

# Hydrogen Bond Interactions in Liquid and Supercritical Hydrofluorocarbons

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Determination of solvent–solute interactions is key to the understanding of solvent properties in liquid and supercritical fluids. The Kamlet–Taft parameters were determined for difluoromethane (HFC 32) and 1,1,1,2-tetrafluoroethane (HFC 134a) as a function of temperature and pressure in the range 40–130 °C and 50–220 bar using three solvatochromic dyes. It is shown that both solvents exhibit considerable hydrogen bond donating and accepting properties, and these parameters also obey the three region density model often invoked when describing the dipolarity/ polarizability parameter in supercritical fluids.

## Introduction

Supercritical (sc) fluids have found use in extraction, chromatography, and catalysis because of the marked changes that can occur in solvent properties as a result of modest changes in temperature or pressure.<sup>1–5</sup> Numerous studies have been made to measure the solvation of solutes in supercritical fluids using solvatochromic shift parameters and fluorescence probes in an attempt to model the solvent properties. Most of the commonly used supercritical solvents have been studied using these techniques,<sup>6–17</sup> and a number of groups have also measured the solvatochromic behavior of binary supercritical fluids.<sup>9,18–20</sup> 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. Tucker<sup>21,22</sup> and Brennecke<sup>23</sup> have reviewed the area of local density augmentation.

Most studies of solvent polarity in sc fluids have used the parameters introduced by Abboud et al.<sup>24</sup> They showed that a variety of solution properties such as reaction rates, equilibrium constants, or Gibbs Energies of solvation could be related via solvatochromic parameters through a schematic equation of the form

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta \quad (1)$$

where XYZ is the solvent property, XYZ<sub>0</sub> is the solvent property in a reference solvent,  $\pi^*$  is the dipolarity/polarizability parameter,  $\alpha$  is the hydrogen bond donor parameter,  $\beta$  is the hydrogen bond acceptor parameter and  $a$ ,  $b$ , and  $s$  are susceptibility constants. The same relationship is obtained for shift absorption maxima of a variety of indicator solutes in a range of solvents, such that

$$\nu_{\max} = \nu_0 + s\pi^* + a\alpha + b\beta \quad (2)$$

where  $\nu_{\max}$  and  $\nu_0$  are the wavenumber of the absorbance maxima in the test solvent and reference solvent (cyclohexane), respectively. The measurement of spectral shifts is the method most commonly used to quantify the  $\alpha$ ,  $\beta$ , and  $\pi^*$  values.

Most solvatochromic studies have been carried out on less polar solvents such as CO<sub>2</sub> and NO<sub>2</sub> where the contribution of hydrogen bonding to solvent polarity is small.<sup>6,7,25–27</sup> Some studies have quantified the hydrogen bond acceptor properties of CO<sub>2</sub>, but these were found to be small and relatively invariant with pressure.<sup>6,26,27</sup> A number of authors have measured the dipolarity/polarizability and hydrogen bond acceptor properties of a number of CO<sub>2</sub>/alcohol binary mixtures as a function of modifier mole fraction, temperature, and pressure.<sup>18,28,29</sup> In this work, it was found that the hydrogen bond acceptor values for the mixtures show a systematic increase with elongation of the alkyl chain. Bulgarevich and co-workers measured the hydrogen bond donor parameter,  $\alpha$ , of CO<sub>2</sub> modified with methanol<sup>30</sup> and found that it decreased with increasing pressure. Kazarian et al.<sup>31</sup> studied the interaction between a proton donor and acceptor in sc SF<sub>6</sub> and determined the equilibrium constant for the free and dissociated species as a function of temperature and pressure.

Employing UV/vis spectroscopy, Kim and Johnston<sup>32</sup> characterized the hydrogen bond donor ability of supercritical fluoroform with the solvatochromic probe phenol blue. It was shown that the hydrogen bond interactions were well developed at the critical density and did not change substantially with pressure up to approximately 350 bar. Bennett and Johnston characterized the hydrogen bond donor strength of supercritical water with the UV/vis spectroscopic solvatochromic probes acetone and benzophenone.<sup>33</sup> They also showed that hydrogen bonding can persist in supercritical media at low densities and specifically as low as 0.1 g cm<sup>−3</sup> in supercritical water at 380 °C.

