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Physical data for a process to separate krypton from air by selective absorption in an ionic liquid

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ABSTRACT

Ionic liquids provide a possible absorption process to extract krypton from air. The feed for such a process is an oxygen stream from a liquid-air plant. An effective ionic liquid is [P(14)666][TMPP]; in that solvent, the solubilities of some pertinent common gases are appreciably larger than those in conventional ionic liquids, and the selectivity Kr/O_2 is close to 3. A nonvolatile ionic liquid is preferred over a hydrocarbon solvent because of safety and simpler solvent recovery. Because, the viscosity of [P(14)666][TMPP] is very high, 20 wt.% [BHMIM][AC] is added to reduce the viscosity by one order of magnitude without significantly reducing solvent capacity and selectivity. This work provides extensive fundamental data (solubility, density and viscosity) required for process design.

1. Introduction

Double (or triple)-pane windows provide an effective way for reducing heat loss in the winter or heat gain in the summer in buildings; such windows commonly use argon for the narrow space between the glass panes [1]. Krypton is a better choice because, like argon, it is safe and chemically inert but, compared to argon, it has a lower thermal conductivity. In addition to multi-pane windows, krypton is used in lighting and electronic devices [2,3].

However, krypton is more expensive than argon. At present, krypton from air is produced by cryogenic distillation of liquefied oxygen [4]. Because the concentration of krypton in air is very small, and because krypton is less volatile than oxygen, this distillation requires much energy [4]. The present work explores a possible alternate method to produce krypton: an absorption process at ambient temperature. The feed to the absorption column is an oxygen stream from a liquid-air plant. The solvent should have a high capacity for krypton and oxygen, and a high Kr/O_2 selectivity.

A possible solvent is a heavy hydrocarbon, but hydrocarbons are volatile and not safe (explosion with oxygen). Ionic liquids are attractive because of their negligible vapor pressure, nonflammability and chemical stability [5,6]. Because the polarizability of Kr (16.8 a_0^3) [7] is larger than that of O_2 (10.6 a_0^3) [8], selectivity Kr/O_2 is likely to be good. Experimental data from our laboratory show that the solubilities of small hydrocarbons in ionic liquid trihexyl tetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate ([P(14)666][TMPP]) [9], are appreciably larger than those in other ionic liquids. Therefore, [P(14)666][TMPP] may be a suitable solvent for an absorption process producing krypton.

However, the viscosity of [P(14)666][TMPP] is too high for a separation process (1004 cP at 298 K [10]). We use 1-butyl-3-H-imidazolium acetate ([BHMIM][AC]) as a diluent to reduce the viscosity of [P(14)666][TMPP]. We choose [BHMIM][AC] because it has low viscosity (7 mPa s at 298 K) [11] and exhibits good solubilities for krypton and oxygen [12]. A simpler alternative is water. However, water is volatile and exhibits very low solubilities for krypton and oxygen.

In this work, we report densities, viscosities and solubilities of krypton, oxygen, nitrogen, xenon and argon in [P(14)666][TMPP] from 313 to 353 K up to 6 MPa. We studied the effect of diluents on solubilities and selectivity for krypton and oxygen in [P(14)666][TMPP]. Because solubiliites of gases in [P(14)666][TMPP] are appreciably larger than those in [BHMIM][AC], we prefer not to use [BHMIM][AC] alone.

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2. Experimental

Krypton and oxygen were purchased from Praxair with purities ≥99.9%. Ionic liquids [P(14)666][TMPP] and [BHMIM][AC] were obtained from Ionic Liquid Technologies (Io-Li-Tec); purities are higher than 95 and 98%, respectively. To remove volatile impurities, the ionic liquids were dried for 24 h in a vacuum oven at 373 K prior to use. Water contents of ionic liquids were measured using the Karl-Fischer method (Aquastar C2000 Titrator); they are less than 0.6 wt.%. The contents of chloride in [P(14)666][TMPP] and [BHMIM][AC] are less than 2.8×10^{-3} ppm and 7.2×10^{-3} ppm, respectively. The contents of bromide in [P(14)666][TMPP] and [BHMIM][AC] are less than 8×10^{-3} ppm and 3.5×10^{-3} ppm, respectively (Information from Ionic Liquid Technologies). The mixtures were prepared gravimetrically using a high-precision balance with uncertainty ±0.0001 g. Miscibility of ionic-liquid mixtures was checked after 48 h.

We used an isochoric-saturation method to measure the solubilities of krypton and oxygen in the pure ionic liquids and in mixtures of [P(14)666][TMPP] with water or [BHMIM][AC]. The essential part of the solubility apparatus is an equilibrium cell with known internal volume, as shown in Fig. S1. The experiment begins with filling the equilibrium cell with a known quantity of dried ionic liquid, removing any air, adding a known quantity of gas from a calibrated pressure vessel of known volume, temperature and pressure. We fix the temperature of the equilibrium cell and then measure the pressure using a calibrated pressure sensor. The pressure decreases due to solubility. Rapid equilibrium is achieved using magnetic stirring. Uncertainties for the pressure and temperature measurements are less than ±0.025% and ±0.1 K, respectively. Details of experimental apparatus and procedure are given in a previous publication [9].

Mass density is necessary for calculating solubility. Mass densities of [P(14)666][TMPP] from 293 to 343 K at atmospheric pressure were reported earlier [9].

Viscosities of ionic liquids were measured using a Brookfield viscometer (model DVII+ Pro); uncertainties are at most 3%.

