Solvatochromic Study of Basic Cosolvents in Supercritical Ethane

K. P. Hafner, F. L. L. Pouillot, C. L. Liotta, and C. A. Eckert
Schools of Chemical Engineering and Chemistry and Specialty Separations Center,
Georgia Institute of Technology, Atlanta, GA 30332

Supercritical fluids (SCFs) are effective solvents for extractions from solid matrices (soil remediation, decaffeination), and for reactions, ranging from polymerization to phase-transfer catalysis (Dillow et al., 1996; Savage et al., 1995; Bruno and Ely, 1991). As paradoxical as it might sound, supercritical fluids are particularly advantageous for industrial applications because they have very little solvating power close to and below their critical point. This tunability of supercritical fluids allows the easy recycling of SCFs in chemical processes. However, used as such, SCFs are not very selective. To improve their loading and/or selectivity, one can "tailor" them by using a cosolvent, usually a small alcohol like methanol, in quantities ranging from 1 to 10 mol %.

Some cosolvent effects can be rationalized in terms of specific molecular interactions occurring between the solute and the cosolvent (Van Alsten and Eckert, 1993; Ekart et al., 1993; Ting et al., 1993), and some studies have focused more specifically on these interactions, whether of the hydrogen-bonding (Kazarian et al., 1993 and references therein) or the charge-transfer type (Knutson, 1994; Kajimoto et al., 1988). Spectroscopic probes, whose absorption and emission spectra are very sensitive to their cybotactic environment, have been used extensively in liquid and supercritical solvents in order to characterize solvent mixture rearrangement upon solvation (Ikushima et al., 1992; Deye and Berger, 1990; Yonker and Smith, 1988; Sigman et al., 1985; Hyatt, 1984).

A very successful quantitative treatment of solvent effects is the linear solvation energy relationship (LSER), of the following form, where XYZ is a free-energy-related observable quantity (Kamlet and Taft, 1983):

$$XYZ = XYZ_o + s\pi^* + a\alpha + b\beta. \qquad (1)$$

The correlation separates the contributions of solute/solvent interactions on the UV/vis absorption of dyes into electrostatic and specific interactions. The first term includes dipolarity and polarizability effects; the α term accounts for the solvent's hydrogen-bond donor ability, and the β term accounts for its hydrogen-bond accepting ability. The coefficients of the regression (a, b, and s) indicate the sensitivity of the probes to such interactions.

We used the methodology associated with this relation to study hydrogen bonding interactions between several basic cosolvents and 4-nitrophenol in SCF ethane ($T_c = 305.4$ K, $P_c = 48.8$ bar), which cannot participate in specific interactions. The results reported are the maximum wavelength of absorption of several probes in SCF ethane and cosolvent-modified SCF solutions from 50 to 100 bar at 35°C.

Experimental Studies

UV-vis absorption experiments were conducted in a double-beam UV-vis spectrophotometer modified for high-pressure applications (Tomasko, 1992). The two identical high-pressure optical cells, a sample cell, and a reference cell, have stir bars for mixing, a path length of 7.55 mm, and an internal volume of 5.88 mL.

A piston-type generator (High Pressure Equipment Co. Model 87-6-5) supplied pressure to the sample and reference cells, and pressure was monitored with a calibrated Heise pressure gauge (Model 901B) with an accuracy of ±0.35%. Temperature was maintained using thermoelectric heaters (MELCOR—Materials Electronic Products Corporation CP 1.4-35-06L) and measured within the sample cell as the resistance of a thermistor probe (Omega type 44032) calibrated to ± 0.1°C. An injector and switching valve (Valco Instruments Model C6UW) were used for direct introduction of cosolvent into the sample and reference cells individually. External sample loop sizes of 2, 5, and 15 μL were used with this cosolvent injection system.

