Kinetics and Phase Equilibria in Supercritical Fluids for Advanced Fuel Composition and Use

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Fuels for advanced high performance aircraft engines will approach and traverse the critical region; therefore, the unique properties of supercritical fluid solvents on solubilities and reaction rates are applicable here. In the past years we have developed models for the prediction of various thermodynamic properties of compounds which are representative of fuel components and we have studied several reactions in supercritical fluids. The reactions studied in the past three years represent both fuel model reactions and reactions which will provide an increased understanding of molecular level events in SCF reaction mixtures, such as local composition effects in ternary systems.
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Advanced high-performance aircraft engines will require special fuels that endure supercritical conditions and alleviate the problem of heat management. These fuels will approach and even traverse their critical region; therefore, the unique effects and properties of supercritical solvents on solubilities and reactions are applicable here. In the past three years we have developed models for the prediction of various thermodynamic properties of compounds which are representative of fuel components and which are necessary for the prediction of their phase equilibria. We have studied several reactions in supercritical fluids. The reactions studied in the past three years represent both fuel model reactions and reactions which will provide an increased understanding of molecular level events, such as local composition effects in ternary reaction systems.

Goal of Project

It was the goal of this project to:

- Develop mathematical models for the prediction of phase equilibrium of coke precursors based on experimental data
- Study the effects of SCF conditions on model reactions which correspond to reactions common in fuel chemistry
• Develop mathematical models to correlate and ultimately predict kinetic behavior in SCFs

This project has successfully completed these projects which have resulted in numerous publications. These publications which are readily available will be outlined briefly. Following this brief outline, a more detailed description of the same projects will follow.

1. Solubility Studies. (VanAlsten and Eckert, 1993) This study resulted in the solubility of many model compounds representative of fuel chemistry. Solubility enhancements due to the highly-compressible nature of near-critical fluids were determined as a function of solute, solute size, and solvent.

2. Model for the Prediction of Solid Solubilities in SCFs. (Bush, 1996) A model which correlates the solid solubilities of solutes in SCF ethane was developed which eliminates the need for solute critical properties—which are usually estimated. In this correlation, the only required parameters are solid properties which are usually readily available.

3. Capacity Factors and Solid Solubilities from Chromatographic Methods and Mathematical Models. (Suleiman and Eckert, 1995a, 1995b; Chandler et al., 1996; and Pouillot et al., 1996a, 1996b). In this series of publications capacity factors of n-alkanes in SCFs obtained from chromatographic methods are reported (Suleiman and Eckert, 1995a, 1995b; Chandler et al., 1996). Also reported is method of determining relevant phase equilibria information from the data by derivation of the thermodynamic equations involved, computation of the pure component properties and by limiting assumptions to a minimum (Chandler et al., 1996; Pouillot et al., 1996a, 1996b).
4. Kinetic Investigation of a Diels-Alder Reaction in SCF Propane. (Knutson et al., 1995)
This study investigated the kinetics of a Diels-Alder reaction which is representative of fuel chemistry in SCF propane. The effects of the near-critical region on the reaction kinetics was determined, as well as the effect of cosolvents on the reaction rate.

5. Effect of the Near-Critical SCFs on Chemical Equilibria. (Dillow et al., 1996a, 1996b).
The effect of density (in the near-critical, highly-compressible region) on the tautomeric equilibrium of a Schiff Base was determined in SCF ethane. A Chemical-Physical analysis was used to model the experimental equilibrium constants (Kc).

Solubility Studies

Supercritical fluid solutions are characterized by liquid-like densities and gas-like transport properties. Solubilities are virtually exponential in density, leading to loadings much greater than predicted by ideal solution theory. Due to high compressibility of SCFs, small changes in pressure result in large density changes and considerable solubility variations. Nonvolatile compounds, including reactants and products, can be pulled into or dropped out of solution preferentially. Tailor SCF selectivity is increased by the addition of a cosolvent. The solubilities of naphthalene, phenanthrene, anthracene, pyrene, fluorene, triphenylmethane, dibenzofuran, acridine, and 9-fluorenone were studied in pure SCF carbon dioxide and carbon dioxide with small amounts of the cosolvents methanol and acetone (Van Alsten and Eckert, 1993).
Theory

