PREDICTION OF THERMODYNAMIC PROPERTIES
OF COAL DERIVATIVES

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N O T I C E

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ABSTRACT

The purpose of this research program is to understand and model the effect of the different intermolecular forces on the thermodynamic properties of systems containing pure compounds and mixtures. The compounds under consideration vary considerably in size, shape and energy. Therefore in order to develop a theory capable of describing accurately the thermodynamic properties and phase behavior of such systems over a wide range of temperature and pressure, one has to take into account explicitly the differences in shape and size among the various compounds as well as the different type of intermolecular interactions.

Over the course of this project, we have developed equations of state for pure-component chain molecules. We have shown that the excellent performance of complicated theories such as the Generalized Flory Dimer (GFD) theory can be mimicked by simpler equations, if certain assumptions for the shape parameters are made. We developed engineering correlations based on the GFD theory, using local composition theory to take into account the attractive contribution. During the current contract period, we compared various methods for the calculation of the repulsive and attractive contributions against computer simulation data for hard and square-well chains, and experimental data from the literature. We also have studied microstructure and local order in fluids that contain asymmetric molecules. In addition, simple cubic equations of state have been applied to calculate physical and chemical-reaction equilibria in non-ideal systems.

In order to obtain a better understanding of the intermolecular forces and to test some of our recent models, we have performed considerable experimental work. We used FT-IR to examine the self-association of aliphatic alcohols due to hydrogen bonding. In addition, FT-IR spectroscopy was used to investigate Lewis acid-base interactions between probe and entrainer-cosolvent molecules.

In the future, we plan to extend our theoretical models for pure components to a more general scheme that would be able to treat mixtures of molecules that differ in molecular size, shape, and type of interaction.

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THEORY

In this section we present briefly our theoretical accomplishments during the last contract period. Details are presented in the papers referenced. Copies of these papers are enclosed; enclosed also are copies of the papers that were published during the current contract period, but were discussed in detail in the last year's report.

- We have shown that the PHCT equation of state is equivalent to the Generalized Flory Dimer (GFD) equation of state, if the shape parameter 'c' in PHCT is written as a linear function of density. This results in a relatively simple expression for the pressure of hard-chain molecules, that is as accurate as the much more complicated GFD theory. Details of the derivation and a comparison of various equations for chain molecules are discussed in "Shape Parameters and the Density Dependence of Hard-Chain Equations of State" by Bokis and Donohue (1992).
- We have improved this simplified equation by fitting the shape parameter 'c' in PHCT directly to molecular simulation data (Gao and Weiner, 1989, and Dickman and Hall, 1988). We have written our equation of state for hard chains in a form which reduces to the correct second virial coefficient limit, as the density approaches zero. For this purpose, we used computer simulation data for the second virial coefficient of hard chains by Hall and co-workers. The resulting expression is very accurate over the entire density range: from the ideal gas limit to liquid-like densities. It is also applicable to both small molecules and polymers. Details of the derivation of this theory are presented in "Thermodynamic Properties of Hard-Chain Molecules" by Bokis *et al.* (1992a).
- The GFD theory has been extended by Yethiraj and Hall (1991) to chain molecules that interact through site-site square-well intermolecular potential. They showed that both the repulsive and the attractive term of the equation of state have the same dependence on the size of the molecule. Thus, they developed a theory for square-well chains by incorporating the Ornstein-Zernike equation for monomers and the Reference Interaction Site Model (RISM) for dimers. Their equation, though in excellent agreement

with simulation data, is very complicated and not explicit with respect to the pressure (it requires numerical solution at each point of interest). We have developed simple expressions for the attractive term of square-well monomers and dimers based on local composition theory, which, when incorporated into the GFD theory, result in a simple and closed-form equation of state. This theory is in very good agreement with simulation data, and also suitable for engineering calculations. The derivation of this theory is discussed in “Local Composition Model for Square-Well Chains Using the Generalized Flory Dimer Theory” by Bokis *et al.* (1992b).

- Besides chain molecules that consist of tangent hard spheres, we also have studied chains of various bond lengths. For this purpose, we have performed Monte Carlo simulations for square-well dimers for bond lengths that are similar to those in real molecules (chlorine and ethane). We developed analytic expressions for the equation of state for square-well dimers using both local composition theory and perturbation theory. Comparison of these theories with the simulation data showed very good agreement. Simulation results and details of the derivation of the theories are presented in “Square-well dimers of different bond lengths: Theory and simulation for the equation of state” by Thomas and Donohue (1992).
- We also have studied the effect of the bond length in square-well chain molecules longer than dimers. Our goal was to develop an accurate equation of state for homonuclear chains, using molecularly based equations for the repulsive and attractive contributions. Four methods to calculate the compressibility factor for the reference hard-chain term were compared. In order to take into account the effect of chain length on the attractive term, two methods were considered: the GFD theory, and the *ei*-model, a model based on a site-site approach assuming that chain molecules are made of two kinds of segments: end and internal. To test these theories, we performed simulations for chain molecules with various bond lengths over a wide range of temperatures and densities. The *ei*-model is in very good agreement with the simulation data for both freely-jointed,

