The Molecular Design Basis for Hydrogen Storage in Clathrate Hydrates

Principal Investigator: Vijay T. John, Tulane University
Co-Principal Investigators: Henry L. Ashbaugh, Tulane University, Gary L. McPherson, Tulane University, Camille Y. Jones, Hamilton College.

Program Scope

Our research objective is to develop new clathrate hydrates as inclusion compounds for hydrogen storage at moderate pressure (<100 bar), approaching 10 wt % hydrogen loading, and at ambient or near-ambient temperatures. This research is focused on a new paradigm in the treatment of clathrate molecular additive design to reinforce the lattice structure of clathrate materials. Specifically, we seek to determine if semi-clathrate materials are capable of encapsulating hydrogen for storage. In semi-clathrate materials, a portion of the guest chemically binds to the host framework, effectively replacing a water molecule in the lattice.[1] The remainder of the guest is then free to interact with the lattice through either van der Waals forces or hydrogen bonding. The strong hydrogen bonding lattice-guest interactions act as an "anchor" to rigidly hold the guest and reduced the translational and rotational degrees of freedom thus increasing the bulk material thermodynamic stability. There are several examples in the literature of semi-clathrate guest interactions with host lattices containing alcohols, phosphine oxides, phosphine sulfides, amines, amides, carbonyls, and aldehyde functional groups. There are also examples of ion pairs acting as host-guest stabilizers.

The research involves a collaboration between the investigators on this project, and a team at Los Alamos National Laboratory (R. Currier and S. Obrey) who are developing novel hydrotrope additives that dramatically reduce the pressure requirements for clathrate formation. The theoretical aspects of the research are complemented by computational studies which is lead by H. Ashbaugh. The research is strongly enhanced by collaboration from C. Jones (Hamilton College) whose expertise is the use of neutron scattering and computational methods for the study of the structure and dynamics of lattice inclusion compounds and molecular solids.

Recent Progress

Research in this project has not yielded any results yet. Due to the effects of hurricane Katrina in New Orleans, the investigators at Tulane have been significantly delayed in starting the work. The University was closed for the Fall of 2005 and the current semester is focused on bringing laboratories back to full operation and rebuilding research. Additionally the intensive teaching schedules to make up for the lost semester have affected faculty progress on research. The PI has just completed hiring research personnel (a post doctoral scholar and Ph.D. student) for the project and is working on setting up the high pressure equipment to characterize hydrogen storage. It is anticipated that results will be forthcoming only in the late summer or Fall of 06.

Future Plans

The following are specific project tasks.

1. Classical thermodynamics and phase behavior of semi-clathrates in the presence of hydrogen. Here we will screen a variety of semi-clathrates for their ability to store hydrogen
2. The Use of Confined Media for Rapid Clathrate Formation. We will evaluate semiclathrate formation in water-in-oil microemulsions (reversed micelles) which have extremely high surface areas for gas-water contact.
3. Characterization of semi-clathrates and hydrogen uptake through neutron scattering (small angle neutron scattering and neutron diffraction) and spectroscopy. We will also undertake novel cryoelectron microscopy techniques to capture the morphology of semi-clathrate structures.
4. Theoretical and Simulation Studies of Semi-Clathrate Stability.

Publications

No publications have resulted from this project to date.

---

1. Jeffrey, G.A. *Accounts of Chemical Research* **1969**, *2*, 344. Franks, F. (ed.),Water in crystalline hydrates; aqueous solutions of simple non-electrolytes, Plenum Press, New York, 1973.