SUPERCRITICAL FLUID SOLVENT PROPERTIES AS A FUNCTION OF TEMPERATURE AND DENSITY MEASURED BY THE SOLVATOCHROMIC METHOD

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INTRODUCTION

In the past few years supercritical fluids have attracted interest as solvents for both analytical and chemical process applications. They possess interesting combinations of solvent properties, such as high diffusivity and liquid-like solvating properties which can be drastically changed with moderate changes in temperature and pressure, making them attractive for a variety of uses.

One hindrance to the further development of supercritical fluid extraction or chromatographic techniques is that relatively little is known about the dependence of solvent properties of supercritical fluids, and fluid mixtures, upon various physical parameters. This study of the interactions between solutes and supercritical fluid solvents was aimed at extending the understanding of supercritical fluids as solvents, and to help in the selection of the most appropriate fluid for a particular application.

EXPERIMENTAL

Absorption spectra were measured on a Cary model 1605 spectrophotometer used in the dual beam mode. The measurements using liquid solvents were made using 1 cm square quartz cells with a solvent blank in the reference beam. The vapor and supercritical fluid spectra were taken versus air in the reference beam.

A specially constructed high pressure cell was used in taking the spectra in the supercritical fluid solvents. This cell has a cylindrical stainless steel body approximately 1" in diameter which has a 3/16" diameter hole drilled along the axis. Two connections for 1/16" tubing are present to allow for inlet and outlet flow. Each end of the cell has a seat for a 1/4" diameter 1/4" thick quartz window and is threaded to accept a brass nut. A 1/4" o.d. Teflon o-ring is placed on each side of each window to provide cushioning and a gas tight seal. The optical path between the windows was approximately 1/4". The absorption cell was wrapped with heating tape, insulated and equipped with a thermocouple. This arrangement allowed temperature regulation to within ±0.5 C.

A Varian 8500 syringe pump was used to supply the supercritical fluid solvent at the appropriate pressure. The pump was connected to the cell via a Rheodyne valve equipped with a 10 μl sample loop. A pressure transducer was connected to the cell outlet to allow accurate pressure measurement.

The experiments were conducted as follows: the sample was loaded in to sample loop and the valve switched to allow fluid from the pump to flow to the cell through the loop. A shut-off valve at the cell outlet was opened to allow solvent flow through the cell and the absorbance at a selected wavelength was measured to detect the appearance of the sample in the cell cavity. Often it was necessary to

partially purge the cell with additional solvent to decrease the sample concentration to the point that the absorbance measurement was on scale. When a usable concentration of sample had been obtained the outlet valve was closed and the absorption spectrum was taken under isobaric and isothermal conditions. After a scan the pressure or temperature was increased to the next level and the cell allowed to equilibrate at the new conditions before the next measurement. In all cases the spectrum of the pure fluid was also recorded to insure that there was no interference with the spectrum of the solute.

RESULTS AND DISCUSSION

Since interest centers on the specific interactions between solute and solvent, and how those interactions change as the density and composition of the supercritical fluid solvent are varied, an experimental technique is needed which is sensitive to the cybotactic environment of the solute. One such technique is the solvatochromic method, which probes the effect of solvent on the optical absorption spectrum of the solute molecule (1).

Using the solvatochromic method to study solvent effects of supercritical fluids is particularly efficacious in view of the extensive work of Taft and coworkers in measuring the solvatochromic shifts of a large number of solute molecules in a wide range of liquid solvents (2). They have been successful in developing a π^* solubility scale which encompasses a wide range of solute types and which can account for variance in several solvent properties, including polarity, polarizability, hydrogen bonding ability, etc.

The π^* polarizability scale was originally developed from observations of solvent effects on $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the probe molecules. By using a select group of solutes and solvents which minimized hydrogen-bonding, Taft and co-workers were able to relate solvent polarity to relative shifts in the position of the absorption maximum. These data were primarily dependent on the interaction between solute and solvent dipoles. Further refinements have since been made to account for solvent-solvent interaction, the presence of induced dipoles, and hydrogen bonding between solute and solvent (3).

Since the π^* scale is well established for the study of conventional solvents it may afford a convenient basis for the comparison of liquid and supercritical solvents. Further, by determining the various scale parameters for these fluids it should be possible to obtain some insight into the specific solvation mechanisms involved, and how those mechanisms change as the solvent composition and conditions are altered.

The compounds 2-nitroanisole (2NA) and 4-ethylnitrobenzene (4ENB) were chosen to be the initial probe molecules in our initial solvatochromic studies of supercritical fluid solvents. These compounds have been previously used by Taft et al. in the studies of conventional liquid solvents, thus making it easier to integrate supercritical fluid solvents into the π^* solvent polarity scale. It is also advantageous that these compounds are liquids and have absorption maxima at convenient wavelengths in the UV.