tangent square-well chain molecules, and fused square-well chain molecules. Furthermore, this model showed very good agreement with experimental data for n -alkanes with carbon numbers ranging from 4 to 20. Details of this work are discussed in “An equation of state for chain molecules using a site-interaction model: Theory, simulation and correlation of experimental data” by Thomas and Donohue (1992a).

- We have developed a framework for calculating the thermodynamic properties of each site on a chain molecule. The difference between this approach and other theories, such as PHCT (Donohue and Prausnitz, 1978), GFD (Honnell and Hall, 1989), and SAFT (Chapman *et al.*, 1990), is that in our model, the bond energy is formally assigned to the bonding between segments and belongs to the molecule as a whole. This distinction between segmental and bond energies is unimportant in analysis of molecular properties; however, proper assignment of the bond energy to molecular segments is necessary for a coherent definition of the segmental chemical potential and access to submolecular information. This formalism provides a method for predicting the formation of microscopically-ordered regions within a macroscopic bulk phase. The simplest of asymmetrical molecules (a dimer consisting of a hard-sphere site and a square-well site) was used to illustrate fluid microstructure with this sphere-and-bond model. Details of this model are discussed in “Local Order and Microphase Formation in Fluids Containing Asymmetric Molecules” by Kuespert and Donohue (1992).
- We have developed a method that combines chemical-reaction equilibrium and phase equilibrium in multicomponent, non-ideal systems. This method is applicable in any fluid or condensed phase and over a wide range of temperatures and pressures. Commonly used cubic equations of state are applied to calculate the chemical and phase equilibria for the water-gas shift reaction, the methylcyclohexane decomposition, and the reaction of carbon monoxide and hydrogen sulfide. Details of this method are discussed in “Equations-of-State Calculations of Chemical Reaction Equilibrium in Non-Ideal Systems” by Economou *et al.* (1992).

EXPERIMENTS

Most of our experimental work has been focused on determining the properties of systems in which specific interactions such as hydrogen bonding occur. Fourier Transform - Infrared (FT-IR) spectroscopy has been shown to be extremely useful in characterizing molecular interactions. Besides, FT-IR can be used to investigate the behavior of liquid mixtures and supercritical fluid solvents.

- A novel spectral analysis technique has been developed for the determination of peak areas from spectra in which there are multiple overlapping peaks. The technique involves a combination of Fourier spectral analysis and profile modeling. It has been applied to the problem of determining, from FT-IR spectra, the peak areas that correspond to monomeric and hydrogen-bonded species. The Voigt profile has been found to be better than either the Lorentzian or Gaussian profiles for FT-IR spectra. Details of this spectral analysis technique are discussed in "Analysis of FT-IR spectroscopic data: the Voigt profile" by Reilly *et al.* (1992).
- FT-IR spectroscopy has been applied for the determination of the self-association of aliphatic alcohols. Analysis of FT-IR spectroscopic data enables one to determine the species present in a mixture, as well as the equilibrium constants. A qualitative analysis of aliphatic alcohol spectra revealed that there at least three types of hydrogen bonds occurring in the mixture. In addition, the formation of these bonds did not occur until a threshold value of the alcohol concentration was reached. These results can be used to test various theories for hydrogen bonding. More details and results of the spectral analysis for alcohols of various chain lengths and at different temperatures are presented in "Analysis of the self-association of aliphatic alcohols using Fourier transform infrared (FT-IR) spectroscopy" by Thomas *et al.* (1992b). This manuscript will be submitted for publication before the end of the current contract period.
- FT-IR spectroscopy also has been applied for the investigation of the Lewis acid-base interactions between probe molecules and entrainer-cosolvents. The probe molecules

that have been used are benzaldehyde, anisole, acetone, and phenol. The entrainers are tri-n-butyl phosphate (TBP) and methanol. The strength of the acid-base interactions between each entrainer and probe was found by determining the chemical equilibrium constants. Methanol was found to associate with all the probe components; TBS on the other hand hydrogen bonds only with phenol. Experimental results and quantitative spectral analysis will be discussed in detail in "Experimental Investigation of the Hydrogen Bonding between Entrainer-Cosolvents (Tri-N-Butyl Phosphate and Methanol) and Probe Molecules" by Reilly *et al.* (1992a). This manuscript will be submitted for publication before the end of the current contract period.

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