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/O₂ 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.

Keywords: selectivity Kr/O₂, mixture of ionic liquids, separation, absorption, diluent

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/O₂ 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 a₀³)⁷ is larger than that of O₂ (10.6 a₀³)⁸, selectivity Kr/O₂ 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 K¹⁰). 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 oxygen¹². 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 solubilities of gases in [P(14)666][TMPP] are appreciably larger than those in [BHMIM][AC], we prefer not to use [BHMIM][AC] alone.

EXPERIMENTAL

Krypton and oxygen were purchased from Praxair with purities $\geq 99.9\%$. 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 hours 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 hours.

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 Figure 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 publication⁹.

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 %.

RESULTS

Table S1 and Figure 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 %. Figure 1 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

$$H = \lim_{x \rightarrow 0} \frac{f}{x} \quad (1)$$

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

Table S2 and Figure 2 show Henry's constants for krypton, oxygen, argon, xenon and nitrogen in [P(14)666][TMPP]. A high Henry's constant corresponds to low solubility. Figures 1 and 2 show that the solubilities of krypton, oxygen, argon and xenon in [P(14)666][TMPP] increase in the order nitrogen < oxygen < argon < krypton < xenon. Krypton and xenon are one order of magnitude more soluble than the other three solutes. Solubilities for the five solutes in [P(14)666][TMPP] increase with rising pressure and decrease with rising temperature. For nitrogen, oxygen and argon, temperature has a small effect on the solubilities.

Henry's constants for krypton, oxygen, argon, xenon and nitrogen in [P(14)666][TMPP] can be represented by¹³:

$$\ln H = \frac{A}{T} + B \quad (2)$$

where temperature T is in kelvins. Table S2 gives coefficients A and B . Figure 2 shows that Eq.(2) agrees well with experiment.

Figures 3-5 compare the solubilities of nitrogen, oxygen and krypton in a variety of ionic liquids studied earlier^{9,12,14-26}. [P(14)666][TMPP] exhibits high solubilities for nitrogen, oxygen and krypton. To our best knowledge, the only published solubility data for xenon are in [BMIM][CH₃SO₄]²⁷ and [HMIM][Tf₂N]²⁸. Henry's constant for xenon in these ionic liquids are 41.7²⁷ and 9.7 MPa²⁸ at 333 K, respectively. Henry's constant for xenon in [P(14)666][TMPP] is 2.2 MPa at 333 K, much lower than those in [BMIM][CH₃SO₄] and [HMIM][Tf₂N]. For argon, the literature gives solubilities in two ionic liquids [BMIM][BF₄]¹⁷ and [BMIM][PF₆]¹⁸. Henry's constants in these solvents are 169 and 113 MPa at 313 K, respectively, one order of magnitude larger than that in [P(14)666][TMPP] (12.4 MPa).

Figure 6 and Table 2 show selectivity Kr/O₂ (H₂O₂/HKr) in several solvents including ionic liquids^{12,25} and alkanes²⁹ at 298 K. Selectivity for Kr/O₂ in [P(14)666][TMPP] is higher than those in other ionic liquids, and similar to those in alkanes.

[P(14)666][TMPP] shows high solubilities for the five gases and high selectivity for Kr/O₂. Therefore, based on these data, it should be a good solvent for separation of krypton from oxygen. However, the high viscosity of [P(14)666][TMPP] makes it unsuitable for industrial application. Unlike other ionic liquids, the viscosity of tetraalkyl phosphonium bis(2,4,4-trimethylpentyl) phosphinate does not decrease when we use a similar ionic liquid with a shorter alkyl chain on the cation³⁰. To reduce the viscosity, we add a co-solvent as a diluent. We studied water and [BHMIM][AC] as possible diluents to reduce the viscosity of [P(14)666][TMPP].

