QUARTERLY PROGRESS REPORT

SUPERCritical FLUID reactions
FOR COAL PROCESSING

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ABSTRACT

Exciting opportunities exist for the application of supercritical fluid (SCF) reactions for the pre-treatment of coal. Utilizing reactants which resemble the organic nitrogen containing components of coal, we propose to develop a method to tailor chemical reactions in supercritical fluid solvents for the specific application of coal denitrogenation. The tautomeric equilibrium of a Schiff base was chosen as the model system and was investigated in supercritical ethane and cosolvent modified supercritical ethane.
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OBJECTIVES

The goal of this work is to develop benign solvent/cosolvent systems for reactions which will achieve optimum denitrogenation in the pretreatment 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 nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general (Johnston, 1989; Ely, 1991; Brennecke, 1989), as well as in many specific applications to environmental control (Leman, 1990; Eckert, 1986).

The objectives of this work are: utilize supercritical fluids and modified supercritical fluids to tune the chemical equilibria of model coal compounds; and, model the density dependence of the equilibrium constant using a chemical-physical approach. This approach allows us to ascertain the contributions of hydrogen bonding of cosolvents, and the density augmentation to the changes in equilibrium constant. By understanding the effects of these contributions to the equilibrium constant we will be able to quantitatively tune reaction equilibria in supercritical fluids.
Keto-Enol Equilibrium Measurements
Recent studies of chemical equilibria have focused on the effects of pressure on the equilibrium constants of solutes in pure supercritical fluids (Yagi, 1993; Kazarian, 1993; Yamasaki, 1990). The presence of a cosolvent complicates the system, especially if the cosolvent is capable of participating in specific interactions with the solute molecule and leads to multiple equilibria. However, it is the purpose of this study to quantify the effect of cosolvents on keto-enol equilibrium constant for the Schiff base, 4-(methoxy)-1-(N-phenylforminidoyl)-2-naphthol (Figure 1), especially in the near-critical region where local composition enhancements are expected to have a large effect on the equilibrium constant.

![Figure 1. Tautomeric equilibrium of the Schiff base 4-(methoxy)-1-(N-phenylforminidoyl)-2-naphthol.](image)

The Schiff base and a blocked Schiff base (Figure 2) were synthesized by a condensation reaction of 2-hydroxynaphthaldehyde and p-methoxy aniline in ethanol (Salman, 1991) and by a condensation reaction of 2-methoxy-1-naphthaldehyde and 4-methoxyaniline in ethanol, respectively. Yellow solids of blocked Schiff base were obtained after filtration, washing twice with cold ethanol and drying under vacuum. $^1$H NMR (CDCl$_3$ and TMS): $\delta =$ 3.78 ppm (s, 3H); 6.94 ppm (d, 2H); 7.18 ppm (d, 1H); 7.30 ppm (d, 2H); 7.36 ppm (m, 1H); 7.56 ppm (m, 1H); 7.74 ppm (d,1H); 7.85 ppm (d, 1H); 9.25 ppm (s, 1H); 9.53 ppm (d, 1H); 13C NMR (CDCl$_3$ and TMS): $\delta =$ 55.30 ppm (s); 56.26 ppm (s); 112.53
ppm (s); 114.38 ppm (s); 117.37 ppm (s); 122.30 ppm (s); 124.23 ppm (s); 126.07 ppm (s); 128.29 ppm (s); 128.40 ppm (s); 129.26 ppm (s); 132.05 ppm (s); 133.39 ppm (s); 146.61 ppm (s); 157.02 ppm (s); 158.22 ppm (s); 159.31 ppm (s). The blocked Schiff base had the phenolic oxygen methylated to prohibit tautomerization so that the extinction coefficients of the enol form of the Schiff could be measured.

Figure 2. Blocked Schiff base.

