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ARTICLES

Investigating the Effect of the Zwitterion/Lactone Equilibrium of Rhodamine B on the Cybotactic Region of the Acetonitrile/scCO$_2$ Cosolvent

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We investigated the effect of adding acetonitrile to supercritical carbon dioxide (scCO$_2$) in the presence of rhodamine B. This spectroscopic investigation of the scCO$_2$/acetonitrile, rhodamine B/scCO$_2$, and rhodamine B/acetonitrile interactions revealed that rhodamine B, which possesses a temperature dependent equilibrium between a zwitterionic form and a neutral form, had a strong affect on the cybotactic region. To confirm that this effect was only dependent upon the rhodamine B/acetonitrile interactions and not merely due to the bulk-phase behavior of the scCO$_2$, we measured the compressibility of the scCO$_2$/acetonitrile mixture and found it to be independent of the acetonitrile concentration to less than ~0.047 mol fraction. We fit the compressibility data using the Peng−Robinson equation of state because it is most appropriate for fluids in the region between 1.72 and 12.45 MPa and between 313 and 333 K.

Introduction

In an attempt to make better use of the world's resources, supercritical CO$_2$ (scCO$_2$) and other supercritical fluids have received much attention during the past decade for their use as solvents. Supercritical CO$_2$ is a functional solvent in many processes for the following reasons: it provides a "green" alternative to commonly used liquid solvents in that CO$_2$ is readily available and relatively harmless to living organisms and the dielectric constant can be varied with the addition of a cosolvent, thereby, "tuning" the ability of the scCO$_2$ to solvate a larger range of molecules.[1,2] This is a very useful feature, especially in selective extraction processes, material processing, and chemical reactions. The variability of the dielectric constant and the excellent mass transport properties due to the low viscosity make this solvent system tremendously useful in both research laboratories and industrial settings.

Much attention has been given to the solubility enhancement of different cosolvents on various solutes and many researchers have published on this subject.[3−5] The solubility of a solute directly depends on the molecular interaction between the solute molecule and the solvent molecule. Solute/solvent, solvent/cosolvent, and solute/cosolvent interactions are of primary interest in the study of supercritical fluids,[6−9] and this work further contributes to the knowledge base.

In this paper, we present an interesting effect when rhodamine B is dissolved in the acetonitrile/scCO$_2$ cosolvent. Rhodamine B is a xanthene dye that exists in solution as a mixture of a pink colored zwitterion form and a colorless, neutral, lactone form. The rhodamine B equilibrium between these two forms depends on temperature, concentration, and solvent parameters and has been measured in the condensed phase using UV−visible absorbance spectroscopy.[21] As the temperature of the solution increases, the equilibrium shifts toward the colorless lactone, resulting in decreased absorbance. The lactone form is entirely soluble in neat scCO$_2$, because of its low polarity. The

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zwitterion is only soluble in cosolvent enhanced $scCO_2$. We chose acetonitrile as our cosolvent, due to its very large dipole moment and inability to form hydrogen bonds.

FT-IR spectroscopy is an excellent method by which to probe the interaction between acetonitrile and rhodamine B; however, one would not be able to differentiate between the bulk phase behavior of the $scCO_2$/acetonitrile mixture (i.e., a change in density) and specific interactions between the rhodamine B and acetonitrile molecules. To differentiate between these two effects, we devised an experiment to determine how the addition of acetonitrile affects the $scCO_2$ in the bulk phase. To investigate this effect on the thermodynamic behavior of the supercritical fluid, we used the compressibility factor and fit the data using the Peng−Robinson equation of state (given below)

