TITLE: PHASE BEHAVIOR OF LIGHT GASES IN HYDROCARBON AND AQUEOUS SOLVENTS

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I. 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 theoretically-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 measured solubilities in several binary systems using a static equilibrium cell over the temperature range from 344.3 to 410.9 K and pressures to 22.0 MPa. The specific systems included carbon monoxide in cyclohexane and n-dodecane; hydrogen in n-dodecane; and nitrogen in n-decane, n-dodecane, cyclohexane, *trans*-decalin, benzene, 1-methylnaphthalene, naphthalene, and pyrene. The uncertainty in these solubility measurements is estimated to be less than 0.001 in mole fraction. The data were analyzed using the Peng-Robinson equation of state, and binary interaction parameters were determined.

We also modified our procedures for measuring liquid-liquid solubilities and tested the new procedures for decane + water at temperatures from 310 to 384 K using our continuous-flow liquid-liquid equilibrium apparatus. The samples were analyzed by gas chromatography. Results agree with some of the diverse literature results on this system. The mutual solubility data were used to estimate enthalpies of solution of decane in water and water in decane.

As part of our modeling efforts, we also pursued an integrated program of model development and testing with the goal of providing more accurate capabilities to predict equilibrium, volumetric and calorimetric properties of mixtures of the type under study.

SIGINFICANCE 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:

- Construct a liquid-liquid equilibrium apparatus which will allow mutual solubility data to be measured at higher temperatures and pressures.
- Extend our experimental studies to include systems which contain aqueous phases and F-T waxes.
- Continue our model development efforts with emphasis on evaluating and developing theoretically-based equations of state.

II. HIGHLIGHT ACCOMPLISHMENTS

- Gas-liquid solubilities were measured for carbon monoxide in cyclohexane and n-dodecane; hydrogen in n-dodecane; and nitrogen in n-decane, n-dodecane, cyclohexane, *trans*-decalin, benzene, 1-methylnaphthalene, naphthalene, and pyrene using a static equilibrium cell over the temperature range from 344.3 to 410.9 K and pressures to 22.0 MPa.
- Mutual solubilities for decane + water were measured from 310 to 384 K using a continuous-flow liquid-liquid equilibrium apparatus.
- Our model development work shows promise for more accurate predictions of equilibrium, volumetric and calorimetric properties of mixtures encountered in coal processing.

III. ARTICLES AND PRESENTATIONS

"Solubility of Methane in Cyclohexane and in *trans*-Decalin at Temperatures from 323 to 423 K at Pressures to 9.6 MPa," N. A. Darwish, K. A. M. Gasem and R. L. Robinson, Jr. (accepted, *J. Chem. Eng. Data.*)

“Solubility of Methane in Toluene at Temperatures from 323 to 423 K at Pressures to 8.9 MPa,” S. Srivatsan, W. Gao, K. A. M. Gasem and R. L. Robinson, Jr. (submitted, *J. Chem. Eng. Data*.)