3. Results

Table S1 and Fig. S2 show the *P*–*x* data for krypton, oxygen, argon, xenon and nitrogen in [P(14)666][TMPP] from 313 to 353 K up to 6 MPa. The uncertainty in mole fraction is less than ±5%. Fig. 1

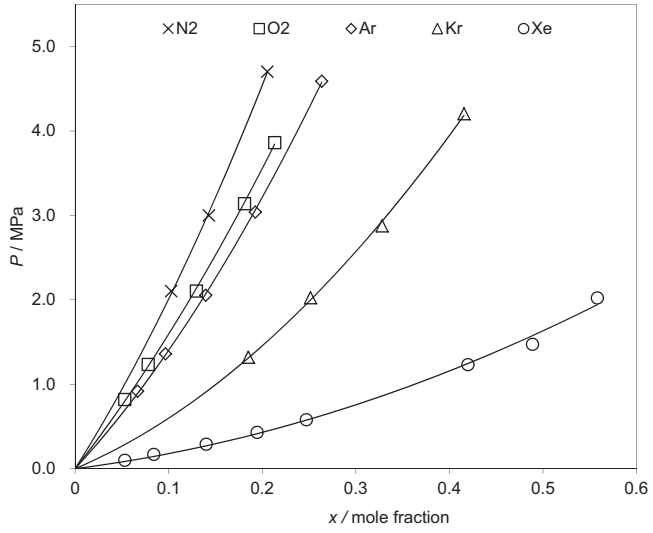

Fig. 1. Solubilities of five gases in [P(14)666][TMPP] at 313 K.

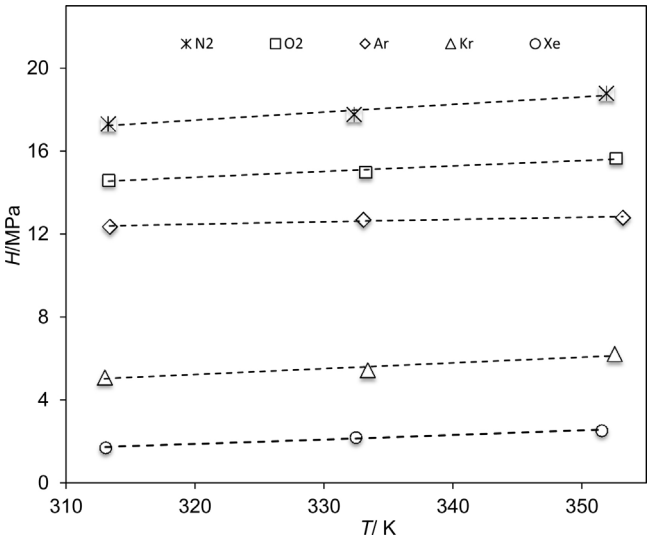

Fig. 2. Henry's constants for five gases in [P(14)666][TMPP].

shows the *P*–*x* data for krypton, oxygen, argon, xenon and nitrogen in [P(14)666][TMPP] at 313 K. From these data, we obtain Henry's constants defined by

$$H = \lim_{x \to 0} \frac{f}{x} \tag{1}$$

where Henry's constant H is in MPa, f is fugacity and x is mole fraction of solute.

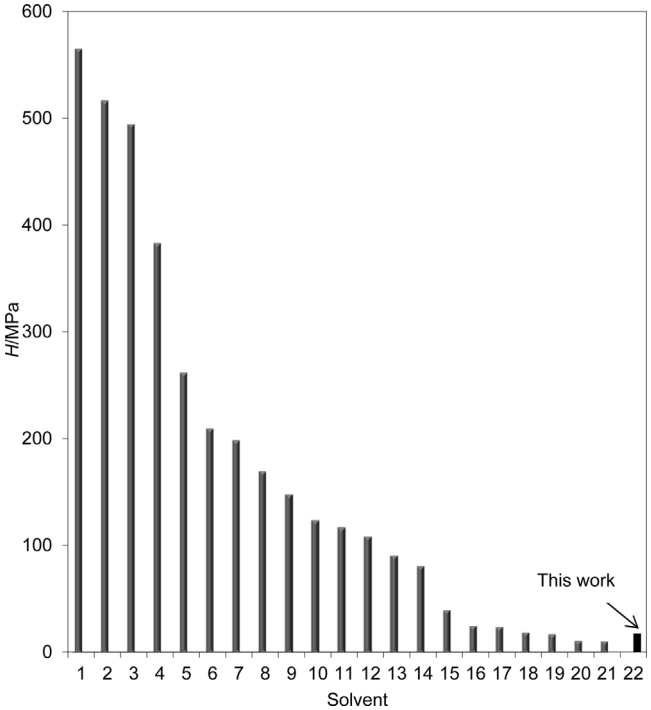

Fig. 3. Henry's constants for nitrogen in a variety of ionic liquids at 313 K. (1) [MMIM][$MeSO_4$] [14]; (2) [S222][Tf_2N] (333 K) [15]; (3) [EMIM][DCA] [16]; (4) [EMIM][BF_4] [14]; (5) [EMIM][CF_3SO_3] [16]; (6) [MP-Piperid][Tf_2N] (333 K) [15]; (7) [BMIM][BF_4] [17]; (8) [BHMIM][AC] [12]; (9) [BMIM][PF_6] [18]; (10) [BMIM][$B(CN)_4$] (333 K) [15]; (11) [EMIM][Tf_2N] [16]; (12) [H-Pyrid][NTf_2] (333 K) [15]; (13) [HMIM][Tf_2N] [14]; (14) [HMIM][FAP] (333 K) [15]; (15) [P(14)666][FAP] (333 K) [15]; (16) [BMIM][eFAP] [19]; (17) [C1C4Pyrro][eFAP] [20]; (18) [N(1)444][Tf_2N] [21]; (19) [BMIM][$CF_3CF_2CF_2COO$] [22]; (20) [MDEA][Cl] [23]; (21) [P(14)666][eFAP] [20]; (22) [P(14)666][TMPP].