Reported here is the modeling of solubilities of such compounds as acridine, anthracene, benzoic acid, biphenyl, naphthalene, 2-naphthol, naphthaquinone, phenanthrene, and triphenylmethane in supercritical fluid ethane for the purpose of SCF solubility predictions. For calculating the solubility of a solid in a supercritical fluid, the thermodynamic relationship

\[ f_2^{\text{solid}} = f_2^{\text{vapor}} \]  

(1)

is the starting point. The solid component is subscript 2, the solvent, 1. Assuming the solid remains pure, is incompressible, and has a low sublimation pressure, the fugacity of 2 in the solid phase is given by

\[ f_2^{\text{solid}} = p_2^{\text{sat}} \exp(v_2^{\text{solid}} (P - p_2^{\text{sat}}) / RT) \]  

(2)

The fugacity in the vapor phase can be determined from an equation of state with appropriate mixing rules; however, this technique has not met with much success beyond correlating isothermal measurements. We are comparing dilute solution models where the solubilities are correlated with properties of the pure fluid. This requires no knowledge of the solute’s critical properties which are almost always estimates. Furthermore, if the regression parameters can then be shown to be functions of the solid properties, for example, heat of fusion, then the method can be used for prediction.
Wang and Tavlarides (1994) have developed a model for $f_2^{\text{vapor}}$ that correlates solid solubilities in supercritical solvents. The model was developed to be consistent with the ideal gas law and Henry's law for dilute liquid solutions. After mathematical manipulation and neglecting the Poynting correction, they arrive at

$$RT[\ln E - \ln Z] = \frac{b}{V_1 + c}$$

(3)

where

$$E = \frac{yP}{P_{sat}^2}$$

$$Z = \frac{PV_1}{RT}$$

(4)

and the coefficients can be calculated from the following identities:

$$b = -[N_A \zeta \exp(-\Gamma_{12} / kT) \Gamma_{12} N_A]$$

$$c = N_A \zeta [\exp(-\Gamma_{12} / kT) - 1]$$

(5)

The parameter $\Gamma_{12}$ is the potential energy between the solute and the solvent, and the parameter $\zeta$ is the average volume occupied by a solvent cluster. $N_A$ is Avogadro's number and $k$ is
Boltzmann’s constant. The coefficients $b$ and $c$ are treated as adjustable parameters for a given solute-solvent system and constant with small changes in temperature (approximately $40^\circ$C).

**Results of models**

We have applied this model to the solubility of solids in SCF ethane (Bush, 1996). All the pure component properties were derived and then calculated from a 32 parameter modified Benedict-Webb-Rubin equation of state proposed by Jacobsen and Stewart (1973). The required parameters have been optimized by Younglove (1982) for ethylene, Younglove and Ely (1987) for ethane, propane, and butane, and Ely and coworkers (1989) for carbon dioxide. A visual basic for windows program was written and compiled.

The Wang model was correlated to solid solubilities in ethane. Only solids with vapor pressures that are reported in the literature were used. The solubility data represent data that have been measured in the past from our research laboratory as well as others. The coefficients are given in Table 1.
<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent b (bar)</th>
<th>c (cm³/mol)</th>
<th>Avg Error</th>
<th>Data Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>acridine</td>
<td>ethane</td>
<td>78.9</td>
<td>153.4</td>
<td>27%</td>
</tr>
<tr>
<td>anthracene</td>
<td>ethane</td>
<td>51.2</td>
<td>70.8</td>
<td>22%</td>
</tr>
<tr>
<td>benzoic acid</td>
<td>ethane</td>
<td>35.9</td>
<td>46.1</td>
<td>16%</td>
</tr>
<tr>
<td>biphenyl</td>
<td>ethane</td>
<td>62.6</td>
<td>116.7</td>
<td>7%</td>
</tr>
<tr>
<td>naphthalene</td>
<td>ethane</td>
<td>52.0</td>
<td>116.0</td>
<td>23%</td>
</tr>
<tr>
<td>2-naphthol</td>
<td>ethane</td>
<td>48.1</td>
<td>96.2</td>
<td>23%</td>
</tr>
<tr>
<td>naphthaquinone</td>
<td>ethane</td>
<td>50.8</td>
<td>108.4</td>
<td>18%</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>ethane</td>
<td>60.7</td>
<td>98.3</td>
<td>21%</td>
</tr>
<tr>
<td>triphenylmethane</td>
<td>ethane</td>
<td>66.6</td>
<td>80.1</td>
<td>18%</td>
</tr>
</tbody>
</table>

