Environmental Management Science Program

Project ID Number 60155

Measurements and Models for Hazardous Chemical and Mixed Wastes

Dr. Cynthia Holcomb
National Institute of Standards &Technology - Boulder
NIST MS 838.07
325 Broadway
Boulder, Colorado 80303
Phone: 303-497-3437
E-mail: cynthia.holcomb@nist.gov

Dr. Laurel Watts
National Institute of Standards &Technology - Boulder
NIST MS 838.01
325 Broadway
Boulder, Colorado 80303
Phone: 303-497-7418
E-mail: laurel.watts@nist.gov

Stephanie L. Outcalt
National Institute of Standards &Technology - Boulder
NIST MS 838.07
325 Broadway
Boulder, Colorado 80303
E-mail: stephanie.outcalt@nist.gov

Beverly Louie
National Institute of Standards &Technology - Boulder
MS 838.01
325 Broadway
Boulder, Colorado 80303
E-mail: beverly.louie@nist.gov

Michael E. Mullins
Michigan Technological University
Houghton, Michigan 49931
E-mail: memullin@mtu.edu

Tony N. Rogers
Michigan Technological University
Houghton, Michigan 49931
E-mail: tnRogers@mtu.edu

June 1, 1998

Measurements and Models for Hazardous Chemical and Mixed Wastes

Dr. Cynthia Holcomb, National Institute of Standards & Technology - Boulder

Dr. Laurel Watts, National Institute of Standards & Technology – Boulder
Stephanie L. Outcalt, National Institute of Standards & Technology – Boulder
Beverly Louie, National Institute of Standards & Technology – Boulder
Michael E. Mullins, Michigan Technological University
Tony N. Rogers, Michigan Technological University

Research Objective

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 May, 1998, nine months into the first year of a three year project, we have made significant progress in the database development, have begun testing the models, and have been performance testing the apparatus on the pure components.

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 permitivities 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. Over 150 data and several dozen modeling articles have been obtained. Data of the highest quality are being used to test the models for the system under study. The gaps in the data and areas where our measurements should be concentrated are being identified and evaluated.

Model Development: Two models are being investigate 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 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 computer program to implement this overall model has been written, and nonlinear least squares programs have been written to optimize the parameters for the model. A test of the model with saturation pressure data for the pure solvents (water, acetone, and isopropyl alcohol) gives a deviation of less than 0.2%.

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 calibrations have been completed for the NIST apparatus. The performance tests on these apparatus are nearly complete. A new high-accuracy low-pressure pressure transducer was acquired for these experiments. The ebulliometer at MTU is being modified. Temperature, pressure and composition calibrations for the ebulliometer are nearly complete. Measurements of the vapor pressures and coexisting densities of water, acetone, and isopropyl alcohol from 280 to 400 K are nearly complete.

Planned Activities

Upon completion and verification of the pure component measurements, VLE and densities of the binary water+solvent mixtures on the NIST apparatus will be measured and completed by Fall of this year. The data will cover the temperature range of 275 to 425° K at pressures to 14 Mpa. Next year, measurements of the VLE and densities of the ternary water+solvent mixtures and binary water+salt mixtures will begin on the NIST apparatus. The activity coefficients measurements of the binary systems will begin on the MTU ebulliometer. In the final year, the VLE and densities of the ternary and quaternary water+solvent+salt mixtures will be measured on the NIST apparatus and their activity coefficients will be measured on the MTU ebulliometer. All of the measurements will be completed about 2.5 years into the project, and the optimization and tests of the models will be completed by the end of the three year project. The model for phase equilibria predictions will be further optimized and tested for the following systems and properties:

- Solvent mixture bubble point pressures. (Some data are available now.)
- Pure solvent and solvents mixture densities. (Some data are available now.)
- Water+solvent+salt mixture vapor pressures and densities. (Most of these data need to be measured before testing.)

---

[1] P.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.