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Review Commentary

Solvatochromic probes in supercritical fluids

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ABSTRACT: Supercritical fluids (SCFs) have in recent years become favored solvents for chemical reactions and separations. In order to be used as solvents, their solvation properties should be known, and solvatochromic probes are effectively used for this purpose. They have been applied foremost for supercritical carbon dioxide (SCCD), which is by far the most widely employed SCFs, but also for supercritical water, fluorocarbons and other substances. The probes have also found use in mixtures involving SCF and a more polar additive that have better solvation properties for polar solutes and in solvents expanded by dissolving in them SCCD. Clustering of the molecules of the SCF around the probe molecule is a common feature of the systems studied and this may reflect on the employment of the probes as stand-ins for other solutes. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: expanded solvents; fluorocarbons; solvation properties; solvatochromic probes; supercritical carbon dioxide; supercritical fluids; supercritical water

INTRODUCTION

There has been a tendency in recent years to switch towards 'green' solvents, i.e. those benign to the environment, as reaction media and for extraction and separation purposes. Such 'green' solvents must not be toxic or flammable, or leave residues that are difficult to deal with after use. Supercritical fluids (SCFs) can serve well as such solvents, provided that the solutes of interest are soluble in them. They have the advantages that their properties can be readily tuned by changes in the pressure and temperature (and hence density) and that they can be readily removed as gases by releasing the pressure, leaving behind the desired reaction products or separated solutes. The resulting gas can be re-compressed for recycling. The abilities of SCFs to dissolve the reactants and products of reactions or the materials to be separated depend on their solvating powers. These, in turn, depend on the polarity (also polarizability), and the hydrogen bond donating and accepting abilities of the SCFs. These properties can be measured by the use of solvatochromic probes that have already found much use for the characterization of ordinary liquid solvents.

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SUPERCRITICAL FLUIDS

On the pressure P vs temperature T diagram[1] for pure substances, the regions corresponding to the vapor and liquid phases are separated by the vaporization/liquefaction (saturation) curve extending from the triple point (where the equilibrium involves also the solid phase) to the critical point (P_c, T_c). Beyond this point ($P > P_c$ and $T > T_c$), only one phase exists, called a supercritical fluid (SCF). The fluid density of an SCF varies rapidly with a slight change in pressure at constant temperature near the critical point, since the compressibility of the substance at the critical point is infinite. The isothermal compressibility κ_T of SCFs even at a few degrees above T_c is still large. The correlation length, measuring the range of density fluctuations, falls from 10 times the mean intermolecular distance at 1 K above T_c to about two times this distance at $T_c + 10$ K.[2] Consequently, the solvent power of an SCF and other physico-chemical properties depend strongly on the P and T variables and can be finely tuned by controlling them. When an SCF is maintained at a pressure $P > P_c$ but at a temperature $T < T_c$ it is called a subcritical liquid and has properties intermediate between those of a supercritical fluid ($P > P_c$ and $T > T_c$) and a liquefied gas ($P < P_c$ and $T < T_c$).

Most applications of supercritical fluids (and subcritical liquids) depend on their density being 'tunable', so that their solvent power can be varied over a wide range.

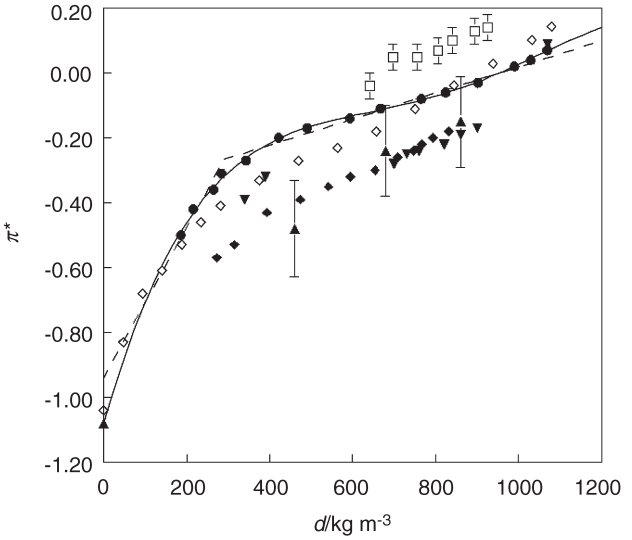

Figure 1. Values of π^* in SCCD as function of its density ▲, Ref. 18 at 309–315 K; ●, Ref. 19 at 308 K; □, Ref. 20 at 306 K; ◇, Ref. 21 at 308 K; ▼, Ref. 25 at 305.7 K; ◆, Ref. 31 at 318 K. The continuous curve is a fourth-degree polynomial drawn through the points (including the gas-phase one) and the dashed lines are drawn according to those in Ref. 19