Table 1. Coefficients for the Wang model

Discussion of the models

The fit is quite surprising; however, several problems arise. The linear transformation takes experimental measurements that are equally spaced in temperature and pressure to being heavily weighted towards low volumes (high densities). The few points that are taken near 0.3 L/mol (below the critical density) ethane have a strong influence on the slope of the line. In some cases, the points in this region give an error over 100 percent in the predicted solubility. It is not certain whether the data or the model is failing.
**Possible Future Work**

Addition measurements of solid solubilities using supercritical fluid chromatography (Suleiman and Eckert, 1994) are being taken to understand the error in the low density regions. We are also evaluating the coefficients in terms of solid and solvent properties to be able to predict solubilities of other solids in heavier solvents such as propane and butane, which are more representative of hydrocarbon fuels.

We have also noticed that the following simple empirical model seems to correlate the data well.

\[ \ln E = \beta_0 + \beta_1 U_r \]  \hspace{1cm} (6)

$U_r$ is the residual internal energy of the pure solvent as previously used in a correlation by Jonah (1986). This promising model is being examined for a theoretical and practical basis.

**PHASE EQUILIBRIA FOR HYDROCARBONS**

The knowledge of the phase behavior of supercritical fluid mixtures of hydrocarbons will be imperative in developing fuels which are capable of meeting the current demands. We have developed a technique to measure capacity factors of n-alkanes in supercritical fluids, including Methane, Ethane, and CO$_2$. We have reported these data (Suleiman and Eckert, 1995a, 1995b; Chandler et al., 1995) and what can be considered a first order approximation of the hypothetical
solubility of these compounds as pure compounds (the solvent is not absorbed by the solute) at infinite dilution conditions (i.e. no solute-solute interactions). We present here a less approximate way of determining the relevant phase equilibria information from chromatographic data by careful derivation of the thermodynamic equation involved, computation of the pure component properties and by limiting the assumptions to a minimum.

**Chromatography and Phase Equilibrium.**

A chromatographic experiment is one which measures how a component distributes itself between two phases. Unless working at overloaded conditions of the column, one gets information on the infinite dilution distribution of the solute eluted. It can be shown that the capacity factor of a solute is defined as:

\[
k_i = \frac{n_i \text{(stationary phase)}}{n_i \text{(mobile phase)}}
\]

(7)

where \( n_i \) is the number of moles, is equal to

\[
k_i = \frac{x_i V^s v^m}{y_i v^s V^m}
\]

(8)

where \( V \) is the volume, \( v \) is the molar volume, and \( s \) and \( m \) denote the stationary and mobile phases, respectively. This is experimentally measured by
\[ k_i = \frac{t_i - t_o}{t_o} \]  

(9)

where \( t_i \) is the retention time of the solute and \( t_o \) the retention time of an unretained solute.

The phase equilibrium between the two phases is written as

\[ x_i \gamma_i \left( T, P, x_i \right) f_i^o \left( T, P^{o,L}, \text{pure} \right) = y_i \Phi_i P \]  

(10)

which is rearranged as

\[ \frac{x_i}{y_i} = k_i \frac{C(T, P)}{\gamma_i \left( T, P, x_i \right) f_i^o \left( T, P^{o,L}, \text{pure} \right)_{\text{Liquid}}} \]  

(11)

where \( C(T, P) \), the ratio of the volumes depends on the temperature \( T \) and the pressure \( P \) because of the molar volume of the mobile phase. What is not apparent in equation (8) is the fact that for a chromatographic experiment, we are at infinite dilution. Therefore, the last equation must be written:

\[ k_i \frac{C(T, P)}{\gamma_i \left( T, P \right) f_i^o \left( T, P^{o,L} \right)_{\text{Liquid}}} = \frac{\Phi_i P}{\left( T, P^{o,L} \right)_{\text{Liquid}}} \]  

(12)