Recently Eckert and co-workers characterized the Kamlet–Taft parameters of near critical and supercritical ethanol and showed that the hydrogen bond donor (HBD) properties decrease with increasing pressure and temperature. The hydrogen bond acceptor (HBA) properties were small and relatively invariant with pressure in the supercritical region.<sup>34</sup>

Hydrofluorocarbons have been shown to be useful for a variety of applications including refrigerants propellants and solvents.<sup>35</sup> They are useful as supercritical solvents because of their accessible critical constants (for HFC 134a:  $T_c = 101$  °C and  $P_c = 40.7$  bar and HFC 32:  $T_c = 78.35$  °C,  $P_c = 58.16$  bar) and high polarity.<sup>15,16</sup> In the current work, we use solvatochromic shift data for three indicator solutes to character-

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**TABLE 1: Susceptibility Constants for the Three Dye Indicators Used in This Work**

dye	<i>a</i>	<i>b</i>	<i>s</i>	<i>v</i> <sub>0</sub> (kK)
<i>N,N</i> -dimethyl-4-nitroaniline	−0.562	N/A	−3.326	27.956
4-nitroaniline	N/A	−3.484	−2.600	30.820
Nile Red	−0.942	N/A	−1.623	19.978

ize the HBD and HBA properties of HFC 134a and HFC 32 as a function of temperature and pressure in the range 40–130 °C and 50–220 bar in what is the most detailed study of pressure and temperature effects on hydrogen bonding in liquid and supercritical fluids.