SCFs can be solvents (reaction media, extraction solvents, chromatographic eluents) with high solvent power at high densities (temperature higher than the critical temperature but not far from it and pressure much above the critical pressure) or become compressed gases with very low solvent power at low densities (temperature near or higher than the critical temperature and pressure lower than the critical pressure). Except for ammonia and water among commonly used SCFs, these generally have a critical pressure between 3 and 8 MPa (see Table 1). Few substances have critical temperatures < 323 K (ethane, ethene, carbon dioxide, dinitrogen oxide and trifluoromethane), and the T_c values increase with the complexity of the molecule[3] (Table 1).

For many substances (conformal fluids), there exists an empirical relationship[1] between the critical temperature, pressure and density, d_c:

$$P_c/T_c d_c = (0.290 \pm 0.005)R/M \qquad (1)$$

The numerical constant corresponds to P_c in Pa, T_c in K, d_c in kg m^{-3}, R, the gas constant, in J K^{-1} mol^{-1} and M, the molar mass of the fluid, in kg mol^{-1}. Therefore, only two of the critical constants P_c, T_c and d_c of the fluid need be known and the third can be obtained from Eqn (1) for approximate calculations.

The transport properties of SCFs are very attractive: SCFs are nearly as dense as ordinary liquids but mobile almost as a gas, having very low viscosities and intermediate diffusivities (Table 2).[2,4] The kinematic viscosity, $\nu = \eta/d$, is therefore very low, owing to the high density and fairly low dynamic viscosity, η. Therefore, the mass and heat transfers in an SCF are fast, compared with liquid organic solvents or water.

Carbon dioxide is a very attractive supercritical fluid [supercritical carbon dioxide (SCCD)] for many reasons.[5] It is very cheap and abundant in pure form (food grade) worldwide, it is non-flammable and non-toxic and it is usually manufactured from waste streams (mainly

Table 1. Critical parameters of SCF solvents (adapted from Refs 2 and 5) and the dipole moments of their molecules

Substance	M (kg mol^{-1})	T_c (K)	P_c (MPa)	ρ_c (kg m^{-3})	μ (D[a])
Methane	0.01604	190.4	4.60	162	0
Ammonia	0.01703	405.5	11.35	235	1.47
Water	0.01802	647.3	22.12	316	1.85
Ethene	0.02805	282.4	5.04	215	0
Ethane	0.03007	305.4	4.88	203	0
Methanol	0.03204	512.6	8.09	272	2.87
Carbon dioxide	0.04401	304.1	7.38	469	0
Dinitrogen oxide	0.04401	309.6	7.24	452	0.16
Propane	0.04409	369.8	4.25	217	0.08
Ethanol	0.04607	513.9	6.14	276	1.66
Dimethyl ether	0.04607	400.0	5.24	256	1.30
Difluoromethane	0.05202	351.6	5.83	431	1.98
n-Butane	0.05812	425.2	3.8	228	0
2-Propanol	0.06010	508.3	4.76	273	1.58
Trifluoromethane	0.07001	299.3	4.86	528	1.65
n-Pentane	0.07215	469.7	3.37	237	0
n-Hexane	0.08618	507.5	3.01	234	0
Diethyl ether	0.07412	466.7	3.64	265	1.15
Benzene	0.07811	562.2	4.89	302	0
1,1,1,2-Tetrafluoroethane	0.10203	374.2	4.06	515	2.06
Chlorotrifluoromethane	0.10446	302.0	3.86	580	0.50
Pentafluoroethane	0.12002	339.3	3.63	571	1.56
Xenon	0.13129	289.7	5.84	1109	0
Sulfur hexafluoride	0.14605	318.7	3.76	735	0

[a] $1\ \mathrm{D} = 3.33 \times 10^{-30}$ C m.

Table 2. Comparison of average ranges of properties of gases, liquids and SCF (adapted from Refs 3 and 4)

