Solvent Properties of Supercritical CO$_2$/HFC134a Mixtures

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The dipolarity/polarizability parameter, π^*, of Kamlet and Taft is used to characterize the solvent properties of CO$_2$/1,1,1,2- tetrafluoroethane (HFC134a) mixtures in the supercritical state. It is shown that preferential solvation of the solute by HFC134a occurs. The local composition of the polar constituent is shown to steadily decrease as the pressure is increased, but the local π^* value does not decrease below that of the bulk fluid. A mixture of 30 mol % HFC134a in CO$_2$ has properties similar to those of bulk HFC134a at high densities. Such a mixture is extremely useful for extraction purposes, as it has a critical temperature that is 42 °C lower than bulk HFC134a.

Introduction

Supercritical fluids have found wide application in extraction, chromatography, and catalysis because of the marked changes that can occur in solvent properties following modest changes in temperature or pressure.[1−5] It is very important, therefore, to characterize the effect of physical conditions on solvent properties. Numerous studies have been made to measure the solvation of solutes in supercritical fluids using solvatochromic shift parameters and fluorescence probes. Solvents studied via these techniques include CO$_2$, SF$_6$, Xe, C$_2$H$_6$, CHF$_3$, NH$_3$, CF$_3$CH$_2$F, CH$_2$F$_2$, and C$_2$HF$_5$.[6−17] These studies have shown that solvent−solute interactions cause an increase in the local solvent density surrounding the solute. This so-called local density augmentation has also been confirmed using molecular dynamics simulations and integral equation calculations. The area of local density augmentation has recently been reviewed by Tucker[18,19] and Brennecke.[20]

The majority of processes using supercritical fluids employ nonpolar molecules such as CO$_2$ or ethane. Modifying solvents are frequently added to supercritical fluids to increase the solvent polarity and hence increase solute solubility. The problems associated with many of the more polar modifying fluids such as water and methanol is that they have limited solubility and are frequently left as residues in the solute when the system is depressurized. Only a limited number of studies have been carried out into the solvent properties of supercritical fluid mixtures. Yonker and Smith[21] used the π^* parameter to study CO$_2$/2-propanol mixtures and found that the local composition of alcohol surrounding the solute could approach 4 times that in the bulk. Kim and Johnston studied a number of modifying cosolvents and showed that at low densities the local composition could be 10 times greater than the bulk value.[22] Both Johnston[23] and Brennecke[24] used fluorescence spectroscopy to study mixtures of CO$_2$ and CHF$_3$ and suggested that preferential solvation of the solute by CHF$_3$ took place.

We have recently shown that 1,1,1,2-tetrafluoroethane (HFC134a) (T_c = 374.21 K, p_c = 40.56 bar) and difluo-

romethane (HFC 32) (T_c = 351.26 K, p_c = 57.82 bar) are excellent solvents for supercritical extraction. Work by Poliakoff et al.[25] showed that mixtures of HFC134a with CO$_2$ have significantly lower critical temperatures than the pure HFC fluids and suggested that they should be good solvents for extraction purposes. The aim of the current work is to investigate how the composition of HFC134a/CO$_2$ mixtures affect the solvent properties of these mixtures and how the composition of the cybotactic region is affected by pressure.

Experimental Section

The experimental apparatus used to measure the solvatochromic shift in both liquid and supercritical states has been described in detail elsewhere.[15] A Beckman model DU 650 spectrophotometer was used to measure the UV/vis absorbance spectra. Light was fed into and out of the high-pressure optical cell via fiber optic cables (Hellma, Müllheim, FRG) equipped with a 662 QX prism adapter. The optical cell was made of 316 stainless steel that was encased in brass to aid heat flow. Sapphire windows 1 cm thick together with copper gas seals were used to allow light to be passed through the cell. The internal volume of the cell was approximately 1 cm^3 with the path length at 1 cm. A model 10−600 pump (Hydraulic Engineering Corp., Los Angeles) driven by compressed air was used to apply the appropriate pressure. An Fe/constantan thermocouple was employed to measure the cell temperature, which was retained (±0.5 °C) using a CAL 9900 heater. A UCC type PGE 1001.600 gauge was used to monitor the pressure (±2 bar). The solvent mixtures (ICI Klea group, 99.99%) and the indicator Nile Red (Aldrich) were used as received. Nile Red concentrations ranged from 10^{-5} to 10^{-6} mol dm^{-3}, such that solute−solute interactions can be ignored. No change in band shape was observed over the range of temperature and pressure used. The solubility of salicylic acid (Fisons, 99.5%) was determined using the dielectric method of Hourri et al.[26]