Apparatus
A schematic of the modified UV spectrophotometer (Perkin Elmer 554) is shown in Figure 3. Single beam spectroscopy was used in this double beam apparatus using air as a constant background for enhanced signal to noise ratio. The spectrophotometer was modified to accommodate a stainless steel high pressure cell (Tomasko, 1992) with quartz windows (Heraeus Amersil). The path length of the cell was 0.75 cm and the volume was 5.88 ml. The cell was stirred continuously using a mini stir plate (Variomag) and a stir bar (Fisher) placed inside the cell.
The temperature inside the cell was monitored with an internal thermistor (Omega, calibrated within ± 0.1°C) and controlled manually using an EPSCO DC power supply (Model D-612T). Heat was supplied by thermoelectric heaters (Melcor). The pressure was controlled using a 60 cm³ piston type high pressure generator (High Pressure Equipment, Model 87-6-5) and measured to within ± 2 psi with a Heise digital pressure gauge (Model 901B). A Valco 6-port sampling valve with external sample loops ranging in size from 20-100μl was used to inject cosolvent directly into the high pressure cell.

Procedure
Single beam spectroscopy was used to monitor absorbance as a function of increasing pressure at constant probe and cosolvent concentrations. All measurements were made at a constant temperature of 35°C (± 0.1°C), and all experiments were carried out in the single phase region, as confirmed by separate miscibility experiments (Yun, Accepted April 1996) (Table 1).
Table 1. Pressure limits of miscibility for SCF ethane/cosolvent mixtures.

<table>
<thead>
<tr>
<th>Cosolvent in SCF Ethane</th>
<th>Cosolvent Concentration (mol/L)</th>
<th>Lower Miscibility Limit (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trifluoroethanol</td>
<td>0.24</td>
<td>800</td>
</tr>
<tr>
<td>Trifluoroethanol</td>
<td>0.12</td>
<td>756</td>
</tr>
<tr>
<td>Trifluoroethanol</td>
<td>0.046</td>
<td>738</td>
</tr>
<tr>
<td>Hexafluoroiso-propanol</td>
<td>0.32</td>
<td>721</td>
</tr>
<tr>
<td>Hexafluoroiso-propanol</td>
<td>0.16</td>
<td>713</td>
</tr>
<tr>
<td>Hexafluoroiso-propanol</td>
<td>0.08</td>
<td>Miscible at all conditions observed.</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.2</td>
<td>Miscible at all conditions observed.</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.1</td>
<td>Miscible at all conditions observed.</td>
</tr>
</tbody>
</table>

Spectra at different pressures were recorded, starting with a low pressure as determined by the miscibility limit, and incrementally going to higher pressures. The absorbance was recorded at the wavelength of maximum absorption for each tautomer at least three times to obtain an average value (standard error ± 2% at higher pressures; ± 5% at pressures below 730 psig). The pressure varied less than 1.5 psi within a single spectral scan, and data were taken with increasing pressure to ensure that the solute concentration remained constant. Since single beam spectroscopy was used in this double beam apparatus, blank runs (no Schiff base) were made for each solvent system at every pressure point, and this subsequent spectrum was subtracted from the spectrum which contained the Schiff base.

The high-pressure cell was loaded with a solution of 20 μl of (0.0437 M) Schiff base in acetone using a syringe to obtain a probe concentration of 1.5 x 10^-4 M, which is below the solubility limit at experimental conditions as determined spectroscopically. The cell was flushed with multiple volumes of low pressure ethane to evaporate the acetone and to displace air from the system. In the experiments without cosolvent, the cell was then pressurized with ethane to the desired initial pressure. In cases where cosolvent was added, the cell was charged with 100 psig of ethane after removing air from the system. Then, the cell was isolated from the rest of the system, and the lines leading to the cell were pressurized with 450 psig of ethane. The external sample loop was then rinsed and filled with the cosolvent, and the sampling valve and the valve leading to the cell were opened simultaneously to force the cosolvent into the cell using the pressure differential. The cell was further pressurized with ethane to the desired pressure set point, and after equilibration of temperature and pressure, absorbance spectra were measured as described above.
Calculation of $K_c$

