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PREDICTION OF THERMODYNAMIC PROPERTIES OF COAL DERIVATIVES

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SUMMARY

In this report, we present our efforts and progress toward understanding molecular behaviour and its effect on thermodynamic properties. This includes work in the following areas: We have constructed an equation based on the Flory lattice model to describe the thermodynamics of polymer solutions. We also have developed a new equation to describe gas sorption in glassy polymers. The APACT has been extended to mixtures of components associating through Lewis acid-base interactions. We have used Monte Carlo simulation of chain molecules to study the partitioning of intermolecular interactions and improve the correlation of the molecular parameters for PSCT. We have used Fourier transform infrared (FTIR) spectroscopy to measure the extent of hydrogen bonding in liquid mixtures, and have developed a new data analysis technique for peak resolving and curve fitting. Finally, we have experimentally measured solute retention times using HPLC and have developed the appropriate theoretical equations to calculate the ratios of the infinite dilution activity coefficients from the measured data.

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INTRODUCTION

In this report, we present our efforts and progress toward understanding molecular behavior and its effect on thermodynamic properties. To this end, we have developed a number of theories applicable to the types of molecules found in coal processing.

To put out current work into context, we present here a brief review of our previous work. Initially the Perturbed Soft Chain Theory (PSCT), a perturbation theory for chain molecules based on the Lennard-Jones potential function was formulated. This was followed by the development of the Perturbed Anisotropic Chain Theory (PACT) which extended the applicability of PSCT to mixtures containing polar molecules. Next, PACT was generalized to include the effect of chemical association (hydrogen bonding) resulting in the Associated Perturbed Anisotropic Chain Theory (APACT). In order to reduce the mathematical complexity of these equations and hence increase their usefulness to practicing engineers, the Simplified Perturbed Hard Chain Theory (SPHCT), which is applicable to non-polar chain molecules, and COMPACT, an equation for hydrogen bonding fluids were developed. In addition to our theoretical work, experiments have been performed to study the phase behavior of binary, ternary and quaternary mixtures containing model coal compounds. Other experimental work involved measurements of selective solubility enhancement of coal chemicals in high-pressure fluids, the partitioning of a dilute solute between two solvents and spectroscopic measurements of chemical association. The various theories developed and experimental work performed under this research program during the current contract period are described briefly in the following sections.

The Modified Generalized Flory Theory

A new equation has been constructed to describe the thermodynamics of polymer solutions. This equation is based on the Flory lattice model, but attempts to correct the

Flory model by taking into account the fact that polymer segments within a molecule are more likely to encounter one another than Flory predicts.

Since Flory first presented his model, several corrections have been made to account that polymer molecules are not infinitely flexible and that a polymer segment is not necessarily the same size as a solvent molecule. Shape, size, and coordination number of the polymer segments have also been taken into account. While these corrections are important, they are not the only flaws in the Flory model.

It is generally assumed that polymer molecules in dilute solutions form "blobs" or "clumps". Since the Flory model assumes a uniform distribution of polymer segments, it does not predict these clumps and is only correct at high polymer concentrations. In our model, clumping is defined as when two non-adjacent segments of a polymer molecule come in contact with one another. Given this definition, clumping does not decrease with increasing polymer concentration. As the polymer concentration increases, not only do the original clumps within the polymer molecules remain, more clumps are formed involving more than one polymer molecule. The model attempts to account for the concentration of the clump formation in polymer solutions. In addition to the χ parameter, one other constant must be fitted for each polymer/solvent system. The model predicts temperature-volume diagrams and reduces to the correct osmotic pressure first virial coefficient, but does not accurately predict solvent activities when an enthalpic term is included.

The Glassy Polymer Lattice Sorption Theory

We began our work in this area by attempting to model gas sorption in glassy polymers using the well-known Flory-Huggins χ theory, which is widely used to describe gas sorption in rubbery polymers. The semiempirical Flory χ parameter reflects the difference in the interaction energies of the polymer segment and the gas. In rubbery polymer systems, these negative interaction energies result in a positive value for χ. For glassy polymers the use of the FH equation results in large negative χ parameters.