Spectra were recorded as a function of increasing pressure at constant probe and cosolvent concentrations. The probe was dissolved in dichloromethane and loaded into the sample cell using a syringe. After allowing for evaporation of the dichloromethane, the sample cell was flushed with multiple volumes of low-pressure ethane to remove trace dichloromethane and to displace air out of the system. When desired, the cosolvent was added to each cell individually by pushing it through a sampling loop while pressurizing the

---

Correspondence concerning this article should be addressed to C. A. Eckert.

cells. The system was pressurized to a desired low-pressure setpoint, and after equilibration, a wavelength scan was done. Spectra were then recorded in order of increasing pressure. The estimated error in wavelength is ± 1 nm. This relatively large error is due essentially to the peak fitting in the data analysis. The probe absorbance of interest is a shoulder on a larger peak that could not be fitted exactly since it had to be cut at 220 nm, the lower limit in the UV region.

Results and Discussion

All of the cosolvents used in this study have a negligible acidity, and the supercritical solvent ethane is polarizable, but nonpolar and aprotic. 4-nitroanisole is a nearly identical aprotic analog of 4-nitrophenol. The two probes have similar sensitivities to polar environments, and they have been found to have very similar s parameters (-2.717 and -2.41, respectively) for use in the LSER equation. Therefore, the effect of basicity on 4-nitrophenol can be separated from that of polarity by subtracting the shift of 4-nitroanisole by the same cosolvent. The addition of triethylamine (TEA) and propionitrile, independently, to SCF ethane (Figure 1) results in a significant shift for 4-nitrophenol, while no shift is observed for 4-nitroanisole in the same cosolvent/solvent environment. These results are consistent with the fact that hydrogen bonding is possible between the cosolvent TEA and 4-nitrophenol, but not with 4-nitroanisole. Also, the effect of polarity (e.g., propionitrile), on the spectral shift for 4-nitroanisole is negligible within experimental error at the same conditions. Therefore, the wavelength shifts of 4-nitrophenol observed with other cosolvents can be attributed to basicity contributions of the cosolvent to the solute environment.

Figure 2 shows the shifts of maximum absorption of 4-nitrophenol in SCF ethane with selected basic cosolvents and pure ethane as a function of density at 35°C. Experimental data are given in Table 1. The shifts are in the same order as the Kamlet-Taft solvent basicity parameters, which are indicated in Figure 2. However, the shift induced by any cosolvent is smaller than the shift computed from direct application of the solvatochromic equation. In effect, the solute environment is not saturated by the cosolvent. To illustrate this point, Figure 3 shows the effect of TEA concentration on the shift of maximum-wavelength absorption of 4-nitrophenol in liquid cyclohexane at 25°C. There are two regimes of solvatochromism; there is a sharp increase in the wavelength shift with increasing cosolvent concentration, which extends from 0 to 4×10^{-4} mol fraction, and there is a long, slow increase upwards to the wavelength shift obtained in pure TEA. The first regime corresponds to complex formation between TEA and 4-nitrophenol, while the second regime corresponds to a gradual modification of the dielectric properties of the solvent.

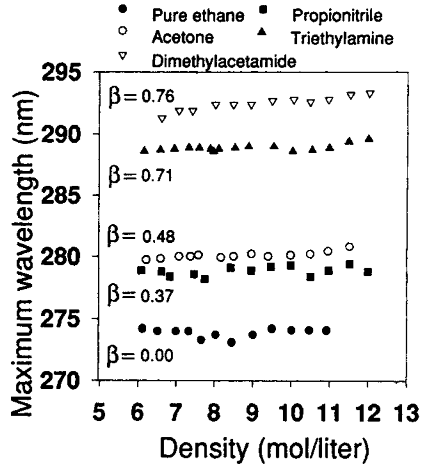


Figure 2. Effect of selected cosolvents on the maximum-wavelength absorption of 4-nitrophenol.

