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1992 Annual Report
**New Generation of Group Contribution and Equation-of-State
Models**

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Introduction

During the past year we have had an extraordinary success in the equation of state portion of our research, and have made steady, but much slower progress in the group contribution part of our research program. We have also made unanticipated contributions in several other areas, as described below. This report briefly describes the work we have accomplished. More detailed information on our work is given below, and in the collection of reprints and preprints which will be sent separately.

Equations of State

Equations of state are very powerful tools for describing the thermodynamic properties of pure fluids and mixtures. When applicable, equations of state provide an internally consistent description of the phase behavior and the thermodynamic properties of mixtures over wide ranges of temperature and pressure with few adjustable parameters. However, a major shortcoming of equations of state is that, until recently, they could only be used for relatively simple mixtures such as mixtures of hydrocarbons, or hydrocarbons with the inorganic gases.

This limited range of applicability to mixtures represented an interesting problem and technologically important challenge in that while a simple equation of state could be used to provide an accurate description of, for example, a pure alcohol and a pure hydrocarbon, it did not provide a good description of an alcohol-hydrocarbon mixture (as occurs in gasohol and some of the reformulated gasolines). This clearly indicated that the problem lies in the mixing rules used to apply an equation of state to mixtures, rather than a problem inherent in the equation of state. Consequently, as a major activity of the past year has been research on equation of state parameter mixing rules in order to extend the range of applicability of equations of state to the sorts of complex mixtures which heretofore could only be described by activity coefficient models.

A major success this year was accomplishing this goal; we have now extended the range of equations of state to mixtures of any complexity which before our work could only be described by activity coefficient models. This work is described in the paper "A Theoretically Correct Mixing Rule for Cubic Equations of State" by D. S. H. Wong and S. I. Sandler that has been published in the AIChE Journal. Our work is based on determining the equation of state parameters in a way that satisfies two well-defined boundary conditions. The first is that at low density the equation of state/mixing rule combination should exhibit the quadratic composition dependence of the second virial coefficient known from statistical mechanics. The second boundary condition is that at liquid densities the (Helmholtz) free energy of mixing calculated from the equation of state/mixing rule combination should exhibit the composition dependence of known free energy (activity coefficient) models. By simultaneously satisfying the low density and high density boundary conditions, we obtain two relations for the equation of state parameters and find that behavior of mixtures of any degree of complexity could be well correlated, and even predicted as will be discussed below.

The importance of this work was evident to the reviewers and editor of the AIChE Journal, as the manuscript was published within 9 weeks of its initial receipt, and was subsequently featured in the Update section of Chemical Engineering Progress. In addition, we have had requests from more than twenty industrial companies and universities for our programs, and our mixing rule is now being incorporated into the process simulators of Simulation Sciences, Aspen and Hypro, as well as the inhouse simulators of Mobil, Union Carbide, Ethyl, Amoco, Toyo Engineering (Japan) and Kobelco (Japan).

One surprising result of our work is that we found that we could correlate data of enormous ranges of temperature (200 C or more) and pressure with temperature independent parameters. As a result, we have been able to use readily available ambient temperature/pressure data to make accurate predictions at much higher temperatures. Similarly, with our mixing rule and data or activity coefficient parameters available in compilations such as the DECHEMA Chemistry Data Series can be used to make accurate predictions can be made at conditions much different from those at which the experimental data were obtained. Finally, we have also found that even in the absence of experimental data, predictive methods such as UNIFAC, which are normally restricted to low temperatures and pressures, can be combined with our mixing rule to produce accurate predictions for very complex mixtures at high temperatures and pressures. This work is described in detail in several of the attached reprints and preprints.

Our most recent work involves the extension of our mixing rules to such asymmetric systems as polymer/solvent mixtures and to mixtures containing hydrogen as occurs in hydro-processing and other applications. One manuscript on this work has already been submitted for publication.

Group Contribution Methods

As described in the original proposal, the goal of this part of the research program is to develop a new generation of group contribution methods which take into account specific chemical forces such as hydrogen bonding, and make use of the information we can obtain from computational quantum mechanics. This research follows on the successful work of Wu and Sandler reported in the last Annual Report. In contrast to the progress described above for our equation of state research, work on this project has progressed slowly. The problem which occurs is that when one introduces the idea of associated compounds resulting in monomers, dimers, etc., many parameters arise which are needed to describe the properties of each of the species and the chemical equilibrium between them as a function of temperature. For the case of carboxylic acids much spectroscopic data have been reported on the extent of hydrogen bonding from which the needed association constants can be obtained. In this case vapor pressure data for the acids are then sufficient to obtain all the remaining model parameters, and we have developed a UNIFAC/association model for such systems which is an improvement over the original UNIFAC model (which does not account for association).

