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Project Title: **Measurements and Models for Hazardous Chemical and Mixed Wastes**

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WASTES**

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PROGRESS REPORT

Research Objectives

Aqueous waste of various chemical compositions constitutes a significant fraction of the total waste produced by industry in the United States. A large quantity of the waste generated by the U.S. chemical process industry is waste water. In addition, the majority of the waste inventory at DoE sites previously used for nuclear weapons production is aqueous waste. Large quantities of additional aqueous waste are expected to be generated during the clean-up of those sites. In order to effectively treat, safely handle, and properly dispose of these wastes, accurate and comprehensive knowledge of basic thermophysical property information is paramount. This knowledge will lead to huge savings by aiding in the design and optimization of treatment and disposal processes. The main objectives of this project are:

- Develop and validate models that accurately predict the phase equilibria and thermodynamic properties of hazardous aqueous systems necessary for the safe handling and successful design of separation and treatment processes for hazardous chemical and mixed wastes.

- Accurately measure the phase equilibria and thermodynamic properties of a representative system (water + acetone + isopropyl alcohol + sodium nitrate) over the applicable ranges of temperature, pressure, and composition to provide the pure component, binary, ternary, and quaternary experimental data required for model development.

Research Progress and Implications

As of June, 1999, seventeen months into the a three year project, we have made significant progress in the database development, have begun testing the models, have completed the pure component measurements, and have been measuring selected binary mixtures.

Database Development: An extensive literature search has been completed and the data are being compiled in a database on the internet shared by NIST and MTU. The database includes the vapor pressures, densities, and permittivities of the pure solvents; and the VLE, densities, and activity coefficients of the mixtures. It also includes a literature search on liquid phase activity models used with these systems. The database has been extended to over 250 data publications and over 100 modeling publications. The database will continue to be updated. These data have been used to determine what compositions and temperatures are needed to complete and validate the data for each binary mixture. Very little data has been reported for the acetone+isopropyl alcohol system. More extensive measurements will be required for this system.

Model Development: Two models are being investigated by NIST and MTU. The NIST model concentrates on the phase equilibria and coexisting densities and the MTU model concentrates on the liquid phase activities. The model under development at NIST for the phase equilibria and the densities of the coexisting phases uses the Peng-Robinson-Stryjek-Vera cubic equation of state for both the liquid and vapor phases. The density correction of Mathias et al.¹ is applied to the liquid density. The Wong-Sandler mixing rule is employed, with the NRTL model used for activity coefficient contributions to the mixing rules. This allows the cubic equation of state to be used for mixtures containing ions and other nonvolatile species. The model has been tested with pure solvents, solvent mixtures and solvent mixtures with salt. The model performs well predicting the vapor pressure and vapor composition, given the temperature and liquid composition, for pure solvents and solvent mixtures. Initial results for mixtures containing salt are encouraging.

The model under development at MTU for the liquid phase activities uses the UNIFAC or UNIQUAC parameters. The models are being evaluated with the preliminary database.

Experimental Measurements: The data for this project are measured on three different apparatus. The three apparatus required are an ebulliometer at MTU, a high temperature/high pressure phase equilibria apparatus at NIST for azeotropic aqueous-organic-salt mixtures, and a coexisting density and vapor-liquid equilibrium apparatus at NIST. The activity coefficients from the ebulliometer measurements will be validated with the activity coefficients calculated from the vapor-liquid equilibrium data.

The pure component measurements are completed. The new ebulliometer at MTU is complete. Currently, gravimetrically prepared aqueous-solvent and solvent-solvent mixtures are

being prepared and measured in the ebulliometer. The sampling system for the phase equilibria apparatus at NIST is being validated with gravimetrically prepared mixtures. Measurements on the aqueous-solvent and solvent-solvent mixtures are in progress. The measurements will cover a temperature range from 275 to 425K. Due to the scarcity of data, more extensive measurements will be performed on the acetone+isopropyl alcohol system.

Planned Activities

Upon completion and verification of the aqueous-solvent and solvent-solvent mixture measurements, the VLE, activity coefficients, and densities of the aqueous+solvent+salt mixtures will begin. All measurements will be completed within the next year. The data will cover the temperature range from 275 to 425 K at pressures to 14 MPa. In the final six months of this project, the data will be used to optimize and test the models developed at NIST and MTU. The remaining tasks are listed below:

- Complete bubble-point pressure, coexisting density, and compressed liquid density measurements on aqueous+solvent and solvent+solvent mixtures.
- Measure bubble-point pressures, coexisting densities, and compressed liquid densities for aqueous+solvent+salt mixtures.
- Test the model predictions for mixtures.

¹P.M. Mathias, T. Naheiri, and E.M. Oh. 1989. A Density Correction for the Peng-Robinson Equation of State, *Fluid Phase Equilibria* **47**: 77-87.