State	Density, d (kg m^{-3})	Viscosity, η (mPa s)	Diffusivity, D (m^2 s^{-1})
Gases, ambient	0.6–2	0.01–0.03	$(0.1–0.4) \times 10^{-4}$
SCFs, at T_c, P_c	200–500	0.01–0.03	$\sim 10^{-7}$
SCFs, at T_c, $4P_c$	400–900	0.03–0.09	$\sim 2 \times 10^{-8}$
Liquids, ambient	600–1600	0.2–3	$(0.2–2) \times 10^{-9}$

gaseous effluents from fertilizer plants). It also has convenient values of $T_c = 304$ K, permitting operations at near-ambient temperature, and $P_c = 7.4$ MPa, leading to operating pressures between 10 and 35 MPa. However, SCCD is a 'weak' non-polar solvent. It dissolves lipids such as vegetable oils and hydrocarbons and essential oils, but has a weak affinity to oxygenated or hydroxylated molecules. It hardly dissolves at all salts and hydrophilic compounds such as sugars and proteins. Addition of a polar co-solvent can, however, increase significantly the solvent power and polarity of SCCD. Water, on the other hand, has properties at subcritical or supercritical conditions [supercritical water (SCW)] that are completely different from those of both SCCD and liquid water at ambient conditions. Its $T_c = 647.35$ K is fairly high, as is its $P_c = 22.12$ MPa. Still, it is very useful, being very cheap and abundant in pure form, non-flammable and non-toxic. The large reduction in the relative permittivity, ε_r (dielectric constant), of SCW compared with water at ambient conditions and the disruption of the three-dimensional network of hydrogen bonds[6] result in a fluid that readily dissolves non-polar organic solutes or gases. Hence SCW has been proposed as a medium for destroying toxic organic substances by complete oxidation with oxygen, both ingredients being soluble in SCW, while the resulting products are either water and carbon dioxide, or also mineral acids that can be precipitated by means of alkali.[7] However, the polarity and the hydrogen bond donating and accepting abilities of individual water molecules are not impaired in SCW, hence its solvent power extends also to polar and hydrophilic molecules.

For the dependence of the solubility of solutes on the density d of the SCF and the temperature, provided that the solubility is relatively low, Chrastil's[8] empirical correlation holds:

$$c = d^k \exp(a/T + b) \tag{2}$$

where c is the solute concentration and a, b and k are empirical constants. The solubility depends strongly on the fluid density since generally $1 < k < 5$, so that it increases with pressure at constant temperature. At a given temperature the solubility has also been described by Gurdial and Foster[9] as

$$\ln x_2 = C_0 + (v_2/RT\kappa_{T1}) \ln d_1 \tag{3}$$

where subscript 2 pertains to the solute and 1 to the SCF, x is the mole fraction solubility, v is the infinite dilution partial molar volume and κ_T is the isothermal compressibility. When the SCF is depressurized at constant temperature, the solubility drastically decreases, by several orders of magnitude. Another way to decrease the solubility of a substance in SCFs is the use of an anti-solvent. For instance, when SCCD is added to a polar organic solvent it significantly decreases its polarity and precipitates compounds previously dissolved in it.

Hence, the solubilities of substances in SCFs play a key role in their applications as reaction media or separating media. The solubilities of solutes in SCFs are closely related to the solvation properties of these solvents. These can be ascertained by means of solvatochromic probes, as described below.

SOLVATOCHROMIC PROBES

The use of solvatochromic probes is based on the premise that their measurable spectral shifts in a given solvent relative to a reference state represent an inherent solvation property of the solvent. If the polarity of a solvent is defined as its 'overall solvating ability',[10] then the Dimroth–Reichardt $E_T(30)$ index can be used for indicating this polarity. This approach relies on a single solvatochromic probe to describe the solvation properties of the solvent, as a representative for all solutes. It has the drawback that in the case of solvent mixtures, the measured spectral shifts may indicate preferential solvation of this probe by one solvent component and not be valid for any other solute.[11]

Another approach is to employ the converging results from several probes, suitably averaged, in order to express a more restricted aspect of the solvation ability. For example, the ability of solvents to act as Lewis bases can be expressed by the Kamlet–Taft β parameter[12] and similarly for other solvation properties. The general linear solvation energy relationship (LSER)

$$XYZ = (XYZ)_0 + s\pi^* + a\alpha + b\beta \tag{4}$$

proposed by Kamlet, Taft, and co-workers was shown to hold for many experimentally measured quantities XYZ of solutions.[13] The coefficients s, a and b describe the sensitivities of the solute to certain solvent properties and $(XYZ)_0$ is the quantity measurable in the gas phase or in inert solvents without solvation abilities. The relevant solvent properties are π^*, α and β, which are the dipolarity/polarizability, hydrogen bond donating (HBD) ability and the hydrogen bond accepting/electron-pair donating (HBA/EPD) ability, respectively. [Note: for

certain properties *XYZ* and aromatic and polychlorinated solvents the term $s\pi^*$ in Eqn (1) has to be modified to $s(\pi^* - d\delta)$, where δ is 1.0 and 0.5 for such solvents, respectively (and zero for others), and $0 \leq d \leq 0.4$. However, this is hardly relevant to SCFs that are non-aromatic and not polychlorinated.]

