

Probing Solute Clustering in Supercritical Solutions Using Solvatochromic Parameters

Andrew P. Abbott,* Eric G. Hope, and Donna J. Palmer

Chemistry Department, University of Leicester, Leicester, LE1 7RH, U.K.

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Kamlet and Taft polarity parameters are presented for three supercritical solutions containing solutes of different polarities at two concentrations. It is shown that the polarizability and hydrogen-bond-donating ability change significantly with pressure. In the lower pressure regime, naphthalene and salicylic acid cause a decrease in the polarity parameters compared with the pure fluid, whereas toluic acid causes an increase. These differences can be explained in terms of solute–solute and solute–indicator clustering. It is shown that there is, however, a direct correlation between the change in the hydrogen-bond-donating ability and polarizability for all solutes and all pressures and concentrations, which is thought to result from changes in the amount of solvent required to solvate the solute.

Introduction

Numerous studies have been conducted on the polarity of supercritical solvents using a variety of solvatochromic shift parameters and fluorescent probes. Most studies of solvent polarity in sc fluids have used the parameters introduced by Abboud et al.¹ They showed that a variety of solution properties such as reaction rates, equilibrium constants, or Gibbs energies of solvation can be related via solvatochromic parameters through an equation of the form

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

where XYZ is the solvent property, XYZ_0 is the solvent property in a reference solvent, π^* is the dipolarity/ polarizability parameter, α is the hydrogen-bond-donor parameter, β is the hydrogen bond acceptor parameter and a , b , and s are susceptibility constants. The same relationship is obtained for shifts in 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 ν_{\max} and ν_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 used most commonly to quantify the α , β , and π^* values.

The majority of common sc fluids have been characterized in this way,^{2–10} and some groups have studied the behavior of simple binary mixtures.^{11–14} These solvents were found to have a wide range of solvent strength, which can be readily and continuously tuned by temperature and pressure changes.

Recently, there has been significant interest in the use of polar sc fluids, which can dissolve higher concentrations of polar solutes.^{15–18} The solvent properties of $\text{CO}_2/\text{CF}_3\text{CH}_2\text{F}$ mixtures have also been quantified by measuring π^* values at a range of temperatures, pressures, and $\text{CF}_3\text{CH}_2\text{F}$ mole fraction;¹⁹ and it was found that only 30 mol % $\text{CF}_3\text{CH}_2\text{F}$ in CO_2 was required to provide properties similar to those of pure $\text{CF}_3\text{CH}_2\text{F}$. A number of other authors have investigated the solvent properties of sc mixtures and shown that there is preferential solvation of

the solute by the more polar solvent in the mixture. As pressure is increased, the local composition of this polar constituent is found to decrease steadily.^{20–25}

With the more polar fluids, the hydrogen-bond donor and acceptor properties (α and β) become important, and these have been quantified by a number of authors.^{5,21,26} More recently, Lu et al. have characterized the α and β parameters of near-critical and sc ethanol. The α -HBD properties were found to decrease with increasing pressure and temperature, whereas the β -HBA properties were found to be small and relatively invariant with pressure in the sc region.⁸

More recently, Abbott and Durling characterized the Kamlet–Taft π^* , α and β parameters for liquid and sc $\text{CF}_3\text{CH}_2\text{F}$ and CH_2F_2 as a function of temperature and pressure. They employed three solvatochromic probe molecules, Nile Red, 4-nitroaniline, and *N,N*-dimethyl-4-nitroaniline, to calculate α and β values by the solvatochromic comparison method.²⁷ Both solvents were shown to have significant hydrogen-bonding properties, which exhibit the characteristic decrease with increasing pressure. The polarity parameters were found to be larger for $\text{CF}_3\text{CH}_2\text{F}$, which has the larger dipole moment. For both solvents, β values were small and positive and similar to those reported by Lu et al. for sc ethanol.⁸ At high pressures, under sc conditions, the HBD α -parameter was found to decrease with increasing temperature. However, at pressures below 100 bar α values were found to increase with increasing temperature. This was attributed to the change in equilibrium between solvent–solvent and solvent–solute interactions. A strong correlation between the parameters π^* and α was shown. This was found to change significantly when solvent–solvent interactions are reduced. This indicates that at densities where the solvation sheath is incomplete preferential solvation around the polar moieties of the probe molecule may occur.

In addition to the investigations discussed above, many other spectroscopic studies, such as infrared^{28–33} and fluorescence,^{34–36} have shown that close to the critical temperature and density the local solvent density around a solute molecule is found to be higher than the actual bulk value. The extent of enhanced solvent density about the solute, commonly referred to as “clustering” or “local density augmentation” has

* Corresponding author. E-mail: andrew.abbott@le.ac.uk.

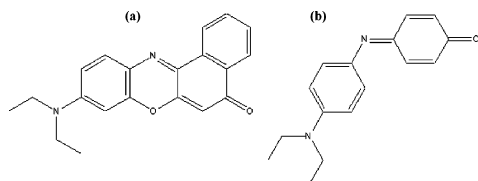


Figure 1. Structures of (a) Nile Red and (b) Phenol Blue.

frequently been calculated by computer simulations,^{37–39} integral equation formulations²³ or compressible electrostatic continuum methods.⁴⁰

The aim of this work is to obtain the first data for the polarizability/dipolarity π^* parameter and the hydrogen-bond donor acidity parameter, α , for three solid solutes dissolved in sc CH_2F_2 . The solutes investigated are *o*-hydroxybenzoic acid (salicylic acid), naphthalene, and *p*-methylbenzoic acid (*p*-toluic acid), and as a result the types of solute–solute and solute–solvent interactions are evaluated.

