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QUARTERLY PROGRESS REPORT

SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

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ABSTRACT

The solubility of the nitrogen bearing dienophile 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) has been measured as a function of pressure at 40 C, with the exception of points at 2500 psig and 3000 psig. When collection of these last points has been accomplished, the collection of all preliminary data needed to begin kinetic studies of the Diels-Alder reaction between PTAD and anthracene at 40 C in supercritical CO_2 will be complete.

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OBJECTIVES

The goal of this work is to design benign solvent/cosolvent systems for reactions which will achieve optimum desulfurization and/or denitrogenation in the pre-treatment of coal or coal liquids. Supercritical fluids present excellent opportunities for the pre-treatment of coal, hence we shall utilize supercritical fluids as a reaction medium. A SCF exists in a single phase just above the critical temperature at elevated pressures. It has a liquid-like density which gives a large capacity for solvation, and it has a high molecular diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer. Further, its high compressibility gives large density variations with very small pressure changes, yielding extraordinary selectivity characteristics, which are most important in the removal of sulfur and nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general [Brennecke, 1989; Ekart, 1991; Johnston, 1989], as well as in many specific applications to environmental control [Eckert, 1986; Leman, 1990].

The specific objectives of this work are three fold. The first objective is the quantification of the intermolecular interactions affecting reaction transition states in SCF's via kinetic measurements using well characterized Diels-Alder reactions. The second objective is the characterization of the thermodynamics of the reacting systems. From the thermodynamics of the reacting species detailed information about the transition state may be determined. The third objective is the development of molecular level mathematical models using the results from the first two objectives. The models shall be developed using both an equation of state approach and linear solvation energy relationships with solvatochromic parameters.

PROGRESS THIS QUARTER

COLLECTION OF SOLUBILITY DATA

The solubility of PTAD in pure CO2 at 40 C is nearing completion. The data set as it currently exists is presented in the Appendix as Figure 1. Additional points will be taken at 2500 psig, and at 3000 psig.

As mentioned in a previous report, some preliminary measurements of the kinetics of anthracene and PTAD in supercritical CO2 have been completed. Results confirmed that this reaction does run in the supercritical phase, and that the reaction has a conveniently short half-life, but that the solubility of PTAD in supercritical CO2 is low. This low solubility necessitated the acquisition of accurate solubility data for the temperatures and pressures at which the reaction will be run. PTAD must be introduced into the reaction cell in quantities below its solubility limit in order to avoid the distortion of results that would occur if the experiments were performed with excess solid PTAD in the bottom of the reaction cell. Obviously, the concentration of the excess reactant PTAD must be known accurately in order to obtain the true rate constant from data in which a pseudo first order rate constant was measured. In order for the concentration of the PTAD to be accurately known, all PTAD introduced into the reaction volume must be present in the fluid phase.

Another more subtle distortion of kinetics in the presence of excess solid PTAD would occur with the reaction of anthracene with PTAD at the solid-fluid interface. In this case, the disappearance of anthracene - which produces the measured signal in fluorescence spectroscopy - would proceed by a complex mechanism involving both supercritcal phase kinetics and solid kinetics. This event would have the effect of distorting the measured value of the observed pseudo first order rate constant.

PLANS FOR NEXT QUARTER

KINETIC MEASUREMENTS

We shall begin collection of kinetic data for the system of PTAD with anthracene in supercritical CO_2 at 40 C. Kinetic data will be collected at various pressures along the 40 C isotherm, and will be correlated with respect to the following equation:

$$\left(\frac{\partial \ln k_x}{\partial P}\right)_T = -\frac{\Delta v^{\ddagger}}{RT}$$

Scouting experiments have been designed which will select among candidate cosolvents for those which provide optimum enhancement of PTAD/anthracene reaction kinetics. These scouting experiments will be run.

THERMODYNAMIC MEASUREMENTS

A recently developed technique uses a supercritical fluid chromatograph for the rapid and facile measurement of the fugacity of dilute solutes in SCF's [Ekart, 1993], which is a variation on several previous successful techniques [Smith, 1987; Bartle, 1990; Bartle, 1990; Bartle, 1990; Shim, 1991]. The chromatograph equilibrates a dilute solute between the stationary phase and a mobile (supercritical fluid) phase. The retention time, t, of solute i defines the capacity factor, k_i

$$k_i = \frac{t_i - t_o}{t_o} \tag{3}$$

Equation (4) gives the infinite dilution fugacity coefficient, ϕ_i^∞, in terms of the capacity factor and column dependent factors.

$$\phi_i^\infty = \frac{k_i H_i}{P v^F} \left(\frac{V^F v^S}{V^S}\right) \tag{4}$$

H_i is the Henry's law constant for the solute and the stationary phase, V is the total volume, v is the molar volume and F & S represent the fluid and the stationary phases, respectively.