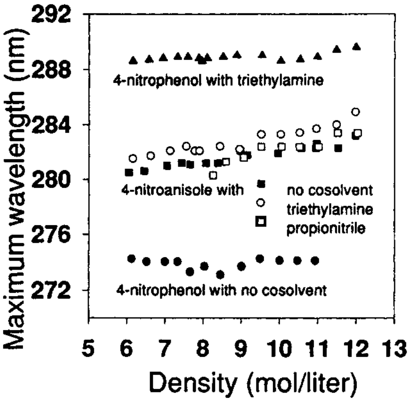
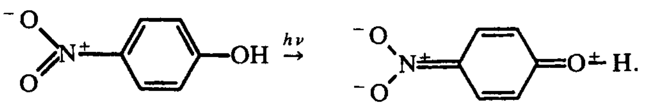


Figure 1. Effect of triethylamine and propionitrile on the maximum-wavelength absorption of 4-nitrophenol.

When excited by UV light, the π electrons of 4-nitrophenol undergo a transition to the π^* state. This electronic transition is connected with an intramolecular charge transfer from the electron donor moiety (here OH, and OCH_3 for 4-nitroanisole), to the electron acceptor moiety (here NO_2) through the aromatic system (Reichardt, 1994). As a consequence, 4-nitrophenol, which is a strong hydrogen-bond donor in its ground state, is an even stronger hydrogen-bond donor in its excited state. This transition can be represented in terms of valence-bond structures (Siverstein et al., 1991; Parker and Brody, 1964).



The more positive oxygen favors the acidity of the hydrogen in the excited state. Hydrogen bonding itself has the effect of displacing sigma electrons, and this is the main reason for the modification of the $\pi \rightarrow \pi^*$ bands upon hydrogen bonding.

When only the complexed form exists, the addition of a basic cosolvent modifies the solvent environment and induces a shift of the complex in terms of the $\pi \rightarrow \pi^*$ electronic transition by differential solvation of its ground and excited states. By elimination of the polarity effect on the observed wavelength shifts, the hydrogen bonding contribution corresponds to an electronic transition *of the complex* from the ground state to the excited state. Thus, our observations at high pressure show the sums of the electronic transitions of pure 4-nitrophenol and hydrogen-bonded complexes between

Table 1. Experimental Data for 4-Nitroanisole and 4-Nitrophenol in Cosolvent/SCF Ethane Solutions

4-Nitroanisole in Pure Ethane		4-Nitroanisole with Triethylamine		4-Nitroanisole with Propionitrile		4-Nitrophenol in Pure Ethane	
Density (mol/L)	λ max (nm)	Density (mol/L)	λ max (nm)	Density (mol/L)	λ max (nm)	Density (mol/L)	λ max (nm)
6.44	280.7	6.15	281.3	8.25	280.3	6.12	274.2
7.04	281.1	6.63	281.6	8.59	281.3	6.52	274.0
7.43	280.5	7.14	281.8	9.06	281.6	7.00	274.0
7.65	280.4	7.55	282.1	9.52	282.4	7.33	274.0
8.07	280.4	7.78	281.6	10.05	282.4	7.66	273.3
8.38	280.4	7.90	281.5	10.52	282.4	8.04	273.7
8.97	281.8	8.44	282.0	11.02	282.4	8.46	273.1
9.15	282.0	8.96	282.0	11.52	283.4	9.01	273.7
9.96	281.5	9.52	282.4	12.04	283.4	9.50	274.2
10.57	281.9	10.04	282.6			10.01	274.1
10.97	282.2	10.53	282.8			10.48	274.1
10.95	282.2	10.97	283.4			10.94	274.1
11.53	282.5	11.50	283.8			11.48	275.3
11.99	282.4	12.00	284.9				