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)} \qquad (1)$$

The Peng−Robinson equation of state can be modified for a binary mixture by the adjustment of two parameters, a and b, according to the following mixing rules:[3]

$$a_{mix} = \sum_i \sum_j x_i x_j a_{ij} \qquad (2)$$

$$a_{ij} = (1 - \delta_{ij})(a_{ii}a_{jj})^{1/2} \qquad (3)$$

$$b_{mix} = \sum_i \sum_j x_i x_j b_{ij} \qquad (4)$$

$$b_{ij} = 0.5(b_{ii} + b_{jj})(1 - \eta_{ij}) \qquad (5)$$

where a_{mix} and b_{mix} are the parameters used in eq 1, x_i and x_j are the mol fractions of components i and j, respectively, a_{ij} and b_{ij} are the mixing coefficients, and δ_{ij} and η_{ij} are experimentally determined, binary interaction parameters.[11] The value for a_{ii} and a_{jj} are the pure component coefficients calculated according to the rules given by Peng and Robinson.[12] The temperature dependence of parameter a(T) is given by

$$a(T) = \left(0.45724\frac{R^2T_c^{\,2}}{P_c}\right)\left[1 + \kappa\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2 \qquad (6)$$

where

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad (7)$$

and the temperature dependence of parameter b(T) is given by

$$b(T) = 0.07780RT_c/P_c \qquad (8)$$

The variable ω is called the *acentric factor* and is specific for each substance in the mixture.[13] The values of the acentric factor for acetonitrile and carbon dioxide are 0.321 and 0.225, respectively.[13,14] The Peng−Robinson equation was used to model the data because it has proven to be very successful in describing the phase behavior of binary mixtures in the liquid−vapor region and the liquid-supercritical fluid region.[3,15−20]

Experimental Methods

Materials. SFE/SFC grade carbon dioxide was obtained from Airliquide. Rhodamine B Lactone and Zwitterion were obtained from Aldrich Chemical Co. Certified HPLC grade acetonitrile was obtained from Pharmcoproducts Inc. All materials were used without further purification.

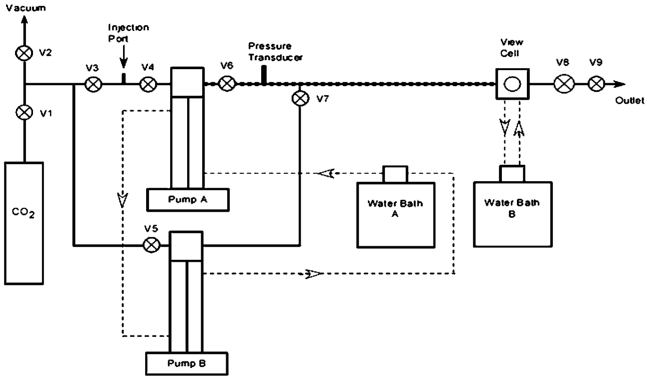

Figure 1. Experimental apparatus used for spectroscopic experiments. The line leading from pump A to the spectroscopic cell was temperature controlled by heat tape.

Spectroscopic Investigation. *Apparatus.* The setup for this experiment is shown in Figure 1. All transfer lines, fittings and valves were constructed of 316 stainless steel. The sample was prepared and controlled using two ISCO 260D syringe pumps. The sample injection port was constructed in house using a Swagelok tee, Teflon O-ring, and a Supelco Thermogreen LB-2 septum, the details of which have been reported in the literature.[22] The system was purged under vacuum using an Alcatel 2002 mechanical roughing pump and monitored with a Kurt J. Lesker thermocouple vacuum gauge. The system pressure was measured by an Omegadyne Inc. model PX01C1-5KGV pressure transducer. The syringe pumps were held at constant temperature by two high volume, high flow rate water baths. The connecting lines were temperature controlled by silicone heat tape. The temperature was monitored at both syringe pumps and at the connecting lines with thermocouples. This system incorporated a high-pressure cell to collect spectroscopic data. The cell had four sapphire windows allowing for two distinct beam paths and was connected to the pumps with 1/16 in. stainless steel tubing. Valve 8 is a Whitey series 31 fine metering valve. All other valves are Swagelok SS ORM2 316 needle valves and used for shutoff. Spectra were collected with a Thermo Nicolet IR 300 spectrometer.