**Case 1: The solute is a pure solid at the system conditions.**

The equilibrium between the solute and the supercritical fluid (solvent) phase is written as
\[ f_i(T, P, \text{pure})_{\text{Solid}} = f_i(T, P^0, \text{pure})_{\text{Solid}} \ast \text{Poynting}(\Phi) \quad (13) \]

\[ f_i(T, P, \text{pure})_{\text{Solid}} = f_i(T, P, y_i)_{\text{Fluid Phase}} = y_i \Phi_i P \quad (14) \]

where the Poynting term is defined as

\[ \text{Poynting}(\Phi) = \int_{P^0}^{P} \left( \frac{\partial f_i}{\partial P} \right)_{T, \text{pure}} dP \quad (15) \]

thus we can write

\[ y_i = \frac{f_i(T, P^0, S, \text{pure})_{\text{Solid}} \ast \text{Poynting}(\Phi)}{\Phi_i P} \quad (16) \]

Substituting \( P \) from equation (11) into \( P \) from (16) we get

\[ y_i = \frac{1}{C(T, P)} \frac{1}{k_i} \frac{1}{\Phi_i} \frac{1}{\gamma_i} \frac{f_i(T, P^0, L, \text{pure})_{\text{Liquid}} \ast \text{Poynting}(\Phi)}{f_i(T, P^0, S, \text{pure})_{\text{Solid}} \ast \text{Poynting}(\gamma)} \quad (17) \]
All the quantities are defined at T and P, except when otherwise noted or defined. If the solute can be considered to be infinitely dilute, then the third term in equation (17) above is equal to one. The computation of the other terms is explained below.

**Case 2. The solute is not a pure solid at the system conditions.**

The ethane-heavy (>20) systems are known to be highly non-ideal and this results in important melting point depressions. Thus, even for high carbon numbers, it is not obvious that one is dealing with a pure solid at temperatures below the melting point of the pure solute. Therefore, care should be taken in applying the correct derivation for that case. Equations (13) and (14) are the equations above that restricted our attention to the particular case of pure solid solutes. For the case of Liquid-Fluid equilibrium (for the solute and the supercritical solvent), we write

\[ x_i \gamma_i(T,P,x_i) f_i^0(T,P,P^{o,L},\text{pure})_{\text{Liquid}} = y_i \Phi_i P \]  

(18)

Again, substituting P in (12) for P in (18), we get
\[ k_i \ C(T,P) = \left( \frac{x_i}{y_i} \right)_{\text{solute/ fluid equilibrium}} \ \frac{\Phi_i^\infty}{\Phi_i} \ \left( \frac{\gamma_i(T,P,x_i)}{\gamma_i^\infty(T,P)} \right)_{\text{solute/ stationary phase equilibrium}} \]  \tag{19}

**Information needed.**

In order to extract information from chromatographic experiments, one therefore needs to know the constant \( C(T,P) \), the reference fugacities of the pure compounds and the activity coefficient of the solute in the stationary phase. The constant calculation was explained elsewhere (Chandler et al., 1995). The reference fugacities are taken as the saturation pressure of the solute (if the solute is a solid at the experimental conditions this is the sublimation pressure; if it is a liquid at experimental conditions this is the vapor pressure. The extrapolation of the vapor pressure line below the melting point of the solutes for the hypothetical subcooled liquid is computed from corresponding state theory as applied by Morgan and Kobayashi (1994b). This also allows the determination of the heat of vaporization in hypothetical states and hence the determination of the solute solubility parameter in the framework of the regular solution theory if needed. The determination of the sublimation pressure of the \( n \)-alkane series is addressed below. Finally, the description of the stationary phase is also addressed.
Vapor Pressure Correlation.

We have developed a correlation for the vapor pressures of n-alkanes (Chandler et al., 1995) based on the data reported by Morgan and Kobayashi (1994a) which ranged from 323 to 588 K for n varying from 10 to 28. The data were fit to an equation of the type

\[ P_{vap}(T,n) = a 10^{b(n-c)} \]  \hspace{1cm} (20)

The coefficients were regressed to be

\[ a = 39.29 + 9.811 \times 10^{-2} T - 2.045 \times 10^{-4} T^2 \]  \hspace{1cm} (21)

\[ b = -1.415 + 4.140 \times 10^{-3} T - 3.353 \times 10^{-6} T^2 \]  \hspace{1cm} (22)

\[ c = 5.412 - 2.776 \times 10^{-2} T + 4.911 \times 10^{-5} T^2 \]  \hspace{1cm} (23)