Densities of mixtures of [P(14)666][TMPP] with 5 or 10 wt. % water or 20 or 50 wt. % [BHMIM][AC] were reported earlier.³¹

Figures S3-S6 and Table S3 show P - x data for krypton and oxygen in binary systems [P(14)666][TMPP] with water or [BHMIM][AC] at 298K, 313K and 323K. Figures 7 and 8 compare the P - x data for krypton and oxygen in mixtures of [P(14)666][TMPP] with water and [BHMIM][AC] at 313K. Figures 9 and 10 and Table 3 show Henry's

constants for krypton and oxygen in mixtures of [P(14)666][TMPP] with water or [BHMIM][AC]. Table S4 gives coefficients A and B in Eq.(1) for krypton and oxygen in binary solvents [P(14)666][TMPP] with water or [BHMIM][AC]. As expected, the solubilities for krypton and oxygen in mixtures of [P(14)666][TMPP] + [BHMIM][AC] and [P(14)666][TMPP] + water increase with rising pressure and decrease with rising temperature. The effect of temperature on the solubility of oxygen is larger than that for krypton in [P(14)666][TMPP] with diluents.

Figures 4 and 5 compare Henry's constants for oxygen and krypton in mixtures of [P(14)666][TMPP] and diluents with those in several ionic liquids^{9,10,19-24} at 313K. Mixtures of [P(14)666][TMPP] with 20 wt. % [BHMIM][AC] show that solubilities of oxygen and krypton are similar to those in [P(14)666][TMPP]. Henry's constants for oxygen and krypton in mixtures of [P(14)666][TMPP] with 50 wt. % [BHMIM][AC] or 5 wt. % water are about twice those in [P(14)666][TMPP]. 10 wt. % water very much reduces the solubilities for oxygen and krypton in [P(14)666][TMPP]. Figure 6 and Table 2 compare selectivities for oxygen and krypton in mixtures of [P(14)666][TMPP] and diluents with those in other ionic liquids^{12,25} and in alkanes²⁹ at 313 K. The effect of water on the selectivity Kr/O₂ in [P(14)666][TMPP] is small. The viscosities of mixtures of [P(14)666][TMPP] with 5 or 10 wt. % or 20 or 50 wt. % [BHMIM][AC] were given previously.³¹ At 298K, addition of 20 wt. % [BHMIM][AC] reduces the viscosity of [P(14)666][TMPP] to 160 cP, lower than the viscosity of [P(14)666][TMPP] with 10 wt. % water, 174 cP. [BHMIM][AC] is a suitable diluent for [P(14)666][TMPP], superior to water.

Figure 11 shows viscosities for [P(14)666][TMPP], [BHMIM][AC], and for two ionic-liquid mixtures as a function of temperature. Viscosities of [P(14)666][TMPP] drop dramatically with addition of 20 wt. % [BHMIM][AC].

Preliminary Process Flow Diagram

Figures 12 and 13 show two possible process flow diagrams for the separation of Kr from a side stream of a liquid-air distillation column containing 2 to 5×10^3 ppm Kr (Private communication from Praxair, Ins.) .

Figure 12 shows a conventional absorption/ stripping process. The feed gas is introduced to a packed-bed column absorber. The solvent enters at the top of the column while the feed is introduced at the bottom. Following counter-current contact, the solvent becomes saturated with gas. The ‘rich’ solvent is introduced to a stripper through a turbine (or a throttling valve) to reduce its pressure and then is heated first, using a heat exchanger with regenerated solvent and then using steam. High temperature and low pressure in the stripper removes gas rich in Kr from the top of the stripper; regenerated liquid leaves at its bottom. The over-head gas stream is cooled and sent to a phase separator where steam is condensed to water and returned to the steam generator. The gaseous stream from the water-removal tank is partly recycled to the bottom of the high-pressure (HP) absorber using a compressor while a part is taken off as product and sent to product storage. The ratio of recycled gas to product significantly influences product purity. In this process, ionic liquid is diluted with co-solvent [BHMIM][AC].

An anticipated drawback in the process presented in Figure 12 is the cost for compression of recycled gas to the pressure of the absorber. To reduce this cost, we considered another process shown in Figure 13 with two strippers, one at high pressure and the other at low pressure. In this process, the operational cost is reduced but the capital cost is larger than that shown in Figure 12.

