Cosolvent Tuning of Tautomeric Equilibrium in Supercritical Fluids

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Cosolvents offer a sensitive tool to tailor equilibria, rates or yields of chemical reactions in supercritical fluid solvents. The tautomeric equilibrium of a Schiff base was chosen as a model system, and small amounts of protic cosolvents shift the position of tautomeric equilibria. The equilibrium was tuned from essentially one tautomer to another by modifying the solvent of pure SCF ethane with less than 2 mol % hexafluoroisopropanol cosolvent. The equilibrium constant was a function of cosolvent concentration and mixture density. A chemical-physical model of equilibrium constants deviates from the measured values in the near-critical region, which may have been caused by local composition enhancement of cosolvent around the Schiff base. Decrease in the degree of hydrogen bonding with pressure or density affects the keto-enol equilibria by decreasing the amount of the keto formation. Thus, solution density, as well as the degree of hydrogen bonding, is manipulated to tune the position of tautomeric equilibria.

Introduction

Supercritical fluids (SCFs) offer several benefits as solvents for reaction chemistry: they are often environmentally benign, may increase mass transfer by orders of magnitude, and remove solvent easily. SCF solvent properties also can be continually adjusted merely by changing from gas-like to liquid-like density without changing the solvent as in corresponding liquid studies. Especially in the near-critical region, SCFs are highly compressible so that small changes in pressure and/or temperature can lead to large density variations.

Cosolvents offer an even more sensitive route to tuning SCF performance; not only do small amounts change solubility behavior, but the specific interactions coupled with local composition enhancement may have profound effects on the reaction chemistry. We have chosen the keto-enol transition of a Schiff base to demonstrate one aspect of such tuning, and that is the effect on chemical equilibria.

Several kinetic and equilibrium studies in pure supercritical fluids have demonstrated that reaction rates (Lee et al., 1985; Paulaitis and Alexander, 1987; Johnston and Haynes, 1987; Ikushima et al., 1992; Randolph and Carlier, 1992; Roberts et al., 1992; Ellington et al., 1994; Knutson et al., 1995; Rhodes et al., 1995), selectivity (Hyatt, 1984; Kim and Johnston, 1988; Collins et al., 1988), and equilibria (Gupta et al., 1993; Kazarian et al., 1993a; Kimura et al., 1989; Peck et al., 1989) can be tuned by adjusting the density of the SCF solvent in the near-critical region. Small amounts of cosolvents can enhance solute solubility in SCFs by orders of magnitude (Dobbs and Johnston, 1987; Brennecke and Eckert, 1989; Lemert and Johnston, 1991; Fulton et al., 1991; Ekart et al., 1993; Tomasko et al., 1993). These increases result from a combination of increasing the solvent mixture density and strong specific interactions between the cosolvent and solute molecule. In addition, local composition enhancements of cosolvents about the solute molecule in the near-critical region contribute to these cosolvent effects (Eckert et al., 1986; Debenedetti, 1987; Kim and Johnston, 1987a,b; Yonker and Smith, 1988; Cochran et al., 1988; Petsche and Debenedetti, 1989; Wu et al., 1990; Brennecke et al., 1990a,b; Knutson et al., 1992; Sun et al., 1992; O'Brien et al., 1993; Phillips and Brennecke, 1993; Eckert and Knutson, 1993).

Recent studies of chemical equilibria have focused on the effects of pressure on the equilibrium constants of solutes in pure supercritical fluids (Peck et al., 1989; Yamasaki and Kajimoto, 1990; O'Shea et al., 1991; Kazarian et al., 1993a; Kimura and Yoshimura, 1992; Yagi et al., 1993). It is the purpose of this study to quantify the effect of cosolvents on

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SCF equilibria, especially in the near-critical region where local composition enhancements are expected to have a large effect on the equilibrium constant.

Focus of This Study

For this demonstration, we have chosen the keto-enol equilibrium of the Schiff base, 4-(methoxy)-1-(N-phenylforminidoyl)-2-naphthol, as shown in Figure 1. Schiff bases are formed from the condensation of aromatic amines with aromatic aldehydes. The Schiff bases which contain an *o*-hydroxy group may exist in two tautomeric forms: a keto-amine and a phenol-imine, referred to as keto and enol forms, respectively (Salman et al., 1991).