The vapor pressure obtained from this correlation at the temperatures of our experiments (308.2 to 348.2 K) compared well with the data measured by Macknick and Prausnitz (1979), and Sasse et al. (1988) for several of the n-alkanes (n = 19 to n = 22). This is shown in the particular case of C_{20}H_{42} on the following figure.
Sublimation Pressure Computation. (Pouillot et al., 1996a)

The sublimation pressure of the n-alkanes is computed according to

\[
\ln P_{\text{sub}}(T) = \ln P_{\text{sub}}(T_m) + \int_{T_m}^{T} \frac{\Delta H_{\text{sub}}(T)}{T^2} dT
\]

The usual procedure is to take the heat of sublimation at the triple point as the reference, and to consider that it does not differ significantly from the one at the melting point. Next, due to the unavailability of the heat of sublimation, it is taken as the sum of the heat of fusion and the heat
of vaporization at the melting temperature. Finally, the temperature dependence of the heat of sublimation is computed as:

\[
\Delta H_{\text{sub}}(T) = \Delta H_{\text{fus}}(T_m) + \Delta H_{\text{vap}}(T_m)
\]

\[
+ \int_{T_{\text{first transition}}}^{T_{\text{second transition}}} \left( C_p^{\text{ideal gas}}(T) - C_p^{\text{solid}}(T) \right) dT + \Delta H_{\text{first transition}}
\]

\[
+ \int_{T_{\text{first transition}}}^{T_{\text{second transition}}} \left( C_p^{\text{ideal gas}}(T) - C_p^{\text{solid}}(T) \right) dT + \Delta H_{\text{second transition}}
\]

This requires that the heat capacities of both the solid and the gas phases, the heat of sublimation and the heats of transitions be known. The heat capacities in the gas state, assumed ideal, are computed with the method of Tinh et al. (1971, 1976). The heat capacities of n-Heptadecane and n-Octadecane have been measured by Messerly et al. (1967) in the temperature range of interest (i.e. 15-25 °C). We compared our method to the correlation of Moaradinia (1986) and to the data of Bradley and Shellard (1949) and found that both methods correlate the data of C_{17}H_{36} well, as can be seen in Figure 2.
Figure 2. The bottom plain line is Moradinia’s correlation (Moradinia, 1986), the “open square–plain line” is the computation according to the method described, and the open circles are the data points (Bradley and Shellard, 1949).

However, we show (Figure 3) the results of our method as well as Moradinia’s correlation on the next figure for the case of C_{22}H_{52}. Moradinia failed to impose that the sublimation pressure equals the vapor pressure at the melting point (326.7 C). There are no data to compare with our predictions.
Figure 3. The top line with + signs is Moradinia’s correlation (Moradinia, 1986), the open circles the extrapolated vapor pressure (Morgan and Kobayashi, 1994), the bottom plain line is the computation according to the method described.

**Phase Transitions of Solid n-alkanes.** (Pouillot et al., 1996b)

In the case of solids, complications arise due to solid-solid transitions, and corresponding discontinuities in heat capacities. We do not discuss the physics of solid-solid transitions here (see e.g. Broadhurst, 1967; Takamizawa, 1982).

**Activity coefficient at infinite dilution in the stationary phase.** (Pouillot et al., 1996b)

The activity coefficient at infinite dilution at T and P of the solute is given by...
\[
\gamma_i^\infty (T,P) = \gamma_i^\infty (T^{0,L}, P^{0,L}) \exp \left[ \int_{P^{0,L}}^{P} \frac{(-\bar{\nu}_i)}{T^{0,L}} dP \right] \exp \left[ \int_{T^{0,L}}^{T} \frac{(-\bar{h}_i)}{RT} dT \right]
\]

which is written as

\[
\gamma_i^\infty (T,P) = \gamma_i^\infty (T^{0,L}, P^{0,L}) \text{Poynting}(\gamma)
\]

The reference temperature \( T^{0,L} \) and pressure \( P^{0,L} \) are taken as 25 °C and 0 atm, for which Patterson and coworkers have developed a corresponding state theory allowing prediction of activity coefficients of n-alkanes in n-alkanes (see e.g. Patterson and Bardin, 1969; and Trejo Rodriguez and Patterson, 1982, 1984). They have shown that their theory allows the prediction of Henry's constants (or activity coefficients at infinite dilution) of n-alkanes in n-alkanes with very good accuracy.