Mixing Technique. Rhodamine B was dissolved in acetonitrile to yield initial 10^{-4} and 10^{-5} M solutions. A 300 μL sample of the solution to be investigated was injected into a previously evacuated syringe pump through a sealed injection port. The sample was forced into pump A using high-pressure CO_2 from the tank. Pump A was filled with compressed CO_2 to a pressure of 9.68 MPa using pump B and the temperature was set at 306 K. The supercritical solution was allowed to mix for ∼2 h. During this period, the sample compartment was repeatedly compressed and expanded, thereby, agitating the solution to ensure complete mixing. Using pump B, the line connecting pump A to the spectroscopic cell was brought to the same pressure as the inside of pump A. Valve 7 was closed to shut off pump B and valve 6 was opened to give pump A control over the pressure of the system. About 50 mL of the $scCO_2$ was allowed to leave the system through valves 8 and 9, which ensured that the spectroscopic cell was filled with a homogeneous solution of rhodamine B/acetonitrile/$scCO_2$. FT-IR spectra were recorded at different temperatures and pressures using a previously collected background of neat $scCO_2$.

Thermodynamic Investigation. *Apparatus.* The setup for this experiment is shown in Figure 2 and is identical to the system used for the spectroscopic study minus the spectroscopic cell, FT-IR spectrometer, and fine metering valve.

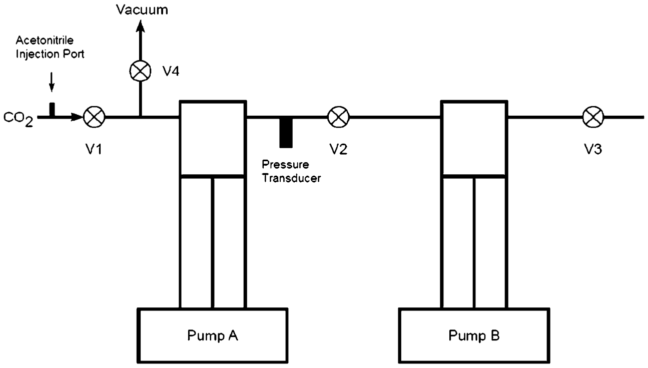

Figure 2. Experimental setup used to collect thermodynamic pressure−volume−temperature data.

Procedure. Pump B was fixed at a volume of ~10 mL, whereas the sample compartment, including the volume of the connecting tubing, had a volume of ~11 mL. Acetonitrile was introduced into the sample compartment by injecting a volume of 500μL via the injection port. The cosolvent was then transferred into the sample compartment using a stream of pressurized CO$_2$ (~6MPa) from the tank. Using pump A, the sample compartment was filled with CO$_2$ to a pressure of 8.30 MPa at a temperature of 393 K and valve 2 was closed. This procedure yielded a mol fraction of acetonitrile of 0.003.

Valve 4 was opened to expose the rest of the system to a vacuum. After sufficient evacuation (<70 milliTorr), valves 1 and 4 were closed and valve 2 was opened. The sample compartment was compressed to give a pressure of ~12 MPa using pump B and the exact pressure, volume, and temperature of the system were recorded. The pressure was reduced by successive ~0.7 MPa intervals by increasing the volume of pump B. At every interval, the pressure, volume, and temperature of the mixture were recorded. After pump B reached a maximum volume of 266 mL, the volume of pump A was increased. When both pumps reached their maximum volumes (532 mL total), the temperature was raised by 5 K and the pressure was increased in ~0.7 MPa intervals until it reached ~12 MPa. Again, the temperature was raised by 5 K and the pressure was decreased in the same manner as above. This cycle was repeated until the temperature reached 333 K.

Results and Discussion

The investigation of the behavior of acetonitrile in scCO$_2$ showed that the absorbance in the region between 2800 and 3100 cm^{-1} is highly dependent on the initial concentration of rhodamine B in solution. The spectrum of 10^{-4} M rhodamine B in the 0.0013 mol fraction acetonitrile/scCO$_2$ cosolvent shows an exceptionally high absorbance in the aforementioned region at a temperature of 313 K as shown in Figure 3.