This tautomeric equilibrium was chosen for several reasons. First, it has large solvent effects in liquids in terms of equilibrium and solvatochromic shifts of the keto tautomer (Dudek and Dudek, 1966; Salman et al., 1994). Tautomerization of the Schiff base and its ability to hydrogen bond, as well as the effect of solvents on these phenomena, has been the focus of much study and debate (Dudek and Dudek, 1971; Herscovitch et al., 1973; Issaf et al., 1974; Ledbetter, 1977; Lewis and Sandorfy, 1982; Mills and Beak, 1985; Ranganathan et al., 1986; Nagy and Herzfeld, 1987; Salman et al., 1989). Schiff bases are also an important group of chemicals with applications in areas ranging from luminescent dyes for solar collectors (Sharma et al., 1990) to medicinal compounds (Ledbetter, 1977). Finally, the UV peaks of each tautomer are well separated (ca. 70–90 nm), which simplifies analysis (Figure 2).

The enol form of this Schiff base is stabilized in nonpolar solvents, while the keto form is more stabilized in polar solvents (Dudek and Dudek, 1971; Ledbetter, 1977; Kamounah et al., 1992; Salman et al., 1994). Solvents which are capable of hydrogen bonding, such as alcohols, interact with the carbonyl oxygen of the keto tautomer and disrupt the intramolecular hydrogen bond, which allows the base to tautomerize to the keto form (Saeed et al., 1988). The solvent effect on such equilibrium is usually explained by the polarity of the solvent and by intermolecular interactions such as hydrogen bonding. However, the equilibrium of some Schiff bases is quite insensitive to even highly dielectric solvents (Dudek and Dudek, 1966; Herscovitch et al., 1973).

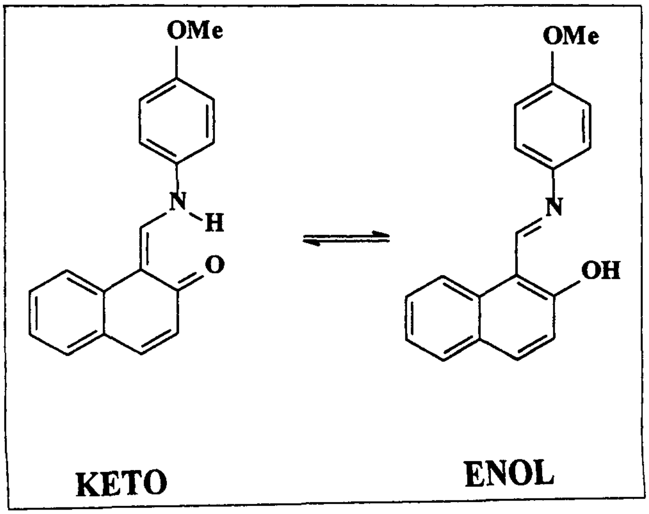

Figure 1. Schiff base tautomeric equilibrium.

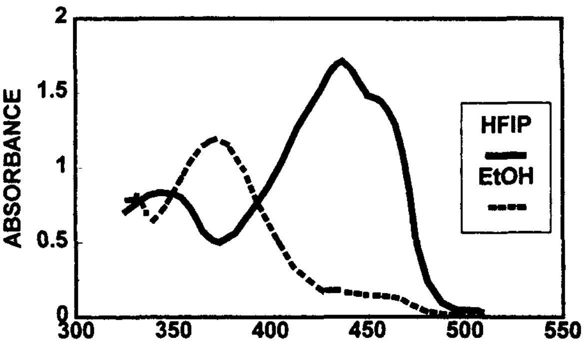

Figure 2. Sample spectrum of Schiff base in SCF ethane plus the following cosolvents at 35°C.

(a) 0.1 M EtOH λ_{max}(enol) = 377 nm, λ_{max}(keto) = 440 nm; (b) 0.08 HFIP λ_{max}(enol) = 355 nm, λ_{max}(keto) = 440 nm.

The Schiff base tautomeric equilibrium was studied in pure SCF ethane as well as in several cosolvent modified SCF solutions. Through the use of small quantities of specific cosolvents, this equilibrium may be adjusted from predominantly one tautomer to another. It would be expected that if local composition enhancements of the colsolvent occur about the Schiff base solute in the near-critical region of these fluids (Eckert and Knutson, 1993; Kazarian et al., 1993a), a given equilibrium position can be obtained with a fraction of the liquid organic solvent needed in traditional liquid solutions.

This tautomeric equilibrium was investigated as a function of density, cosolvent, and concentration of added cosolvent. Concentration equilibrium constants (K_c) were calculated from absorbance spectra. General chemical-physical theory and the Peng-Robinson equation of state were then used to model the experimental results and to infer the effect of the local composition enhancement of cosolvent on the equilibrium constant in the near-critical region.