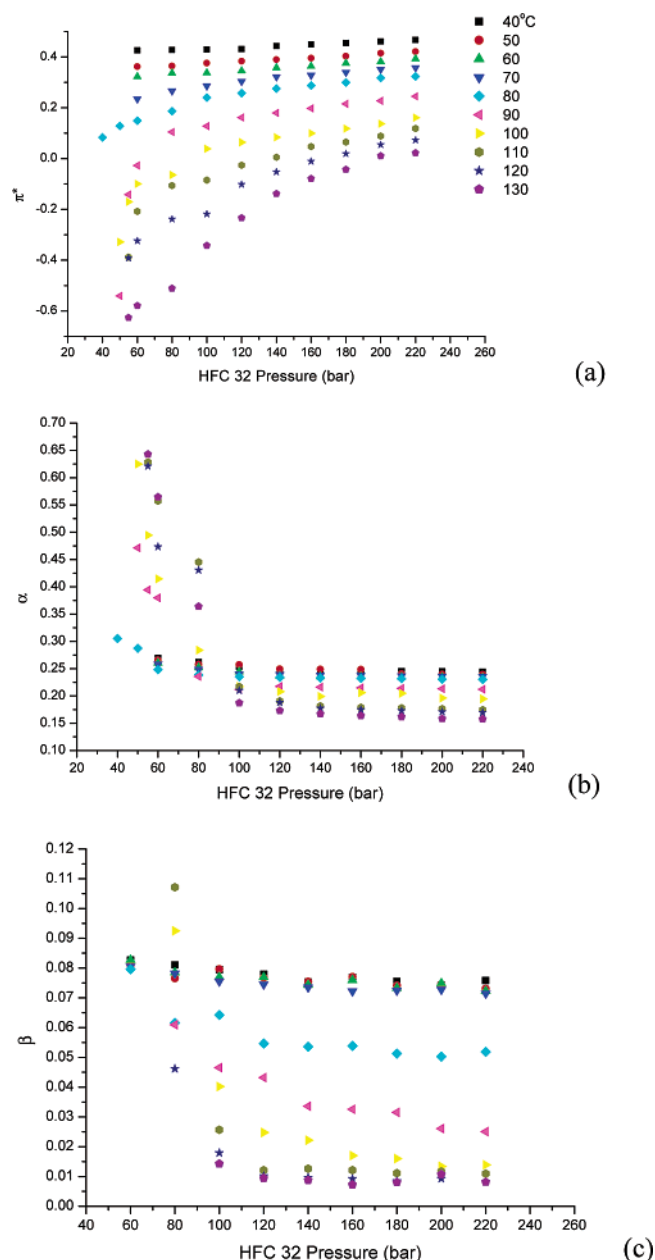
### Experimental Section

The experimental apparatus used to measure the solvatochromic shift in both liquid and supercritical states has been described in detail elsewhere.<sup>15</sup> A Shimadzu model UV-1601 spectrophotometer was used to measure the UV/vis absorbance spectra. Light was fed in to 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 and brass using 1 cm thick sapphire windows together with copper gas seals. The internal volume of the cell was approximately 1 cm<sup>3</sup> 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 cell temperature, which was retained ( $\pm 0.5$  °C) using a CAL 9900 heater. A UCC type PGE 1001.600 gauge was used to monitor the pressure ( $\pm 2$  bar). The HFCs (Ineos Fluor; 99.99%) were used as received. *N,N*-dimethyl-4-nitroaniline (Lancaster; 98%) and 4-nitroaniline (Aldrich; 99%) were used as received as indicator dyes with both solvents. The data for Nile red were taken from the literature.<sup>15,16</sup> Dye concentrations ranged from 10<sup>−5</sup> to 10<sup>−6</sup> mol dm<sup>−3</sup>, such that solute–solute interactions can be ignored. No change in band shape was observed over the range of temperature and pressure used. Solution density values were taken from the literature.<sup>36,37</sup> The molecular volumes of the solvents and solutes were determined using a commercial molecular modeling package.<sup>39</sup>

### Results and Discussion

To obtain the  $\alpha$ ,  $\beta$ , and  $\pi^*$  values for the two HFC fluids the susceptibility constants *a*, *b*, and *s* values for the three indicator dyes used in the current study were first obtained by measuring their absorption spectra in 16 solvents of different polarity and solvent type, i.e., HBD, HBA, and NHB. The data obtained were fitted to eq 2 using a multiple regression analysis. Very good correlation was obtained in all cases ( $R^2 > 0.95$ ). The *a*, *b*, and *s* values for the three solutes used are listed in Table 1 and are in close agreement with those published in the literature.<sup>24</sup> For details of the spectral shifts, see the Supporting Information.

**Polarizability/Dipolarity Parameter  $\pi^*$ .** We have previously reported the pressure and temperature dependency of  $\pi^*$  for HFC 134a and HFC 32 using Nile red as an indicator solute.<sup>16</sup> Lagalante and co-workers have also measured the Kamlet–Taft parameters,  $\pi^*$  and  $\beta$ , for six liquid and supercritical fluorinated ethane solvents, including HFC 134a.<sup>17</sup> The  $\pi^*$  values of HFC 134a previously reported by us were consistently slightly higher (ca. 0.07) than those determined by Lagalante and colleagues in both the liquid and supercritical phases. It is, therefore, implied that the difference in  $\pi^*$  values results from the neglect of hydrogen bonding interactions between HFC 134a and Nile red. Similar inconsistencies in  $\pi^*$ , however, have been observed



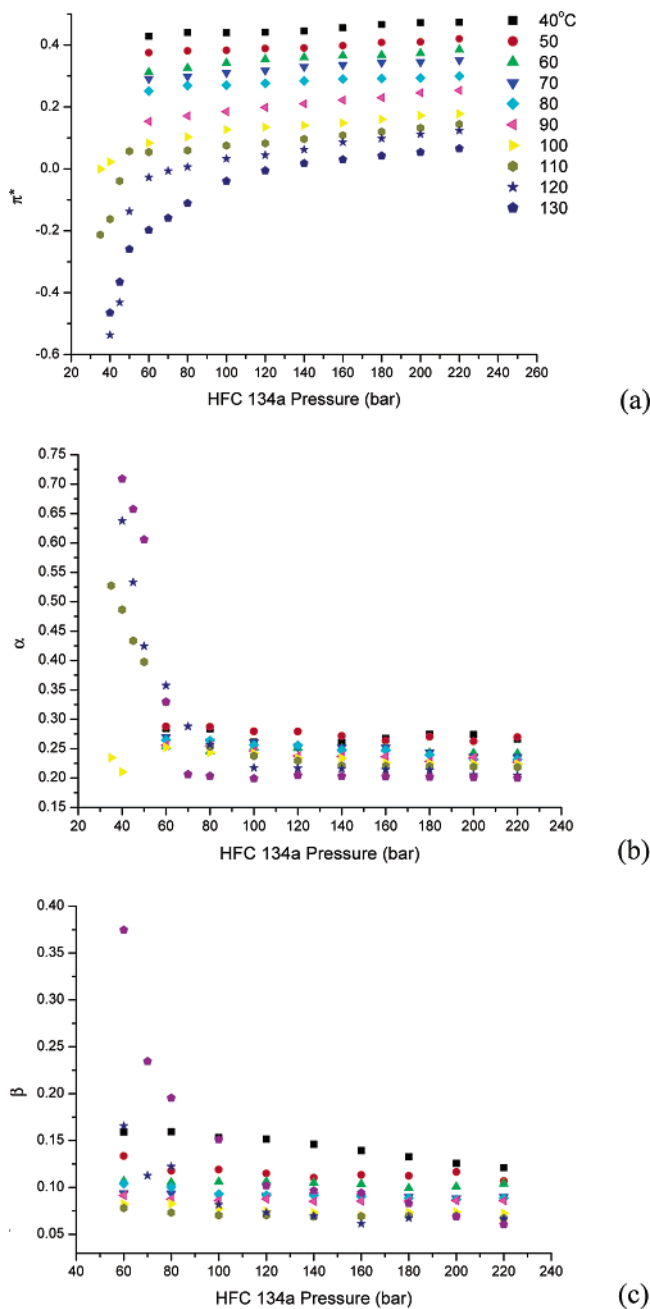
**Figure 1.**  $\alpha$ ,  $\beta$ , and  $\pi^*$  values for HFC 32 as a function of pressure and temperature.