Experimental Section

The experimental apparatus used to measure the solvatochromic shifts was similar to that described previously.^{16–19,27} A Shimadzu Model UV-1601 spectrophotometer was used to measure the UV/visible absorbance spectra. Light was fed into and out of the high-pressure cell by fiber-optic cables (Hellma, Müllheim, FRG) fitted with a 662 QX prism adapter. The high-pressure optical cell was constructed from 316 stainless steel with 1-cm-thick sapphire windows. The gas seals were made from Teflon. The cell path length was 6 cm, and the cell volume was 100 cm^3 . Pressure was applied using a model P50-series piston controlled pump (Thar Technologies inc.; Pittsburgh, PA) and monitored (± 2 bar) using a swagelok manometer. At the center of the cell, the tip of an iron/constantan thermocouple was in contact with the solvent and a constant temperature (± 0.5 °C) was retained using a CAL 9300-controlled heater. The solvatochromic shift of the two indicator dyes were measured at 90 °C as a function of pressure and solute concentration. The cell was loaded with the desired solute, heated to the required temperature, and a small amount of dye was added to the cell. The cell was then pressurized to the desired conditions. The system was left to equilibrate for 20 min; then, the absorbance spectra were taken. The wavelength of absorbance maximum was calculated from an average of three spectra. Difluoromethane was obtained from Ineosfluor (99.99%) and used as received. The solvatochromic dyes, Nile blue A oxazone (Nile Red) (99%) and *N,N*-dimethylindoleaniline (Phenol Blue) (97%), were used as received from Aldrich. Dye

TABLE 1: Susceptibility Constants for the Solvatochromic Probes Employed

solvatochromic probe	<i>a</i> value	<i>s</i> value	ν_0	R^2 value
Nile Red	1.180	−1.437	19.923	0.999
Phenol Blue	2.629	−1.765	18.048	0.993

concentrations ranged from 10^{-5} to 10^{-6} mol dm^{-3} such that solute–solute interactions could be ignored. The solutes employed were *o*-hydroxybenzoic acid (salicylic acid) (Fison, 97%), naphthalene (Fison, 98%), and *p*-methylbenzoic acid (*p*-toluic acid) (Aldrich, 98%). Each was used as received.

Results and Discussion

In the current study, two solvatochromic probes were employed to investigate the variations in π^* and α parameters for three solutes as a function of pressure. These were Nile blue A Oxazone (Nile Red) and *N,N*-dimethylindoleaniline (Phenol Blue), and the structures are shown in Figure 1. It was not possible to obtain values for the β parameter due to a lack of a suitable solvatochromic dye with sufficient absorption in a region free of overlap or interference from the absorption spectra of the solutes. The three solutes under investigation, salicylic acid, naphthalene, and *p*-toluic acid, all exhibited an absorption maximum at wavelengths below 400 nm.

The susceptibility constants were obtained by fitting the wavelength of absorption maxima, ν_{max} , for the probe molecules in CH_2F_2 at 90 °C to the π^* and α values published previously by Abbott and Durling.²⁷ The susceptibility constants *a* and *s* were obtained by this method with excellent correlations for each dye (Table 1). This approach is valid because the aim of the process is to determine relative changes in polarity parameters with pressure.

Polarizability Parameter π^*

Figure 2 shows how π^* for the three solute systems ($c = 0.01$ mol dm^{-3}) varies with pressure. For comparison, the π^* parameter for the pure CH_2F_2 sc fluid is also shown. It is clear that the addition of a solute to the sc fluid alters the interactions of the solvent molecules with the probe dye. The difference in π^* values, $\Delta\pi^*$, between the pure sc fluid and the 0.01 mol dm^{-3} solute systems is also shown in Figure 2 for ease of comparison.

Salicylic acid causes the largest deviation in π^* from that of the pure fluid. Surprisingly, it causes large negative deviations at lower pressures and large positive deviations at high pressures. To explain these observations, it is necessary to consider the

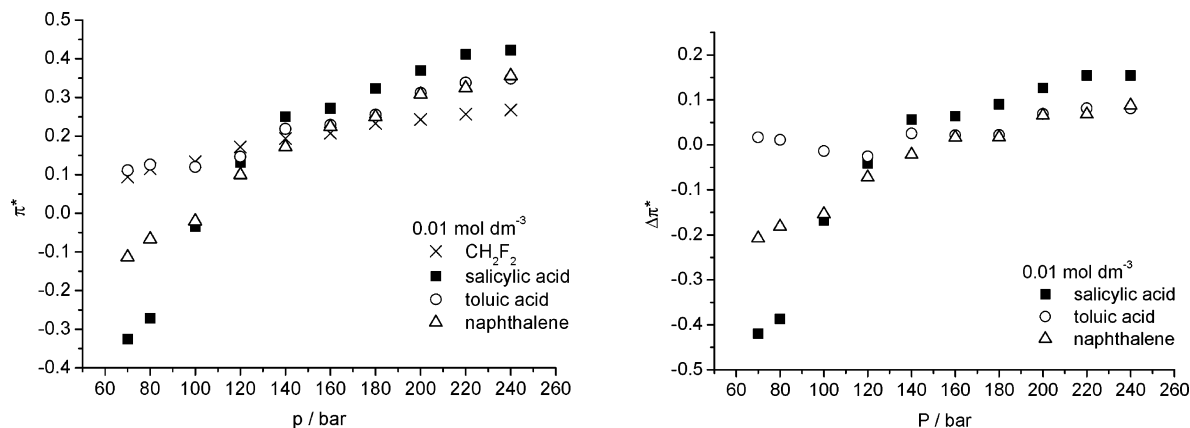


Figure 2. Polarizability/dipolarity parameter, π^* (left), and change in polarizability/dipolarity parameter, $\Delta\pi^*$, (right) for 0.01 mol dm^{-3} solutes in CH_2F_2 at 90 °C as a function of pressure.