The equilibrium constant ($K_c$) was calculated from the following equation:

$$K_c = \frac{c_{\text{keto}}}{c_{\text{enol}}} \quad (1)$$

where $c_{\text{keto}}$ is the concentration of the keto tautomer and $c_{\text{enol}}$ is the concentration of the enol tautomer. Concentration is related to the measured absorbance through Beer's law, thus,

$$K_c = \left( \frac{\varepsilon_{\text{enol}}}{\varepsilon_{\text{keto}}} \right) \left( \frac{A_{\lambda_{\text{max,keto}}}}{A_{\lambda_{\text{max,enol}}}} \right) \quad (2)$$

where $A$ represents the absorbance at the maximum wavelength for each tautomer for a given solvent system. The ratio of extinction coefficients and absorbances were obtained as described previously. The wavelength of maximum absorption changes for the various cosolvent modified SCF solutions due to solvochromatic shifts.

Results and Discussion

The experimental equilibrium constant was found to be a function of cosolvent acidity, cosolvent concentration, and density. Polar cosolvents such as acetone, chloroform, and dimethylacetamide (DMA) did not affect the position of tautomer equilibria. Only cosolvents capable of hydrogen bonding (EtOH, TFE, and HFIP) led to any significant amount of Schiff base tautomerization; the equilibrium constant shifted towards the keto tautomer in the presence of cosolvents which were capable of forming hydrogen bonds. The equilibrium constant also increased with increasing acidity of the cosolvent as can be seen in Figure 4.

The equilibrium constant was also found to shift substantially with varying amounts of cosolvents as can be seen in Figure 5 with the TFE modified SCF ethane solvent system.
Figure 4. Equilibrium constant ($K_c$) as a function of density for approximately 0.1 M cosolvent (EtOH, TFE, HFIP) in SCF ethane. (Equilibrium constant ($K_c$) as a function of density for approximately 0.1 M cosolvent in SCF ethane.)
Figure 5. Equilibrium constant ($K_c$) as a function of density for 0.046 M, 0.12 M, and 0.24 M TFE in SCF ethane. (Equilibrium constant ($K_c$) as a function of density for Schiff base in TFE modified SCF ethane.)

It is important note that miscibility limits and critical mixture densities are different for each cosolvent system and for each cosolvent concentration; therefore, experimental data do not all begin at the same density. The same trend of shift in equilibrium constant was also found with ethanol and HFIP as cosolvents.

These results indicate large changes in tautomerization equilibrium may be obtained with small amounts of carefully selected cosolvents; however, the most interesting and informative result is the variation of the equilibrium constant with density. This effect can be seen in Figure 6 for ethanol and TFE modified SCF ethane solvent systems. The ethanol cosolvent system exhibits the largest density dependence. In all cases, the lowest concentration of added cosolvent results in a larger density effect on the equilibrium constant than the corresponding higher cosolvent concentrations. At the lowest cosolvent concentrations, miscibility limits permit the experiment to extend into the near-critical region of pure SCF ethane where local composition enhancements due to solute-solvent or solute-solute clustering are significant. At the higher concentrations, the experiments are further removed from this near-critical, compressible region. In addition, the shift in equilibrium constant towards the keto tautomer in the lower density regions
may be enhanced by the reduction in self-association of the alcohols which occurs in this same region. These free alcohols have a greater tendency to form intermolecular hydrogen bonds with the keto tautomer.

![Equilibrium constant (Kc) as a function of density in cosolvent/SCF ethane in 0.1 M ethanol and 0.12M (Equilibrium constant (Kc) as a function of density in several cosolvent/SCF ethane systems.]

**Figure 6.** Equilibrium constant (Kc) as a function of density in cosolvent/SCF ethane in 0.1 M ethanol and 0.12M (Equilibrium constant (Kc) as a function of density in several cosolvent/SCF ethane systems.)