As the temperature of the mixture increased, the volume of the sample compartment was increased automatically by the pump controller to maintain a constant pressure of 9.68 MPa. The volume increase caused a decrease in density of the mixture; thereby, decreasing the number of molecules in the beam path. One would expect that the absorbance should scale with the decrease in density, which does not appear to be the case as shown in Figure 3. Therefore, to eliminate bulk-phase behavior as the source of this dramatic absorbance enhancement, we measured the compressibility factor of the acetonitrile/scCO$_2$ cosolvent at the identical temperatures that we used in the spectroscopic investigation. The overlay plot of the three isotherms in Figure 4 shows that the general thermodynamic behavior of scCO$_2$ is unaffected by the addition of small amounts of acetonitrile when compared with standard data for CO$_2$.[10] Furthermore, between the temperatures of 313 and 333 K, the density decreased by a factor of 2, whereas the absorbance decreased by a factor of 12.

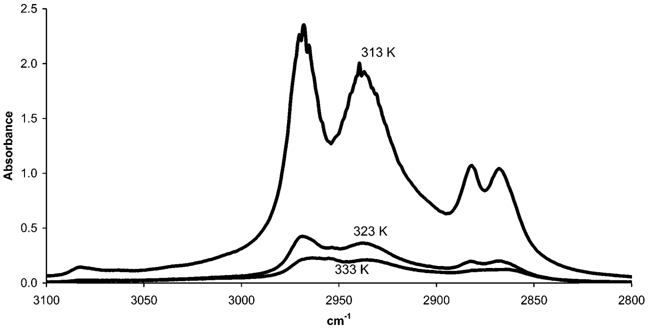

Figure 3. Acetonitrile (mol fraction = 0.0013 in scCO$_2$) in the presence of rhodamine B shows a dramatic increase in absorbance as temperature decreases in the infrared region between 2800 and 3100 cm^{-1}.

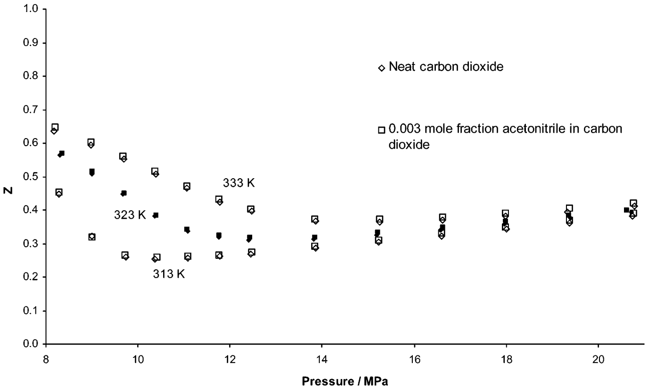

Figure 4. Overlay plot of different concentrations of acetonitrile in scCO$_2$ shows that the general thermodynamic behavior of scCO$_2$ is unaffected.

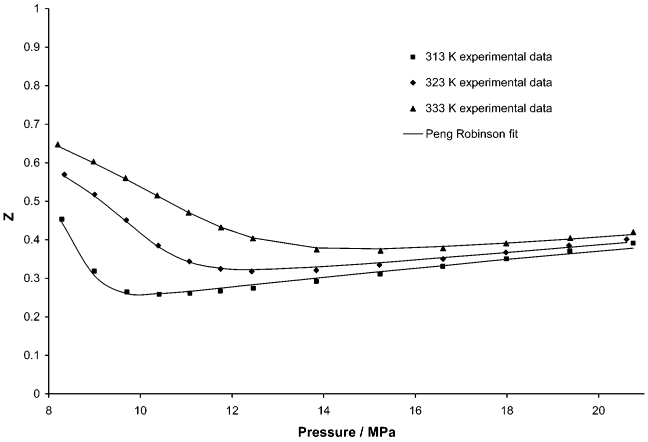

Figure 5. Pressure−volume−temperature data of 0.003 mol fraction acetonitrile in scCO$_2$ is modeled by a parameter-adjusted Peng−Robinson equation of state.

The Peng−Robinson equation of state provided an excellent fit of the experimental data when the parameters were adjusted using the mixing rules given in eqs 2 through 5. A close fit was obtained by the least-squares method using the binary interaction coefficients δ_{ij} and η_{ij} as variational parameters. The experimental data along with the theoretical fits are shown in Figure 5 for the binary mixture of 0.003 mol fraction acetonitrile in scCO$_2$, and Table 1 is a list of the standard errors for the fits to the data.