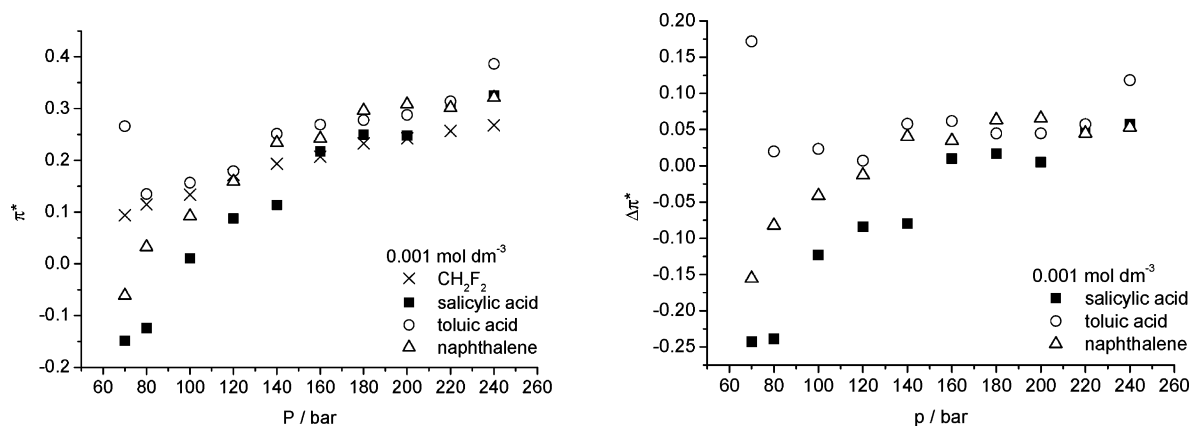


Figure 3. Polarizability/dipolarity parameter, π^* (left), and change in polarizability/ dipolarity parameter, $\Delta\pi^*$, (right) for 0.001 mol dm⁻³ solutes in CH₂F₂ at 90 °C as a function of pressure.

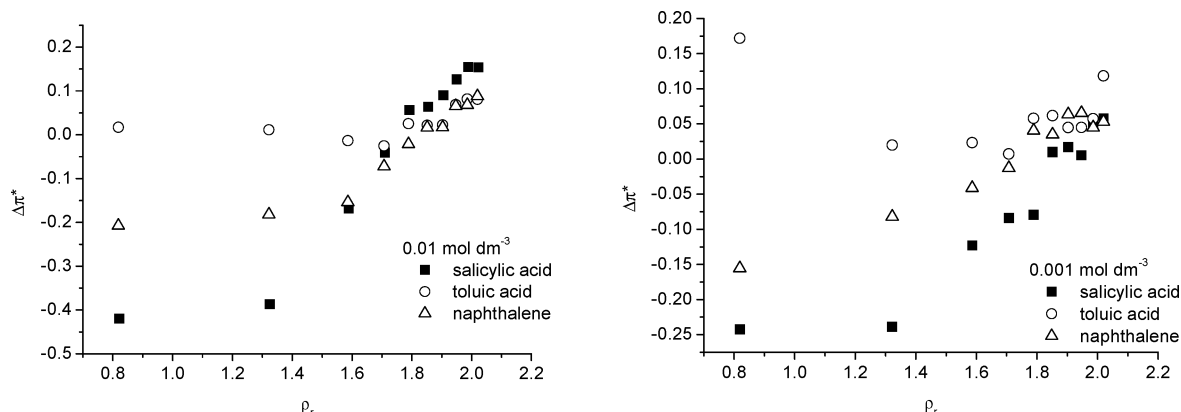


Figure 4. Change in polarizability/ dipolarity parameter, $\Delta\pi^*$, for 0.01 mol dm⁻³ solutes (left) and 0.001 mol dm⁻³ in CH₂F₂ at 90 °C as a function of reduced density.

relative interactions between the solvent, solute, and the indicator molecules. Salicylic acid is known to form dimers through hydrogen bonding, which will significantly increase the size of the solute species in solution. Although it would be possible to form hydrogen bonds between salicylic acid and the probe molecules used in this work, both of the dyes are weaker hydrogen-bond acceptors than salicylic acid. It is not surprising, therefore, that salicylic acid prefers to aggregate with itself under these conditions. In the region where negative deviations in π^* are observed, it has been shown previously that the solvation sheath around the indicator molecule is largely incomplete. The addition of a relatively high concentration of salicylic acid will require a significant amount of solvent to solvate it, which will decrease the amount of bulk solvent capable of solvating the indicator; and, hence, π^* appears to fall. As the pressure is increased, hydrogen bonding decreases and the association between the salicylic acid molecules is reduced. The salicylic acid dimers break up and the increase in free solvent molecules allows the probe molecule as well as the individual salicylic acid molecules to be solvated. This is seen as $\Delta\pi^*$ becomes less negative and above approximately 150 bar becomes positive. From previous studies, it is around this pressure that the cybotactic region around the probe dye is known to become complete.²⁷ The shift in π^* to positive values indicates the completion of the primary solvation sheath around the probe molecule and the inclusion of salicylic acid into the sheath of the indicator as pressure is increased further.

Figures 2 also show how π^* varies upon the addition of naphthalene. In the low-pressure region, $\Delta\pi^*$ for the naphthalene system is negative. This decrease in π^* with naphthalene is caused by the solvation of naphthalene molecules and conse-

quent decrease in solvent free density. However, unlike salicylic acid, naphthalene is unable to aggregate through hydrogen bonding; therefore, the solvated species is of a smaller size, requiring fewer solvent molecules. As the pressure is increased, a similar trend in increasing $\Delta\pi^*$ exists. Above ~150 bar, $\Delta\pi^*$ becomes positive indicating that the cybotactic region around the probe molecule is complete and naphthalene molecules become included in the solvation sheath.

