TITLE: Phase Behavior of Light Gases in
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Hydrocarbon and Aqueous Solvents

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ABSTRACT

OBJECTIVES: The present project focuses on measuring the phase behavior of light gases and water in Fischer-Tropsch (F-T) type solvents at conditions encountered in indirect liquefaction processes and evaluating and developing therorectically-based correlating frameworks to predict the phase behavior of such systems. Specific goals of the proposed work include (a) developing a state-of-the-art experimental facility to permit highly accurate measurements of equilibrium phase compositions (solubilities) of challenging F-T systems, (b) measuring these properties for systematically-selected binary, ternary and molten F-T wax mixtures to provide critically needed input data for correlation development, (c) developing and testing models suitable for describing the phase behavior of such mixtures, and (d) presenting the modeling results in generalized, practical formats suitable for use in process engineering calculations.

WORK DONE AND CONCLUSIONS: During the present reporting period, we have designed and constructed a liquid-liquid equilibrium (LLE) apparatus that will allow us to measure the mutual solubility of hydrocarbon-water systems at higher temperatures and pressures. The mutual solubilities of decane + water and benzene + water were measured using this new continuous-flow LLE apparatus at temperatures form 300 to 550 K and pressures to 10 MPa. Our error analysis indicates that the uncertainty in these data is within 10% in mole fraction.

In addition, we have evaluated the predictive capability of the modified Park-Gasem-Robinson (MPGR) equation of state (EOS) for bubble point pressures of selected carbon dioxide + normal paraffin, ethane + normal paraffin, and hydrogen + normal paraffin mixtures. A set of mixing rules was proposed for the modified EOS to extend its predictive capabilities to mixtures. The predicted bubble point pressures for the ethane + n-paraffin and carbon dioxide + n-paraffin binaries were compared to those of the Peng-

Robinson (PR), simplified-perturbed-hard-chain theory (SPHCT) and original PGR equations. The predictive capability of the proposed equation is better than or comparable to the PR, SPHCT and original PGR equations of state for the ethane binaries (absolute-average-percent deviation [%AAD] of 1.9) and the carbon dioxide binaries (%AAD of 2.0). For the hydrogen binaries, the modified PGR EOS showed much better performance (%AAD of 1.7) than the original PGR equation and comparable to the PR equation.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The experimental portion of this project aims at (a) developing state-of-the-art experimental facilities capable of functioning accurately over a wide range of operating conditions, and (b) acquiring critically-needed experimental data to develop models to represent phase behavior of coal fluids. Our expanded experimental capability permits us to handle the formation of multiple liquid phases and to address effectively the development of more theoretically-based, accurate equations of state.

Parallel to our experimental program, we are pursuing integrated model development and testing with the goal of providing more accurate capabilities to predict equilibrium, volumetric and calorimetric properties of mixtures encountered in coal processing. Our model development activities strive to strike a balance between (a) fulfilling immediate needs in coal processing by using semi-empirical models (such as van der Walls-type equations), and (b) the ultimate goal of providing rigorous, accurate and *a priori* predictive capabilities based on more rigorous theories.

PLANS FOR COMING YEAR:

- Continue mutual solubility measurements of selected hydrocarbon-water systems.
- Develop improved correlations for the critical properties and the acentric factor of heavy n-paraffins, based on recently published experimental measurements.
- Develop improved temperature dependence functions for Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state; such efforts will lead to more accurate EOS property predictions for the heavy hydrocarbon.
- Develop generalized correlations for the binary interaction parameters of the cubic EOS (SRK and PR equations) and the theoretically-based equations (MPGR).

HIGHTLIGHT ACCOMPLISHMENTS

- A new liquid-liquid equilibrium (LLE) apparatus was designed and constructed to measure the mutual solubility of hydrocarbon-water systems at higher temperatures and pressures.
- The mutual solubilities of decane + wa.ter and benzene + water were measured using our new continuous-flow LLE apparatus at temperatures form 300 to 550 K and pressures to 10 MPa.
- We continue to make significant progress in developing more accurate EOS models. The MPGR EOS appears promising in providing more accurate *a priori* predictions for the mixtures encountered in coal processing.

ARTICLES AND PRESENTATIONS

Articles

Gao, W., Robinson, R. L., Jr. and K. A. M. Gasem. "Solubilities of Nitrogen in Selected Naphthenic and Aromatic Hydrocarbons at Temperatures from 344 to 433 K and Pressures to 22.8 MPa." J. Chem. Eng. Data, 44 (2): 185-189, 1999.

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Srivatsan, S., W. Gao, K. A. M. Gasem and R. L. Robinson, Jr. "Solubilities of Methane in Toluene at Temperatures from 323 to 423 K and Pressures to 8.9 MPa." J. Chem. Eng. Data, 43 (4): 623-625, 1998.

Gao, W., K. A. M. Gasem and R. L. Robinson, Jr. "Solubilities of Carbon Monoxide, Hydrogen, and Nitrogen in Dodecane from 344 to 410 K and Pressures to 13.2 MPa." J. Chem. Eng. Data, in press, 1999.

Gao, W., Robinson, R. L., Jr. and K. A. M. Gasem. "Solubilities of Nitrogen in Heavy Normal Paraffins from 323 to 423 K and Pressures to 18.0 MPa." J. Chem. Eng. Data, submitted 1998.

Trivedi, N. J., R. L. Robinson, Jr. and K. A. M. Gasem. "An Amended Framework for Vapor-Liquid Equilibrium Calculations." Fluid Phase Equilibria, Submitted, 1997.

Presentations

K. A. M Gasem, W. Gao, and R. L. Robinson, Jr. "The Modified Park-Gasem-Robinson Equation of State." Presented at the AIChE Spring National Meeting, Houston, Texas, March 14-18, 1999.

Gao, W., K. A. M. Gasem, and R. L. Robinson, Jr. "Experimental Measurements and Equation-of-State Representation of Asymmetric Mixtures." Presented at the AIChE Spring National Meeting, Houston, Texas, March 14-18, 1999.

Gasem, K. A. M., K. S. Chunang, K. C. Row, and R. L. Robinson, Jr. "Predicting Calorimetric Properties Using the Original and the Modified SPHCT EOS." Presented at the AIChE Annual Meeting, Chicago, IL, November 10-15, 1996.

Gasem, K. A. M., S. Raghunathan, M. S. Bader, and R. L. Robinson, Jr. "Predicting the Phase Behavior of Six Supercritical Fluids." Presented at the AIChE Annual Meeting, Chicago, IL, November 10-15, 1996.