

Advanced Membrane Reactors in Energy Systems: A Carbon-Free Conversion of Fossil Fuels

Task 2: Ceramic hydrogen membranes and development

Investigators and starting date

TU Delft

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Introduction

In the statement of work, presented for the period 01 April 2005 to 31 March 2008 the technical description of the work to be performed by ECN and TUDelft has been presented in detail. In Task 2: Hydrogen membranes and development, TUDelft identified three innovative methods to produce novel hydrogen separation membranes, i.e., Multi-component alloy membrane, Functionally-graded porous membrane, and Metal-organic framework membrane. ECN and TUDelft have decided that functionally-graded porous membranes will have the highest potential with respect to efficiency and cost for “carbon-free” production of hydrogen or electricity.

In order to achieve this target the starting ceramic membrane was selected to be a macro-porous support with pore sizes in the order of micrometers. It was proposed to use Chemical Vapor Infiltration (CVI) to create a top layer of this macro-porous support to be converted into an intermediate layer with a much narrower pore-size distribution. The CVI process was followed by Atomic Layer Deposition (ALD) to decrease the pore diameter to the kinetic diameter of the hydrogen molecule in a very controlled way in order for the *in-situ* separation of hydrogen from the reaction gas mixture. Literature studies and scientific discussions with separation membrane scientists have lead to a modification of the Task.

In Task 3: CO₂ membranes and developments, both ECN and TUDelft contribute to the CO₂ separation in a hydrogen production reactor. The ECN and TUDelft contributions and reports will be presented separately. In particular, the role of Ionic Liquids will be emphasised in this report.

Background

For membrane reactor concepts, a hydrogen selective membrane capable of operating in a high-temperature, high-pressure environment is needed. While inorganic membranes are the topic of research for more than two decades, recent gas phase deposition techniques can be employed to design molecular separation processes for mixtures of methane, steam, carbon monoxide, and hydrogen at elevated temperatures in order to obtain pure hydrogen. The microporous inorganic membrane must exhibit a good thermal stability and a mean pore size ≤ 0.3 nm (based on the kinetic diameter of H₂) with an associated narrow pore size distribution.

Results and Progress

A survey of companies, which provide porous ceramic membranes, as well as, of the literature on ceramic membranes revealed that it is not possible to obtain commercially available ceramic alumina membranes with a narrow pore size distribution in the micrometer regime. This is an essential condition for applying Chemical Vapour Infiltration. Therefore, it was decided to start a collaboration with the membrane group of ECN and of the ceramic membrane group of Twente University, which both provide the knowledge to deposit nano-porous ceramic membranes on commercial porous alumina substrates. Both ECN and Twente University use sol-gel techniques to deposit thin films of alumina or silica on the commercial porous alumina substrates. It was, therefore, decided to extend the TUDelft project with the sol-gel deposition of an intermediate mesoporous ceramic alumina layer with a narrow pore-size distribution in order to have an optimised substrate for the ALD. Dr. Stoitas is an expert in sol-gel thin-film techniques. The ALD equipment is currently being improved for automated operation to deposit in a controlled way Al_2O_3 inside the mesopores. After this step, the experimental conditions of deposition will be studied in order to obtain a mean pore size of 0.3 nm with a narrow pore size distribution.

Future Plans

The targets are the following:

1. Modified mesoporous $\gamma\text{-Al}_2\text{O}_3$ by ALD

- Support: $\alpha\text{-Al}_2\text{O}_3$

thickness: 2 mm

Pore diameter: 100-200 nm

- Mesoporous layer: $\gamma\text{-Al}_2\text{O}_3$ by sol-gel

Thickness: 3 μm

Pore diameter: 4 nm and narrow pore size distribution

- Modification of the mesoporous layer by ALD of Al_2O_3 inside the mesopores:

Selected Precursors: AlCl_3 and O_2 and objective: pore diameter ≤ 0.3 nm for the microporous layer, based on the kinetic diameter of H_2 .