Results and Discussion

The dipolarity/polarizability parameter, π^*, introduced by Kamlet and Taft[27] has been determined for a number of nonpolar

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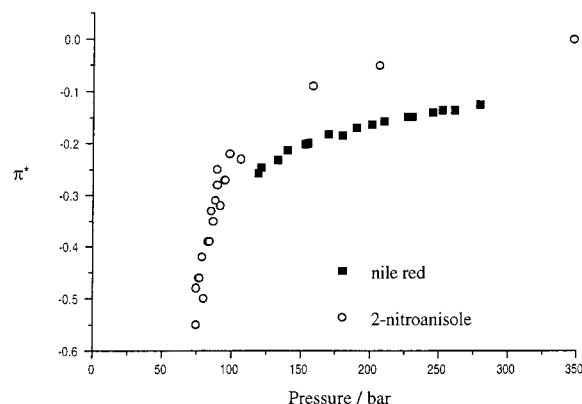
Figure 1. π^* for CO_2 as a function of pressure at 50 °C using Nile red and 2-nitroanisole.
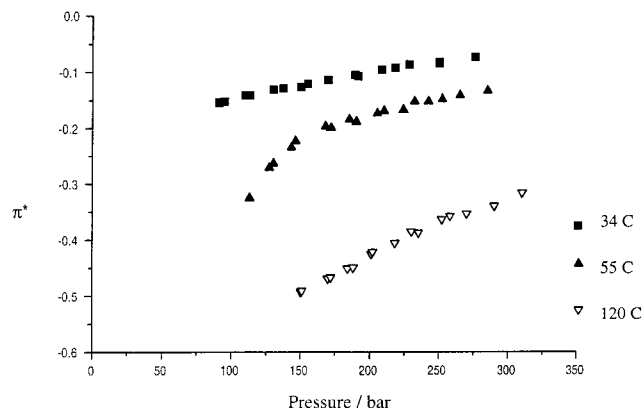

Figure 2. π^* for CO_2 as a function of temperature and pressure using Nile red as an indicator.

supercritical fluids. The parameter is determined by measuring the shift in absorbance maximum of an indicator solute

$$\pi^* = \frac{\nu_{max} - \nu_0}{s} \qquad (1)$$

where ν_{max} and ν_0 are the wavenumber of the absorbance maxima in the test solvent and reference solvent (cyclohexane) respectively and s is the susceptibility constant.

There is a wide discrepancy in the reported π^* values for CO_2. Sigman et al.[6] showed that the value obtained was critically dependent upon the indicator solute used. In the current investigation Nile Red ($s = -2300$ cm^{-1} and $\nu_0 = 20.51 \times 10^3$ cm^{-1})[28] was used as the indicator because of its high extinction coefficient and susceptibility constant. Figure 1 shows a comparison of the values obtained with Nile red to those obtained using 2-nitroanisole by Yonker and Smith.[7] Significant divergence appears to occur at pressures in excess of 150 bar. Measurements could not be made below 130 bar using Nile red because of insignificant solubility. There is, however, even a significant discrepancy between the values published for scCO₂ using the same indicator (2-nitroanisole), as shown by O'Neill et al.[29] Such disparities between indicators are common but since π^* measurements are used as a comparative tool rather than an absolute measurement, they are not significant as long as the same indicator is used for all measurements.

Figure 2 shows the change in π^* for Nile red in scCO₂ as a function of temperature and pressure. At all temperatures the low-pressure data are in good agreement with the values reported previously. As the pressure is increased, however, the values obtained in the current study are lower than those reported previously. For all of the conditions measured, the π^* value
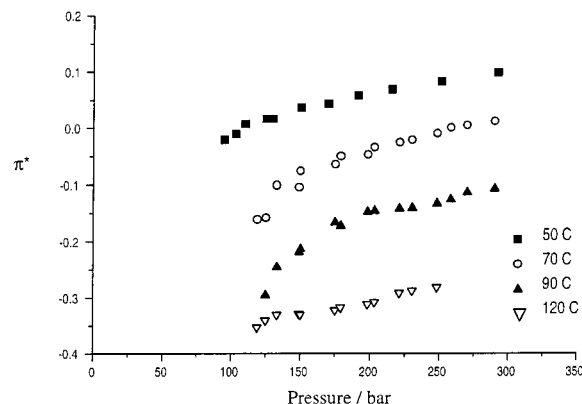

Figure 3. π^* vs pressure for a 5.3 mol % HFC134a in CO_2 mixture at a series of temperatures.

was less than that for cyclohexane. The low polarizability per unit volume of scCO₂ results in a low solubility of most polar solutes. HFC134a should be an ideal solvent for modifying CO_2 because of its high polarity, but the fact that it is a gas at ambient conditions means that it will not be left as a residue in the extract.