for CO<sub>2</sub> when employing the solvatochromic probes Nile red and 4-nitroanisole,<sup>20,25</sup> and hence, this may not be the sole reason.

Figures 1 and 2 show the  $\alpha$ ,  $\beta$ , and  $\pi^*$  values for HFC 32 and HFC 134a respectively as a function of pressure and temperature. The first point to note is that the  $\pi^*$  values are similar, although slightly lower than those published previously<sup>15,16</sup> and the agreement with the Lagalante<sup>17</sup> data for HFC 134a is also improved.

Application of the mean sphere approximation (MSA) to this solvent showed  $\pi^*$  and the relative permittivity,  $\epsilon$ , to be strongly related in both the liquid and supercritical states. It was shown that  $\pi^*$  can be related to a complex function of the solution relative permittivity,  $\alpha(\epsilon)$  by

$$\pi^* = \pi^*_{\text{gas}} + \frac{2\alpha(\epsilon)\mu_G(\mu_G - \mu_E)}{s4\pi\epsilon_0 chD^3} \quad (3)$$



**Figure 2.**  $\alpha$ ,  $\beta$ , and  $\pi^*$  values for HFC 134a as a function of pressure and temperature.

where

$$\alpha(\epsilon) = \frac{8(\epsilon - 1)}{2uR^3\rho^3 + 2\epsilon[1 + R(1 - 2u)]^3 + [1 + R\rho]^3} \quad (4)$$

$$R = d/D$$

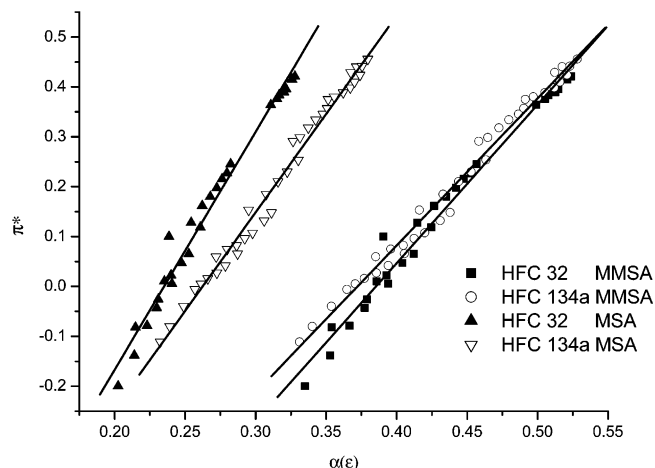
$$\rho = \frac{(1 - u)}{(1 - 2u)}$$

$$u = \frac{3\xi}{(1 + 4\xi)}$$

$$\xi = \frac{1}{2} \left[ 1 - \frac{9}{4 + f^{1/3} + f^{-1/3}} \right]$$

$$f = 1 + 54\epsilon^{1/2} \left[ 1 - \left[ 1 + \frac{1}{27\epsilon^{1/2}} \right]^{1/2} \right]$$

and where  $\pi^*_{\text{gas}}$  is the vapor phase limit,  $R$  is the ratio of the



**Figure 3.** Application of the mean sphere approximation (MSA) and modified MSA (MMSA) to the  $\pi^*$  data shown in Figures 1 and 2.