Permeation experiments (first at low temperature) will follow to evaluate H_2 permeability of the system. If the results are satisfying, we will study the separation of H_2 from mixtures $\text{H}_2/\text{H}_2\text{O}$, H_2/CO , H_2/CH_4 (still at low temperature).

Then, the thermal stability of the pore structure will be studied. To improve the stability of $\gamma\text{-Al}_2\text{O}_3$, against sintering, doping with La will be investigated, as already reported in the literature [1]. In the meantime, we investigate the following system:

2. Modified mesoporous La-doped $\gamma\text{-Al}_2\text{O}_3$ by ALD

- Support idem as for 1.

- Sol-gel synthesis of the mesoporous layer La-doped γ -Al₂O₃ with an optimisation of the synthesis conditions to obtain a mean pore size of 4 nm with a narrow pore size distribution.

Selected precursors: Al[OCH(CH₃)C₂H₅]₃ and LaNO₃

- Modification of the mesoporous layer by ALD of Al₂O₃ inside the mesopores as described in 1.

3. Microporous γ -Al₂O₃ or mesoporous/microporous La-doped γ -Al₂O₃ by sol-gel

References

[1] K.-N. P. Kumar, J. Tranto, J. Kumar, J. E. Engell, J. Mater. Sci. Letters **15** (1996), 266.

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Task 3: A potential ionic liquid for CO₂-separating membranes: selection and gas solubility studies

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Introduction

Due to a range of attractive properties, ionic liquids are receiving exponentially increasing attention in a range of different disciplines. One of the remarkable properties of ionic liquids is their almost nonexistent vapour pressure. As opposed to liquid absorption techniques commonly used for gas separation, this lack of vapour pressure in ionic liquids prevents the loss of the “capturing agent” into the gas stream, thus making these materials highly attractive for gas processing. A scattered number of researchers have recently started investigating the possibility of using ionic liquids as “stable” membranes for selectively separating gases.

Room temperature ionic liquids are defined as organic salts, consisting of anions and cations, which melt at or below room temperature. Some common ionic liquid cations include imidazolium, pyrrolidinium, and pyrrodonium, where among the most popular anions one can name chloride (Cl), nitrate (NO₃), hexafluorophosphate (PF₆), tetrafluoroborate (BF₄), and bis(trifluoromethylsulfonyl)imide (TF₂N). In addition, an alkyl chain is usually attached to the cation of an ionic liquid. Task specific ionic liquids with modified physical and chemical properties can be engineered with the suitable combination of anions, cations, and alkyl chain lengths.

The solubility of CO₂ in ionic liquids is high compared to other gases. Hydrogen solubilities are much lower. On the other hand no appreciable amounts of ionic liquid dissolve in CO₂ or in H₂. These properties render ionic liquids as potential materials for the separation of CO₂ from H₂ in the form of supported membranes. The goal of this study is to further investigate this idea. The initial step involves a literature survey of the numerous ionic liquids, collecting the available data of significance to the separation task of concern. Based on these data, a promising ionic liquid is selected for further investigation. The next step involves the experimental measurement of the solubilities of the different gases involved in the gas-shift reactions, in order to verify the possibility of using the ionic liquid as a potential gas separating medium.

Background

In order to select an ionic liquid for CO₂ separation in an H₂ production reactor, the following criteria were taken into account:

- High CO₂ solubility and low H₂ solubility are desirable for optimal separation
- High solubility of CO in the ionic liquid is also preferred in order to prevent CO emissions as well.
- A manageable viscosity is desired: A low viscosity is favourable for mass transfer rate considerations, yet the viscosity must not be too low for its adhesion to the membrane support.

- A high thermal stability is necessary to withstand reaction temperatures. Each aspect will be considered in the following sections.