In contrast to these results, the pattern exhibited by toluic acid is somewhat different. $\Delta\pi^*$ does not change significantly with pressure and is positive in the low-pressure region. This suggests that there is no competition between the probe molecule and toluic acid for the solvent molecules. It has been shown previously that the addition of cosolvents to sc fluids can increase π^* values.^{20–25} This work has shown that there is preferential clustering of the cosolvent around the probe molecule at low pressures and as the pressure is increased it is replaced by the solvent molecules. However, in this work the increase in π^* is not as significant as would be expected if preferential clustering of toluic acid around the probe molecule was solely present. Toluic acid is not known to form aggregates like salicylic acid, but it is capable of hydrogen bonding and could solvate the probe molecules used in this work. If these associated species were present in the low-pressure region (below 150 bar), then the observed slight increase in $\Delta\pi^*$ would be accounted for. When pressure is increased, the association between these species is weakened.

For naphthalene, no specific dipole–dipole interactions occur; hence, naphthalene is less likely to be incorporated in the solvation sphere around the indicator solute, and the apparent decrease in π^* at low-pressure results from the decreased

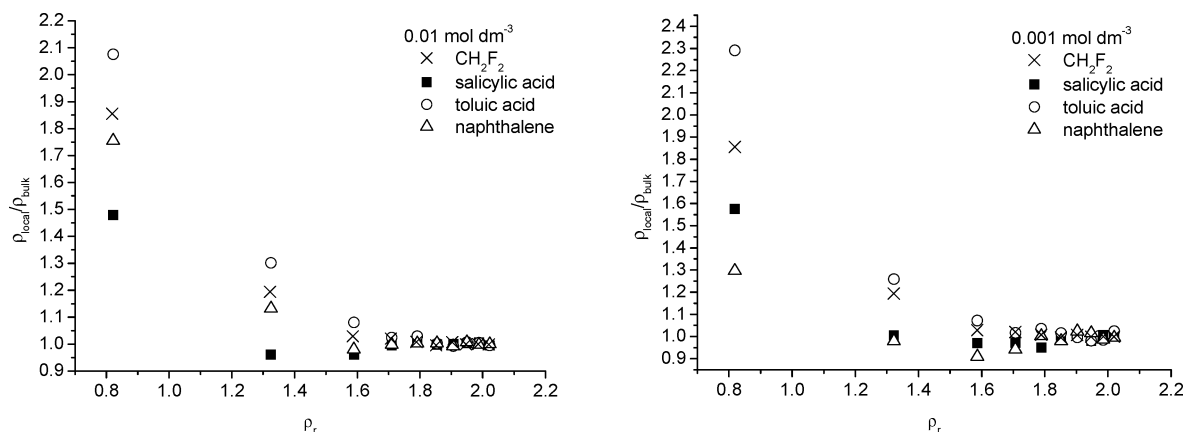


Figure 5. Ratio of local to bulk density as a function of reduced density for 0.01 mol dm⁻³ (left) and 0.001 mol dm⁻³ (right) solutes

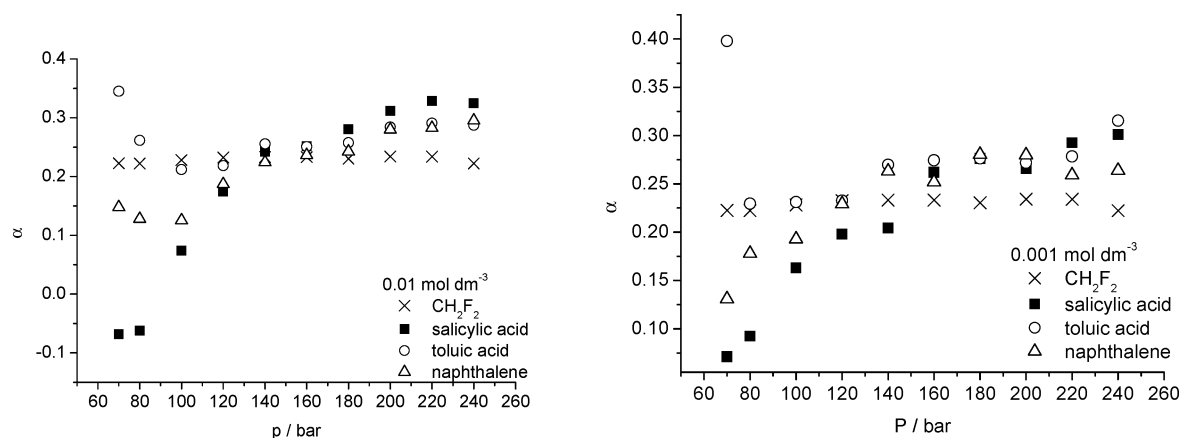


Figure 6. Hydrogen-bond-donor acidity, α , values for 0.01 mol dm⁻³ (left) and 0.001 mol dm⁻³ (right) solutes in CH₂F₂ at 90 °C as a function of pressure.

concentration of unassociated solvent molecules. The increased π^* at higher pressures is again due to an increased solvation density arising from the dissolution of solute.