**SCF REACTIONS**

The effects of SCF solvents on reactions are not well understood. However, reactions provide an excellent probe to the reactant's microenvironment. We can dramatically alter reaction rates and selectivities in SCF solvents by slight adjustments in temperature, pressure, or
the addition of a cosolvent. Understanding the effects of reaction rates and selectivities at a molecular level is important in carefully designing a fuel that may undergo an endothermic decomposition that results in combustible products. This supercritical reaction would also ameliorate the cooling load problem that exists with these advanced aircraft.

**Diels–Alder Investigation.**

We have investigated the effects of temperature, pressure, and supercritical solvents on the reaction rates of the well-characterized, bimolecular, Diels–Alder reaction of maleic anhydride (MA) and 2,3-dimethylbutadiene (DMB) (Knutson et al., 1995). In addition, we studied the reaction with the addition of the cosolvent trifluoroethanol (TFE). Therefore, we were able to determine the effects of near-critical conditions and cosolvent additions on reaction rates in supercritical fluids. With the cosolvent system, we were able to determine the role of specific reactant/cosolvent interactions on reaction rates.

An unusual density-dependence on the reaction rate was observed for the Diels–Alder reaction of DMB and MA in SCF propane. Over the range of supercritical conditions studied, a minima in rate constant was observed at 100 °C and 120 °C in the mid-range of solution densities. The effect of pressure on this rate constant is inconsistent with previous investigations of Diels–Alder reactions SCF carbon dioxide. In SCF carbon dioxide, the large, negative activation volumes become increasingly negative in the near critical region, in agreement with the large negative partial molar volumes of a large solute in a near-critical fluid. The rates of Diels–Alder
reactions in liquids also increase with increasing pressure and the activation volume is relatively insensitive to solvent effects.

The activation volumes in the SCF propane system were predicted from the SRK equation of state by assuming the structure of the product and transition state were equivalent. The resulting activation volumes were used to predict DMB/MA rate constants at 100 C in SCF propane with reference to the highest density point. The predicted and experimental rate constants in the near critical region differ by a factor of two. The density dependence at 140 C more closely follows predicted trends.

The addition of cosolvent is an excellent way to alter reaction rates. However, with the addition of 2.3 to 10 mole% TFE to the Diels-Alder reaction of MA and DMB, which shows minimal solvent effects, the rate was increased by only a small factor. However, this is typical of a reaction with an isopolar transition state.

The overall solvent insensitivity of this reaction suggests that the unusual rate constant minima observed as a function of density results from a local composition enhancement in the near-critical vicinity. This would result in the measurement of an apparent rate constant that was a function of the local composition of the DMB (the reactant in great excess) rather than the bulk composition. The use of the bulk DMB composition in locally enhanced solutions would result in an apparent rate constant that was greater than the true rate constant. This is exactly what we observed. These type of local compositions enhancements are associated with near-critical ternary solutions.

There are a number of reasons why our observed rate trends differ from those previously reported. One may be the SCF solvent itself. Carbon dioxide is capable of specific
intermolecular interactions, whereas propane is not. Also, we swamped with one reactant, whereas other researchers have used stoichiometric amounts of both reactants. These observations will lead to a subsequent study of the effect of relative reactant concentrations on reaction rates.

Results on this research suggest that local reactant composition, as well as pressure, temperature, and cosolvent can be used to manipulate the reaction rate in the near critical region. The phenomena of local composition enhancement has significant applications to reaction rates. An understanding of these effects of reactions in SCF solvents are necessary to fine-tune reaction rate and selectivities in supercritical fluids.

**Tautomeric Equilibrium in SCFs**

The keto-enol equilibrium constant for the Schiff base reaction shown below
was determined to develop a more complete molecular level understanding of the effects of local
density and local composition on reactions in SCFs (Dillow et al., 1996a;1996b). The
equilibrium of this reaction was followed spectroscopically using UV-VIS spectroscopy. This
reaction was ran in pure SCFs ethane at a reduced temperature of 1.01. The keto form of this
Schiff Base is more polar by nature and, therefore, is expected to be stabilized to a greater extent
in a more dielectric environment. The dielectric constant of SCF ethane is comparable to that
of liquid cyclohexane and does not change significantly as the fluid’s density is changed. It is,
therefore, not surprising that the equilibrium of the base, within experimental error, lie totally in
the less polar enol form of the compound.