Figure 13 presents a process flow diagram where the rich solvent coming from the bottom of the absorber is fed into a high-pressure regenerator; the gaseous stream from the top of the high-pressure regenerator is recycled and sent to the bottom of the absorber; liquid solvent containing a substantial amount of Kr is sent to a low-pressure stripper for enhanced recovery of Kr and O₂ and for regeneration of solvent. As in Figure 12, the solvent is diluted with [BHMIM][AC].

Because small amounts of methane may be present, we also measured the solubility of methane in the diluted ionic liquid; these solubility data are reported in Table S5.

CONCLUSIONS

This work reports extensive experimental physico-chemical data required to design a potential new separation process for obtaining krypton from the oxygen stream of an air-liquefaction plant. Experimental results suggest that diluted trihexyltetradecylphosphonium bis (2,4,4-trimethylpentyl) phosphinate [P(14)666][TMPP] is a suitable solvent for an absorption process. It has high capacity for dissolved gases as desired to permit a small solvent flow. Also, the diluted ionic liquid exhibits good selectivity for krypton relative to oxygen as desired for using an absorption tower with relatively few stages. The selectivity is about 3.

Experimental studies show that [BHMIM][AC] is more suitable than water for a diluent. When [P(14)666][TMPP] is mixed with 20 wt. % [BHMIM][AC], the viscosity is much reduced while solubilities and selectivity in the diluted solvent are similar to those in undiluted [P(14)666][TMPP]. Two preliminary process flow diagrams are proposed.

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Table 1. Henry's constants for five gases in [P(14)666][TMPP]

T/K	H/MPa	T/K	H/MPa	T/K	H/MPa	T/K	H/MPa	T/K	H/MPa
N_2		O_2		Kr		Xe		Ar	
297	15.8	313	14.6	313	5.1	313	1.7	313	12.4
313	17.3	333	15.0	333	5.4	332	2.2	333	12.7
332	17.8	353	15.7	353	6.2	352	2.5	353	12.8

Table 2. Selectivity Kr/O₂ in a variety of solvents at 298 K*

Solvent	Selectivity Kr/O ₂
heptane ²⁹	3.5
hexane ²⁹	3.5
hexadecane ²⁹	3.4
pentadecane ²⁹	3.4 (305 K)
decane ²⁹	3.3
n-dodecane ²⁹	3.1
[P(14)666][TMPP]	3.1
[P(14)666][TMPP] + 5.0 wt. % water	3.0
[P(14)666][TMPP] + 10.0 wt. % water	3.0
[BHMIM][AC] ¹²	2.9 (303 K)
[P(14)666][TMPP] + 20.0 wt. % [BHMIM][AC]	2.4
[P(14)666][TMPP] + 50.0 wt. % [BHMIM][AC]	2.2
[EMIM][Tf ₂ N] ²⁵	2.0 (313 K)

*: The selectivity in a hydrocarbon solvent is high but hydrocarbons are not safe for a process that includes oxygen.

Table 3. Henry's constants for oxygen and krypton in [P(14)666][TMPP] with diluents

T/K	H/MPa	T/K	H/MPa
oxygen		krypton	
[P(14)666][TMPP] with 5 wt. % water			
299	50.7	299	16.7
313	51.8	314	18.5
324	54.5	324	19.7
[P(14)666][TMPP] with 10 wt. % water			
299	93.2	299	31.4
314	96.3	313	34.9
323	99.1	323	37.4
[P(14)666][TMPP] with 20 wt. % [BHMIM][AC]			
299	22.2	299	9.4
313	22.9	313	10.3
323	23.0	323	11.1
[P(14)666][TMPP] with 50 wt. % [BHMIM][AC]			
299	41.1	299	18.4
313	43.9	313	19.5
323	47.2	323	21.2

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

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

Figure 3. Henry's constants for nitrogen in a variety of ionic liquids at 313K.