The data for 0.001 mol dm⁻³ solute solutions are shown in Figure 3. Trends similar to the 0.01 mol dm⁻³ data are observed, although more scatter in the data is present. This indicates that even at lower concentrations the same solute–solute interactions and variations in solvation are present. Many research groups have shown that three distinct density regions exist with marked changes occurring in solvent properties at reduced densities, ρ_r , of approximately 1 and 2.^{16–19}

Figure 4 shows the dependency of $\Delta\pi^*$ on reduced density ($\rho_r = \rho/\rho_c$ where ρ_c for CH₂F₂ is 0.424 g cm⁻³) at 0.01 mol dm⁻³ and 0.001 mol dm⁻³, respectively. Although data below $\rho_r = 1$ and above $\rho_r = 2$ are limited, a noticeable change in the shape of the plot is observed over the pressure range studied. For dilute sc fluid solutions, the bulk fluid density and local solute density about the probe molecule have been shown to be similar in the liquid-like region ($\rho_r > 2$). The data presented here for different solutes is shown to converge with a steep slope close to this region. This is in agreement with the bulk density being akin to the local density around the indicator dye. Below this region, (approximately $1 < \rho_r < 2$), the local solvent density about the probe molecule is believed to be considerably higher than the bulk value. This is evident from the decrease in the slope and again is present in the systems investigated here. The slope in the gas-like region of a dilute sc fluid ($\rho_r < 1$) has been shown to again increase. This trend suggests that the local density approaches that of the bulk as ρ_r tends to zero. Although data in this region is more limited, it is in this region that the

distinction between the three solutes becomes even more apparent as they appear to diverge. The overall shape of the plots indicates that local density augmentation occurs with each of the solute systems.

If the linear region at high reduced density is extrapolated to lower reduced density, then a baseline is obtained of how π^* should change if the local density was equal to the bulk density. Extrapolation of the measured π^* value to this baseline will give the local solvent density around the probe molecule. A similar approach was used by Johnston et al.⁴¹ and by Abbott and Eardley for hydrofluorocarbon solvents.¹⁷ Figure 5 shows the ratio of the local to bulk densities as a function of bulk fluid density for 0.01 mol dm⁻³ and 0.001 mol dm⁻³ solute solutions, respectively. For comparison, the pure CH₂F₂ fluid is also shown. It is clear for each solute investigated that as reduced density increases toward 2 the local density becomes more akin to the bulk fluid density. However, in the region of lower reduced density distinct variations between the three solutes become apparent. There is an overall increase in the ratio of the local to bulk density for each solute but to different extents. Salicylic acid exhibits the lowest ratio of local to bulk density, indicating that the local solvent density around the indicator molecule is greater than the bulk fluid density; but this is not as great as those for naphthalene or toluic acid. This is in agreement with the variations in $\Delta\pi^*$ because if at pressures below approximately 150 bar ($\rho_r = 1.82$) the solvent molecules are effectively used up, solvating salicylic acid dimers, then the local solvent density around the probe molecule would be lower than that if no salicylic acid was present in solution. This is also shown to be true for the naphthalene systems but to a

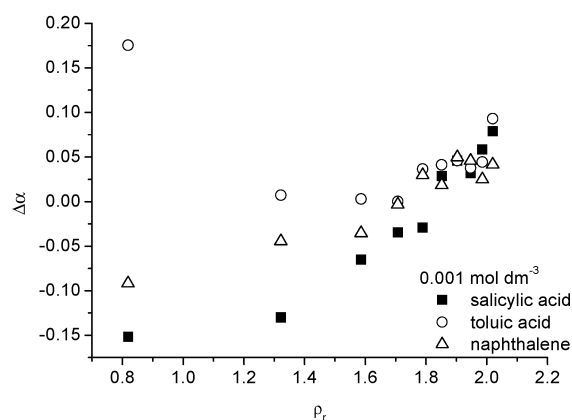
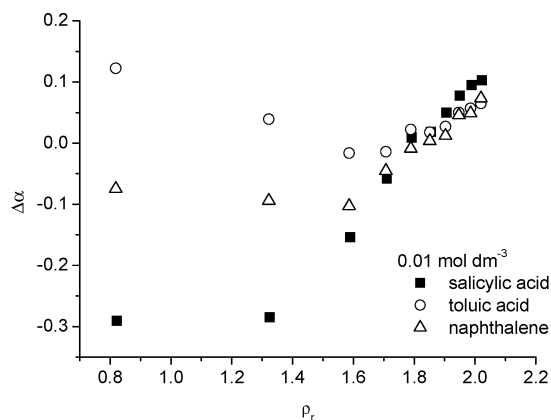


Figure 7. Change in hydrogen-bond acidity, $\Delta\alpha$, for 0.01 mol dm⁻³ (left) and 0.001 mol dm⁻³ (right) solutes in CH₂F₂ at 90 °C as a function of reduced density.

lesser extent, suggesting that fewer solvent molecules are required to solvate naphthalene molecules than the salicylic acid aggregates. This is in agreement with the relative sizes of the species ($V_{\text{salicylic acid dimer}} = 291.84 \text{ \AA}^3$ and $V_{\text{naphthalene}} = 159.12 \text{ \AA}^3$). Toluic acid demonstrates the largest increase in local density around the indicator molecule. This is indicative of a system in which preferential clustering around the indicator is present as seen with sc fluid/cosolvent systems.^{20–25}

It is surprising that although the solute concentration is very low its effect on π^* is significant. It is generally accepted that in the lower pressure region the solvation sheath around the indicator solute (which is present at 10^2 to 10^4 times lower concentrations than the solute) is incomplete. The addition of any species that will preferentially remove free solvent from the bulk solution will affect the solvation equilibrium and cause a significant change in the polarizable environment. Although the magnitude of the change is unexpected given the low concentration of indicator and solute, the effect can be seen clearly in Figure 4 and there seem to be no other reasonable explanations for this observation. The $\rho_{\text{local}}/\rho_{\text{bulk}}$ values for the solutions in Figure 5 deviate by only a small amount compared to the pure fluid, which would equate to changes of only one or two molecules in the solvation sheath around the indicator solute.