The maxima of the absorption spectrum of each of these compounds are shifted in wavelength when in liquid solvents of varying polarities (Table 1). The position of the absorption band of the vapor (essentially a solvent with no polarity or hydrogen bonding ability) is used as a reference. As the solvent becomes more polar the absorption maximum is shifted to longer wavelengths (lower energies). This type of shift indicates that the excited electronic state is being stabilized

TABLE 1. Wavelength of Absorption Maximum of 2NA and 4ENB in Various Solvents

Solvant[a]	2NA Observed[b]	2NA π^*[c]	4ENB Observed	4ENB π^*
Vapor	286	285	250	251
CO_2(a)	295	--	257	--
N_2O(a)	297	--	--	--
$CClF_3$(a)	299	--	--	--
NH_3(a)	303	--	260	--
Pentane(d)	306	305	263	265
Tetrahydrofuran	318	312	273	275
Acetonitrile	324	325	276	278
Methanol	322	322	272	275

(a) The supercritical fluids (CO_2, N_2O, $CClF_3$, and NH_3 had $T_r = 1.01$ and $P_r = 1.05$.
(b) Observed wavelength of absorption maxima, in nm.
(c) Predicted by π^* scale using parameters from Table 2.
(d) Predicted wavelength using parameters for heptane.

with respect to the ground electronic state, thus decreasing their energy gap. These results are in accord with the prediction of the π^* model when the proper coefficients are used for each of the solutes and solvents (Table 2) (4).

Having established the behavior of the probe molecules in conventional solvents, it is possible to compare their behavior in some common supercritical fluids. It is evident from Table 1 that supercritical fluid solvents at moderate reduced temperatures and pressures have relative solvating abilities in accordance with their polarities. The less polar fluids CO_2, N_2O, and $CClF_3$ (Freon-13) shift the absorption maxima to an intermediate position between that measured in the vapor phase and pentane. NH_3 is more polar and the wavelength of the maximum falls close to that of pentane.

The interest in using supercritical fluids as solvents for extraction processes and chromatography is in great extent due to the fact that it is possible to change the solvent properties of the fluid by changing the density and temperature. A large part of the interest in using the solvatochromic method to study these solvents is to see if it is possible to observe and quantify these changes in solvating ability via the absorption shift.

TABLE 2. π^* Solubility Scale Parameters

Solvent	π^*	Solute	ν_o (cm^{-1})	-s
Vapor (4)	-1.06	2NA (2)	32.56 kK	2.428
Heptane (4)	-0.08	4ENB (2)	37.60 kK	2.133
Tetrahydrofuran(4)	0.58			
Acetonitrile(4)	0.75			
Methanol (3)	0.60			

Figure 1 shows that the wavelength of the absorption maximum changes most rapidly at pressures just above the critical pressure. This observation can be explained by examining the relationship between pressure and density is a non-linear function of pressure, and changes most rapidly at reduced pressures near 1. The data are re-plotted in Figure 3 to illustrate the relationship between the energy of the transition (in wave numbers) and the fluid density. This plot also contains data obtained by maintaining a constant pressure and varying the temperature to change the density. It is apparent from this data that fluid density, and not temperature, is of primary importance in determining the amount of spectral shift. This correlation with fluid density is in agreement with the predictions of numerous solubility studies. Finally, Figure 4 shows how the absorption maximum varies with pressure for 2NA in NH_3.

Clearly, the solvatochromic method holds promise for comparison of supercritical fluid solvents with conventional liquid solvents, due to sensitivity to changes in solvation arising from varying the density of the fluid solvent. By using the data on pure fluid solvents as a foundation it should be possible to extend this work to the study of mixed supercritical fluid solvent systems. Since this technique probes the cybotactic environment of the solute it should be feasible to determine how the solvating power of a fluid changes as small amounts of a modifier are added.