1. [MMIM][MeSO₄]¹⁴; 2. [S222][Tf₂N](333 K)¹⁵; 3. [EMIM][DCA]¹⁶; 4. [EMIM][BF₄]¹⁴; 5. [EMIM][CF₃SO₃]¹⁶; 6. [MP-Piperid][Tf₂N](333 K)¹⁵; 7. [BMIM][BF₄]¹⁷; 8. [BHMIM][AC]¹²; 9. [BMIM][PF₆]¹⁸; 10. [BMIM][B(CN)₄](333K)¹⁵; 11.[EMIM][Tf₂N]¹⁶; 12. [H-Pyrid][NTf₂](333 K)¹⁵ 13. [HMIM][Tf₂N]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][Tf₂N]²¹; 19. [BMIM][CF₃CF₂CF₂COO]²²; 20. [MDEA][Cl]²³; 21. [P(14)666][eFAP]²⁰; 22. [P(14)666][TMPP].

Figure 4. Henry's constants for oxygen in a variety of ionic liquids at 313 K.

1. [Bu3MeP][TOS](343 K)²⁴; 2. [BMIM][BF4]¹⁷; 3. [BHMIM][AC]¹²; 4. [BMIM][BF6]¹⁸; 5. [MeBuPyr][Tf2N](323 K)²⁴; 6. [BMIM][Tf2N](321 K)²⁴; 7. [MeBu3N][Tf2N](322 K)²⁴; 8. [P(14)666][TMPP] +10 wt. % water; 9. [EMIM][Tf2N]²⁵; 10. [HMIM][Tf2N]²⁶; 11. [P(14)666][TMPP] +5 wt. % water; 12. [P(14)666][TMPP] +50 wt. % [BHMIM][AC]; 13. [P(14)666][TMPP] +20 wt. % [BHMIM][AC]; 14. [BMIM][CF3CF2CF2COO]²²; 15. [N(1)444][Tf2N](303 K)²¹; 16. [MDEA][Cl]²³; 17. [P(14)666][TMPP]. Solvent 17 shows highest solubility for oxygen.

Figure 5. Henry's constants for krypton in a variety of ionic liquids at 313 K.

1. [EMIM][AC](303 K)²⁵; 2. [BHMIM][Ac]¹²; 3. [EMIM][Tf2N]²⁵; 4. [P(14)666][TMPP] + 10 wt. % water; 5. [P(14)666][TMPP] + 50 wt. % [BHMIM][AC]; 6. [P(14)666][TMPP] + 5 wt. % water; 7. [P(14)666][TMPP] + 20 wt. % [BHMIM][AC]; 8. [P(14)666][TMPP].

Solvent 8 shows highest solubility for krypton.

Figure 6. Selectivities Kr/O₂ in ionic liquids and alkanes at 298 K. 1. Heptane²⁹; 2. Hexane²⁹; 3. hexadecane²⁹; 4. Pentadecane(305 K)¹²; 5. decane²⁹; 6. n-dodecane²⁹; 7. [P(14)666][TMPP]; 8. [P(14)666][TMPP] +5 wt. % water; 9. [P(14)666][TMPP] +10 wt. % water; 10. [BHMIM][AC](303 K)¹²; 11. [P(14)666][TMPP] +20 wt. % [BHMIM][AC]; 12. [P(14)666][TMPP] +50 wt. % [BHMIM][AC]; 13. [EMIM][Tf2N](313 K)²⁵

Figure 7. Solubilities of krypton and oxygen in mixtures of [P(14)666][TMPP] and water at 313 K.

Figure 8. Solubilities of krypton and oxygen in mixtures of [P(14)666][TMPP] and [BHMIM][AC] at 313 K.

Figure 9. Henry's constants for krypton and oxygen in mixtures of [P(14)666][TMPP] and water.

Figure 10. Henry's constants for krypton and oxygen in mixtures of [P(14)666][TMPP] and [BHMIM][AC].

Figure 11. Semi-log plot of viscosities for mixtures of [P(14)666][TMPP] and [BHMIM][AC].

Figure 12. Process flow diagram for krypton absorption using a single stripper for solvent and gas recovery

Figure 13. Process flow diagram for krypton absorption using 2-step regeneration of solvent and gas recovery. The rich solvent is sent first to the high-pressure regenerator for partial recovery of gases and then to the low-pressure regenerator (stripper) for enhanced recovery.