Ionic liquid gas solubility data is severely lacking in literature. Even the data available are mostly in the form of Henry's constants (H) at very low gas concentrations (x) and pressures (P), a highly idealized case:

$$H = \lim_{x \rightarrow 0} \frac{P}{x}$$

But due to the absence of more suitable data, Henry's constant has been chosen as the comparison index for the selection of a potential gas-separating ionic liquid.

1. Carbon dioxide solubility

Compared to other gases, the Henry's constants are very low for CO₂ in ionic liquids, indicating high solubilities. The CO₂ solubility is particularly high in ionic liquids based on the imidazolium cation. However, it is the anion of the ionic liquid that has the dominant effect on the interaction with CO₂, with the cation playing a secondary role.

In Table 1, Henry's constants are given for CO₂ in various ionic liquids found in literature [Cadena et al. (2004), Baltus et al. (2004), Aki et al. (2004)]. It is seen that the family of ionic liquids with the [Tf₂N] anions have the among the lowest Henry's constants, corresponding to the highest solubilities.

Table 1, Henry's constants for CO₂ at atmospheric conditions in various ionic liquids found in literature

Ionic liquid	k _H , MPa ^{a,b,c}
[bmim][BF ₄]	5.65
[bmim][PF ₆]	6.18
[bmim][TfO]	3.7 < k _H < 6.18
[emim] [Tf ₂ N]	3.56
[bmim][Tf ₂ N]	3.7
[hmim][Tf ₂ N]	3.5
[omim][Tf ₂ N]	k _H < 3.5
[bmim][methide]	3.5 < k _H < 3.7

Ref: ^a Cadena et al. (2004), ^b Baltus et al. (2004), ^c Aki et al. (2004)

2. Carbon monoxide solubility

In Table 2, the Henry's constants are given for carbon monoxide in various ionic liquids [Ohlin et al.]. Similar to CO₂, it is clear that ionic liquids with the [Tf₂N] anion show a better CO solubility than most of the other ionic liquids, probably due to the presence of the fluoroalkyl groups.

Table 2. Henry's constants for CO at atmospheric conditions in various ionic liquids found in literature

Ionic liquid	k _H , MPa ^a
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[emim][BF ₄]	667
[bmim][BF ₄]	337
[hmim][BF ₄]	161
[bmim][PF ₆]	327
[bmim][SbF ₆]	201
[bmim][CF ₃ CO ₂]	191
[emim][Tf ₂ N]	118
[bmim][Tf ₂ N]	95
[hmim][Tf ₂ N]	76

Ref: ^a Ohlin et al. (2004)

3. Hydrogen solubility

Table 3 gives the Henry's constants for hydrogen in various ionic liquids found in literature [Dyson et al.]. From the three-digit valued Henry's constants, it can be concluded that in most ionic liquids, hydrogen solubility at atmospheric conditions is much lower than the corresponding solubility of CO₂ and somewhat lower for CO. Ionic liquids with [Tf₂N] anions show higher hydrogen solubility than most of the other ionic liquids as is shown in Table 3.

Table 3. Henry's constants for H₂ at atmospheric conditions in various ionic liquids found in literature

Ionic liquid	k _H , MPa ^a
[bmim][BF ₄]	580
[hmim][BF ₄]	570
[bmim][PF ₆]	660
[bmim][SbF ₆]	490
[bmim][CF ₃ CO ₂]	490
[bmim][Tf ₂ N]	450
[bmmim][Tf ₂ N]	380

Ref: ^a Dyson et al. (2003)

4. Thermal stability

An ionic liquid is only suitable as a gas separating membrane medium, if it can withstand the temperatures involved in the H₂ production reaction. For natural gas conversion into H₂ and CO₂, the temperature should at least be 400°C. The separation enhanced water gas shift of gas from a coal gasifier can occur at temperatures from 150°C.

The vast majority of the data available in literature are obtained by fast TGA (Thermogravimetric Analysis) scans collected under an atmosphere of nitrogen. These data, however, do not imply a *long-term* thermal stability below the given temperature [Kosmulski et al., 2003].