This shows that solute–solute–solvent interactions are complex in supercritical solutions and change with the polarity of the solute and the pressure of the solution. Results suggest that the solute molecules are capable of drawing the solvent molecules around them and hence imparting structure on the solution. This could influence the bulk properties of the sc solution and explain the fluctuations in density often seen around the critical point.

Hydrogen-Bond-Donor Properties α

The temperature and pressure dependence of the hydrogen-bond acidity parameter, α , for CH₂F₂ and CF₃CH₂F has been characterized by Abbott et al.²⁷ The magnitude of α values were found to be comparable to related compounds and consistent with the findings of other authors.^{15,42} The α values were found to be almost constant with increasing pressure in the liquid state and to decrease with increasing pressure in the sc state. The three-region density model was shown to exist for the α parameter, and it was shown that in the low-density region the polarity of these fluids is dominated by hydrogen-bond-donor properties. It was highlighted that in this region the solvent molecules are likely to preferentially interact with the polar groups of the probe molecule. These findings support the work of other authors.³⁹

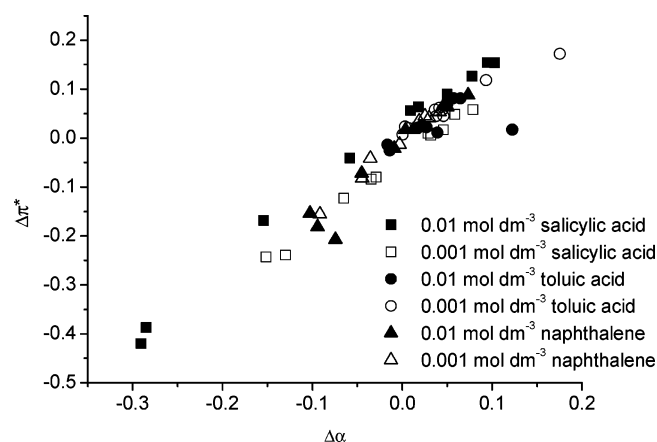


Figure 8. Correlation between $\Delta\pi^*$ and $\Delta\alpha$ for 0.01 mol dm⁻³ solute solutions.

Figure 6 shows, for the first time, the pressure dependency of the HBD parameter for sc solute solutions at concentrations of 0.01 mol dm⁻³ and 0.001 mol dm⁻³. It is clear that the addition of a solute to a sc fluid has a significant effect on the hydrogen-bond-donor properties of the solvent and that these results confirm the findings discussed above for the polarizability parameter.

The change in α with respect to the pure fluid, $\Delta\alpha$, is shown in Figure 7 as a function of reduced density. Although data in the low and high-density regions are more limited, the reduced density plots demonstrate that the three-region density model still exists when a solid solute is dissolved in a sc solution. Close to the high-density region ($\rho_r > 2$), the data for each solute begin to converge with positive $\Delta\alpha$ values. This indicates that solvent–solute interactions are similar under these conditions regardless of the type of solute. The positive value of $\Delta\alpha$ suggests that the solute molecules surround the indicator molecule and are capable of donating a proton to form a hydrogen bond with the indicator. We have shown previously that in the absence of the solute molecules α has been found to not change significantly with pressure in this region. This is thought to be due to self-association between the solvent molecules, which reduces the ability of the solvent to act as a hydrogen-bond donor to the probe molecule.

Figure 7 shows that at lower pressures and densities ($\rho_r < 2$) the trend for each solute becomes different. Salicylic acid is shown to cause a considerable reduction in α with respect to the pure fluid. This could be caused by the interactions of the solvent molecules with the highly associated salicylic molecules present under these conditions. This would mean that there are

