_2O is the major source of NO_x in the stratosphere and therefore an important natural regulator of stratospheric ozone [21]. N_2O is produced by both natural and anthropogenic sources. The main N_2O emission source is from agriculture activities and represents approximately 62% of total emissions. The industrial sources of N_2O include nylon production, nitric acid production, fossil fuel fired power plants, and vehicular emissions. Technological options for emission reduction of N_2O may be categorized into three groups: (1) reduced emissions from fluidized bed combustion; (2) use of selective catalytic reduction; and (3) fuel shift and reduction in fossil fuel consumption [22,23]. However, all these processes aimed at reducing N_2O emissions require large energy consumption and may increase the carbon dioxide emission.

Methane is another important greenhouse gas with a global warming potential. Atmospheric CH_4 is primarily emitted from biological sources and this accounts for more than 70% of the global total [24]. CH_4 is consumed primarily through oxidation by way of OH within the troposphere [24,25] and exerts strong influence over the chemistry of the troposphere and the stratosphere [26].

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http://dx.doi.org/10.1016/j.fluid.2014.03.015
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Therefore, CH_4 has a considerable impact on the earth's climate system, second anthropogenic greenhouse gas after CO_2.

In this work, it is proposed to check the ability of ionic liquids as greenhouse gases absorption solvents. The solubilities of CO_2, N_2O and CH_4 in 13 ionic liquids were measured in an equilibrium cell with a constant volume at pressures close to atmospheric. The solubility determination was based on the measurement of saturation pressure for a mixture of greenhouse gas and ionic liquid with a known composition at different temperatures. The influence of the nature of cation/anion in gas solubility was also investigated. A group contribution method was carried out in order to determine the Henry's law constant of CO_2 in different ionic liquids.

2. Experimental

2.1. Materials

High-purity carbon dioxide, methane and nitrous oxide were obtained from Messer (see Table 1). The 13 following ILs were considered in this work: 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4-mim][BF_4]), 1-butyl-3-methylpyridinium tetrafluoroborate ([C_4-mpy][BF_4]), 1-ethanol-3-methylimidazolium tetrafluoroborate ([C_2OH-mim][BF_4]), 1-ethanol-3-methylimidazolium hexafluorophosphate ([C_2OH-mim][PF_6]), 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_2OH-mim][Tf_2N]), 1-(2-methoxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([$CH_3O(CH_2)_2$-mim][Tf_2N]), trimethyl(hexyl)ammonium bis(trifluoromethylsulfonyl)imide ([$N_{(6)111}$][Tf_2N]), trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ([$P_{(14)666}$][Tf_2N]), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_2-mim][Tf_2N]), 1-butyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide ([C_4-mim][beti]), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([C_4-mim][CF_3SO_3]), 1,3-dimethylimidazolium methylphosphonate ([C_1-mim][$MePO_3$]), 1-butyl-3-methylimidazolium octylsulfate ([C_4-mim][$OctSO_4$]). Purities and suppliers are listed in Table 1.

2.2. Apparatus and procedure

The experimental apparatus based on an isochoric saturation technique is applied to measure the gas solubility in different ILs at pressures close to atmospheric. It has been presented in other publications [27,28]. In this technique, a known quantity of gaseous solute is put in contact with a determined quantity of IL at a constant temperature. When thermodynamic equilibrium is reached, the pressure above the liquid solution is constant and is directly related to the solubility of the gas in the IL.

The experimental apparatus is schematically depicted in Fig. 1. The equilibrium section of the apparatus is constituted with an equilibrium cell EC together with the precision manometer PM and glass bulbs limited by valves V4 and V5. The simple designed equilibrium cell is able to appropriately study relatively viscous liquid solvents like the ILs presented in this work. Moreover, it allows handling volumes of liquid solvent varying from 5 to 15 mL and a proper contact between gas and liquid can be achieved by means of an efficient stirring using a magnetic bar.