For many ionic liquids, degradation temperatures were observed to be lower than 200°C. However ionic liquids based on imidazolium cations and fluoride containing anions, in general, show higher thermal stability [Anderson et al., 2003; Fox et al., 2003], for example 1-butyl-3-methylimidazolium [Tf₂N], is stable at 200°C [Kosmulski et al.,

2003]. Ionic liquids with nucleophilic anions decompose about 150°C lower than ionic liquids with fluoride containing anions. The thermal stability of the imidazolium based ionic liquids increase with increased alkyl substitution, as long as linear alkyl groups are used [Ngo et al., 2000; Fox et al., 2003]. However, the alkyl chain length doesn't have a large effect on the thermal stability of the ionic liquids investigated [Fox et al., 2003]. The thermal stability of ionic liquids increases with increasing anion size [Fredlake et al., 2004]. The onset of thermal decomposition appears to decrease as the anion hydrophilicity increases [Chiappe et al.]. The onset decomposition temperature was found to be more dependent upon the anion than the cation.

Ionic liquids that are stable at much higher temperatures are the dicationic ionic liquids. They exhibit a much higher thermal stability, with onset temperatures ranging from 330 to over 400 °C [Han et al., 2005].

More relevant to practical applications are results obtained from ionic liquids in the presence of impurities. The effect of typical impurities (water and chloride) on the thermal stability of ionic liquids is insignificant [Kosmulski et al., 2003]. But ionic liquids with [PF₆] anions show larger thermal decomposition in the presence of air compared as compared to nitrogen. However for ionic liquids with a [Tf₂N] anion the presence of air is rather insignificant on their thermal degradation as compared to pure nitrogen [Kosmulski et al., 2003].

In Table 4, the onset and start temperatures for thermal decomposition are given for some ionic liquids [Huddleston et al., 2001, Fredlake et al., 2004]. These temperatures are based on the TGA method, and are therefore much higher than long-term degradation temperatures. They can, however, be used to compare the thermal stability of different ionic liquids. As discussed above, ionic liquids with the [Tf₂N] anion in general show high thermal stability. Also the ionic liquids [emim][BF₄] and [bmim][methide] show good thermal stability.

Table 4. Onset and start temperatures for thermal decomposition for various ionic liquids found in literature

Ionic liquid	Onset and start temperatures for thermal decomposition	
	$T_{\text{onset}} (^{\circ}\text{C})$ ^{a,b,c}	$T_{\text{start}} (^{\circ}\text{C})$ ^b

[bmim][Cl]	264	150
[bmim][Br]	273	215
[bmim][dca]	300	240
[emim][BF ₄]	412	-
[bmim][[BF ₄]	361	290
[bmmim][BF ₄]	380	285
[bmim][methide]	413	360
[bmim][triflate]	392	340
[emim][PF ₆]	375	-
[bmim][PF ₆]	349	-
[bmmim][PF ₆]	373	235
[emim][Tf ₂ N]	440/455	-
[pmim][Tf ₂ N]	452	-
[bmim][Tf ₂ N]	422	330
[pmmim][Tf ₂ N]	462	385

Ref: ^aHuddleston et al. (2001), ^bFredlake et al. (2004), Camper et al. (2005)

5. Viscosity

The viscosity of the ionic liquid is also an important criterion when selecting an ionic liquid to use as a membrane. A high viscosity leads to low mass transfer. On the other hand, the viscosity of the ionic liquid must not be too low for application as a supported membrane. An optimum has to be found.

The viscosities of most of the ionic liquids are comparable to the viscosities of oils, and thus about two or more orders of magnitude higher than the typical values found for most organic solvents. The viscosity of an ionic liquid is mainly governed by the electrostatic attraction between the cations and anions, the tendency to form hydrogen bonds, the strength of Van der Waals interactions, and the degrees of freedom within the ions. The viscosity of ionic liquids decreases with increasing temperature. The viscosity is also expected to decrease in the presence of CO₂ in the liquid phase, because CO₂ can disrupt the ionic bond between the anion and cation [Blanchard et al., 2001; Baltus, 2004].