solvent,  $d$ , and solute,  $D$ , radii,  $\mu_G$  and  $\mu_E$  are the dipole moments of the solute in the ground and excited states,  $c$  is the speed of light in a vacuum,  $\epsilon_0$  is the permittivity of free space and  $h$  is Planck's constant. Hence,  $\pi^*$  should be proportional to  $\alpha(\epsilon)$ . This was shown to be valid for HFCs 134a, 32, and 125 over the temperature range 30–130 °C and the pressure range 40–300 bar. Although the slopes of  $\pi^*$  vs  $\alpha(\epsilon)$  plots were all very similar they were considerably offset from each other in reference to eq 3 which predicts that all the solvents should be coincident since  $\pi^*_{\text{gas}}$  should be common to all solvents. It was postulated that this discrepancy may result from hydrogen bonding but the changes in  $\pi^*$  from those published previously are too small to account for this difference. Analysis of eq 4 shows a critical dependence of  $\alpha(\epsilon)$  on the ratio of the solvent and solute radii. The previously reported method for determining the molecular radii was an additive method based upon average atomic Stokes radii<sup>38</sup> that was relatively inaccurate and may result in the previously observed offset. In the current study, a computer simulation was used to determine the solvent and solute volumes. The equilibrium geometry and charge distributions of the solute and solvent were calculated using a Hartree-Fock method utilizing an STO-3G model.<sup>39</sup> Figure 3 shows plots of  $\pi^*$  vs  $\alpha(\epsilon)$  for the new  $\pi^*$  data and shows that both solvents are in much closer agreement to eq 3. The model does, however, still assume that the indicator solutes are spherical, which in the case of Nile red in particular is clearly not accurate as it is more oblate. Redefining  $d$  and  $D$  as the volume/area ratio (rather than the radius) of the solvent and solute respectively yields a parameter that more accurately accounts for the contribution of the molecular geometry to the solvent solute interaction; that is, an oblate molecule has a larger surface of interaction with the surrounding environment than a spherical molecule of the same molecular formula. Figure 3 shows that the modified MSA approach yields a much closer agreement between the two solvents and a  $\pi^*_{\text{gas}}$  value in close agreement with the theoretical value of  $-1.06$  ( $\pi^*_{\text{gas}}$  is  $-1.10$  and  $-1.22$  for HFCs 134a and 32, respectively).<sup>40</sup> The polarizability/dipolarity parameter can accurately be modeled for HFC 32 and HFC 134a using the MSA although critical parameters such as molecular radii significantly affect the accuracy of the parameter  $\alpha(\epsilon)$  which is a weakness of this approach.

**Hydrogen Bond Acceptor Properties,  $\beta$ .** The  $\beta$  values for both solvents are small but positive. This is a slight contradiction to the data presented by Lagalante et al.,<sup>17</sup> who showed that HFC 134a is a poor hydrogen bond acceptor, because  $\beta$  was found to be slightly negative. The discrepancy probably occurs

from the assumption made by Lagalante that the indicator solute, 4-nitroanisole, does not act as a hydrogen bond acceptor. For HFC 32, the  $\beta$  value is almost invariant with either temperature or pressure in the liquid state (i.e., below 78 °C). At  $T \geq T_c$ , a decrease in  $\beta$  with increasing temperature and pressure is observed. At supercritical temperatures, the  $\beta$  values for HFC 134a are slightly larger than those for HFC 32, and at low pressures, both solvents are relatively good HBAs. The  $\beta$  values for both fluids are similar to those reported recently for sc ethanol by Lu et al.<sup>34</sup>

**Hydrogen Bond Donor Properties,  $\alpha$ .** This is the first time that  $\alpha$  values have been presented for these solvents in the sc state. Given the relatively acidic protons on both solvents, it would be expected that they would be relatively good HBDs. The magnitude of the  $\alpha$  values are comparable with related compounds, e.g., methylene chloride at ambient conditions where  $\alpha = 0.3$  and similar to the value reported by Corr<sup>35</sup> for liquid HFC 134a ( $\alpha = 0.48$ ) at ambient temperature and an approximate density of 1.22 g cm<sup>-3</sup>. The decrease in  $\alpha$  with increasing pressure in the sc state is consistent with the data presented recently for ethanol.<sup>34</sup> The  $\alpha$  values for both solvents are shown to be almost constant with increasing pressure in the liquid state and decrease with increasing pressure in the supercritical state. Similar results were also obtained using the previously published data.<sup>41</sup>