The gas solubility measurement starts by making the entire apparatus vacuum with the help of a vane pump by opening valves except the gas supply valve. The apparatus is kept in an oven, with a precision of ±0.1 K in order to maintain its temperature constant. In a second step, gas in introduced in the apparatus and the corresponding pressure and temperature (respectively P_{ini} and T_{ini}) are recorded. P_{ini} is measured with the precision manometer PM (Druck DPI 282 series 0007, precision of 0.0001 bar). Valve V4 is then closed in order to capture the gas in the largest glass bulb and the gas contained in the other part of the apparatus is evacuated. Thirdly, a precise amount of ionic liquid is put into the equilibrium cell using a Pasteur pipette through the connection C2. High vacuum is imposed in this part of the apparatus and the valve V3 is closed to isolate the system. The mass of ionic liquid, which varied from 4 to 6 g, is determined by a balance (Sartorius Analytic model A200S-F1) with an accuracy of 0.0001 g. Before using ILs, they are dried in vacuum at a temperature around 80 °C and a pressure about 10 Pa for at least 8 h. In a last step, valve V4 is opened and the gas solute is introduced into the equilibrium section containing the IL. Once thermodynamic equilibrium is reached, the corresponding pressure and temperature respectively noted P_{eq} and T_{eq} are recorded. The solubility of the gaseous solute in a given ionic liquid is carried out at different temperatures by only changing the temperature of the oven and by waiting for a new thermal and mechanical equilibrium. The pressure and the temperature of the equilibrium state are then recorded. A single operation is thus required for measuring the solubility of gases in a wide range of temperatures.

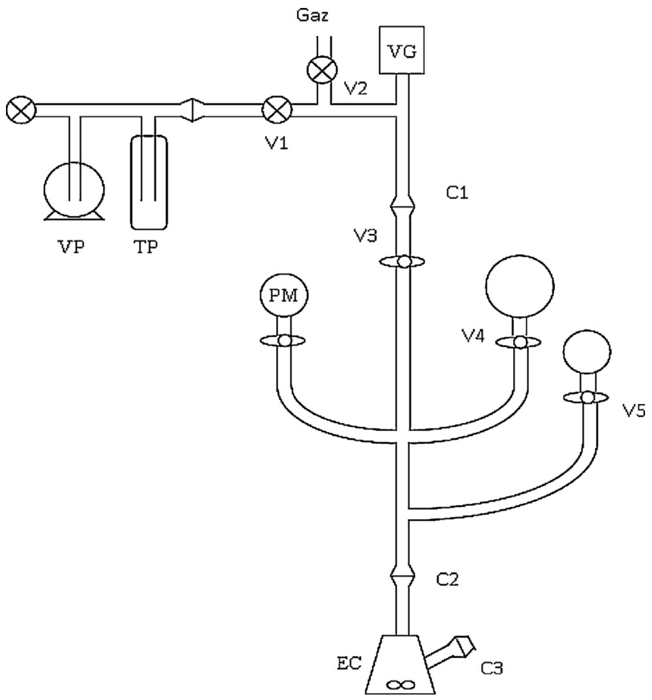

Fig. 1. Schema of the solubility apparatus: VP, vacuum pump; TP, cold trap; VG, vacuum gauge; PM, precision manometer; EC, equilibrium cell; V3, V4, V5, constant volume glass valves; C1, C2, vacuum O'ring connections.

The volumes of the various sections of the apparatus are now given: the volume of the equilibrium cell delimited by V3, V4, V5 and PM has a total volume of:

$$V_{EC} = 61.29\,\text{cm}^3 \tag{1}$$

The two bulbs were calibrated at 303 K by argon. After considering corrections due to thermal expansion, the volume of each bulb is:

$$\begin{cases} V_{\text{bulb},V_4} = (58.15 \pm 0.02)\,\text{cm}^3 \\ V_{\text{bulb},V_5} = (31.95 \pm 0.02)\,\text{cm}^3 \end{cases} \tag{2}$$

The vacuum gauge (ACS 2000, ALCATEL model) which allows controlling the pressure of the upper part of the apparatus, and which is delimited by V1, V2, and V3 has a volume of:

$$V_{VG} = 17.04\,\text{cm}^3 \tag{3}$$

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