The viscosity, in general, increases with increasing length of the alkyl side chain of the cation, due to the increase of Van der Waals interactions [Zhou et al., 2005]. Branching of the alkyl side chain in 1-alkyl-3-methylimidazolium salts always reduces viscosity [Chiappe et al., 2005]. Ionic liquids with a fluorinated cation have a viscosity much larger than ionic liquids with nonfluorinated cations [Baltus et al., 2004].

The influence of the anion is much less well understood. The geometry and molar mass of the anions strongly influence the viscosity of an ionic liquid. Chiappe and coworkers (2005) concluded that the viscosity increases with increasing symmetry of the anions. Ions with low polarizability, high degree of freedom, good charge distribution, and somewhat flat shape are favourable for producing low-viscosity ionic liquids [Zhou et al., 2005]. Fluorination of the alkyl chain in the anion leads to lower viscosity, due to the better charge distribution and lower polarizability for the fluorinated anions. This makes a contribution to reducing the strength of cohesive forces, including coulombic interactions, Van der Waals interactions, and hydrogen bonding, thus lowering the viscosity [Zhou et al., 2005; Chiappe et al., 2005].

In Table 5, the viscosities for various ionic liquids are shown [Huddleston et al.,2001; Zhou et al., 2005]. The [Tf₂N] family seems to exhibit the most workable viscosities.

Table 5. Viscosity of various ionic liquids at 25°C

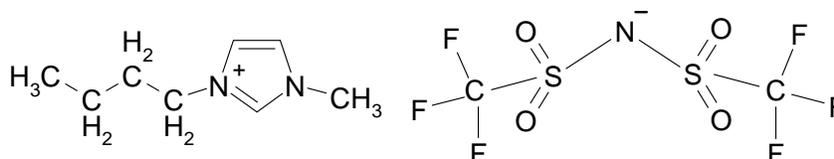
Ionic liquid	Viscosity at 25°C (cp) ^{a,b}
[hmim][Cl]	716
[emim][BF ₄]	43/38
[bmim][BF ₄]	233
[hmim][BF ₄]	314 (at 20°C)
[bmim][PF ₆]	450
[hmim][PF ₆]	585
[bmim][CF ₃ CO ₂]	73
[emim][Tf ₂ N]	28
[bmim][Tf ₂ N]	52
[emmim][Tf ₂ N]	88
[bmmim][Tf ₂ N]	97

Ref: ^a Huddleston et al. (2001), ^b Zhou et al. (2005)

Choice of ionic liquid

Examining the above-mentioned considerations among the various ionic liquids for which a reasonable amount of information is already available, the choice of the ionic family to be considered as a possible CO₂ separating membrane is rather straightforward. The [Tf₂N] family of ionic liquids shows very low Henry's constants for CO₂, suggestive of high solubilities of this gas in the ionic liquid. At the same time, the solubilities of H₂ in this family of liquids are also higher than in other ionic liquids. This difference is however small compared to the much higher solubility of CO and CO₂ in [Tf₂N]-based ionic liquids. In other words, the ratios of CO₂/H₂ solubilities are expected to be higher in the [Tf₂N] family. In addition, the greater thermal stabilities and lower viscosities of this family make it stand out further as the most promising class of ionic liquids for further consideration. It is also of great significance that the [Tf₂N] ionic liquids are mostly water immiscible, a characteristic of utter significance for membrane stability in a reaction involving steam.

However, the choice of the specific member of this family is less obvious. Various characteristics of the different members of this family, where available, are summarized in Table 6. A larger alkyl side chain is favoured when solubility considerations are a priority, while the smaller members of the [Tf₂N] family are preferred for their higher thermal stability and lower viscosity. [bmim] [Tf₂N], with the molecular structure shown below, has been selected as the initial component to be investigated further due to its moderate values in all the properties of concern. The [emim] [Tf₂N] member will be the second component to be investigated later on in this research.