Figure 3 shows a plot of π^* vs pressure for a 5.3 mol % HFC134a in CO_2 mixture at a series of temperatures. The trend in π^* with temperature and pressure is similar to that found for pure CO_2. The trends are also the same as those presented for the π^* of 2-propanol/CO₂[21] mixtures of the same composition. However, it is clear that π^* of the mixture is significantly increased over that in pure CO_2. This results partly from the increase in solvent density in the mixture, but partially from preferential solvation of the solute by the more polar HFC134a molecules. What is interesting to note, however, is that the change in π^* following the addition of the polar modifier is greater for HFC134a than for 2-propanol.[21] This is not wholly surprising given the larger dipole moment of the former (2.06 compared with 1.66 D). Ikushima et al.[30] studied mixtures of CO_2 with ethanol and DMSO (both 8.9 mol %). The estimated π^* parameter for both modifiers was comparable with those found for HFC134a in Figure 3. To be strictly accurate, the solvatochromic shift for HFC134a should be correlated not only with the π^* parameter but also with the hydrogen bond donor parameter α and acceptor parameter β. Lagalante[17] recently showed that the β parameter for HFC134a was negligible, which is consistent with the liquid chlorinated analogue under ambient conditions. Comparison of the solvatochromic shift data published recently[15–17] shows good agreement in the π^* parameter for different indicators and a negligible contribution for the hydrogen bond donor character, α, of HFC134a. Hence, changes in the solvent–solute hydrogen bond interaction with temperature and pressure can be ignored in these systems.

A significant increase in π^* is observed for a 30.1 mol % mixture of HFC134a in CO_2, as shown in Figure 4. The lack of published π^* data for mixed fluids makes the comparison difficult, but the values for this mixture are comparable with the recently published data for Nile red in the HFC fluids close to T_c.[15–17] The critical temperature of a 30.1 mol % mixture of HFC134a (58 °C)[25] is also significantly below that of the pure HFC134a (101.2 °C). It is interesting to note that at the same pressure the π^* of the 30.1 mol % HFC134a mixture at 70 °C is similar to that of 100% HFC134a at 120 °C. The high polarity of this solvent mixture makes it extremely useful for supercritical extraction applications. Preliminary solubility measurements show that salicylic acid has a solubility of 1 mol % in a 30.1 mol % HFC134a mixture with CO_2 at 70 °C and 250 bar. This
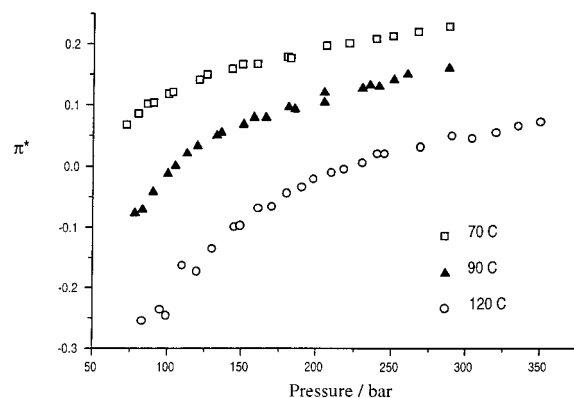
Figure 4. π^* vs pressure for a 30.1 mol % HFC134a in CO_2 mixture at a series of temperatures.

Figure 5. π^* as a function of density for four different CO_2/HFC134a compositions at 120 °C.

is approximately 2 orders of magnitude larger than that in unmodified CO_2.[31-33]

As with all studies in mixed supercritical fluids, there are difficulties with data analysis arising from the lack of experimental density data. In this work the densities of the mixed fluids were calculated by the same technique used by Johnston et al.[23] The Peng–Robinson a and b parameters were obtained for HFC134a and CO_2 by fitting the experimental data obtained previously to the equations

$$a = 0.45724R2T_c^2/P_c[1 + m(m - \sqrt{T_r})] \quad (2)$$

$$b = 0.0778RT_c/P_c \quad (3)$$

where $m = 0.37464 + 1.54226\omega - 0.2699\omega^2$ and ω for HFC134a and CO_2 was 0.140 and 0.145, respectively. The value for CO_2 is less than that used previously[23] because it provides a much better fit to the experimentally determined data at 120 °C. The parameters for the mixtures, a_m and b_m were determined from

$$a_m = y_1^2 a_1 + y_2^2 a_2 + 2y_1 y_2 a_{12} \quad (4)$$

$$b_m = y_1 a_1 + y_2 a_2 \quad (5)$$

where y is the mole fraction of the solvent in the mixture and a_{12} is given by

$$a_{12} = \sqrt{(a_1 a_2)}(1 - k_{12}) \quad (6)$$

where k_{12} is the binary interaction parameter. A value of $k_{12} = 0.1$ was used, which is consistent with other systems studied.[23]