Therefore, the density effect observed can be attributed to a combination of factors. First, even in a compressed gas far from its critical point, density changes cause shifts in chemical equilibria due to changes in fugacity. However, in the near critical fluids we also have large effects due to local density and composition enhancements. Finally, hydrogen bonding of the keto tautomer to the cosolvent prevents tautomerization back to the enol form. As pressure is increased beyond the critical region, the equilibrium constant of hydrogen bonding decreases (Gupta et al., 1993; Kazarian et al., 1993a; Kazarian et al., 1993b), which would reduce the concentration of the hydrogen bonded keto form and result in a decrease in the equilibrium constant.
Modeling Based on General Chemical Physical Analysis

A physical-chemical model has been developed to characterize the behavior of the equilibrium constant as a function of density. Possible equilibria describing this solute in a cosolvent modified solvent system are shown below. The equilibrium constant $K_1$ is the actual tautomerization between the keto and enol forms of the Schiff base. The equilibrium constants $K_2$ and $K_3$ indicate the equilibrium between the cosolvent, a hydrogen bond donor, and the Schiff base tautomers which are hydrogen bond acceptors, along with the hydrogen bonded complex of each form. Finally $K_4$ is the equilibrium constant for the dimerization of the alcohol cosolvents. Other equilibria such as the formation of the higher self-associates of the alcohol cosolvents are neglected. In addition, HFIP exists in an equilibrium between two rotamer forms which have slightly different acidities. This equilibrium is known to vary with density (Kazarian and Poliakoff, 1995), however, should have negligible effects on the Schiff tautomerization and will be ignored.

\[
\begin{align*}
K_1 & \quad (1) \\
K_2 & \quad (2) \\
K_3 & \quad (3) \\
K_4 & \quad (4)
\end{align*}
\]

Where $K$, $E$, and $H$ designate the keto tautomer, enol tautomer, and cosolvent, respectively.

For simplification, only cosolvent systems with minimal self-association were modeled. The self association of fluorinated alcohols such as TFE is minimal, and with HFIP, there is essentially no dimerization at the concentrations used (Schrems et al., 1992; Kazarian et al., 1993b; Marco et al., 1994). Additionally, it was found from gas phase hydrogen bonding data between the fluoro-alcohols and various ketonic and enolic (phenolic, in particular, such as the enol form of the Schiff base used in this investigation) compounds that the third equilibrium ($K_3$) may be ignored (Abraham, 1993; Marco et al., 1994) because the equilibrium constant for hydrogen bonds between fluoro-alcohols and ketones is so much greater in comparison to that between the fluoro-alcohols and the phenolic compounds. This results in a model based on only two equilibrium constants:

\[
K_1 = \frac{z_K \Phi_K}{z_E \Phi_E}
\]
where \( z, z_E, \) and \( z_{KH} \) are the true concentrations of the keto and enol tautomers of the Schiff base, respectively, and the keto hydrogen bonded complex; and the \( \phi_K, \phi_E, \) and \( \phi_{KH} \) are the fugacity coefficients for these species.

In order to compare the model directly to the experimental results, an expression in terms of the experimental equilibrium constant was derived. For this derivation, it was assumed that the fugacity coefficients for each of the free Schiff tautomers (\( \phi_K \) and \( \phi_E \)) were equal and the free cosolvent concentration was constant, because in all cases the added cosolvent was in great excess of the Schiff base concentration. Then, the experimental equilibrium constant is given by,

\[
K_{C,exp} = \frac{c_K + c_{KH}}{c_E}
\]  

where the concentration of the keto tautomer is now a combination of the free and hydrogen bonded form of the tautomer. Then, the equilibrium constant calculated from a physical-chemical analysis becomes,

\[
K_{C,calc} = K_1(1 + K_2 C_{cos} \phi^*)
\]  

where

\[
\phi^* = \frac{\phi_K \phi_{KH}}{\phi_{KH}}.
\]

\( K_1, K_2 \) are defined previously in equations 4 and 5, and \( C_{cos} \) is the bulk cosolvent concentration.