At higher pressures ( $> 100$  bar), the  $\alpha$  value decreases with increasing temperature as would be expected. However, at lower pressures when  $T > T_c$ , the  $\alpha$  value increases with increasing temperature. This is an unusual result and is observed for both solvents. Lu et al.<sup>34</sup> suggested that for ethanol the change in  $\alpha$  with pressure was due to the change in the equilibrium between solvent–solvent and solvent–solute interactions with the latter dominating at high temperature. It can be argued that because the  $\alpha$  parameter gives a measure of the equilibrium constant,  $K$ , between the solvent–solvent and solvent–solute interactions in a liquid then at low density it can be used to obtain an apparent enthalpy of hydrogen bond formation  $\Delta H'$  because

$$\frac{d \ln K}{d(1/T)} = \frac{\Delta H'}{R} = \frac{d\alpha}{d(1/T)} \quad (5)$$

Hence when  $p < 100$  bar and  $T > T_c$ ,  $d\alpha/dT$  is negative and hydrogen bond formation is exothermic. At 55 bar, for example, the data obey eq 5 well and yield an apparent enthalpy of hydrogen bond formation of 9.2 kJ mol<sup>-1</sup>. The exothermic behavior is also observed for HFC 134a although less data display this characteristic because of the higher  $T_c$ . It is interesting to note that for all of the data where  $d\alpha/dT$  is negative the density of the solvent is less than the critical density,  $\rho_c$ . It is around this density that the solvation sheath is assumed to be complete and hence the decrease in hydrogen bonding is most probably due to the competing solvent–solvent interactions with neighboring solvent molecules. This suggests that the same three-region density model should also be evident for  $\alpha$  as is observed for  $\pi^*$ .<sup>16</sup>

Figure 4 shows the  $\alpha$ ,  $\beta$ , and  $\pi^*$  values for HFC 32 as a function of solvent density. The first point to notice is that HFC 32 is such an excellent solvent partly because of the high density exhibited in the sc state. The density in the sc state is higher than many common solvents in the liquid state at ambient conditions. It is also clear from Figure 4 that this three-region density model does indeed exist for the  $\alpha$  parameter. Unfortunately, it was not possible to confirm this for the  $\beta$  parameter although the trend observed over the obtainable density range is remarkably linear suggesting that density augmentation has

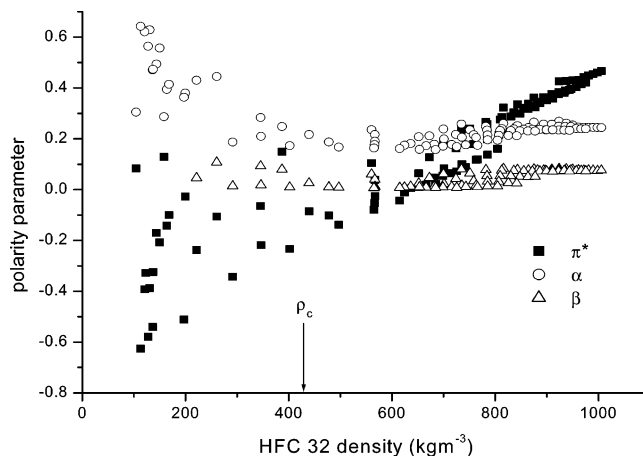


Figure 4. Polarity parameters for HFC 32 as a function of density.