ACKNOWLEDGMENTS

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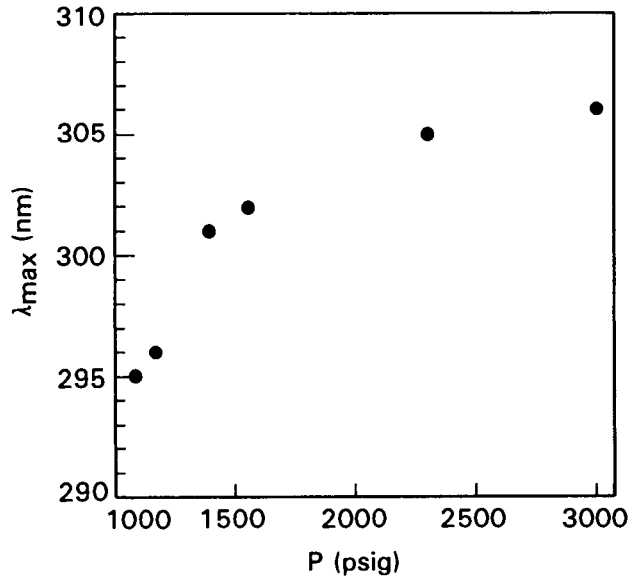
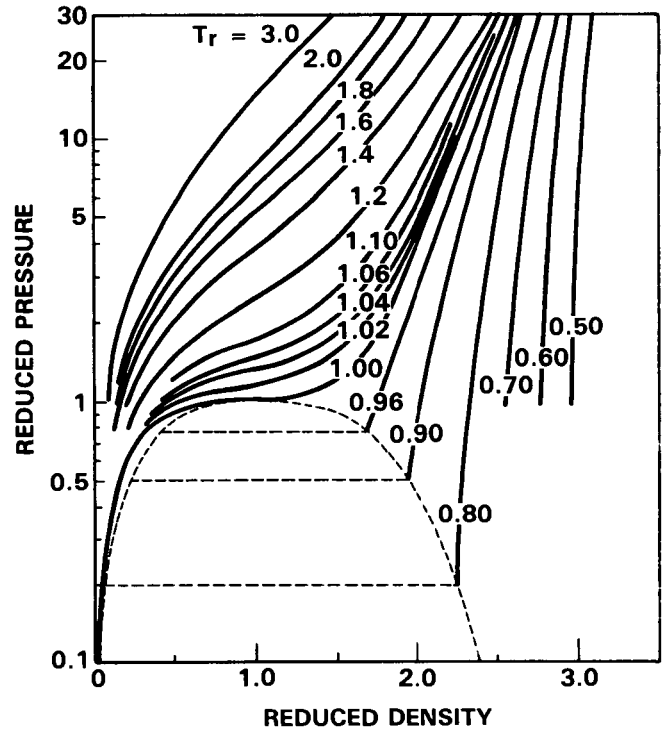


FIGURE 1. 2-Nitroanisole in CO_2. Temperature = 50°C.

TYPICAL PRESSURE-DENSITY BEHAVIOR



T_r = REDUCED TEMPERATURE

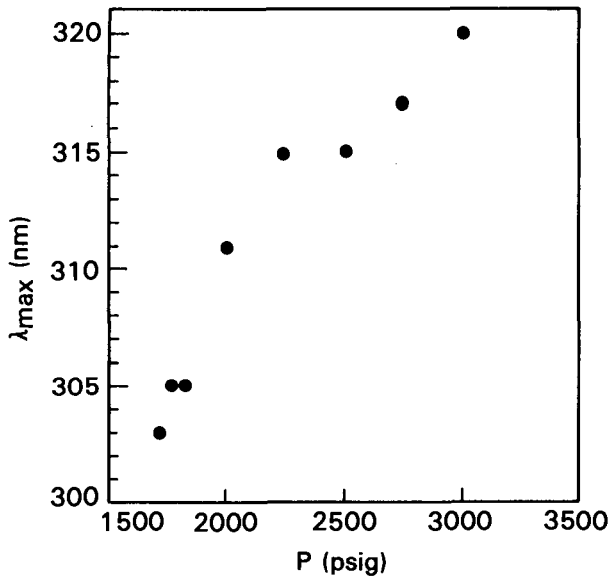


FIGURE 4. 2-Nitroanisole in NH_3. Temperature = 140°C.

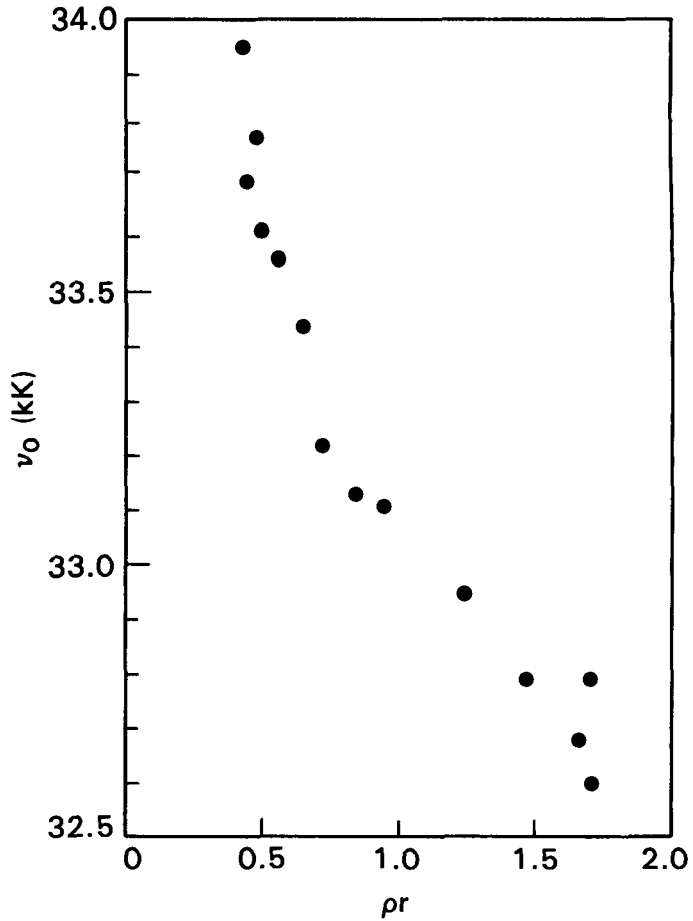


FIGURE 3. 2-Nitroanisole in CO_2.