A POTENTIAL IONIC LIQUID FOR CO_2-SEPARATING MEMBRANES: SELECTION AND GAS SOLUBILITY MEASUREMENTS

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Introduction

The steam reforming and the water gas shift equilibria are the key reactions for the production of hydrogen from fossil fuels. By removing carbon dioxide from the reaction mixture as it is produced, the equilibrium can be shifted to the product side. The aim of this study is to find an ionic liquid suitable as membrane, for use in a separation-enhanced reactor (membrane reactor) for carbon-free hydrogen production.

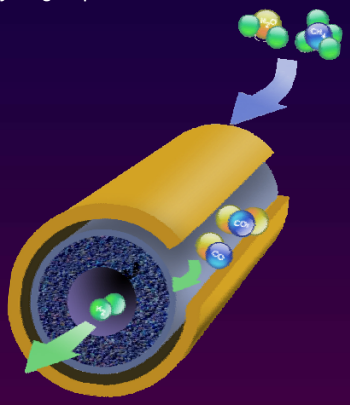
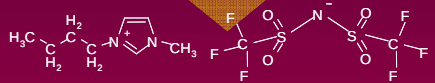


Figure 1. Schematic diagram of separation-enhanced membrane reactor

Ionic liquid selection criteria for CO_2 separation membrane

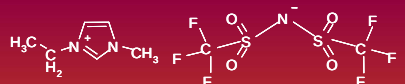
- High solubility for CO_2
- Low solubility for H_2
- High solubility for CO is favourable
- Thermal stablity at T≥150°C
- Workable viscosity

Suitable ionic liquid candidates



1-butyl-3-methyl-imidazolium-bis-(trifluoromethylsulphonyl) imide

abbreviation: [bmim][Tf_2N]



1-ethyl-3-methyl-imidazolium-bis-(trifluoromethylsulphonyl) imide

abbreviation: [emim][Tf_2N]

Experimental

To obtain the solubilities of the reaction gases in the two selected ionic liquids, measurements were carried out in the Cailletet apparatus. This apparatus allows the visual observation of the disappearance of gas upon pressure increase at a fixed temperature for a mixture of known fixed composition.

Results

The measured solubilities of CO_2, CH_4, and H_2 in the ionic liquid [bmim][Tf_2N] is shown below at various temperatures. It is shown that CO_2 has indeed very high solubilities in the ionic liquid, reaching as high as 60 mol% at 8 MPa. On the other hand, as desired, H_2 has much lower solubilities (by one order of magnitude). It is also seen that while CO_2 and CH_4 solubilities decrease with increasing temperature, H_2 shows the opposite trend, increasing its solubility in the ionic liquid with increasing temperature.

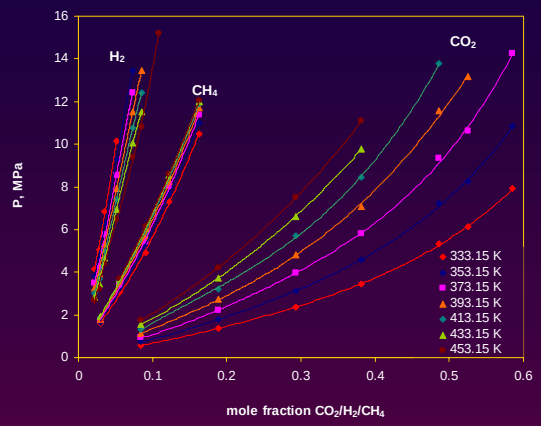


Figure 2. Measured gas solubilities in the ionic liquid [bmim][Tf_2N]

Similar results were also obtained for the ionic liquid [emim][Tf_2N]. However, the solubilities of both CO_2 and H_2 were slightly lower in [emim][Tf_2N] than in [bmim][Tf_2N]. While solubility is higher in [bmim][Tf_2N], separation selectivity is better in [emim][Tf_2N]. For example at T=373.15 K and P=10 MPa:

[emim][Tf_2N] CO_2/H_2 = 9.8

[bmim][Tf_2N] CO_2/H_2 = 8.6

Conclusions

- Two ionic liquids have been selected for possible use in CO_2-separating membranes.
- CO_2 has indeed very high solubilities in both ionic liquids.
- solubility measurements indicate favorable selectivities, pointing to solubility ratios ranging between 5<CO_2/H_2<15 or more
- Solubility ratios vary significantly depending on T and P.
- CO_2-H_2 seperation improves as temperature decreases.
- CO_2-H_2 seperation probably has an optimum pressure.
- [bmim][Tf_2N] has slightly higher solubility for CO_2 than [emim][Tf_2N].
- However, the CO_2/H_2 selectivity of [bmim][Tf_2N] is less than [emim][Tf_2N].
- The lower viscosity of [emim][Tf_2N] allows for faster kinetics.

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