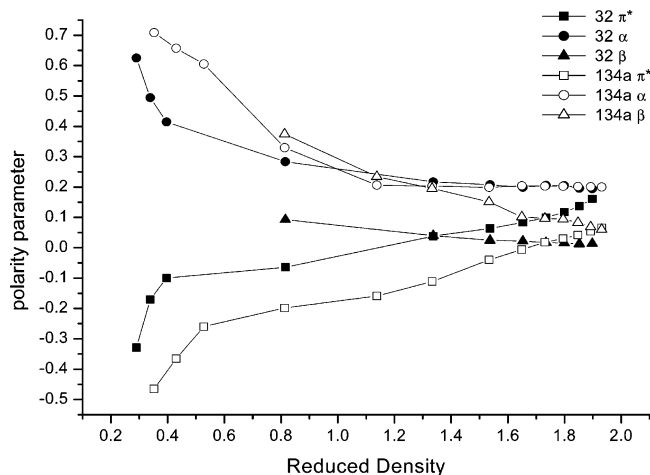


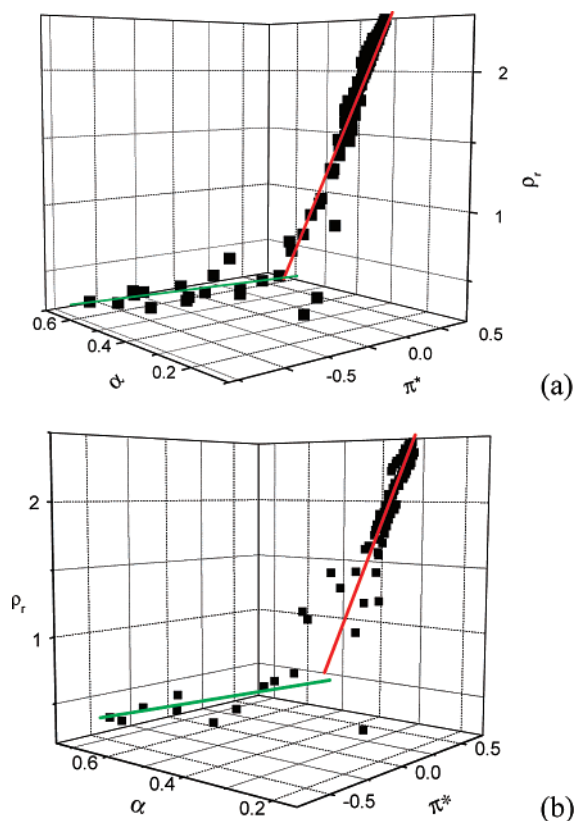
Figure 5. Polarity parameters for HFC 32 and 134a as a function of reduced density at a constant reduced temperature (1.128).

little effect on the HBA properties of the solvent. Figure 4 shows that at low density the polarity of these HFCs is dominated by hydrogen bond donor properties which suggests that in the low-density region the solvent interaction is different to that at higher densities.

Figure 5 compares the polarity parameters for HFCs 32 and 134a as a function of reduced density at a reduced temperature of 1.128 (HFC 32:  $T = 100$  °C; HFC 134a:  $T = 130$  °C). It can be seen that at a given reduced density the HBA and HBD parameters for HFC 134a are larger than those for HFC 32 that may be expected given the differences in dipole moment (2.058 and 1.987 D, respectively). In contrast, the  $\pi^*$  for HFC 32 is larger than that for HFC 134a possibly because of the difference in size and the ability to pack more of the smaller solvent molecules around the indicator solute. The two solvents show points of inflection for all three parameters at approximately the same reduced density confirming that they both obey the same three-region density model.

Cross correlation of the parameters presented above also yields some interesting results. Figure 6 shows the correlation between  $\alpha$  and  $\pi^*$  for HFC 32 as a function of reduced density. Two distinct regions are observed, one with a positive and one with a negative correlation between the parameters. At high densities in the “liquidlike” region ( $\rho_r > 1$ ) there is a small, positive correlation of  $\alpha$  and  $\pi^*$ , and this is linearly dependent on density, suggesting it is just the packing of solvent molecules around the solute that affects these two parameters. In the “gaslike” region, both parameters change more significantly with



