A POTENTIAL IONIC LIQUID FOR CO₂-SEPARATING MEMBRANES: SELECTION AND GAS SOLUBILITY MEASUREMENTS

Sona Raeissi¹, Astrid Schilderman², L.J. Florusse², Cor J. Peters²

¹Department of Chemical and Petroleum Engineering, School of Engineering, Shiraz University, Shiraz 71345, Iran
²Physical Chemistry & Molecular Thermodynamics, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

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.

Suitable ionic liquid candidates

- High solubility for CO₂
- Low solubility for H₂
- High solubility for CO is favourable
- Thermal stability at T ≥ 150°C
- Workable viscosity

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 CO₂, CH₄, and H₂ in the ionic liquid [bmim][Tf₂N] is shown below at various temperatures. It is shown that CO₂ has indeed very high solubilities in the ionic liquid, reaching as high as 60 mol% at 8 MPa. On the other hand, as desired, H₂ has much lower solubilities (by one order of magnitude). It is also seen that while CO₂ and CH₄ solubilities decrease with increasing temperature, H₂ shows the opposite trend, increasing its solubility in the ionic liquid with increasing temperature.

Similar results were also obtained for the ionic liquid [emim][Tf₂N]. However, the solubilities of both CO₂ and H₂ were slightly lower in [emim][Tf₂N] than in [bmim][Tf₂N]. While solubility is higher in [bmim][Tf₂N], separation selectivity is better in [emim][Tf₂N]. For example at T=373.15 K and P=10 MPa:
- [emim][Tf₂N] CO₂/H₂ = 9.8
- [bmim][Tf₂N] CO₂/H₂ = 8.6

Conclusions
- Two ionic liquids have been selected for possible use in CO₂-separating membranes.
- CO₂ has indeed very high solubilities in both ionic liquids.
- Solubility measurements indicate favorable selectivities, pointing to solubility ratios ranging between 5<CO₂/H₂<15 or more.
- Solubility ratios vary significantly depending on T and P.
- CO₂/H₂ separation improves as temperature decreases.
- CO₂/H₂ separation probably has an optimum pressure.
- [bmim][Tf₂N] has slightly higher solubility for CO₂ than [emim][Tf₂N].
- However, the CO₂/H₂ selectivity of [bmim][Tf₂N] is less than [emim][Tf₂N].
- The lower viscosity of [emim][Tf₂N] allows for faster kinetics.