1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

Table 6. Characteristics of various members of the [Tf₂N] family of ionic liquids

Ionic liquid	[H ₂], MPa	[CO], MPa	[CO ₂], MPa	T _{onset} (°C)	Viscosity at 25°C	Commercial availability	Purity	Price \$/5g
[emim][Tf ₂ N]	-	118	3.56	440/455	28	>97%		330
[pmim][Tf ₂ N]	-	-	-	452	-	-	-	-
[bmim][Tf ₂ N]	450	95	3.7	422	52	>98%		262
[hmim][Tf ₂ N]	-	76	3.5	-	-	-	-	-
[omim][Tf ₂ N]	-	-	<3.5	-	-	-	-	-
[bmmim][Tf ₂ N]	380	-	-	-	97	-	-	-
[pmmim][Tf ₂ N]	-	-	-	462	-	-	-	-

Results and Progress

Figure 1 shows the solubility data obtained for the system [bmim][Tf₂N] within the temperature and pressure range of the Cailletet apparatus. It is seen that as temperature rises, increasingly higher pressures are necessary to dissolve a fixed amount of CO₂ in the ionic liquid.

The interpolation of this data onto a more descriptive pressure-composition diagram is shown in Figure 2. This figure shows the remarkable solubility of CO₂ in [bmim][Tf₂N], going as far as 60 mole percent at pressures exceeding 8MPa. At lower pressures, for example at 4MPa, CO₂ concentration range between 20-40 mole percent depending on the temperature. Figure 2 also emphasises the strong functionality of solubility on temperature and pressure, especially at higher gas concentrations where pressures start to approach a diverging behaviour with gas concentrations. This diverging region should be avoided in any membrane operation, as it would result in excessive compressor energy loss with no gain in gas solubility. The curvature of the isotherms on this plot indicates the non-ideality of the system, and hence the extent of errors that will be obtained by extending the linear Henry's law to inapplicable regions of high gas solubility.



Figures 3a and 3b compare CO₂ solubility in two other ionic liquids having the same cation as [bmim][Tf₂N], but with different anions. Comparing these experimental data further confirms the excellence of the selected ionic liquid, showing solution capacities for CO₂ to be typically 1.5 times higher in [bmim][Tf₂N] than in other ionic liquids.

A literature survey through the limited data available on solubility of gases in various ionic liquids, together with other considerations such as suitable viscosity and high thermal decomposition temperatures, has led us to select [bmim][Tf₂N] as a potential ionic liquid for CO₂ separation in the coal-gasification process. The solubilities of CO₂ were then experimentally determined using a synthetic phase equilibrium measurement technique. The experimental results indicated that the solubility is strongly dependent on temperature and pressure, decreasing with temperature and increasing with pressure. The results obtained have confirmed the hypothesis of very high CO₂ solubility in [bmim][Tf₂N], reaching values up to 60 molar percent, and possibly even higher at higher

pressures. Such CO₂ solubilities are considerably higher than in the various other ionic liquids for which such data is available.

The results obtained so far have indicated the success of [bmim][Tf₂N] as a potential membrane for transferring CO₂. However a successful membrane must also have no or very little transfer of H₂ to the permeate side. But, as shown by the curvature leading to steep-sloped pressure-composition curves in this work, extrapolating available Henry's constant data to higher gas concentrations can be seriously misleading and erroneous. Therefore, it is absolutely necessary to measure the corresponding solubilities of hydrogen gas in the selected ionic liquid over a whole range of concentrations and pressures, before any conclusive statement can be made about the capability of [bmim][Tf₂N] in separating CO₂ from H₂. This will cover the next step in this ongoing investigation.

