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NOVEL CO₂ - PHILIC ABSORBENTS

Summary

The ability to separate a high pressure mixture of CO₂ and H₂ such that a high pressure stream of CO₂ for sequestration *and* a high pressure stream of H₂ for energy are produced remains an elusive goal. This research has identified a class of compounds that melt in the presence of high pressure CO₂, forming a liquid phase composed of roughly 50wt% CO₂ and 50wt% of the compound. Unlike conventional solvents that require substantial depressurization during regeneration to release a low pressure CO₂ stream, these novel compounds completely release the CO₂ at many hundreds of psia as the compound solidifies. This work will reveal whether one of more of these compounds can selectively remove CO₂ from a mixture of CO and H₂ at high pressure and release the CO₂ after a modest depressurization.

Problem

One version of an IGCC plant gasifies coal and then employs the water-gas shift reaction to produce a high pressure process stream that is rich in CO₂ and H₂. It would be advantageous to process this mixture such that it simultaneously yields a high pressure CO₂ stream for geologic sequestration and a high pressure H₂ stream for the generation of electricity. Commercial separation technologies, such as membranes, PSA and gas absorption columns, have the ability to produce high pressure CO₂ or high pressure H₂, but not both. The goal of this work is to determine if the ability of novel CO₂ - philic compounds (that liquefy and absorb significant amounts of high pressure CO₂, and then release the CO₂ via a very small pressure drop that causes the compound to solidify) can be used to establish a separation process that yields a high pressure hydrogen stream and a high pressure CO₂ stream.

Methodology

It is anticipated that prior work in CO₂ - philic solids, coupled with molecular modeling contributions (which recently helped us to design new CO₂ - philic compounds), will lead to the development of a truly unique CO₂ - solvent. Prior research identified two classes of compounds, sugar acetates and tert-butylated aromatics, that are extremely "CO₂ - philic". Examples of sugar acetates include glucose pentaacetate and maltose octaacetate, and examples of tert-butylated



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aromatics include tri-tert-butylbenzene and tri-tert-butylphenol. Tri-tert-butylphenol (TTBP) is a commercially available compound (~\$3/lb) that is a solid at room temperature with a melting point (in the absence of CO₂) of 135 °C. In the presence of CO₂ at 50 °C and a pressure of about 1500 psia, the TTBB melts and a liquid phase containing as much as 50wt% TTBP forms. This liquid phase can be slightly depressurized to a slightly lower pressure, roughly 1450 psia, in order to produce a solid TTBP powder that contains no CO₂ and a high pressure CO₂ phase that contains trace amounts of TTBP. Similar experiments conducted with pure H₂ demonstrate that these compounds do not experience a similar melting point depression; these compounds are not H₂ - philic.

Our intention is to exploit this property for the separation of a CO₂ - H₂ mixture. If the TTBP is capable of selectively absorbing CO₂ from the mixture, the process would yield a H₂ - rich gas stream and a TTBP - CO₂ high pressure liquid. The TTBP - CO₂ liquid could be slightly depressurized to release 100% of the CO₂ as the solid TTBP forms. However, this process would have to deal with the handling of solid particulate TTBP.

The objectives would be to determine (using TTBP as an example) the phase behavior of TTBP - CO₂ over a wide range of T, the phase behavior of TTBP - H₂ over the same range of temperature, the separation of H₂ and CO₂ over a wide range of temperature, pressure, gas composition, and gas-TTBP ratio. During this experimentation, various configurations of IGCC cycles would be examined to determine the optimal placement of this separation system, which (based on our preliminary results) appear to be high pressure and relatively low temperature (below 300 °C).

Expected Outcomes

- The phase behavior of CO₂, H₂, CO₂+H₂ mixed with the CO₂ - phile (e.g., TTBP) can be determined from non-sampling visual phase behavior experiments or from sampling VLE experiments.
- Proof-of-concept gas separations can be conducted using either closed systems (in which pressure changes could be used to monitor gas absorption or release) or open systems that would introduce and withdraw a gas stream from the vessel that contains the solid or molten TTBP (in which the composition of the gas in the vessel and/or the effluent gas would be determined using GC).