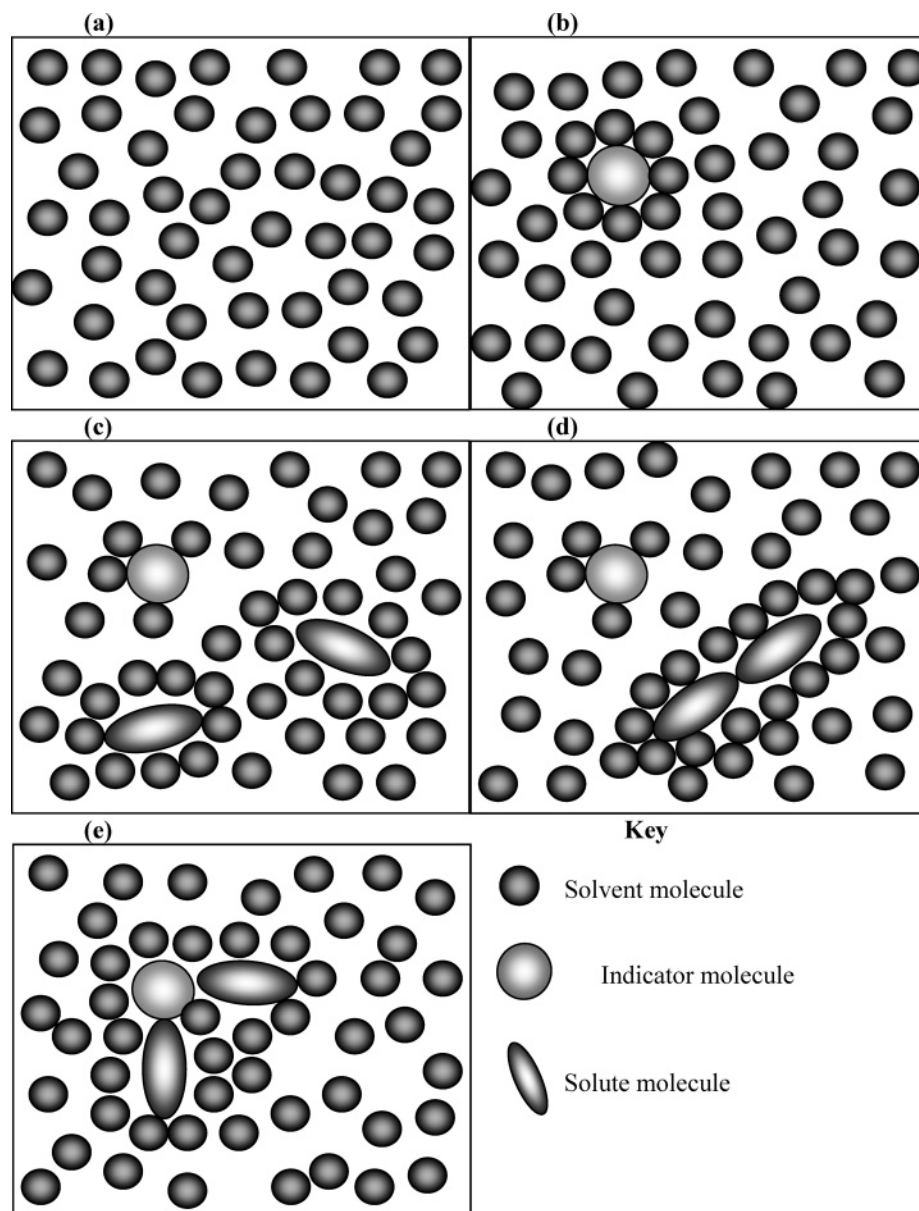


Figure 9. Illustration depicting solvent–solute interactions present in solution, (a) Solvent molecules; (b) solvent and indicator molecule; (c) solvent, indicator, and unassociated solute molecules; (d) solvent, indicator, and associated solute molecules; and (e) solvent and solute solvating the indicator molecule.

fewer solvent molecules available to interact with the indicator molecule than in the absence of salicylic acid. A similar trend is observed for naphthalene; however, fewer solvent molecules would be required to solvate a naphthalene molecule compared to a salicylic acid aggregate. Interestingly, $\Delta\alpha$ values for toluic acid begin to increase as the density is reduced below $\rho_r \approx 1.8$. Above this reduced density, the cybotactic region around the probe molecule is known to be complete and the data converge with the other solute data. The remarkable increase in α below this reduced density may be a consequence of hydrogen-bond interactions between toluic acid and the indicator molecule.

Data was also collected for a concentration of $0.0001 \text{ mol dm}^{-3}$, and the trends were found to be similar to the higher concentrations, although the scatter of points was enhanced. Despite this, it is clear that the hydrogen-bond interactions are consistent for each solute over the pressure and concentration range investigated. It is also clear from Figures 2 and 6 that the trends for α and π^* are similar with pressure.

Figure 8 shows the correlation between the change in the polarizability parameter and hydrogen-bond-donor ability of the

solvent for each solute investigated at 0.01 and $0.001 \text{ mol dm}^{-3}$. It is clear that the two polarity parameters are closely related and suggests that the main cause of changes in solution polarity is the change in local density of the solvent. Figure 9 shows a schematic representation of the proposed solvent–solute interactions present in these systems. Schematic a shows a system only containing sc fluid solvent molecules, and in picture b an indicator probe molecule is solvated by the sc fluid molecules. Picture c could represent the scenario when an unassociated solute molecule like naphthalene is present in solution along with the indicator molecule. The solvent density around the indicator molecule should be slightly lower than that in b because the naphthalene solute molecules draw the solvent molecules around themselves. In contrast to this schematic, d shows the situation that could occur when an associated molecule like salicylic acid is added to the system. The associated salicylic molecules are solvated by the solvent molecules, whereas the indicator molecule is surrounded by fewer solvent molecules than shown in picture b. We propose that the scenarios shown in c and d could explain the apparent

reduction in π^* and α values because in both cases there are fewer solvent molecules available to solvate the probe and participate in hydrogen-bonding interactions. In picture e, the converse situation is represented. In this case, the solute molecule solvates the indicator molecule and both are fully solvated by solvent molecules. This situation is seen to occur at high pressures for each solute investigated and is indicative of the apparent increase in π^* that is observed. Positive deviations in the hydrogen-bond-donor parameter can also be explained by this scenario. Salicylic acid presents the largest positive increase in α and is capable of hydrogen-bond interactions with the indicator molecules.

Conclusions

This work has shown how the addition of a solid solute to a sc fluid affects the polarity parameters of the solution, and a model for solvation has been proposed. It has been found that when a solute capable of forming self-associated aggregates such as salicylic acid is examined there is a significant reduction in the solvent free density. This is shown by a decrease in the polarizability parameter and the HBD properties of the solvent. Because the association between these species is weakened with increasing pressure, the solvent molecules reorientate to complete the solvation sheath of the indicator molecule. Under these conditions, the solute molecule is included in the solvation sheath, and this is indicated by a positive increase in the polarizability parameter with respect to the pure sc fluid. When a nonpolar solute, naphthalene, was examined, a similar trend was found. Conversely, when the polar species, toluic acid, was examined, the general trend was found to differ. This is perceived to be due to the ability of toluic acid to associate with the solvatochromic dyes in a manner similar to that seen with cosolvents in sc CO₂ at low densities. In the high-density region, toluic acid is shown to exhibit behavior similar to the other solutes examined. The ability of a solute molecule to influence the solvent structure is of great significance because bulk solutions properties may be affected.