Unfortunately, for many other associating systems, such as alcohols and ethers, spectroscopic data from which association constants can be computed are not available. In this

the case are UNIFAC/association model contains too many adjustable parameters, and there is no way that we have yet identified which yields an unambiguous determination of the needed parameters and results in a clear improvement over the unadorned UNIFAC model.

We will continue working on this problem during the coming year. Our immediate attack will be to use computational quantum mechanics to compute the association constant as a function of temperature. If successful, this would reduce the number of fitted parameters in the model, and make the UNIFAC/association model tractable. We will be testing this idea by first using the computational quantum mechanics to make predictions for the association constants of the carboxylic acids for which the results are already known.

Chain and Polymer Molecules

Another aspect of our work is the study of chain molecules and eventually polymers. So far we have developed a molecular dynamics simulation code for hard sphere chains and square-well chains, and studied the cases of chains of 2, 4, 8 and 16 segments. Our results show good agreement with the results of Hall et al. for 2 and 4 segment chains, a slight deviation for the 8 segment chain, and a more significant deviation for the 16 segment chain. Since Hall et al. used an unconventional algorithm, and our results are in better agreement with some theories than theirs, we have confidence in our results. This work will be written up for publication in the near future.

Together with the simulations, we have been developing a perturbation theory for chain molecules. An interesting side aspect of this work is that we have re-examined the integral equation theory for the hard sphere fluid, since radial distribution function information for hard spheres is needed for our perturbation theory work. In this study we have shown that the Percus-Yevick integral equation for the hard sphere fluid can be converted into a differential equation which has a closed-form analytic solution containing only real functions. This has made it possible, for the first time, to get completely analytic (rather than merely numeric) solutions from perturbation theory using the hard sphere reference potential. This work, entitled "A Real Function Representation of the Radial Distribution Function for the Hard Shpere Fluid" done in collaboration with J. Chang, has been submitted to the Journal of Chemical Physics for publication.

Our continuing effort in this research is to use this analytic solution in our perturbation theory models for both spherical and chain molecules. This work is well underway, and we expect three manuscripts describing various aspect of this work to be completed in the next year.

The Viscosity of Hydrocarbons and Petroleum Reservoir Fluids

Though not part of the original proposal, we have also spent some time studying the correlation of the viscosity of hydrocarbons and petroleum reservoir fluids. The motivation for this effort was continued requests from my colleagues in the oil industry for accurate prediction methods for the viscosity of petroleum reservoir fluids (for reservoir simulation), of

petroleum reservoir fluids with carbon dioxide and other light gases (for enhanced oil recovery simulations), and of bitumens (for heavy oil and shale processing). Together with H. Orbey, we have developed a new viscosity model, which can be used for either correlation or prediction. This correlation is more accurate and general than any other available viscosity correlation for hydrocarbons. This work is described in a manuscript which has been accepted for publication by the Canadian Journal of Chemical Engineering.

Interestingly, this correlation has now been tuned and tested with real fluids ranging from light Arabian crude oils to heavy bitumens by the reservoir engineering group the the Chevron Oil Field Research Company (now the Chevron Petroleum Technology Company). In this work they showed that by using our correlation the average error in viscosity predictions for there diverse range of fluids was reduced to less than 10% over all ranges of temperature, pressure and injected gas concentrations compared to an average error in excess of 140% with their previous correlations. This work, co-authored by W. S. Fong, A. S. Emmanuel and S. I. Sandler, has been submitted for publication to the Society of Petroleum Engineers, and has been incorporated into the Chevron reservoir simulator. At present, no future work in this area is anticipated.

PUBLICATIONS SUPPORTED BY THIS CONTRACT

Books published

1. "The Kinetic and Thermodynamic Lumping in Multicomponent Mixtures" edited by G. Astarita and S. I. Sandler. Published by Elsevier, Amsterdam, 1991.

Papers published

1. "The Use of *ab initio* Quantum Mechanics Calculations in Group Contribution Methods. I. Theory and the Basis for Group Identifications" by H. S. Wu and S. I. Sandler. IEC Research, 30, 881-889 (1991).
2. "The Use of *ab initio* Quantum Mechanics Calculations in Group Contribution Methods. II. Test of New Groups in UNIFAC" by H. S. Wu and S. I. Sandler. IEC Research, 30, 889-897 (1991).
3. "Equations of State from Generalized Perturbation Theory I. The Hard-Core Lennard-Jones Fluid" by G. M. Sowers and S. I. Sandler. Fluid Phase Equilibria, 63, 1-25, (1991).
4. "A Study of Buckingham Exponential-Six Fluid Mixtures" by L. R. Dodd and S. I. Sandler. Fluid Phase Equilibria, 63, 279-315, (1991).
5. "Relative Measurements of Activity Coefficients at Infinite Dilution by Gas Chromatography" by H. Orbey and S. I. Sandler. IEC Research, 30, 2006-2011 (1991).
6. "Lumping or Pseudocomponent Identification in Phase Equilibrium Calculations" by S. I. Sandler in "Chemical Reactions in Complex Mixtures" edited by A.V. Sapre and F. J. Krambeck, Van Nostrand Reinhold, New York, 1991, pp. 60-74.
7. "A Note on the Method of Moments in the Thermodynamics of Continuous Mixtures" by S. I. Sandler and M. C. Libby, in "Kinetic and Thermodynamic Lumping of Multicomponent Mixtures," edited by G. Astarita and S. I. Sandler, Elsevier, Amsterdam, 1991, 341-350.
8. "Equations of State from Generalized Perturbation Theory II. The Soft-Core Lennard-Jones Fluid" by G. M. Sowers and S. I. Sandler. Fluid Phase Equilibria, 67, 127-150 (1991).