Ethane was chosen as the primary SCF solvent for this investigation of the Schiff base equilibria because it cannot participate in specific interactions with the Schiff base or with the cosolvents, thus simplifying the interpretation of the density and solvent effects on the equilibrium. Ethane was also chosen because of its moderate critical properties ($T_c = 305.4$ K; $P_c = 49.8$ bar). T_c is critical temperature, and P_c is critical pressure. Carbon dioxide is often the SCF solvent of choice because of its environmentally benign characteristics. However, other research with tautomeric equilibria has shown that in pure SCF carbon dioxide, shifts in position of equilibria are attributed to Lewis acidity and the large quadrupole moment of CO_2 (O'Shea et al., 1991).

The cosolvents were selected so that effects of polarity/polarizability and hydrogen bonding could be examined separately. Table 1 shows the cosolvents investigated along with their Kamlet-Taft values for rating solvent strength: α is a measure of solvent hydrogen bond donating ability; β indicates solvent hydrogen bond accepting ability; and π^* is a measure of a solvent polarity/polarizability. Acetone, chloroform, and dimethylacetamide (DMA) were used to examine effects of polarity. For the hydrogen bonding ethanol (EtOH), 2,2,2-trifluoroethanol (TFE), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) afford increasing degrees of proticity.

Table 1. Cosolvent Structures and Properties

Cosolvent	α^*	β^*	π^*	ϵ^{**}
CH_3CH_2OH Ethanol	0.83	0.77	0.54	24.55
CF_3CH_2OH 2,2,2-Trifluoroethanol	1.51	0.00	0.73	
$CF_3CH(OH)CF_3$ 1,1,1,3,3,3-hexafluoro-2-propanol	1.96	0.00	0.65	16.6†
CH_3COCH_3 Acetone	0.08	0.48	0.71	20.7**
$CHCl_3$ Chloroform	0.44	0.00	0.58	4.8**
$CH_3CON(CH_3)_2$ Dimethylacetamide	0.00	0.76	0.88	

*Kamlet et al. (1983); **Schneider (1975); †Murto et al. (1970).

Experimental Studies

Materials

The Schiff base was synthesized by a condensation reaction of 2-hydroxynaphthaldehyde and *p*-methoxy aniline in ethanol (Salman et al., 1991). A blocked Schiff base (see Figure 3) was also synthesized with the phenolic oxygen methylated to prohibit tautomerization so that the extinction coefficients of the enol form of the Schiff could be measured. This compound was prepared by the condensation reaction of 10 g of 2-methoxyl-1-naphthaldehyde in 50 mL ethanol and 6.6 g of 4-methoxyaniline in 20 mL of ethanol. The mixture was stirred overnight. Yellow solids of blocked Schiff base were obtained after filtration, washing twice with cold ethanol and drying under vacuum. ^1H NMR ($CDCL_3$ and TMS): δ = 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): δ = 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).

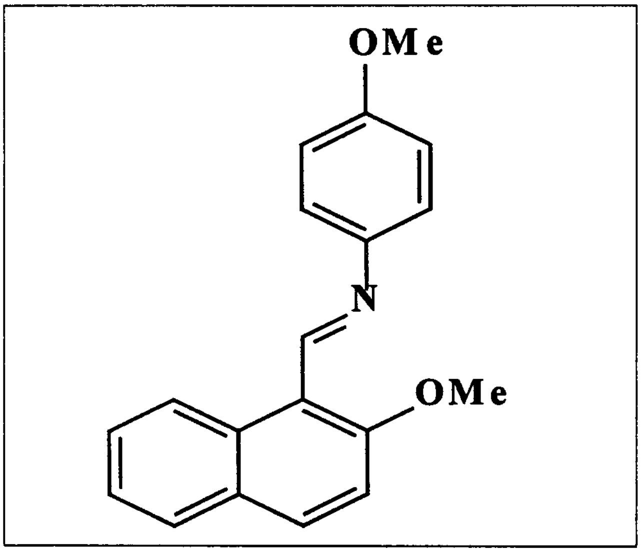

Figure 3. Blocked or methylated Schiff base.

The ethane gas (Matheson, C. P. grade 99.0%) was used as received. Other chemicals used as received were: acetone (Aldrich, HPLC grade, 99.9+%); chloroform (Aldrich, HPLC grade, 99.9%); cyclohexane (Aldrich, 99%); dimethylacetamide (Aldrich, HPLC grade, 99.9%); ethanol (Quantum Chemical, 99.9%); 1,1,1,3,3,3-hexafluoro-2-propanol (Aldrich, 99.8+%); methanol (Aldrich, HPLC grade, 99.9+%); 2,2,2-trifluoroethanol (Aldrich, 99+%).

Apparatus

The modified UV spectrophotometer (Perkin Elmer 554) is shown in Figure 4. 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).

