PREDICTION OF THERMODYNAMIC PROPERTIES
OF COAL DERIVATIVES

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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 the Acid-Base-Perturbed-Anisotropic-Chain-Theory (ABPACT), a rigorous theory that takes into account the differences in size and shape between the constituent species in the system. In addition, it accounts explicitly for the repulsive, attractive and association interactions exhibited in the system. During the current contract period, we compared our theory to other theoretical models for associating fluids. These models are based on the perturbation theory of Wertheim and on the quasi-chemical theory of Guggenheim. We showed that all three theories, though based on different assumptions, result in equivalent expressions for associating systems. In addition, we compared the Perturbed-Hard-Chain-Theory (PHCT) with the Generalized-Flory-Dimer (GFD) equation of state and showed that the two equations are equivalent if some assumptions are made concerning the parameter 'c' in the PHCT.

In order to get a better understanding of the intermolecular forces and to test some of our recent models, we have performed considerable experimental work. We used FTIR to examine hydrogen bonding interactions between small molecules and between small molecules and polymers. In addition, we investigated experimentally the high pressure phase behavior of ternary and quaternary systems exhibiting polar and hydrogen bonding interactions.

In the future, we plan to extent our theoretical model to a more general scheme that would be able to treat multicomponent systems containing components with multiple associating sites that would vary considerably in size (from small molecules to polymers) and in shape (from linear molecules to branched and cyclic molecules). We intend to incorporate all the information we obtained from perturbation and quasi-chemical theory for association into this model.

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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 which are enclosed.

- We have compared extensively thermodynamic models for hydrogen bonding systems. Three different classes of theories have been developed specifically to treat hydrogen-bonding systems. The first is based on the assumption that hydrogen bonding results in the formation of new species and is referred to as "chemical theory". The second is based on lattice-fluid theory that is used to describe different types of specific interactions and is known as "quasi-chemical" theory. Unlike chemical theory, in quasi-chemical theory the number of intermolecular bonds is calculated rather than the number of association species (Panayiotou and Sanchez, 1991). The last theory, known as perturbation theory, accounts for hydrogen bonding through the use of a potential function that mimics that of a hydrogen bond. This theory was initially introduced by Wertheim (1984, 1986a-c, 1987). It has been postulated in the past that Wertheim's perturbation theory "treatment is distinguished from earlier 'chemical' theories of association by a precise statistical-mechanical definition of what constitutes a monomer, dimer, etc. In contrast to these other theories, which are by essence largely empirical in nature, Wertheim's theory is completely deterministic" and rigorous (Joslin et al., 1987). However, we have shown that chemical, quasi-chemical and perturbation theory result in expressions that are essentially the same, i.e. the analytic expressions derived (though written in terms of completely different physical parameters) are analytically identical in their functional form and are indistinguishable numerically. Hence, claims that one is more rigorous than the other are not justifiable. Moreover, chemical theory is written in terms of experimentally measurable quantities, i.e. the equilibrium constant, whereas perturbation theory is written in terms of quantities, i.e. the association volume and association energy, that can not be measured experimentally. Therefore, the equivalence of chemical theory

and perturbation theory allows the experimentally unmeasurable quantities in perturbation theory to be related to the experimentally measurable equilibrium constant. This is very useful from the user's point of view since one is able to apply perturbation theory using quantities obtained directly through experimental measurements. These results are discussed in "Chemical, Quasi-Chemical and Perturbation Theories for Associating Fluids" by Economou and Donohue (1991a).

- We extended the Associated-Perturbed-Anisotropic-Chain-Theory (APACT) to compounds with three associating sites per molecule. Association species are taken into account using an expression based on the first-order Thermodynamic-Perturbation-Theory of Wertheim as simplified by Huang and Radosz (1990). As explained above, the equivalence of chemical and perturbation theories allows us to incorporate one theory's results into the other. The new equation describes quantitatively vapor-liquid equilibria, liquid-liquid equilibria and vapor-liquid-liquid equilibria for mixtures of water with aliphatic and aromatic hydrocarbons over a wide range of temperature and pressure with the use of only one adjustable parameter. Details of the derivation and results are discussed in "An Equation of State with Multiple Associating Sites for Water and Water - Hydrocarbon Mixtures" by Economou and Donohue (1991b).

- In many equations of state for associating fluids the assumption is made that physical and chemical interactions are separable. We have shown that chemical and physical interactions are coupled and one can not assume *a priori* that each can be calculated separately and their arbitrary separation leads to a thermodynamic inconsistency. This is discussed in "On the Separability of Physical and Chemical Interactions in Equations of State for Associating Fluids" by Economou and Donohue (1991c).