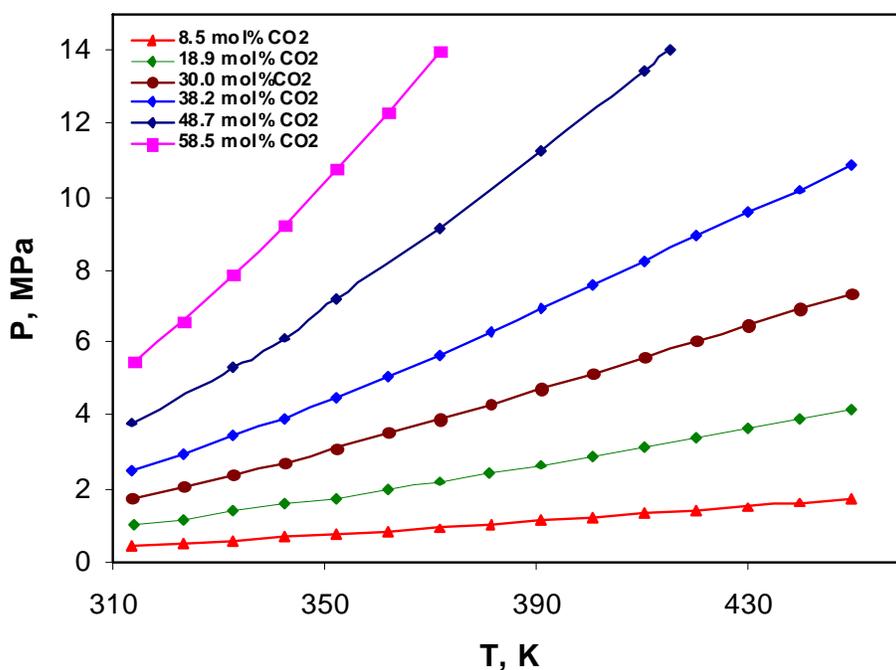


Figure 1. Experimental pressure-temperature results for the binary mixtures of CO₂ + [bmim][Tf₂N] with varying concentrations.