4-Nitrophenol with Triethylamine		4-Nitrophenol with Dimethylacetamide		4-Nitrophenol with Acetone		4-Nitrophenol with Propionitrile	
Density (mol/L)	λ max (nm)	Density (mol/L)	λ max (nm)	Density (mol/L)	λ max (nm)	Density (mol/L)	λ max (nm)
6.15	288.6	6.12	291.1	6.22	279.7	6.08	278.8
6.57	288.7	6.61	291.3	6.59	279.8	6.61	278.9
6.94	288.8	7.06	291.9	7.07	280.0	6.83	278.8
7.32	288.9	7.41	291.9	7.38	280.0	7.46	278.4
7.59	288.9	8.01	292.4	7.59	280.1	7.74	278.6
7.88	288.8	8.48	292.4	8.17	279.9	8.42	278.2
8.10	288.8	8.94	292.4	8.50	280.0	8.95	279.1
7.96	288.6	9.49	292.7	8.97	280.2	9.47	278.9
8.52	288.9	10.05	292.8	9.40	280.0	9.99	279.2
8.88	289.0	10.48	292.6	9.99	280.1	10.50	279.3
9.54	289.0	10.96	292.8	10.50	280.2	10.97	278.4
10.03	288.6	11.53	293.2	10.96	280.4	11.52	278.9
10.54	288.7	12.02	293.3	11.52	280.8	12.03	279.4
10.99	288.9						
11.49	289.4						
12.00	289.6						

the solute and the cosolvent; the maximum wavelength of absorption is not affected by the change in solvent density. This is not surprising considering that at 35°C, the dielectric constant of ethane varies only from 1.22 to 1.47 over the range of densities investigated.

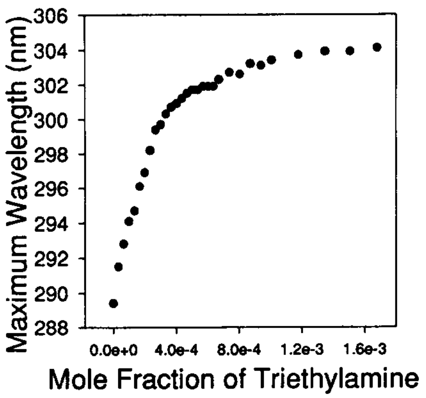


Figure 3. Effect of triethylamine mole fraction on the maximum wavelength absorption of 4-nitrophenol (in cyclohexane at ambient conditions).

Conclusions

Solvatochromism has been applied to supercritical fluid mixtures by several investigators, and it has been shown that the solute's cybotactic region is different from the bulk environment. A study of specific interactions between a basic solute and protic cosolvents has been reported previously (Knutson et al., 1995). Here, the interaction of protic solutes through hydrogen bonding in supercritical ethane with basic cosolvents has been shown. These strong interactions play an important role in the loading ability and selectivity of modified supercritical fluids. To be quantitative, measurements of thermodynamic effects are necessary for solvent/cosolvent/SCF systems, for example, cosolvent effects and solubility. More information on the equilibrium involving 4-nitrophenol and the basic cosolvents could be obtained by doing experiments at varying concentrations. Previous investigators have shown that preferential solvation occurs in supercritical fluids due to strong electrostatic interactions. We have also shown that specific interactions can readily take place between solutes and cosolvents in the whole range of densities studied, from 6 to 12 mol/L in supercritical ethane at 35°C. Also, the Kamlet-Taft solvent parameters for the cosolvents permit the qualitative ranking of the wavelength shifts observed and provide a reasonable basis for cosolvent selection in SCF processing.

Acknowledgments

We are grateful for the financial support of E. I. DuPont de Nemours and Company.

Literature Cited

Bruno, T. J., and J. F. Ely, *Supercritical Fluid Technology: Reviews in Modern Theory and Applications*, CRC Press, Boca Raton, FL (1991).

Deye, J. F., and T. A. Berger, "Nile Red as a Solvatochromic Dye for Measuring Solvent Strength in Normal Liquids and Mixtures of Normal Liquids with Supercritical and Near Critical Fluids," *Anal. Chem.*, **62**, 615 (1990).

Dillow, A. K., S. L. J. Yun, D. Suleiman, D. L. Boatright, C. L. Liotta, and C. A. Eckert, "Kinetics of a Phase Transfer Catalysis Reaction in Supercritical Fluid Carbon Dioxide," *Ind. Eng. Chem. Res.*, **35**, 1801 (1996).