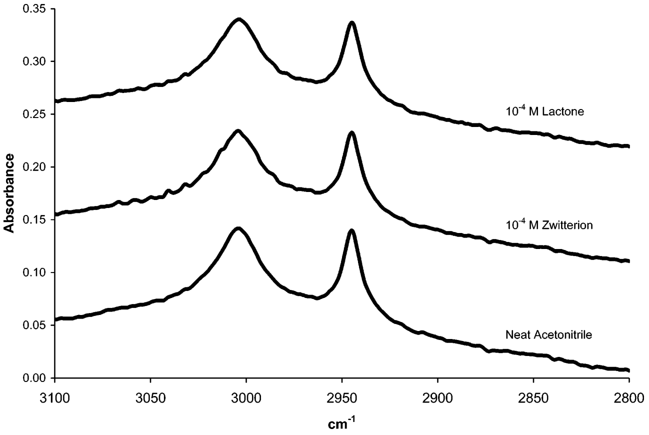

Figure 6. Combined, condensed phase FT-IR spectra of neat acetonitrile, 10^{-4} M rhodamine B zwitterion in acetonitrile, and 10^{-4} M rhodamine B lactone in acetonitrile (the spectra have been offset for display).

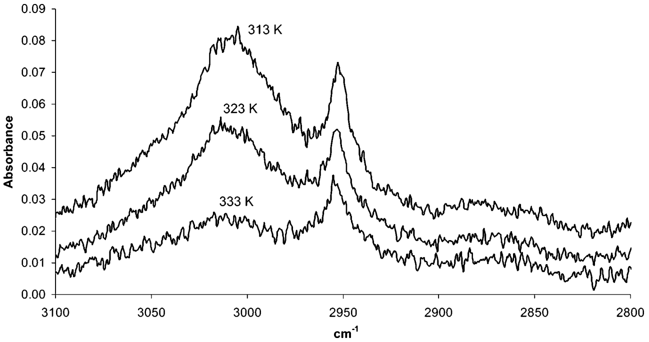

Figure 7. Acetonitrile (mol fraction 0.0013 in $scCO_2$) without rhodamine B at a pressure of 9.68 MPa.

TABLE 1: Binary Interaction Coefficients, δ_{ij} and η_{ij} and Standard Errors for the Peng−Robinson Fits to the Data

temp/K	δ_{ij}	η_{ij}	standard error
313	2.118	−754.784	0.0076
323	2.871	−739.826	0.0049
333	3.350	−726.541	0.0036

The compressibility data show that the bulk-phase behavior of the cosolvent is not the source of the absorbance enhancement; therefore, we must consider the molecular interactions between rhodamine B and acetonitrile as the source of this effect. A possible explanation could be that the rhodamine B itself absorbs in this region, thereby, causing the peaks to be a convolution of the vibrational modes of rhodamine B with the vibrational modes of acetonitrile in the region between 2800 and 3100 cm^{-1}. To test this theory, we collected the FT-IR absorbance spectra of 10^{-4} M rhodamine B zwitterion in acetonitrile, 10^{-4} rhodamine B lactone in acetonitrile, and neat acetonitrile. These spectra, shown in Figure 6, reveal that rhodamine B at this concentration or lower does not exhibit a measurable absorbance in the region between 2800 and 3100 cm^{-1}.

To determine how acetonitrile behaves in $scCO_2$ without rhodamine B, we collected spectra at the temperatures that we used for the $scCO_2$/acetonitrile/rhodamine B solution. Figure 7 shows the FT-IR spectra of 0.0013 mol fraction acetonitrile in $scCO_2$ at 313, 323, and 333 K.

We cannot make any general conclusions about the behavior of acetonitrile in $scCO_2$ from these spectroscopic data because the absorbance is extremely low (<0.1 in all cases) and the peaks at 3009 and 2954 cm^{-1} appear to rise from a sloping baseline. That said, when one compares the spectra of Figure 7 with the spectra of Figure 3, it is clear that acetonitrile in $scCO_2$ without rhodamine B behaves dramatically different than it does in the presence of rhodamine B.