The temperature 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 cm^3 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 20–100 μL 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 et al., 1996). Spectra at different pressures were recorded, starting with a low pressure just beyond 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, 5

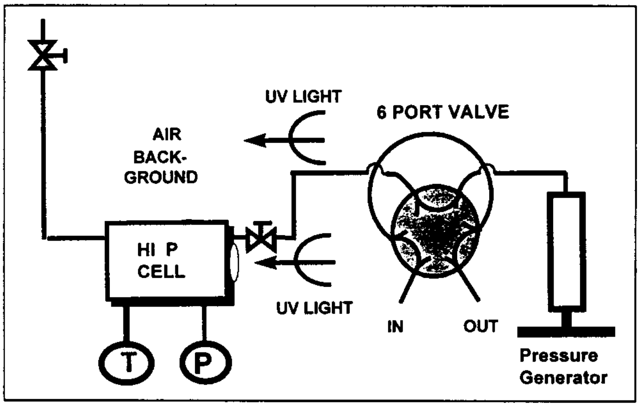

Figure 4. UV spectrophotometer modified for high-pressure applications.

MPa). 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 the spectra were subtracted from the spectra 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 1.5×10^{-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 to 100 psig (690 KPa) with 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 to 450 psig (3.1 MPa) with 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 setpoint, and after equilibration of temperature and pressure, absorbance spectra were measured as described above.

Data analysis

For each cosolvent/SCF ethane system, the equilibrium constant as a function of density is the information of interest. Mixture densities for each pressure were measured experimentally for each cosolvent/ethane system, and the equilibrium constants were calculated using extinction coefficients and absorbance measurements for the keto and enol tautomers. Absorbances for the tautomer peaks were determined from spectra taken at various pressure points. The extinction coefficient for the enol tautomer was estimated using a blocked form of the Schiff base, and the ratio of extinction coefficients (enol to keto) was calibrated using a literature value from liquid data.

Analysis of Spectra. The baseline spectra of the solvent system (pure ethane or cosolvent/ethane) were subtracted from the spectra containing the Schiff base at equivalent pressure data points, and the absorbance at the maximum wavelength for each tautomer was determined using SpectraCalc software. Since the peaks of the Schiff tautomers were separated, deconvolution of the peaks was not necessary. Deconvolution of example spectra using Peakfit software resulted in corrected absorbances which were within the experimental error of the absorbances calculated without using a deconvolution method.

Calculation of extinction coefficients

Extinction coefficients are a function of not only the solute of interest, but also the environment around the solute (Rice et al., 1995). In order to estimate the density dependence of the extinction coefficient of the Schiff base, a blocked form of the Schiff base was synthesized with a methylated oxygen group as shown in Figure 3. The blocked form of the Schiff base is representative only of the enol tautomer of the Schiff base. Since this blocked form cannot tautomerize, it is used to estimate the extinction coefficient of the enol tautomer of the Schiff base. The absorbance for this blocked Schiff base varied only slightly throughout the density range investigated: 15% in pure SCF ethane and 4.4% for HFIP, 8.5% for TFE, and 16% for ethanol cosolvent modified systems. From these data, it was shown that the extinction coefficients (ϵ) vary minimally with density. Also, any slight variations in the extinction coefficients of the tautomers should vary in the same manner with changes in solvent density (Kimura and Yoshimura, 1992). From these facts, it is assumed that the *ratio* of the enol to keto extinction coefficient is a constant.

The extinction coefficients for the Schiff base used in this study, or compounds analogous in structure, have been measured in several liquid solvents (Dudek and Dudek, 1966, 1971; Issaf et al., 1974; Ranganathan et al., 1986; Kamounah et al., 1992). Because the measured extinction coefficient of the blocked Schiff base in pure SCF ethane at 100 bar (12,800 L/mol cm^2; $\lambda_{\max} = 370$ nm) agreed well with the literature value for the enol extinction coefficient (13,000 L/mol cm^2; $\lambda_{\max} = 377$ nm) in cyclohexane (Dudek and Dudek, 1966), the experimentally determined liquid enol/keto ratio of extinction coefficients was used as a calibration value. The experimentally determined extinction coefficients for the blocked Schiff base in SCF ethane were then used to determine the variation in this enol/keto ratio of extinction coefficients as a function of changing solvent environment.