Ekart, M. P., K. L. Bennett, S. M. Ekart, S. G. Gurdial, C. L. Liotta, and C. A. Eckert, "Cosolvent Interactions in Supercritical Fluid Solutions," *AIChE J.*, **39**, 235 (1993).

Hyatt, J. A., "Liquid and Supercritical Carbon Dioxide as Organic Solvents," *J. Org. Chem.*, **49**, 5097 (1984).

Ikushima, Y., N. Saito, and M. Arai, "Supercritical Carbon Dioxide as Reaction Medium: Examination of Its Solvent Effects in the Near-Critical Region," *J. Phys. Chem.*, **96**, 2293 (1992).

Kajimoto, O., M. Futakami, T. Kobayashi, and K. Yamasaki, "Charge-Transfer State Formation," *J. Phys. Chem.*, **92**, 1347 (1988).

Kamlet, M. J., J.-L. Abboud, M. H. Abraham, and R. W. Taft, "Linear Solvation Energy Relationships. 23. A Comprehensive Collection of the Solvatochromic Parameters, π^*, α, β, and Some Methods for Simplifying the Generalized Solvatochromic Equation," *J. Org. Chem.*, **48**, 2877 (1983).

Kazarian, S. G., R. B. Gupta, M. J. Clarke, K. P. Johnston, and M. Poliakoff, "How is Hydrogen-Bonding Influenced by Solvent Density? The Spectroscopic Study and Modeling of the Interaction between a Proton Donor and Acceptor from the Gas to Supercritical Fluid State," *J. Amer. Chem. Soc.*, **115**, 11099 (1993).

Knutson, B. L., "Charge-Transfer Complex Formation in a Supercritical Fluid," PhD Thesis, Chap. IV, Georgia Inst. of Technol., Atlanta, GA (1994).

Knutson, B. L., K. L. Bennett, C. L. Liotta, and C. A. Eckert, "Benzophenone as a Probe of Local Cosolvent Effects in Supercritical Ethane," *Ind. Eng. Chem. Res.*, in press (1997).

Parker, A. J., and D. Brody, "Solvation of Ions. Part IV. The Electronic Absorption Spectra of Some Group VI Anions and their Conjugate Acids in Protic and Dipolar Aprotic Solvents," *J. Chem. Soc.*, 4061 (1963).

Reichardt, C., "Solvatochromic Dyes as Solvent Polarity Indicators," *Chem. Rev.*, **94**, 2319 (1994).

Savage, P. E., S. Gopalan, T. I. Mizan, C. J. Martino, and E. E. Brock, "Reactions and Supercritical Conditions: Applications and Fundamentals," *AIChE J.*, **41**, 1723 (1995).

Sigman, M. E., S. M. Lindley, and J. E. Leffler, "Supercritical Carbon Dioxide: Behavior of π^* and β Solvatochromic Indicators in Media of Different Densities," *J. Amer. Chem. Soc.*, **107**, 1471 (1985).

Siverstein, R. M., G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 5th ed., Wiley, New York (1991).

Ting, S. S., D. L. Tomasko, S. J. Macnaughton, and N. R. Foster, "Chemical-Physical Interpretation of Cosolvent Effects in Supercritical Fluids," *Ind. Eng. Chem. Res.*, **32**, 1482 (1993).

Tomasko, D. L., "Spectroscopic and Thermodynamic Studies of Supercritical Fluid Solutions Containing a Cosolvent," PhD Thesis, Univ. of Illinois at Urbana-Champaign (1992).

Van Alsten, J. G., and C. A. Eckert, "Effect of Entrainers and of Solute Size and Polarity in Supercritical Fluid Solutions," *J. Chem. Eng. Data*, **38**, 605 (1993).

Yonker, C. R., and R. D. Smith, "Solvatochromic Behavior of Binary Supercritical Fluids: The Carbon Dioxide/2-Propanol System," *J. Phys. Chem.*, **92**, 2374 (1988).

Manuscript received Oct. 16, 1995, and revision received Sept. 9, 1996.