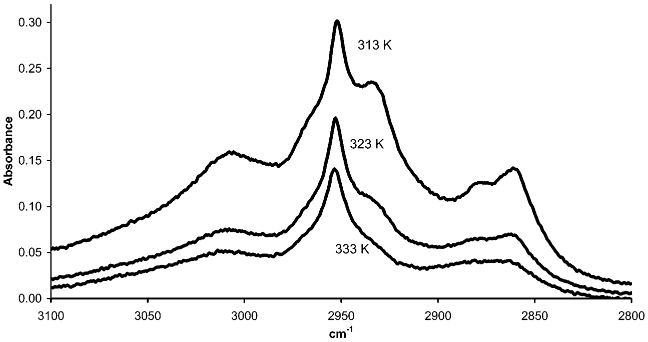

Figure 8. FT-IR spectrum of 10^{-5} M rhodamine B in 0.0013 mol fraction acetonitrile in $scCO_2$.

Hinckley and Seybold have demonstrated in their work that, in a variety of solvents, the equilibrium between the zwitterion and lactone of rhodamine B favors the lactone form at high temperatures.[21] As we increased the temperature of the $scCO_2$/acetonitrile/rhodamine B solution from 313 to 323 K, the equilibrium shifted to favor the lactone, which is soluble in both the acetonitrile and the neat $scCO_2$. Initially, the acetonitrile forms a cluster of molecules around the zwitterion in the cybotactic region. The lactone leaves the acetonitrile solvent sphere and migrates into the $scCO_2$, which in the bulk phase, has nearly unlimited solvation capacity. As the lactone leaves the acetonitrile solvent sphere, the equilibrium concentration is reestablished according to Le Châtelier's principle until all the zwitterion is depleted and all the rhodamine B exists in the lactone form. If the absorbance enhancement of the acetonitrile is caused by the acetonitrile molecules clustering around the rhodamine B zwitterion, then the abrupt decrease in absorbance as a function of the increasing temperature could be explained as the acetonitrile molecules leaving the cluster formation and becoming dispersed in the solution. We found that this decrease is less pronounced in solutions containing a lower initial concentration (10^{-5} M rhodamine B) of zwitterion as shown in Figure 8. The acetonitrile absorbance at high temperatures decreases because the zwitterion has been depleted and the decrease is similar to that observed in the absence of rhodamine B. Also, the spectrum of the 10^{-5} M rhodamine B shows peaks that we observe in neat acetonitrile as well as those present in the 10^{-4} M rhodamine B solution.

Although the absorbance trend observed at a concentration of 10^{-4} M rhodamine B is still evident at 10^{-5} M, the spectrum for the lower concentration is quite different, in that the peaks present in neat acetonitrile appear along with the peaks present in the 10^{-4} M rhodamine B solution. Acetonitrile possesses C_{3v} symmetry, and we assign the peak at 2954 cm^{-1} as the $\nu_1(a_1)$ vibration, the peak at 3009 cm^{-1} is the $\nu_5(e)$ vibration, and the peak at 2868 cm^{-1} is the $2\nu_6(A_1)$ vibration.[23] Perhaps, the interaction between rhodamine B and acetonitrile causes the peaks to shift depending on the local environment. Work done by Ke and co-workers on benzoic acid in $scCO_2$ with methanol as the cosolvent revealed that the hydrogen bonding that occurred between methanol/benzoic acid and benzoic acid/benzoic acid caused the peak due to the C═O stretch to shift such that three distinct peaks were present in the infrared spectrum near 1745 cm^{-1}.[24] All three peaks were attributed to the C═O stretch where the peak at 1745 cm^{-1} was due to benzoic acid monomer, the peak at 1725 cm^{-1} was due to the