The pressure and temperature derivatives of the fugacity coefficient, give the partial molar volume, v_i^∞, and partial molar enthalpy, h_i^∞. Equations (5) and (6).

$$RT\left(\frac{\partial \ln \phi_i^\infty}{\partial P}\right)_T = v_i^\infty \tag{5}$$

$$RT\left(\frac{\partial \ln \phi_i^\infty}{\partial T}\right)_P = -\frac{h_i^\infty}{T} \tag{6}$$

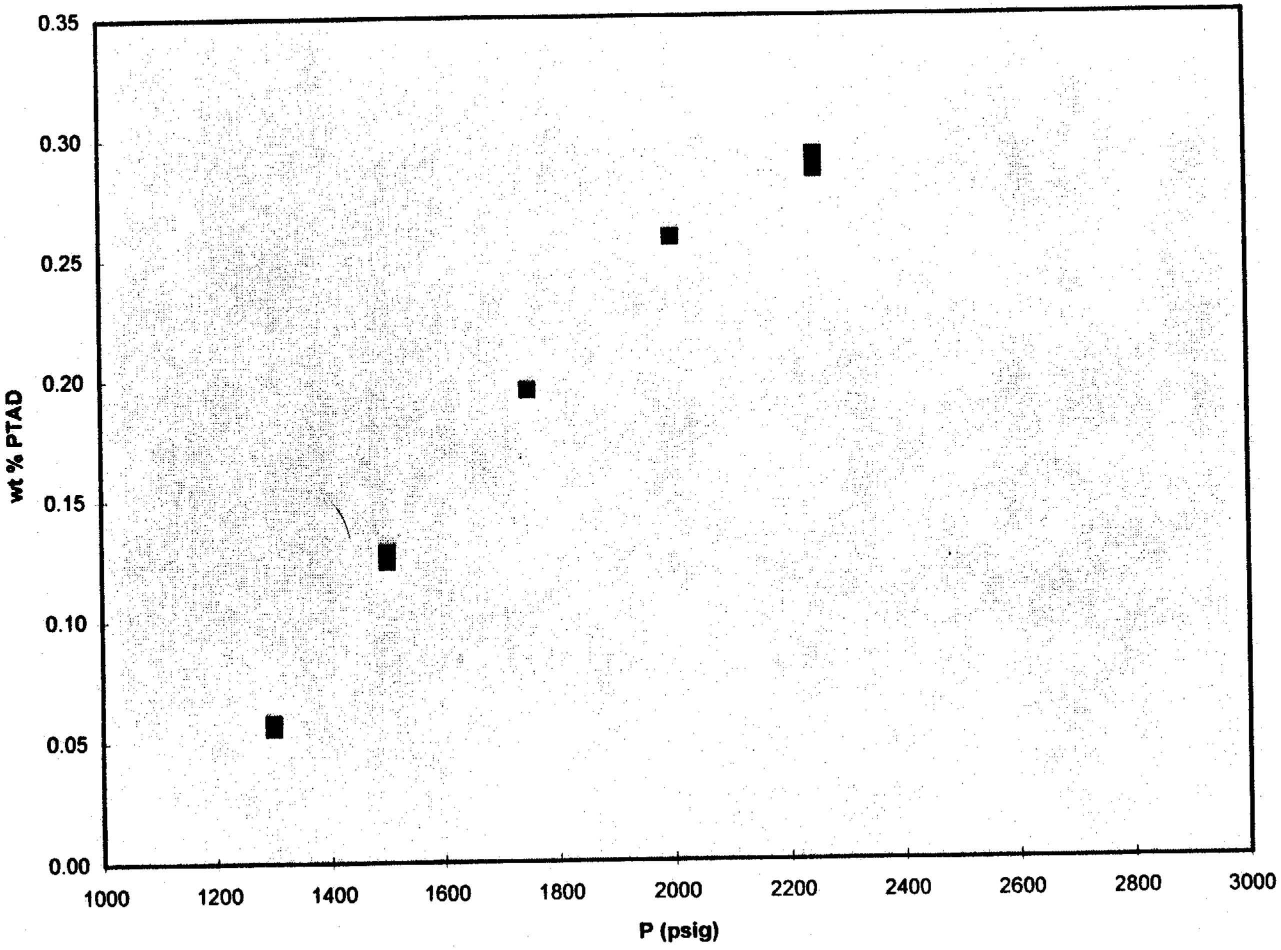
Combining Equations (5) & (6) with Equation (4) allow the partial molar properties to be determined with retention time data only.

SUMMARY

Acquisition of the data needed for kinetic studies of the Diels-Alder reaction of PTAD with anthracene in pure CO_2 at 40 C is nearly complete. When the solubility measurements have been completed, the collection of kinetic data for the PTAD/anthracene system in supercritical CO2 will begin. It is reasonable to expect that at least one isotherm of kinetic data can be completed during this quarter.

Appendix

Figure 1. Solubility of PTAD in Pure CO2 at 40 C



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