We have developed a new lattice-based model for gas sorption in glassy polymer systems. This equation takes into account the immobility of the polymer segments in the glassy state, the presence of holes in the glassy polymer matrix and the swelling due to penetrant gas molecules. Swelling is related to changes in the number of polymer segment-segment interactions, and in the absence of swelling there is no contribution due to the these interactions upon addition of penetrant gas molecules.

The Gibbs free energy of mixing is a sum of the energy of mixing term, the volume of mixing term, and the entropy of mixing term. The entropy term in our model differs from that of the FH equation in that the polymer segments are assumed to be immobile in the glassy state and do not contribute to the entropy. Also, the number of holes on a total polymer segment basis is a function of both temperature and pressure. The energy term is similar to the FH χ term except that a composition dependance is included. The composition dependance takes into account that there are more gas-gas interactions broken than gas-segment interactions due to the gas molecules that occupy the holes, and that a gas molecule entering the lattice can occupy a hole without breaking a segment-segment interaction. The volume term reflects the fact that gas molecules can sorb into a hole in the polymer matrix and not add to the volume of the system.

Using experimental dilation data this model gives excellent predictions for the gas sorption for the polymers and gases studied.

Extension of the APACT to Mixtures of Components Associating Through Lewis Acid-Base Interactions

The Associated-Perturbed-Anisotropic-Chain-Theory (APACT) has been extended to treat multicomponent mixtures in which the components associate through Lewis acid-base interactions. Using the Lewis acid-base approach accurate treatment of systems containing amphoteric (eg. alcohols), acidic (eg. chloroform), and basic (eg. ketones), and non-associating components is possible. Originally, interactions among amphoteric components were taken into account through chemical equilibria, and the components which can only solvate were treated as diluents. For example, in an alcohol-ketone system, the original APACT takes only the self association of the alcohol into account explicitly and the ketone is treated as a diluent. Solvation between the alcohol and the ketone is ignored. This results in poor prediction of phase equilibria even with large values of a binary interaction parameter.

In the extended APACT, all associations are taken into account explicitly based on the acidic and basic properties of each component in the mixture, and a closed-form equation of state has been derived. The extended APACT can accurately predict phase equilibria for systems containing any combination of amphoteric, acidic, basic or non-associating components. The equation of state parameters reflect the actual physical interactions among molecules.

Phase equilibria for ternary mixtures can be predicted based on the constituent binaries without introducing any additional parameters. This can be extended to systems containing any number of components. A general equation for a N-component mixture has been derived and tested.

Monte Carlo Simulations of Chain Molecules

Using computer simulations it is possible to evaluate each term in a model independently. Comparison with experimental data yields only a net effect due to all the terms.

On comparing the repulsive and attractive terms for chain molecules using the Perturbed Soft Chain Theory (PSCT), it was seen that the partitioning between the two terms does not match that calculated from Monte Carlo Simulations. This partitioning is important in calculation of phase equilibria for mixtures. Also, the molecular parameters that are calculated from regressing experimental data do not correlate linearly. This discrepancy systematically increases with chain length.

On comparing the attractive helmholtz free energy calculated from Monte Carlo simulations for 8-mers and spheres, several similarities and important differences are noticed. At higher densities both the 8-mers and spheres show linear behaviour although the slopes and intercepts are different. At lower densities the behaviour of the 8-mers shifts toward the behaviour of the spheres. When this density dependant behaviour is included in the PSCT and the parameters are regressed from experimental data, the parameters show a linear correlation. This indicates that these parameters can be calculated from molecular size and shape.