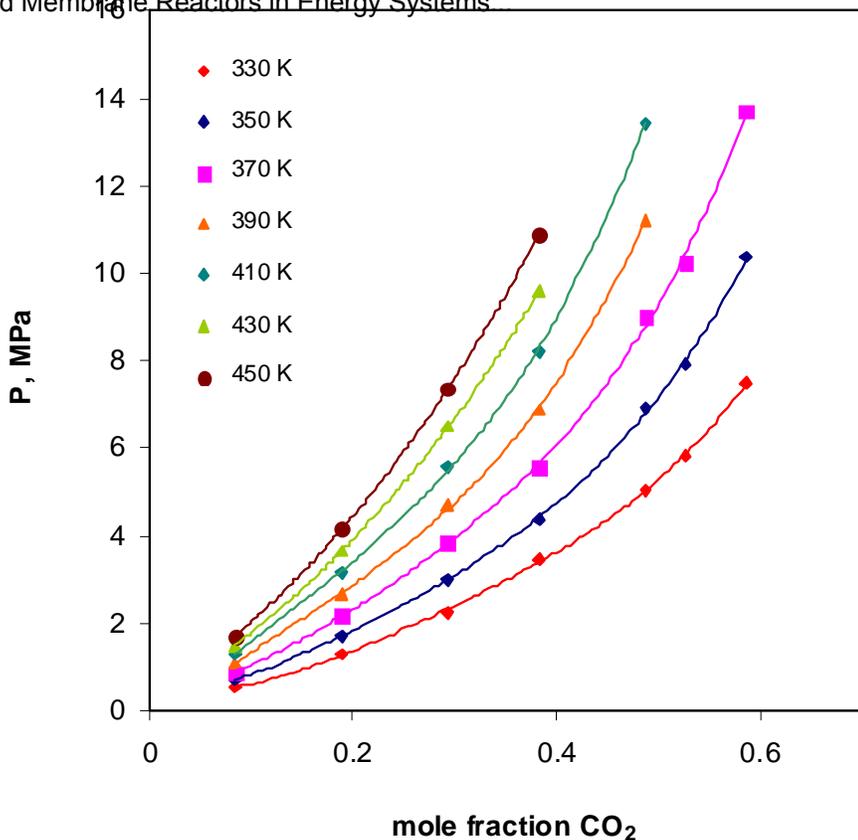


Figure 2. Interpolated Pressure-composition isotherms for the system of CO₂ + [bmim][Tf₂N] with varying concentrations.

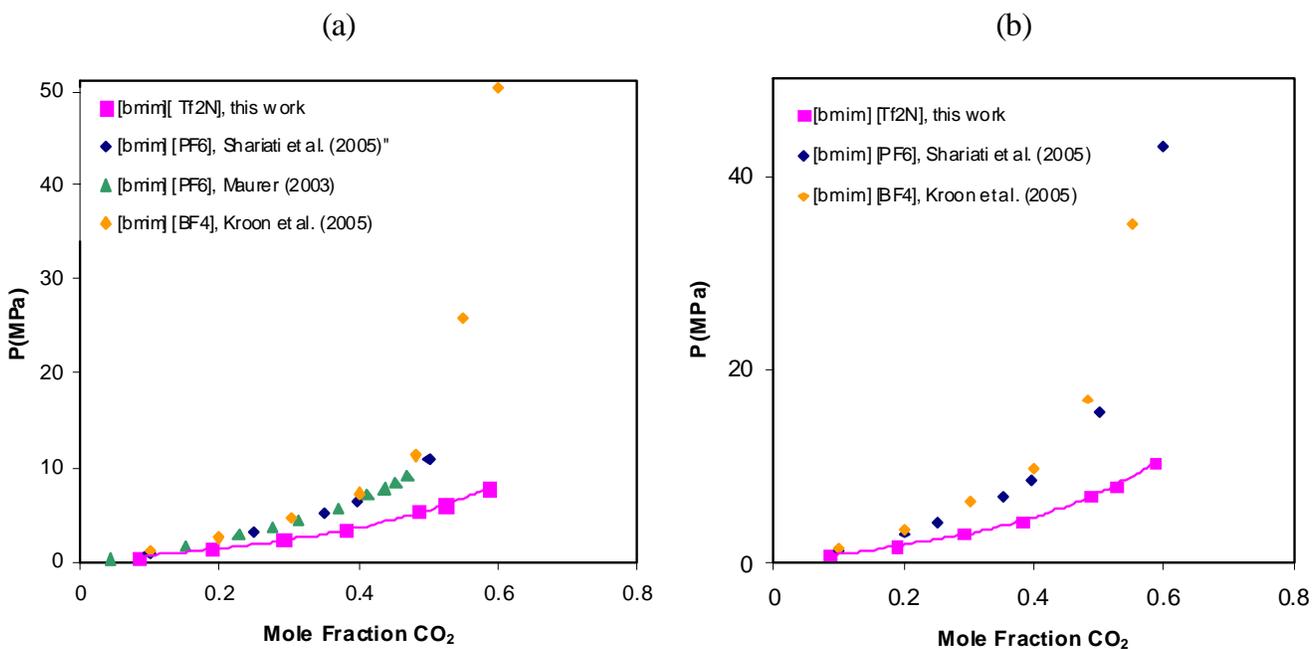


Figure 3. Comparison of CO₂ solubility in several ionic liquids with varying anions but having the same cations (a) 333.15 K (b) 350 K.

Future Plans

Solubility measurements of hydrogen (H₂), methane (CH₄) and carbon monoxide (CO) in the two selected ionic liquids will be performed. After that an analysis will be carried out to test the applicability of the ionic liquids in the developed membranes.

Publications

The collected experimental information is suitable for publication. Preparing these papers will be done shortly.

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