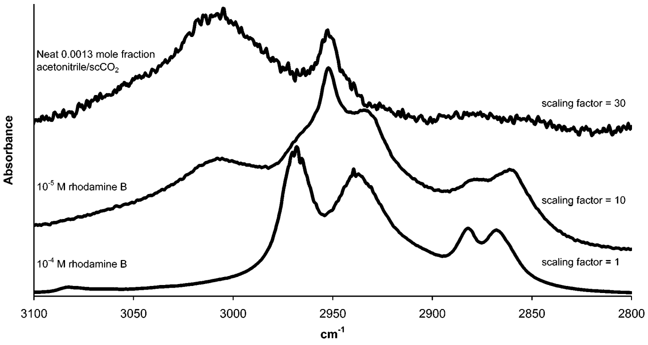

Figure 9. Scaled FT-IR spectra of the 10^{-4} M rhodamine B, 10^{-5} M rhodamine B, and neat 0.0013 mol fraction acetonitrile/scCO$_2$ at 313 K.

TABLE 2: Peak Assignments for the 2800 cm^{-1} to 3100 cm^{-1} Region of the FT-IR Spectra

peak position/cm^{-1}	assignment
Neat Cosolvent	
3009	ν_5
2954	ν_1
2868	$2\nu_6$
10^{-4} M Rhodamine B in Cosolvent	
2968	ν_5 perturbed
2939	ν_1 perturbed
2882	?
2868	$2\nu_6$unperturbed
10^{-5} M Rhodamine B in Cosolvent	
3009	ν_5 unperturbed
2968	ν_5 perturbed
2954	ν_1 unperturbed
2938	ν_1 perturbed
2882	?
2864	$2\nu_6$unperturbed

benzoic acid/methanol hydrogen bonded complex, and the peak at 1705 cm^{-1} was due to the benzoic acid hydrogen bonded dimer. Using this same argument for the interaction between rhodamine B and acetonitrile, we would reason that the solvated complex causes theν_1 and ν_5 vibrations of acetonitrile to redshift in the 10^{-4} M rhodamine B solution and these same modes to each split into two distinguishable peaks in the 10^{-5} M rhodamine B solution due to the two different environments in which acetonitrile exists. Figure 9 is an overlay of the 10^{-4} M rhodamine B, 10^{-5} M rhodamine B, and neat 0.0013 mol fraction acetonitrile/scCO$_2$ at 313 K. Please note that the spectra have been scaled independently (the scaling factors are given in the figure) and offset in order to compare the peak profiles. Table 2 summarizes the assignments of the peaks in the spectra where the peaks that result from the interaction of rhodamine B with acetonitrile are defined as “perturbed” vibrations.

Although this argument addresses the additional peaks that we observe in the FT-IR spectra, it does not explain either the absorbance enhancement that we observe at 313 K or the fact that the unperturbed modes of acetonitrile are enhanced to the same degree that the perturbed modes are enhanced in the 10^{-5} M solution. Furthermore, the spectra shown in Figure 6 of rhodamine B in neat acetonitrile reveal that rhodamine B perturbs the vibrations of acetonitrile only when acetonitrile is at low concentration in scCO$_2$. Given the spectroscopic data on-hand and our investigation of the bulk-phase behavior of the acetonitrile/scCO$_2$ cosolvent, we can only confirm what is not responsible for the absorbance enhancement.

Conclusion

We discovered a dramatic absorbance enhancement between 2800 and 3100 cm^{-1} for acetonitrile while in the presence of rhodamine B in scCO$_2$. The results of the compressibility study allowed us to eliminate bulk-phase solvent behavior as the source of this dramatic enhancement. Though we cannot be certain about the specific molecular interactions that cause this effect, we propose that it is solely dependent upon the presence of rhodamine B. One possible explanation for this phenomenon is that the absorption cross-section of the acetonitrile is increased while in the presence of rhodamine B. If that is true, then one ought to observe a different spectrum using Raman spectroscopy. Conveniently, all of the vibrational modes of acetonitrile are both IR and Raman active. Also, the strong interference due to the absorbance of CO$_2$ appears in different regions because of the rule of mutual exclusivity. Therefore, further investigation of the scCO$_2$/acetonitrile/rhodamine B mixture at varying concentrations using both FT-IR and Raman spectroscopy may lead to greater understanding of the molecular interactions between acetonitrile and rhodamine B in supercritical CO$_2$.

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