As described above, it was assumed that the *ratio* of the density dependence of extinction coefficients of the enol and keto tautomers was constant throughout the density range investigated (Kimura and Yoshimura, 1992). This assumption is supported by the minimal density effects on the extinction coefficient of the blocked form of the Schiff base. The ratios of SCF $\epsilon_{\text{enol}}/\epsilon_{\text{keto}}$ calculated are 0.81, 1.3, and 2.11 for the HFIP, TFE, and ethanol/SCF solvent systems, respectively. No extinction coefficients were obtained for the other cosolvents (acetone, chloroform, and DMA) since these cosolvents had only a minimal effect on the position of tautomeric equilibria.

Calculation of K_c

The equilibrium constant (K_c) was calculated from

$$K_c = \frac{c_{\text{keto}}}{c_{\text{enol}}} \tag{1}$$

where c_{keto} is the concentration of the keto tautomer and c_{enol} is that of the enol tautomer. Concentration is related to the measured absorbance through Beer's law

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

where A represents the absorbance at the maximum wavelength for each tautomer for a given solvent system. The wavelength of maximum absorption ($\lambda_{\max}$) changes for the various cosolvent modified SCF solutions due to solvochromatic shifts.

Determination of miscibility limits and mixture density calculations

The pressure limits of miscibility for all cosolvent/SCF ethane mixtures were determined in a stirred, thermostated Jerguson sight gauge to ensure that all experiments were carried out under single-phase conditions. The miscibility limits for the solvent systems capable of supporting formation of the keto tautomer are given in Table 2.

Equation of state (EOS) models do not predict mixture densities accurately in the near-critical region, and errors based on the use of these equations can lead to large uncertainties. Therefore, mixture densities were determined experimentally at all pressures for each cosolvent/SCF ethane system (Yun et al., 1996).

Results and Discussion

The experimental equilibrium constants were 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 tautomeric equilibria. Only cosolvents capable of hydrogen bonding (EtOH, TFE, and HFIP) led to significant amounts 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 increased with increasing acidity of the cosolvent (Figure 5). (The corresponding solvatochromic parameters for these cosolvents are given in Table 1.) The equilibrium constant was also found to shift substantially with varying amounts of cosolvents as can be seen in Figure 6 with the TFE modified SCF ethane solvent system. Because miscibility limits and critical mixture densities are different for each cosolvent system and for each cosolvent concentration, 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.

The variation of the equilibrium constant with density can be seen in Figure 7 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 region.

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 may also have large effects due to local density and composition enhancements. Finally, hydrogen bonding of the keto tautomer to the cosolvents shifts the equilibrium toward this keto form. As pressure is increased beyond the critical region, the equilibrium constant of hydrogen bonding decreases (Gupta et al., 1993; Kazarian et al., 1993a,b) which would reduce the concentration of the hydrogen bonded keto form and result in a decrease in the equilibrium constant.

Table 2. Pressure Limits of Miscibility for SCF Ethane/Cosolvent Mixtures

Cosolvent in SCF Ethane	Cosolvent Conc. (mol/L)	Lower Miscibility Limit (psig)
TFE	0.24	800
TFE	0.12	756
TFE	0.046	738
HFIP	0.32	721
HFIP	0.16	713
HFIP	0.08	Miscible at all conditions observed
EtOH	0.2	Miscible at all conditions observed
EtOH	0.1	Miscible at all conditions observed

SI Conversion: kPa = psi × 6.89.

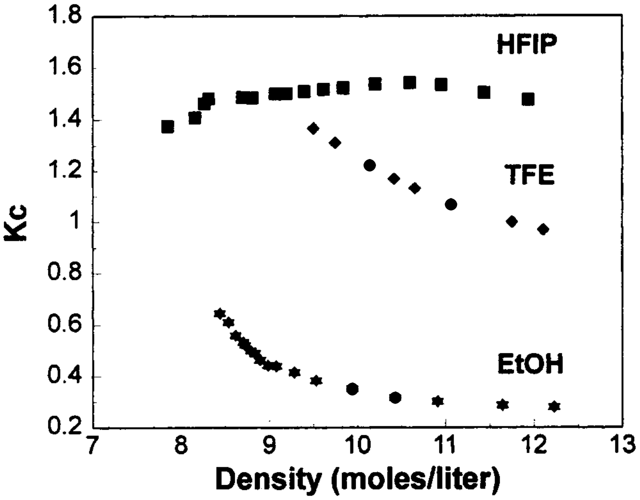

Figure 5. Equilibrium constant (K_c) as a function of density for approximately 0.1 M cosolvent (EtOH, TFE, HFIP) in SCF ethane.