The fugacity coefficients were calculated from the Peng-Robinson equation of state (Reid et al., 1987). The binary interaction parameters \( (k_{ij}) \) for the cosolvent/ethane systems were regressed from measured mixture densities and are given in Table 2. The binary interaction parameters for the cosolvent/Schiff complex in SCF ethane \( (k_{14}) \) arbitrarily were set equal to those for the cosolvent. The binary interaction coefficient for the Schiff base/SCF ethane \( (k_{13}) \) were set equal to 0.1 and all other interaction parameters were set equal to zero. The critical properties of ethane, ethanol (Reid et al., 1987), and TFE (Suresh et al., 1994) were obtained from the literature. The critical temperatures of HFIP, Schiff base, and Schiff base/cosolvent hydrogen bonded complex were estimated from Fedors method; the critical pressure and volume for the same compounds were estimated using the Joback method; and the acentric factor was estimated from the critical volume (Reid et al., 1987).
**Table 2.** Binary interaction parameters for SCF ethane/cosolvent systems regressed from experimental data using the Peng-Robinson equation of state.

<table>
<thead>
<tr>
<th>Cosolvent in SCF Ethane</th>
<th>Cosolvent Composition (mol%)</th>
<th>( k_{ij} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFE</td>
<td>0.98</td>
<td>0.055</td>
</tr>
<tr>
<td>TFE</td>
<td>1.98</td>
<td>0.194</td>
</tr>
<tr>
<td>HFIP</td>
<td>0.68</td>
<td>-0.053</td>
</tr>
<tr>
<td>HFIP</td>
<td>1.36</td>
<td>0.033</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.7</td>
<td>0.061</td>
</tr>
</tbody>
</table>

The equilibrium constant for the Schiff base keto tautomer/cosolvent hydrogen bonded complex (\( K_2 \)) was assumed to be equal to the gas phase equilibrium constant for the same hydrogen bond donors with similar ketone compounds. These were obtained from the literature (Marco et al., 1994) and are given in Table 3. The gas phase data were given for 25°C and were corrected to experimental conditions of 35°C using gas phase enthalpy of formation literature data for the appropriate cosolvent/ketone complex (Kivinen and Murto, 1969; Tucker and Christian, 1976). The equilibrium constant of tautomerization for the free Schiff base in the keto and enol forms was fit to the experimental data at the highest pressure data to avoid the effect of the anomalous behavior associated with the SCF critical region is absent.

**Table 3.** Equilibrium constants (\( K_2 \)) for keto Schiff base/cosolvent hydrogen bonded complex at 25°C and corrected to 35°C.

<table>
<thead>
<tr>
<th>Schiff Base/Cosolvent Hydrogen Bonded Complex</th>
<th>( K_2 ) (L/mol) at 22°C</th>
<th>( K_2 ) (L/mol) at 35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFE</td>
<td>53</td>
<td>37</td>
</tr>
<tr>
<td>HFIP</td>
<td>250</td>
<td>154</td>
</tr>
</tbody>
</table>

The results of the model for the highest and lowest cosolvent concentration of TFE and HFIP are shown in Figures 7 and 8. With both cosolvent systems, the model agrees with the experimental data much better at the highest cosolvent concentration. In all cases, however, the model diverges from the experimental data in the area closest to the critical region. The model takes into account the changes in the \( K_c \) which result from changes in solution fugacity. Therefore, it is likely that the differences between the theory and the experimental data are a result of solute-cosolvent clustering resulting from local...
composition enhancements and increases in hydrogen bonding approaching the critical region.

Figure 7. Results of equilibrium model: 0.046 M and 0.24 M TFE/SCF ethane at 35°C. (Results of equilibrium model for Schiff base in TFE/SCF ethane solvent system.)
A sensitivity analysis of the variables associated with the prediction of the equilibrium constant was performed to ensure that the differences between predicted and experimentally measured data were not due to inaccuracies in estimated values and literature constants. From the perturbation of estimated and literature values, it was found that the only variable in the model which could account for the magnitude of the discrepancy between the model and experiment was the cosolvent concentration. The local concentration of cosolvent needed for the model and experimental data to agree at the lowest density point for each data set is given in Table 4. The local composition enhancement needed for this local concentration is also given in this table. For both cosolvent/SCF systems modeled, the local concentration of cosolvent around the Schiff
base is equal (within experimental error) for the highest and lowest bulk cosolvent concentrations. This is consistent with the possibility of saturation of the local cosolvent concentration about the Schiff solute.

