THERMOPHYSICAL PROPERTIES OF AMMONIA-WATER MIXTURES

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KEY WORDS

interagency agreement, Kalina cycle, energy conversion, National Institute of Standards and Technology (NIST), binary working fluid, aqua-ammonia

PROJECT BACKGROUND AND STATUS

Geothermal binary cycles using ammonia-water mixtures have been estimated to have efficiencies 20 to 50% greater than those using pure fluids. Unfortunately, while accurate thermophysical properties are needed to properly evaluate their performance, experimental data and models for the properties of the mixture in this region of the phase diagram have been lacking or contradictory. The range of operating conditions for typical geothermal binary cycles using ammonia-water are temperatures of 280 to 450 K (44°F to 350°F), pressures up to 3.5 Mpa (500 psi), and mixture compositions ranging from 80 to 100 percent ammonia by mass.

On the basis of work done under this Interagency Agreement, NIST has already provided preliminary estimates for the properties of ammonia-water mixtures to interested industrial concerns as well as to Department of Energy researchers. Experimental vapor-liquid equilibrium, pressure-volume-temperature (PVT), heat capacity, and thermal conductivity measurements have been performed; these estimates can be used for much of the basic design work. Additional heat capacity and thermal conductivity data will be obtained over the next few months. The experimental data and a final model for thermophysical properties will be used for optimization of design and operation, as well as for performance evaluation and warranty. A workshop on ammonia-water properties was held to establish and prioritize additional property needs for this working fluid for geothermal and other energy conversion technologies.

PROJECT OBJECTIVES

The overall objective of this project is to develop reference-quality formulations for the thermophysical properties of ammonia-water mixtures in the ranges needed for application to geothermal energy conversion.

Technical Objectives

- Evaluate existing data for the thermophysical properties of ammonia-water mixtures.
- Develop preliminary property formulations based on these data and fundamental thermodynamic relationships.
- Measure vapor-liquid equilibrium (VLE), density or pressure-volume-temperature (PVT) relations, heat capacity, and thermal conductivity for several ammonia-water compositions in the temperature and pressure ranges of geothermal interest.

- Establish reference quality formulations for the ammonia-water system over the ranges of interest to geothermal applications.

Expected Outcomes

- Distribute accurate formulations for ammonia-water properties to engineers interested in geothermal applications.

- Decisions made on whether or not to implement this technology; if these are positive, design decisions can be made on heat exchanger sizing, etc.

APPROACH

The National Institute of Standards and Technology (NIST) has collected and critically evaluated the thermodynamic data for ammonia-water mixtures which are currently available in the literature. Although there are some earlier bibliographic efforts, there has been no comprehensive study of the data situation for this mixture. These existing data will serve several purposes: important gaps in the data will be identified so that new experimental efforts will be well focussed; discrepancies among the data may be resolved by this critical evaluation; and preliminary formulations for the property surfaces can be developed.

The initial study of the thermodynamic surface will be based on an extended corresponding states (ECS) algorithm using a propane reference fluid system; this approach is straightforward and the results are quite successful for many mixture systems. A study of the critical locus and its vicinity, based on a modified Leung-Griffiths (renormalization group) model, will produce a satisfactory description of the high pressure VLE which will assist in the development of the more general models. Standard reference formulations for the pure fluid water and ammonia surfaces will be introduced to improve the ECS description of the thermodynamic surface, and a preliminary mixture model will be generated from this approach. This model and a description based on a two-fluid Helmholtz energy model will be optimized with the existing literature data.

Selected experimental measurements will be carried out as inconsistencies and gaps in the data are identified. NIST will do selected state-of-the-art vapor-liquid equilibrium (VLE), pressure-volume-temperature (PVT), heat capacity, and thermal conductivity measurements for several ammonia-water compositions at temperatures from 250 to 450 K (-10°F to 350°F) at pressures up to 10 Mpa (1450 psi). NIST will then optimize the thermodynamic models using these measurements in order to improve the required binary interaction parameters for the ECS model or the residual function in the alternative Helmholtz energy approach.

In these efforts, existing NIST apparatus and facilities will be used at no direct cost to the project; the capital costs of the three experimental apparatus used in this project are in excess of $1.5M. In addition, NIST will fund some aspects of the ammonia-water project through internal funds, and will use other funding sources to allow some measurements and study of the system outside the range of state variables required for geothermal applications. This research (which currently provides about 20% additional resources to the study, but may be projected to allow a project of substantially larger scope) yields results which permit a more accurate validation of the models' ability to describe the property surfaces within the range of primary concern of the current project. Guest researchers from the University of Hanover in Germany and Cracow University of Technology in Poland and bibliographic resources from the Russian Research Center for Standardization, Information, and Certification of Materials contributed to this project with no direct costs charged to the Interagency Agreement.