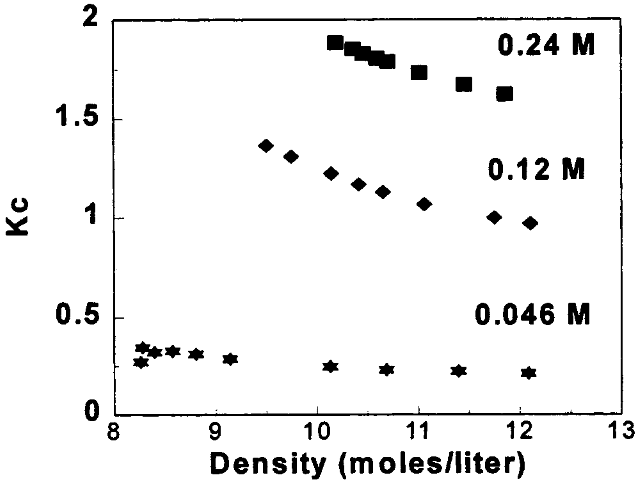

Figure 6. Equilibrium constant (K_c) as a function of density for 0.046 M, 0.12 M, and 0.24 M TFE in SCF ethane.

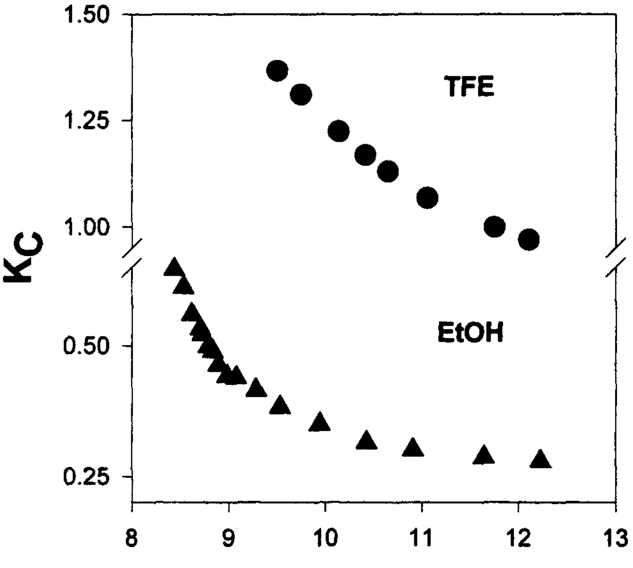

Figure 7. Equilibrium constant (K_c) as a function of density for 0.1 M ethanol and 0.12 M TFE in SCF ethane.

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, it should have negligible effects on the Schiff tautomerization and will be ignored.

$$\begin{gathered} K \overset{K_1}{\leftrightarrow} E \\ K + H \overset{K_2}{\leftrightarrow} KH \\ E + H \overset{K_3}{\leftrightarrow} EH \\ H + H \overset{K_4}{\leftrightarrow} HH \end{gathered} \tag{3}$$

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 virtually no dimerization at the concentrations used (Schrems et al., 1984; 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

$$K_1 = \frac{z_K \phi_K}{z_E \phi_E} \tag{4}$$

$$K_2 = \frac{z_{KH} \phi_{KH}}{z_K \phi_K z_H \phi_H} \tag{5}$$

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. The ϕ_K, ϕ_E, and ϕ_{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 (ϕ_K and ϕ_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

$$K_{c,\text{exp}} = \frac{[c_K + c_{KH}]}{[c_E]} \tag{6}$$

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

$$K_{c,\text{calc}} = K_1(1 + K_2 C_{\cos} \phi^*) \tag{7}$$

where

$$\phi^* = \frac{\phi_K \phi_H}{\phi_{KH}}, \tag{8}$$

K_1, K_2 are defined previously in Eqs. 4 and 5, and $C_{\cos}$ is the bulk cosolvent concentration. $K_{c,\text{calc}}$ is the predicted concentration equilibrium constant from the model. ϕ^* is the ratio of fugacity coefficients.

The fugacity coefficients were calculated from the Peng-Robinson equation of state (Reid et al., 1987). The binary interaction parameters (k_{12}) for the cosolvent/ethane systems were regressed from measured mixture densities and are given in Table 3. 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}) was set equal to 0.1 and all other interaction parameters were set equal to zero, also arbitrarily. All critical properties used are shown in Table 4. The critical properties of ethane, ethanol (Reid et al., 1987), and TFE (Suresh et al., 1994) were obtained from

Table 3. Binary Interaction Parameters for SCF Ethane/Cosolvent Systems Regressed from Experimental Data Using the Peng-Robinson Equation of State

Cosolvent in SCF Ethane	Cosolvent Comp. (mol %)	k_{ij}^*
TFE	0.98	0.055
TFE	1.98	0.194
HFIP	0.68	−0.053
HFIP	1.36	0.033
EtOH	1.7	0.061

$^*k_{ij}$ is the binary interaction parameter.