Table 4. Local composition enhancement and local concentration of cosolvent about the Schiff base from modeled results using chemical-physical theory.

<table>
<thead>
<tr>
<th>Cosolvent</th>
<th>Bulk Concentration (M)</th>
<th>Mole Fraction Ratio $x_{\text{local}}/x_{\text{bulk}}$</th>
<th>Local Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFE</td>
<td>0.046</td>
<td>9.2</td>
<td>0.423</td>
</tr>
<tr>
<td>TFE</td>
<td>0.24</td>
<td>1.7</td>
<td>0.401</td>
</tr>
<tr>
<td>HFIP</td>
<td>0.032</td>
<td>6.5</td>
<td>0.208</td>
</tr>
<tr>
<td>HFIP</td>
<td>0.164</td>
<td>1.3</td>
<td>0.213</td>
</tr>
</tbody>
</table>

There are several possible explanations for the observations above. At the highest cosolvent concentrations, miscibility limits dictate that the experiments are carried out beginning at densities which are well removed from the near critical region of the solvent system. In the cases of the lowest cosolvent concentrations, it was possible to extend the spectroscopic measurements into the critical region of the solvent system without phase splitting, where local composition enhancements are known to occur. In addition, with nearly 2 mol% of added cosolvent, the fluid is much less compressible in general than at lower cosolvent concentrations. It is also known that the equation of state fugacity coefficient calculations are more accurate at pressures well removed from the critical region.

PLANS FOR NEXT QUARTER

We shall study the reaction of anthracene and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) in supercritical carbon dioxide and supercritical carbon dioxide modified with acetone. The nitrogen bearing compound PTAD has demonstrated superior reactivity and sensitivity to cosolvent additions. A convenient half-life of the reaction is expected under our conditions.
SUMMARY

Densities of binary supercritical mixtures of ethane with cosolvents, ethanol, 2,2,2-trifluoroethanol, and 1,1,1,3,3,3-hexafluoro-2-propanol, have been measured by a constant volume apparatus. Measurements were made in the range 0.7 to 2.0 mol% cosolvent and pressure from 49.8 to 105.7 bar at 308.2 K. The tautomeric equilibrium constant was measured as a function of density in supercritical ethane modified with three different concentrations of hexafluoroisopropanol (HFIP). The measured equilibrium constant was found to be a function of fluid density and cosolvent concentration.

The position of Schiff base tautomeric equilibria was tuned from essentially one tautomer to another by modifying the solvent of pure SCF ethane with less than 2 mol% of cosolvents capable of hydrogen bonding interactions. For the cosolvents of EtOH, TFE, and HFIP, it was found that the equilibrium constant was a function of cosolvent concentration and mixture density. Modifying the equilibrium constants using general chemical-physical analysis results in differences in predicted and experimentally calculated equilibrium constants which are greater than accountable by theory alone. This evidence of solute-cosolvent clustering is consistent with the effects of density on hydrogen bonding (Kazarian et al., 1993). Hydrogen bonding has been shown to decrease with increasing density. A local composition enhancement of cosolvent about the Schiff base in the low density, near-critical region would result in an increased amount of hydrogen bonding which in turn shifts the equilibria to the keto tautomer. As the density of the solution is increased, the solute-cosolvent clustering decreases as the fluid becomes less compressible which also reduces the degree of hydrogen bonding. This decrease in hydrogen bonding in turn affects the keto-enol equilibria by decreasing the amount of the keto formation. Thus, it is possible to utilize density dependence of hydrogen bonding in SCF solutions to “tune” tautomeric equilibrium between the keto-enol forms of the Schiff base.
Literature Cited