References and Notes

- (1) Kamlet, M. J.; Abboud, J.-L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027.
- (2) Sigman, M. E.; Lindley, S. M.; Leffler, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 1471.
- (3) Yonker, C. R.; Frye, S. L.; Kalkwarf, D. R.; Smith, R. D. *J. Phys. Chem.* **1986**, *90*, 3022.
- (4) Smith, R. D.; Frye, S. L.; Yonker, C. R.; Gale, R. W. *J. Phys. Chem.* **1987**, *91*, 3059.
- (5) O'Neill, M. L.; Kruus, P.; Burk, R. C. *Can. J. Chem.* **1993**, *71*, 1834.
- (6) Maiwald, M.; Schneider, G. M. *Ber. Bunsen. Phys. Chem.* **1998**, *102*, 960.
- (7) Lu, J.; Brown, J. S.; Boughner, E. C.; Liotta, C. L.; Eckert, C. A. *Ind. Eng. Chem. Res.* **2002**, *41*, 2835.
- (8) Lu, J.; Boughner, E. C.; Liotta, C. L.; Eckert, C. A. *Fluid Phase Equilib.* **2002**, *198*, 37.
- (9) Minami, K.; Mizuta, M.; Suzuki, M.; Aizawa, T.; Arai, K. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2257.
- (10) Kim, S.; Johnston, K. P. *Ind. Eng. Chem. Res.* **1987**, *26*, 1206.
- (11) Blitz, J. P.; Yonker, C. R.; Smith, R. D. *J. Phys. Chem.* **1989**, *93*, 6661.
- (12) Yonker, C. R.; Smith, R. D. *J. Phys. Chem.* **1988**, *92*, 2304.
- (13) Ikushima, Y.; Saito, N.; Arai, M. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1817.
- (14) Abbott, A. P.; Eardley, C. A.; Scheirer, J. E. *J. Phys. Chem. B* **1999**, *103*, 8790.
- (15) Lagalante, A. F.; Hall, R. L.; Bruno, T. J. *J. Phys. Chem. B* **1998**, *102*, 6601.
- (16) Abbott, A. P.; Eardley, C. A. *J. Phys. Chem. B* **1998**, *102*, 8574.
- (17) Abbott, A. P.; Eardley, C. A. *J. Phys. Chem. B* **1999**, *103*, 2504.
- (18) Abbott, A. P.; Eardley, C. A.; Scheirer, J. E. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3722.
- (19) Abbott, A. P.; Eardley, C. A.; Scheirer, J. E. *J. Phys. Chem. B* **1999**, *103*, 8790.
- (20) Yonker, C. R.; Smith, R. D. *J. Phys. Chem.* **1988**, *92*, 2374.
- (21) Kim, S.; Johnston, K. P. *AIChE J.* **1987**, *33*, 1603.
- (22) Sun Y.-P.; Bennett, G.; Johnston, K. P.; Fox, M. A. *J. Phys. Chem.* **1992**, *96*, 10001.
- (23) Zhang, J.; Lee, L. L.; Brennecke, J. F. *J. Phys. Chem.* **1995**, *99*, 9268.
- (24) Kelley, S. P.; Lemert, R. M. *AIChE J.* **1996**, *42*, 2047.
- (25) Chen, J.; Shen, D.; Wu, W.; Han, B.; Wang, B.; Sun, D. *J. Chem. Phys.* **2005**, *122*, 204508.
- (26) Bennett, G. E.; Johnston, K. P. *J. Phys. Chem.* **1994**, *98*, 441.
- (27) Abbott, A. P.; Corr, S.; Durling, N. E.; Hope, E. G. *J. Phys. Chem. B* **2003**, *107*, 10628.
- (28) Blitz, J. P.; Yonker, C. R.; Smith, R. D. *J. Phys. Chem.* **1989**, *93*, 6661.
- (29) Ikushima, Y.; Saito, N.; Arai, M. *J. Phys. Chem.* **1992**, *96*, 2293.
- (30) Gupta, R. B.; Combes, J. R.; Johnston, K. P. *J. Phys. Chem.* **1993**, *97*, 707.
- (31) Bulgarevich, D. S.; Sako, T.; Sugeta, T.; Otake, K.; Takebayashi, Y.; Kamizawa, C.; Horikawa, Y.; Kato, M. *Ind. Eng. Chem. Res.* **2002**, *41*, 2074.
- (32) Bulgarevich, D. S.; Otake, K.; Sako, T.; Sugeta, T.; Takebayashi, Y.; Kamizawa, C.; Shintani, D.; Negishi, A.; Tsuruni, C. *J. Chem. Phys.* **2002**, *116*, 1995.
- (33) Barlow, S. J.; Bondarenko, G. V.; Gorbaty, Y. E.; Yamaguchi, T.; Poliakoff, M. *J. Phys. Chem. A* **2002**, *106*, 10452.
- (34) Brennecke, J. F.; Tomasko, D. L.; Peshkin, J.; Eckert, C. A. *Ind. Eng. Chem. Res.* **1990**, *29*, 1682.
- (35) Betts, T. A.; Zagrobelny, J.; Bright, F. V. *J. Am. Chem. Soc.* **1992**, *114*, 8163.
- (36) Heitz, M. P.; Bright, F. V. *J. Phys. Chem.* **1996**, *100*, 6889.
- (37) Adams, J. E. *J. Phys. Chem. B* **1998**, *102*, 7455.
- (38) Ingrosso, F.; Ladanyi, B. M.; Mennucci, B.; Scalmani, G. *J. Phys. Chem. B* **2006**, *110*, 10120.
- (39) Tucker, S. C. *Chem. Rev.* **1999**, *99*, 391.
- (40) Yonker, C. R.; Smith, R. D. *J. Phys. Chem.* **1988**, *92*, 236.
- (41) Johnston, K. P.; Kim, S.; Combes, J. *ACS Symp. Ser.* **1989**, *406*, 52.
- (42) Corr, S. *J. Fluorine Chem.* **2002**, *118*, 55.