Table 5. Equilibrium Constants (K_2) for keto Schiff Base/Cosolvent Hydrogen Bonded Complex at 25°C and Corrected to 35°C

Schiff Base/Cosolvent Hydrogen-Bonded Complex	K_2 (L/mol) 22°C	K_2 (L/mol) 35°C
TFE	53	37
HFIP	250	154

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_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 5. 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 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 8 and 9. 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 possible 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 (including the arbitrarily set binary interaction coefficients) 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 6. 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 base solute.

Table 4. Critical Properties Used for the Peng-Robinson Equation of State

Compound	T_c (K)	P_c (bar)	ω^*
Ethane	305.4	48.8	0.09
EtOH	513.9	61.4	0.64
TFE	490.2	42.7	0.78
HFIP	461.6	37.3	0.66
Schiff Base	860	25	0.74
hydrogen-bonded complex	905	25	0.74
Schiff Base/HFIP hydrogen-bonded complex	908	25	0.74

$^*\omega$ is the Pitzer acentic factor.

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. For the lowest cosolvent concentrations, it was possible to extend spectroscopic measurements into the critical region of the solvent system without phase splitting, where local composition enhancements are known to occur. It is also known that the equation of state fugacity coefficient calculations are more accurate at pressures well removed from the critical region.

This model was chosen for simplicity of demonstrating the effects seen. One might achieve a superior fit of the data with more elaborate thermodynamic models (as, for example,

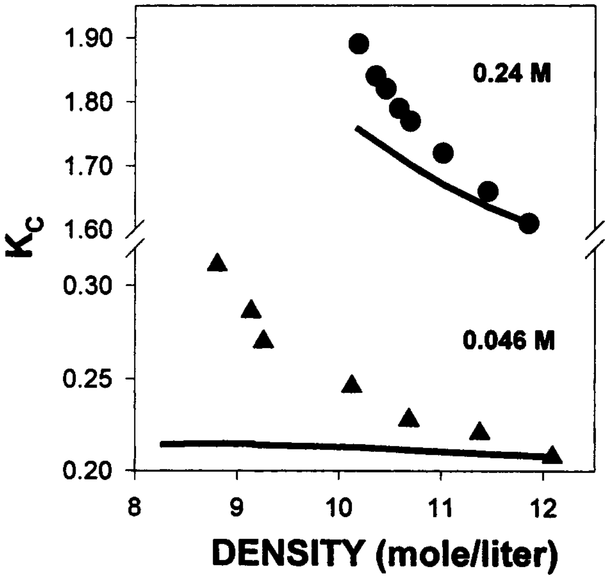

Figure 8. Equilibrium model: 0.046 M and 0.24 M TFE in SCF ethane at 35°C.

Symbol = experimental; line = model.

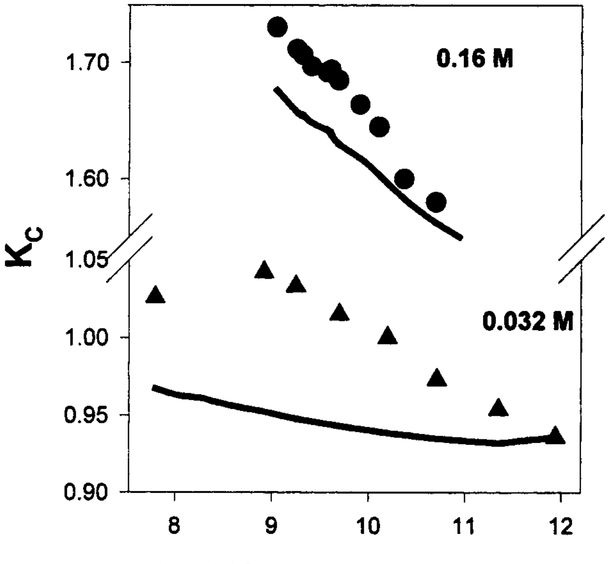

Figure 9. Equilibrium model: 0.032 M and 0.16 M HFIP in SCF ethane at 35°C.

Symbol = experimental; line = model.

that of Gupta et al., 1993), perhaps, however, at the cost of even more arbitrary assignments of parameters. The focus of this work is on the reaction chemistry and cosolvent tuning rather than on comparing equations of state.

Conclusions

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. Modeling the equilibrium constants using general chemical-physical analysis results in differences in predicted and experimentally calculated equilibrium constants could be interpreted in terms of local composition enhancement in the near-critical region. This evidence of solute-cosolvent clustering is consistent with the effects of density on hydrogen bonding, which 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.