RESEARCH RESULTS

Available thermodynamic data for the ammonia-water system have been collected, entered into machine-readable format, and analyzed. The manuscript *Survey and Assessment of Available Measurements on Thermodynamic Properties of the Mixture (Water + Ammonia)* has been completed and is in the final stages of review. About 6000 experimental data points and some 50 literature references were evaluated for the system. The initial property formulations, based on ECS algorithms, were completed and forwarded to the Department of Energy and to several interested corporate research and design engineers.

The experimental measurements for the vapor-liquid equilibrium and pressure-valve-temperature relations have been completed, and these data have been analyzed and compared to the preliminary property formulations. Measurements of the density and isochoric heat capacity for an ammonia mass fraction of about 0.8 have been completed. These experimental results have been used to validate the thermodynamic surfaces, and have provided good support for the property models. Improvements to the twin-cell calorimeter have been finished, and measurements for additional ammonia-water compositions are now scheduled for completion. Some new data have been obtained with the transient hot-wire thermal conductivity apparatus. This apparatus has also been modified to improve the compatibility with this mixture system, and additional measurements are in progress.

Two approaches have been pursued to establish the reference quality formulations. The two-fluid Helmholtz energy model has been optimized to the existing literature data; a manuscript *A Helmholtz Free Energy Formulation of the Thermodynamic Properties of the Mixture (Water + Ammonia)* has been completed and is in the final stages of review. Some preliminary computer code to implement this model and tabular material from this property surface, have been provided to the Department of Energy and to members of the research/design community who have requested this material. The general uncertainties associated with this formulation are about 0.01 for the liquid and vapor compositions (in mass fraction), 0.3% in densities of the single-phase fluid, and 200 J/mol for enthalpies. The extended corresponding states approach to the problem has been modified to take into account the complex interactions in the ammonia-water system; a report on this approach with extensive comparisons between the model and experimental data is being prepared for presentation at the 13th Symposium on Thermophysical Properties in June of 1997.

Discussions have been ongoing between the project participants and industrial users of the properties of ammonia-water systems in the context of geothermal conversion applications and other energy technologies. A workshop was held in the summer of 1996 to bring together members of these communities, in order to present some intermediate results of the project and to establish any additional requirements in terms of ranges, properties, and uncertainty.

FUTURE PLANS

Measurements will continue through the first part of calendar 1997, in order to provide the deliverables as specified. The formulations can be re-optimized to the new data as necessary to improve the accuracy of the thermodynamic surfaces. The scope of the project may be expanded, pending further funding from other sources, to include significantly higher temperatures, additional properties, and the complete composition range for the ammonia-water system.

INDUSTRY INTEREST AND TECHNOLOGY TRANSFER

Organization	Type and Extent of Interest
General Electric Power	NH_3-H_2O for combined cycle technologies
ABB Power Plant Laboratories	NH_3-H_2O for direct fired power technologies
Exergy, Inc.	Commercialization of Kalina cycle technologies
Oak Ridge National Laboratory	NH_3-H_2O for cooling applications

REFERENCES

Department of Energy Interagency Agreement; No. DE-AI36-CH10558; Dated March 31, 1993.

Standard Thermophysical Properties of the Ammonia-Water Binary Fluid, D.G. Friend, A.L. Olson, and A. Nowarski" in **Physical Chemistry of Aqueous Systems**, Proc. 12th Intern. Conf. on the Properties of Water and Steam: Meeting the Needs of Industry, Begell House, New York, 1995, H.J. White, Jr., J.V. Sengers, D.B. Neumann, and J.C. Bellows, eds., pp. 854-861.

This paper summarizes the extended corresponding states model for the description of ammonia-water thermodynamic properties. Other papers in this volume describe the Kalina cycle and illustrate its use in an energy conversion technology.

Report of the Workshop on Thermophysical Properties of Ammonia/Water Mixtures: June 26, 1996, D.G. Friend and W. M. Haynes, National Institute of Standards and Technology Interagency Report, in press, 1997.

This report summarizes progress of the project, and establishes current and projected properties needs for the ammonia-water system for a variety of technologies.

Survey and Assessment of Available Measurements on Thermodynamic Properties of the Mixture (Water + Ammonia), R. Tillner-Roth and D.G. Friend, to be submitted to J. Phys. Chem. Ref. Data, 1997.

This paper summarizes and evaluates the available data on thermodynamic properties of the system; it provides a very complete bibliography of the experimental literature.

A Helmholtz Free Energy Formulation of the Thermodynamic Properties of the Mixture (Water +Ammonia), R. Tillner-Roth and D.G. Friend, to be submitted to J. Phys. Chem. Ref. Data, 1997.

This paper completely describes the two-fluid Helmholtz energy model and provides limited tabular information on the thermodynamic properties of the mixture.