- We have shown that the PHCT equation of state is equivalent to the GFD equation of state if the parameter 'c' in PHCT is a linear function of density. This is an important result since a theoretically derived equation of state such as the GFD is proven to be equivalent with an equation that was derived based on phenomenological arguments. In

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addition, PHCT is simpler than the GFD and thus is preferable from the user's point of view. Details of the derivation are discussed in "Shape Parameters and the Density Dependence of Hard-Chain Equations of State" by Bokis and Donohue (1991).

- We derived a new expression for the Gibbs free energy of mixing. The entropy of mixing is essentially the Guggenheim's random mixing term whereas the energy of mixing is a simple Boltzmann-weighted surface fraction averaged energy. The new equation is simple and in excellent agreement with the much more complicated but accurate equation of Freed and coworkers for polymer solution phase behavior (Freed and Bawendi, 1989; Freed and Pesci, 1989; Douglas *et al.*, 1990; Dudowicz *et al.*, 1990). Comparisons were also made with other widely used expressions for the free energy of mixing. Details of the derivation of the new theory and comparisons with other theories and simulation data are presented in "Entropy and Energy of Mixing in Polymer Solutions: Mixture Properties Based on Freed Theory" by Cui and Donohue (1991).

- We determined the local composition effects on the properties of the pure fluid. Using the square-well potential, we derived an expression for the local composition that was incorporated into the Simplified-PHCT (SPHCT). The new equation is slightly more complicated, but shows a considerable improvement for the vapor pressure and liquid density of simple spherical fluids such as argon and methane and of non-polar chain and polar fluids such as n-decane, carbon dioxide and water. The derivation of the new theory is discussed in "Effect of Hard-Sphere Structure on Pure-Component Equation of State Calculations" by Vimalchand *et al.* (1991).

EXPERIMENTS

Most of our theoretical work is focused on systems where specific interactions such as hydrogen bonding occur, on systems where components vary considerably in size such as mixtures containing polymers and on systems in extreme conditions such as the near critical and supercritical regions. In most of these cases, no experimental data are available in the literature or the available data are not sufficient in order to adequately test

the models we have developed. As a result, we have made considerable effort to experimentally determine the thermodynamic behavior and phase behavior of these systems.

- We developed a novel spectral analysis technique to determine quantitatively the peak areas from spectra when there are multiple overlapping peaks. The technique involves a combination of Fourier spectral analysis and profile modeling. The technique is used to determine the peak areas from Fourier Transform Infrared (FTIR) spectra that correspond to monomeric and hydrogen-bonded species. The Voigt profile is used in fitting the spectral data. Use of the Voigt profile instead of the more widely used Lorentzian or Gaussian profiles leads to more accurate and descriptive shape parameters and in turn to more accurate determinations of concentrations of monomeric and hydrogen-bonded species. Details of the technique are discussed in "Voigt Profile Analysis of FT-IR Hydrogen Bonding Spectra" by Walsh *et al.* (1991).

- We investigated hydrogen bonding between solvent molecules and between solvent and polymer molecules using FTIR spectroscopy. The solvents used in this work were methanol, chloroform and tetrahydrofuran. Methanol can self-associate and solvate whereas chloroform and tetrahydrofuran can only solvate. The polymer used was a polyketone capable of solvating with molecules having acidic properties. In addition, hydrogen bonding between an ether with five bonding sites per molecule and methanol was examined. The spectroscopic results were modeled using chemical theory expressed in terms of segment-segment interactions. Details of this work are presented in "Hydrogen Bonding in Polymer-Solvent Mixtures" by Economou *et al.* (1991).

- We measured high-pressure vapor-liquid equilibria of several ternary and quaternary systems containing anisole, benzaldehyde, methanol, supercritical carbon dioxide and supercritical ethane. The phase equilibria of the systems containing carbon dioxide are measured at 373 K and pressures up to 22 MPa whereas for the systems containing ethane measurements were made at the same temperature and pressure up to 12 MPa. Anisole and benzaldehyde hydrogen bond with methanol and therefore for the

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systems where methanol was present, the solubility of these aromatic hydrocarbons increased. Quantitative studies of the hydrogen bonding between the aromatic hydrocarbons and methanol were made using FTIR spectroscopy. Details of the experimental work and results are presented in "The Extraction of Model Coal Compounds from 1-Methylnaphthalene Mixtures: The Entrainer Effect" by Reilly *et al.* (1991).

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