Table 6. Local Composition Enhancement and Local Concentration of Cosolvent about the Schiff Base Estimated from a Chemical-Physical Theory Analysis

Cosolvent	Bulk Conc. (M)	Mole Fraction Ratio ($x_{\text{local}}/x_{\text{bulk}}$)	Local Conc. (M)
TFE	0.046	9.2	0.423
TFE	0.24	1.7	0.401
HFIP	0.032	6.5	0.208
HFIP	0.164	1.3	0.213

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Appendix

Tables A1–A3 include experimental data of mixture density vs. equilibrium constant (K_c) for all Schiff base/SCF ethane/cosolvent systems which exhibited significant degrees of tautomerization. The raw absorbance data for the synthesized blocked Schiff base are also included (Table A4). A recent study of tautomeric equilibrium of a Schiff base (Kamounah, 1996) in solvent mixtures supports the suggestion that the keto form is stabilized via H-bonding with alcohol solvents.

Table A1. Schiff Base Data 1.5×10^{-3} M with HFIP Cosolvent in SCF Ethane

20 μL HFIP 0.032 M		50 μL HFIP 0.08 M		100 μL HFIP 0.136 M	
Mixture Density (mol/L)	K_c	Mixture Density (mol/L)	K_c	Mixture Density (mol/L)	K_c
7.80	1.026	7.85	1.375	9.05	1.731
7.88	1.092	8.16	1.409	9.26	1.712
7.97	1.067	8.26	1.462	9.32	1.707
8.06	1.069	8.31	1.481	9.41	1.697
8.29	1.070	8.70	1.487	9.57	1.692
8.37	1.065	8.81	1.485	9.61	1.694
8.55	1.060	9.06	1.500	9.69	1.685
8.93	1.042	9.19	1.500	9.91	1.664
9.25	1.033	9.40	1.508	10.11	1.650
9.70	1.015	9.62	1.516	10.37	1.601
10.20	1.002	9.84	1.523		
10.71	0.973	10.20	1.537		
11.35	0.954	10.60	1.542		
11.94	0.936	10.95	1.533		
		11.44	1.502		
		11.94	1.476		

Table A2. Schiff Base Data 1.5×10^{-3} M with TFE Cosolvent in SCF Ethane

20 μL TFE 0.046 M		50 μL TFE 0.12 M		100 μL TFE 0.24 M	
Mixture Density (mol/L)	K_c	Mixture Density (mol/L)	K_c	Mixture Density (mol/L)	K_c
8.28	0.349	9.50	1.366	10.19	1.883
8.40	0.323	9.75	1.310	10.36	1.852
8.57	0.329	10.14	1.224	10.46	1.829
8.81	0.314	10.42	1.168	10.59	1.806
9.14	0.288	10.65	1.130	10.70	1.788
8.26	0.272	11.06	1.067	11.02	1.733
10.13	0.247	11.75	0.999	11.46	1.673
10.69	0.230	12.11	0.969	11.86	1.624
11.40	0.222				
12.09	0.210				

Table A3. Schiff Base Data 1.5×10^{-3} with EtOH Cosolvent in SCF Ethane

50 μL EtOH 0.1 M		100 μL EtOH 0.2 M	
Mixture Density (mol/L)	K_c	Mixture Density (mol/L)	K_c
8.44	0.646	9.34	0.425
8.54	0.612	9.42	0.412
8.62	0.560	9.59	0.405
8.71	0.532	9.76	0.406
8.73	0.522	9.82	0.399
8.79	0.499	9.87	0.399
8.84	0.489	9.93	0.394
8.90	0.463	9.99	0.393
8.99	0.442	10.06	0.390
9.08	0.439	10.21	0.380
9.28	0.415	10.45	0.372
9.53	0.383	10.66	0.359
9.94	0.351	10.92	0.344
10.43	0.316	11.36	0.332
10.91	0.301	11.78	0.320
11.65	0.287	12.10	0.315
12.23	0.279		

Table A4. Blocked Schiff Base Data 1.5×10^{-3} M in SCF Ethane

100 μL EtOH		100 μL TFE		100 μL HFIP	
P (psig)	Absorb.	P (psig)	Absorb.	P (psig)	Absorb.
750	0.825	822.4	1.3	798	0.988
800	0.868	877.9	1.296	842.4	1.01
849.6	0.88	920.5	1.272	914.5	1.025
914.2	0.895	1020.1	1.244	1,015.8	1.023
1,038.4	0.94	1,249	1.22	1,194.7	1.027
1,192.4	0.959	1,428.4	1.2	1,425	1.033
1,435.7	0.985				

SI Conversion: kPa = psi × 6.89.

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