Next, a series of cosolvents was used to determine and separate the effects of
dielectric/polarity and specific interactions/hydrogen bonding. Cosolvents used included:
chloroform, DMA, acetone, ethanol, trifluoroethanol, and hexafluoroisopropanol. As expected,
it was found that the dielectric cosolvents caused an equilibrium to exist between the keto and enol isomers, but the effect was small. On the other hand, the protic cosolvents caused an enormous effect on the equilibrium. Both increasing acidity and increasing concentration of cosolvent caused the equilibrium of the reaction to shift towards the keto tautomer. We found that through the use of appropriate cosolvents, the equilibrium constant could be shifted approximately 3 orders of magnitude, essentially from one tautomer to the other. These experiments were carried out over an entire density range at temperatures very close to critical.

A chemical-physical model of the equilibrium constants exhibits deviations from the measured values in the near-critical region, which may be due to local composition enhancement of cosolvent about the Schiff base. As the degree of hydrogen bonding decreases with pressure or density, this in turn affects the keto-enol equilibria by decreasing the amount of the keto formation. Thus, solution density, as well as the degree of hydrogen bonding, are manipulated to tune the position of tautomeric equilibria.

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 $K_d$ 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 know to vary with density (Kazarian and Poliakoff, 1995), however, should have negligible effects on the Schiff tautomerization and will be ignored.

\[
\begin{align*}
K_1 & \quad K \leftrightarrow E \\
K_2 & \quad K + H \leftrightarrow KH \\
K_3 & \quad E + H \leftrightarrow EH \\
K_4 & \quad H + H \leftrightarrow HH
\end{align*}
\]

(28)

Where $K_1$, $E$, 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; Yee 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:

\[
K_1 = \frac{z_K \phi_K}{z_E \phi_E} \tag{29}
\]

\[
K_2 = \frac{z_{KH} \phi_{KH}}{z_K \phi_K z_H \phi_H} \tag{30}
\]

where \(z_K\), \(z_E\), 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,

\[
K_{C,\text{exp}} = \frac{c_K + c_{KH}}{c_E} \tag{31}
\]
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,

\[ K_{c,\text{calc}} = K_1(1 + K_2 C_{\text{cos}} \phi^*) \]  \hspace{1cm} (32)

where

\[ \phi^* = \frac{\phi_K \phi_H}{\phi_{K\text{H}}} \]  \hspace{1cm} (33)

K_1, K_2 are defined previously, and C_{\text{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_{i2}) for the cosolvent/ethane systems were regressed from measured mixture densities. The binary interaction parameters for the cosolvent/Schiff complex in SCF ethane (k_{i4}) arbitrarily were set equal to those for the cosolvent.

The binary interaction coefficient for the Schiff base/SCF ethane (k_{i3}) were set equal to 0.1 and all other interaction parameters were set equal to zero, also arbitrarily. 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).

The equilibrium constant for the Schiff base keto tautomer/cosolvent hydrogen bonded complex (K_c) 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). 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.

The results of the model for the highest and lowest cosolvent concentration of TFE and HFIP are shown in Figures 4. 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.

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.

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.
Figure 4. Chemical-Physical Model and Experimental data for Equilibrium Constant vs Density for the Schiff Base/SCF Ethane/TFE (cosolvent) System at 2 Concentrations.

Conclusions

The research conducted in the past three years has lead to an increased understanding of supercritical fluids at a molecular level. We have gained much insight concerning solid solubilities which is directly applicable to the dissolution of coke precursors. Models have been developed and applied to predict relevant thermodynamic properties of compounds which represent fuel chemistry. We have also investigated two reactions which are directly applicable to SCF fuels. In addition, a study has been completed which will allow us to develop of better fundamental understanding of molecular level events in SCF reaction mixtures. Thermodynamic theory has been used to model these kinetic results for a deeper understanding of the parameters.
responsible for the experimental observations. These all represent significant contributions to an understanding which will aid in the development fuel which utilizes SCF regions and will best serve the current needs.
Current Relevant Publications


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