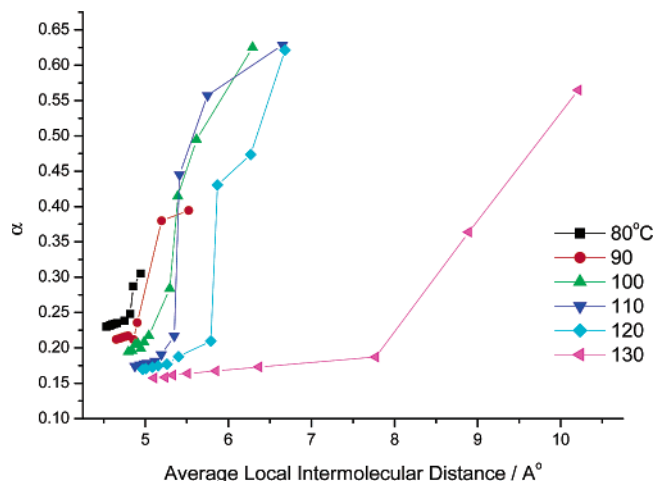


**Figure 6.** Cross-correlation between  $\alpha$ ,  $\pi^*$ , and  $\rho_r$  for (a) HFC 32 and (b) HFC 134a.

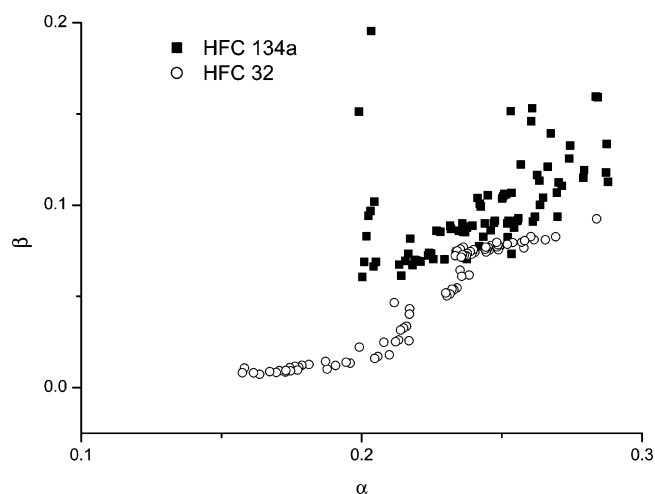
density. Importantly, a negative correlation is observed between the parameters and  $d\alpha/d\pi^*$  increases with increasing temperature. Exactly the same trend is observed for HFC 134a (Figure 6b). The two solvents differ only in the reduced density at which the point of inflection occurs (for HFC 32 it is ca. 0.6 whereas for HFC 134a it is ca. 0.4).

There are two possible scenarios that could lead to this effect; either the solvent–solvent interactions are weakened as the intersolvent separation increases (allowing the solvating molecules to interact more strongly with the solute) or the solvation sheath is incomplete and the solvent molecules cluster preferentially around the hydrogen bonding moieties. To analyze these scenarios, it is important to determine the local density around the solute. Using the  $\pi^*$  data, it is possible to determine the local solvent density by assuming that if local density augmentation did not occur then  $\pi^*$  would increase linearly with density as it does in the liquid state (and the sc state at high pressure).<sup>42</sup> Figure 7 shows the value of the  $\alpha$  parameter as a function of the average local intermolecular separation for HFC 32. Increasing the distance between the solvating molecules to about 5–6 Å causes a significant increase in  $\alpha$  suggesting that decreased solvent–solvent interactions play a key role in influencing solvent–solute interactions. However, because under the low-density conditions where  $\alpha$  increases significantly the solvation sheath is incomplete, hydrogen bond interactions will be larger than dipole–dipole or dipole–induced dipole interactions, and it is probable that the solvent interacts with the indicator solute preferentially at the polar groups. The computer simulation by Tucker<sup>22</sup> that showed the local solvent density around a solute was larger around a polar functional group supports this idea.

Figure 8 shows the correlation between  $\alpha$  and  $\beta$  for both solvents, and although this cannot interrogate the low-density region because of the lack of  $\beta$  data, it is clear that the two parameters are related. For HFC 32, a well-defined correlation



**Figure 7.** Change in  $\alpha$  with intermolecular distance for HFC 32.



**Figure 8.** Cross-correlation between  $\alpha$  and  $\beta$  for HFC 32 and 134a.

is shown where  $d\beta/d\alpha$  is small under liquid and supercritical conditions and larger in the near critical regime. Considerably more scatter is seen for HFC 134a, although a general positive correlation is observed which would be expected. The difference between the two solvents is difficult to rationalize although the generally larger  $\beta$  value for HFC 134a suggest that solvent–solvent interactions through hydrogen bonding may be more important than in HFC 32.

## Conclusions

This work has shown that HFCs 32 and 134a have significant hydrogen bond donor characteristics particularly in the supercritical state. The hydrogen bond donor properties of the solvents decrease with increasing pressure and this trend is suggested to be due to a decrease in solvent–solvent interactions and an increase in the preferential solvation around the polar moieties as the local solvent density decreases. A strong correlation is observed between the polarizability/dipolarity parameter,  $\pi^*$ , and the hydrogen bond donor character,  $\alpha$ , and the relation changes significantly at the conditions where the solvent–solvent interactions decrease.

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**Supporting Information Available:** Solvatochromic shift data for a variety of solvents with the dyes are shown in Table 1. Plots showing accuracy of fit parameters to eq 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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