9. "Practical Equation of State and Activity Coefficient Models Based on the Exp-6 Fluid" by L. R. Dodd and S. I. Sandler. *Fluid Phase Equilibria*, 69, 99-139 (1991).
10. "Vapor-Liquid Equilibrium From Infinite Dilution Activity Coefficients: Measurement and Predication of Oxygenated Fuel Additives with Alkanes" by K. A. Pividal, C. Sterner, S. I. Sandler and H. Orbey. *Fluid Phase Equilibria*, 72, 227-249 (1992).
11. "A Theoretically Correct New Mixing Rule for Cubic Equations of State", by D. S. H. Wong and S. I. Sandler. *AIChE Journal*, 38, 671-680 (1992).
12. "An Equation of State Mixing Rule for Nonideal Mixtures Using Available Activity Coefficient Model Parameters and Which Allows Extrapolation Over Large Ranges of Temperature and Pressure" by D. S. H. Wong, H. Orbey and S. I. Sandler. *IEC Research*, 31, 2033-2039 (1992).
13. "Infinite Dilution Activity Coefficients of Halogenated Hydrocarbons in Water at Ambient Temperatures," by D. A. Wright, S. I. Sandler and D. DeVoll. *Envir. Sci. and Technology*, 26, 1828-1831 (1992).
14. "Simulations Results and Corresponding States Correlations for Pure Rigid Molecular Fluids" by G. M. Sowers and S. I. Sandler. *Molecular Physics*, 77, 351-379 (1992).
15. "Infinite Dilution Activity Coefficients and Henry's Law Coefficients of Some Priority Water Pollutants Determined by a Relative Gas Chromatographic Method" by G. Tse, H. Orbey and S. I. Sandler. *Envir. Sci. and Tech.* 26, 2024-2028 (1992).

Books in press

1. "Thermodynamic Modelling" edited by S. I. Sandler. Submitted for publication to Marcel-Dekker, July, 1992.

Papers in press

1. "The Thermodynamics of Long-Lived Organic Pollutants" by S. I. Sandler and H. Orbey. Accepted for publication by Fluid Phase Eq.
2. "Accurate Equation of State Predictions at High Temperatures and Pressures Using the Existing UNIFAC Model" by H. Orbey, S. I. Sandler, and D. S. H. Wong. Accepted for publication by Fluid Phase Equilibria.
3. "Vapor-Liquid Equilibria of Hydrocarbons and Fuel Oxygenates. II." by A. Bennett, S. Lamm, H. Orbey, and S. I. Sandler. Accepted for publication to J. Chem. Eng. Data.
4. "Computer Simulation of Molecular Fluid Mixtures: Results and Two New One-Fluid Models" by G. M. Sowers and S. I. Sandler. Accepted for publication by the AIChE Journal.
5. "The Prediction of the Viscosity of Liquid Hydrocarbons and Their Mixtures as a Function of Temperature and Pressure" by H. Orbey and S. I. Sandler. Accepted for publication by the Canadian Journal of Chemical Engineering.
6. "Equations of State" by S. I. Sandler, H. Orbey and B. I. Lee for publication in "Thermodynamic Modelling" edited by S. I. Sandler. Submitted for publication to Marcel-Dekker, July, 1992.
7. "A Real Function Representation for the Radial Distribution Function of the the Hard Sphere Fluid" by J. Chang and S. I. Sandler. Submitted for publication to J. Chem. Phys.
8. "Prediction of Vapor-Liquid Equilibria at High Pressures Using Activity Coefficient Parameters Obtained from Low Pressure Data: A Comparison of Two Equation of State Mixing Rules" by H. Huang and S. I. Sandler. Submitted for publication to Ind. Eng. Chem Res.
9. "The Correlation and Prediction of the Vapor-Liquid Equilibrium of Hydrogen-Hydrocarbon Systems" by H. Orbey, H. Huang and S. I. Sandler. Submitted for publication to IEC Res.
10. "The Viscosity of Petroleum Fluids" by W. Fong, A. S. Emmanuel and S. I. Sandler. Submitted for publication to the Soc. Pet. Engrs. J.

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