Figure 5 shows π^* as a function of density for four different compositions at 120 °C. A significant difference is observed between the values obtained with the 5.3 mol % HFC134a mixture and the pure CO_2. The π^* values for these two media converge as the density increases. It is interesting to note that π^* values for the 30.1 mol % mixture converge with those for pure HFC134a at high density; i.e., at high density the value of π^* is relatively unchanged by increasing the polar component of the mixture. Figure 6 shows that there is a rapid rise in π^* following the addition of a small amount of polar constituent, but there is very little change above a mole fraction of 0.3. These results are remarkably similar to those obtained by Johnston et al.[23] who studied the fluorescence of a twisted intramolecular charge transfer state in CO_2/CHF_3 mixtures.

Figure 7 shows the same data as Figure 5 in terms of the concentration (or molar density) of solvent molecules, which compensates for the wide disparity between the molecular
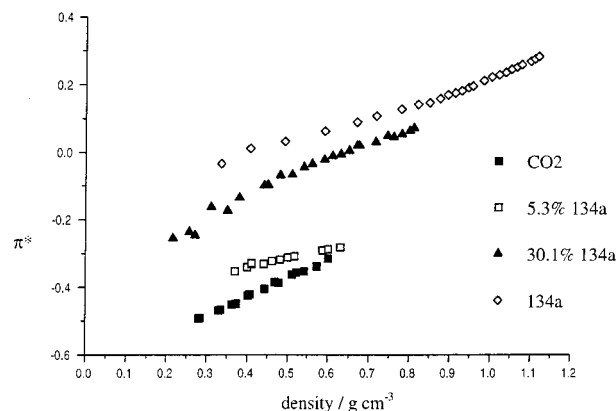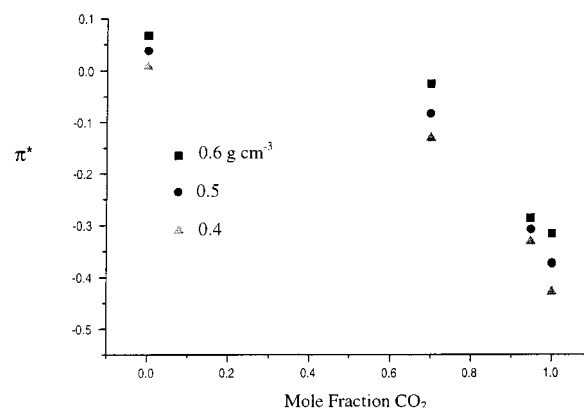

Figure 6. π^* as a function of mole fraction of HFC134a at 120 °C at a range of densities.

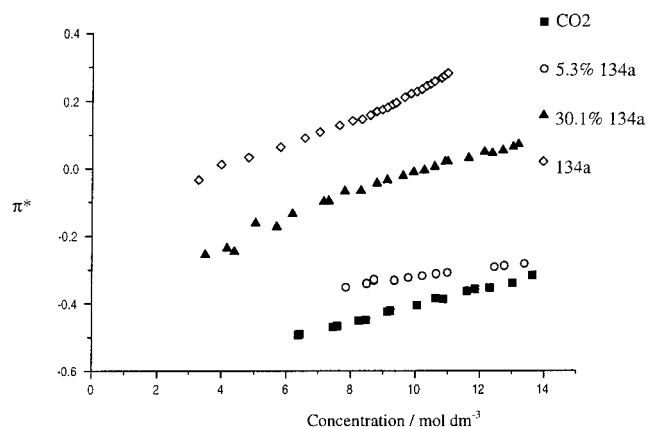**Figure 7.** π^* as a function of solvent concentration for four different CO_2/HFC134a compositions at 120 °C.

weights of the two solvents. From this representation an alternative picture of the solute solvation can be acquired. The π^* values for the 5.3 mol % HFC134a mixture and pure CO_2 converge. This could be ascribed to a number of factors such as a change in the specific solvent–solute interaction or a difference in the van der Waals interaction arising from a change in the asymmetry of the system. Most probably, however, the increase in pressure causes dipole–dipole repulsions and the cybotactic region close to the solute becomes depleted of HFC134a. This trend is also seen in the divergence of the π^* of the 30.1 mol % HFC134a mixture from that of the pure HFC134a. This mechanism was suggested by Brennecke et al.[24] who studied mixtures containing 84.2 and 15.0 mol % CHF_3 in CO_2 at 35 and 50 °C. For all of the systems studied, local density augmentation was observed because the temperature was