FTIR Spectroscopy of Hydrogen Bonding Systems

As a separation technology, supercritical extraction has considerable potential for commercial utilization. The limitation is the lack of knowledge of the phase behavior and chemical interactions of multicomponent mixtures near the critical points. Finding the appropriate cosolvents or "entrainers" that maintain or improve selectivity and increase solubility is important.

We have studied systems in which acid-base (hydrogen bonding) interactions between solute, solvent, and cosolvent (entrainer) are prevalent. Three types of mixtures have been defined according to the type of hydrogen bonding. Type 1 mixtures contains a solute dissolved in an inert solvent with a cosolvent added at low concentrations (eg. carbon tetrachloride, acetone, and methanol). In this mixture we have measured the solute-cosolvent interactions. Type 2 mixtures contain cosolvent at higher concentrations and self-associate. Thus, in addition to solute-cosolvent interactions there are cosolvent-cosolvent interactions as well. Finally, type 3 mixtures are similar to type 2, except that an inert solvent is not used (eg. carbon tetrachloride is replaced with diethyl ether). We now have to consider the interactions of type 2 mixtures plus the solvent-cosolvent interactions.

We have used Fourier transform infrared (FTIR) spectroscopy to measure the chemical associations that occur in the solution. In using FTIR spectroscopy we found it necessary to develop a new data analysis technique that is able to resolve the overlapping peaks that occur in such mixtures. In addition to resolving the peaks we have developed a curve fitting technique for peaks which observe Gaussian or Lorentzian behavior.

Thus far we have used FTIR spectroscopy and our data analysis technique to measure the extent of hydrogen bonding in liquid mixtures. As an example we used acetone (electron donor) as a base probe and measured its interactions with a weak electron acceptor (diethyl ether), a strong electron acceptor (chloroform), and a strong electron acceptor-donor (methanol). As for acid probes (electron acceptor) we have used methanol and will be using pyrrol. We are using these liquid probes as references for the study of SCF and entrainer mixtures. As an example we are measuring the extent of hydrogen bonding between a SCF and an entrainer such as CO_2 and methanol. The ability to measure and compare the hydrogen bonding of an entrainer with a SCF will prove to be valuable to predicting the feasibility of the entrainer and SCF for SCF extraction.

In addition to the above we have extended the work on model coal compounds. We previously measured the solubility of the model coal compounds in a high -pressure fluid, with and without an entrainer, using vapor-liquid equilibrium data. Using FTIR spectroscopy and our data analysis techniques we have measured the extent of hydrogen bonding between the model coal compound and the entrainer methanol. We have found there is little chemical association between methanol and anisole and methanol and benzaldehyde. This is believed to be caused by the self-association of the methanol.

Measurement of Infinite Dilution Activity Coefficients Using High Performance Liquid Chromatography

We have measured the retention time of a solute in different solvents using High Performance Liquid Chromatography (HPLC). We have used a reverse phase packing HPLC column with C_{18} as the stationary phase. The solvents under consideration were used as the mobile phase. The solvents used were aqueous solutions of methanol, ethanol, i-propanol and acetonitrile and the solutes used were benzene, toluene, p-xylene, and cumene. We also have developed the appropriate theoretical equations to calculate ratios of infinite dilution activity coefficients (γ^{∞}) of a particular solute in two different solvents from the ratios of the retention times.

This method seems to be fast and simple compared to other static methods using more elaborate setups. If Gas Liquid Chromatography is used in conjunction with HPLC, the activity coefficients can be calculated. In principle, only one absolute value is needed. The results that we got from this method were compared to values obtained from different equations of state such as, UNIFAC, NRTL and APACT. The agreement between our results and the theoretical predictions is, in principle, satisfactory. In fact, a considerable deviation is observed between the predictions obtained from the various equations. This results from the chemical and physical complexity of the systems examined. The chemical complexity is due to the strong hydrogen bonding interactions that between water and organic solvents and the physical complexities are due to the dipole-dipole and dipole-induced dipole interactions because of the strong dipole moments of the solutes.

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