

U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY



MOLECULAR DESIGN OF CO₂ LIGANDS IONIC LIQUIDS AND POLY (IONIC LIQUIDS)

Justification and Background

The potential for various ionic liquids (ILs) and poly(ionic liquids) (PILs) to capture CO₂ is being investigated. Papers published by Radosz and co-workers indicate that PILs can have very larger CO₂ uptake compared with ILs. One of their most surprising results was that four of the IL monomers they tested had essentially zero uptake capacity for CO₂, whereas when polymerized, the corresponding PILs showed very large uptake at a temperature of 22 °C and a pressure of about 0.8 bar. Molecular modeling combined with COSMOtherm is being used to gain insights into these surprising findings

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Approach

Turbomole ab initio calculations have been used to predict the σ profiles for the following PIL/IL pairs: PVBIH/VBIH, PVBIT/VBIT, PBIMT/BIMT, PVBTMA/VBTMA, PMATMA/MATMA, PVBBI/VBBI and on the [bmim][BF₄] and other ionic liquids. In cooperation with an industrial researcher, COSMOtherm calculations using the σ profiles have been used to estimate the Henry's law constants and solubilities for CO₂ in the ILs and PILs at the experimental condition of 22 °C and 0.8 bar. Results from these calculations are summarized in Table 1. Good agreement for some of the PILs and ILs tested have been found but there are discrepancies for several systems. Therefore an experimental program has been initiated to confirm the computational results.

Table 1. Experimental and calculated CO₂ solubilities for various poly(ionic liquid)s.

Poly(ionic liquid)s	Experiments	Calculations
PVBtMA+BF ₄	10.2	2.2
PMATMA+BF ₄	8.0	1.2
PVBIH+PF ₆	2.7	3.3
PVBBI+Tf ₂ N	2.2	3.1
VBBI+Tf ₂ N	N/A	3.0
PVBIT+BF ₄	2.2	2.7
PBIMT+BF ₄	1.8	1.9
BIMT+BF ₄	1.3	1.8
bmim+BF ₄	1.3	1.7
VBIH+PF ₆	0.0	3.1
VBIT+BF ₄	0.0	2.5
VBTMA+BF ₄	0.0	0.7
MATMA+BF ₄	0.0	1.0