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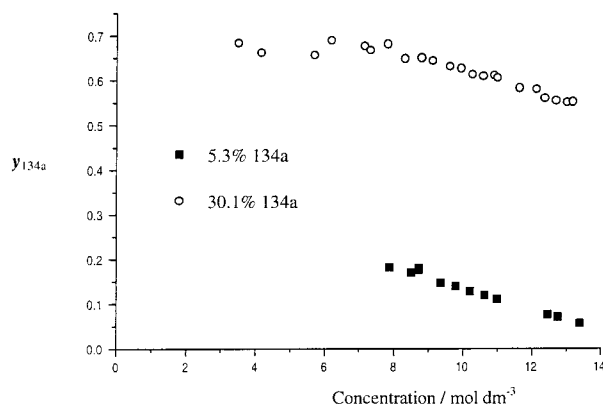*J. Phys. Chem. B, Vol. 103, No. 41, 1999* **8793**

Figure 8. Local mole fraction of HFC134a for both the 5.3 and 30.1 mol % mixtures as a function of total solvent concentration.

relatively close to the critical temperature. The changes in solvent polarity (in this case the fluorescence intensity ratio I_1/I_3) were relatively small but clearly showed a divergence at high pressure for the 84.2 mol % CHF$_3$ mixture. Anomalous results were obtained at low CHF$_3$ concentrations where divergence from the value for pure CO$_2$ was observed at high pressure. This led to an apparent initial decrease followed by a subsequent increase in the local mole fraction of CHF$_3$ as the pressure was increased. This results from the conditions under which the measurements were made. At $T_r \approx 1$ both the composition and density of the cybotactic region change with respect to the bulk values as the pressure is increased. Thus, it is impossible to determine whether the change in polarity parameter in the mixed fluid is caused by a change in local density or local composition.

In the current investigation, because the measurements were carried out at $T_r \gg 1$, local density augmentation can be ignored for all but pure HFC134a. Extrapolation of the π^* data at high density can be used, as previously,[16] to determine values without local density augmentation. The π^* of the mixture at each concentration is therefore given by

$$(\pi^*_{12})_c = (y_{134a})(\pi^*_{134a})_c + (1 - y_{134a})(\pi^*_{CO_2})_c \quad (7)$$

Figure 8 shows the local mole fraction of HFC134a for both the 5.3 and 30.1 mol % mixtures as a function of total solvent concentration. For the 30.1 mol % mixture the local composition remains approximately constant at low pressures. The local mole fraction of 0.7 is approximately double the bulk composition, but no sign of complete saturation of the solvation sheath was observed, as suggested by Yonker and Smith. At concentrations above ca. 8 mol dm^{-3} a steady decrease in local mole fraction of HFC134a is observed, caused either by solvent−solute repulsion or cosolvent clustering. The same trend is observed for the 5.3 mol % mixture, although the low solubility of Nile red does not allow measurements at low solvent concentrations; hence, the maximum concentration could not be determined. Figure 8 shows, however, that it must be in excess of 4 times the bulk composition. It is also interesting to note that the decrease in polar constituent with solvent concentration is almost identical for both mixtures.

Under the conditions used in these experiments the local mole fraction of the polar constituent does not decrease below that of the bulk solution for either mixture. This is in agreement with the majority of studies in mixed fluids but is contrary to the results of Brennecke et al.[24] What is not proven by these results but what is suggested by the results in Figure 8 is that the concentration of the more polar component in the cybotactic region could decrease below that of the bulk when the bulk HFC134a concentration is low and the pressure is high.

Conclusions

This work shows conclusively that in mixed supercritical fluids preferential solvation of the solute by the more polar constituent occurs. The local composition of polar solvent can exceed 4 times that in the bulk fluid but saturation of the solvation sheath was not observed. It was shown that as the pressure is increased the polar constituent is expelled from the solvation sheath and the local composition tends toward that of the bulk at high pressures. A mixture of 30 mol % HFC134a with CO$_2$ is shown to have solvent properties similar to those of pure HFC134a at the same density, which shows that it is a useful mixture for extraction purposes. Preliminary measurements show that polar molecules such as salicylic acid have relatively high solubilities in this mixed fluid.

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