If the solute is a solvatochromic probe, then *XYZ* is generally the wavenumber ν of the longest wavelength peak of its light absorption in the UV–visible region, or its emission wavenumber, if fluorescent. Useful solvatochromic probes have large ranges of signal values $\Delta\nu = \nu - \nu_0$ obtained for solvents with extreme solvating properties, from the least to the largest. The values should be only slightly dependent on the concentration of the probe molecule in the solvent, but may depend on the temperature (thermochromism). Solvatochromic shifts, $\Delta\nu = \nu - \nu_0$, in a series of solvents with increasing solvating properties may be positive (hypsochromic or blue shifts to shorter wavelengths, higher wavenumbers and energies), or negative (bathochromic or red shifts to longer wavelengths, lower wavenumbers and energies). Since the solvating solvent generally interacts with the probe by means of its dipole moment, the direction of the shift depends on whether the dipole moment of the probe molecule in the excited state is larger or smaller than in the ground state.[10]

Probes suitable for the measurement of π^* should be devoid of HBD and HBA abilities. Those used for the measurement of α or β are commonly applied in the solvatochromic comparison mode. That is, a pair of probes is used that are homomorphs of each other, one with HBD (or HBA) properties and the other so substituted that it has none of these. The latter of the pair of probes corrects for the general dipolarity of the former so that only the HBD (or HBA) abilities of the SCF are measured. Typical probe pairs are 4-nitrophenol–4-nitroanisole and 4-nitroaniline–*N*,*N*-dimethyl-4-nitroaniline for obtaining β values. Other often used probes for SCF polarity assessment are dyes such as Nile Red or Phenol Blue and the betaine dye used for the $E_T(30)$ scale. Nile Red and the betaine dye are sensitive to both the polarity and the HBD properties of the solvent to different extents.

The π^* scale is normalized so that $\pi^* = 0.00$ for cyclohexane and $\pi^* = 1.00$ for dimethyl sulfoxide. The α scale was initially normalized to 1.0 for methanol, later revised to 0.98 for this solvent (and $\alpha \equiv 0$ for aprotic and non-protogenic solvents). The β scale was normalized so that $\beta = 0$ for the *n*-alkanes and $\beta = 1.0$ for hexamethylphosphoric triamide, a value that was later revised to 1.05.[13] Comprehensive lists of values for ordinary liquid solvents of these solvatochromic parameters as also of $E_T(30)$ have been published.[3,10,13–15] It should be noted that there are solvents for which the values are outside these normalization points. For instance, fluorocarbons have negative π^* values, ranging down to -0.48 for perfluorohexane and other solvents range up to 1.08 for aniline[14] or 1.20 for 2-cyanopyridine.[15] The high α value of 1.96 for hexafluoro-2-propanol and the high β value of 1.43 for 1,2-diaminoethane, recorded so far,[15] still need not be the highest that can be achieved by strong HBD or HBA solvents.

SOLVATOCHROMIC PROBES IN SUPERCRITICAL CARBON DIOXIDE (SCCD)

The most extensive use of solvatochromic probes was made for SCCD, which, in turn, is the most widely used and extensively studied SCF. Hyatt[16] was the first to place SCCD on a polarity scale comparable to organic solvents on the basis of results for solvatochromic probes. Whereas the betaine dye used for the determination of $E_T(30)$ is practically insoluble in SCCD, its pentakis(4-*tert*-butyl)-substituted analog is sufficiently soluble. It yielded in SCCD at 315 K and 7 MPa an $E_T'(30)$ value of 34.3 kcal mol^{-1} (1 kcal = 4.184 kJ) that, according to the (later established)[17] conversion expressions $E_T(30) = 1.061E_T'(30) - 1.919$ and $E_T^N = [E_T(30) - 30.7]/32.4$ yields $E_T(30) = 34.5$ kcal mol^{-1} and the normalized $E_T^N = 0.116$. These values are higher than expected (in analogy with alkanes) for the non-polar solvent SCCD having low polarizability (although carbon dioxide has an appreciable quadrupole moment). On the other hand, the probes 4-(*N*,*N*-diethylamino)-4′-nitrodiazobenzene and its 3′-trifluoromethyl further substituted analog yielded linear correlations of their absorption wavenumbers with the Kamlet–Taft π^* values, so that the resulting $\pi^* = -0.52 \pm 0.19$ and -0.60 ± 0.10 for SCCD (at unspecified temperature and pressure) could be reported.[16]

Subsequent studies by Sigman *et al.*[18] and Yonker *et al.*[19] provided π^* values as functions of the densities. The former group used seven probes [4-nitroanisole, *N*,*N*-diethyl-3-nitroaniline, 4-methoxy-β-nitrostyrene, 4-nitroethylbenzene, *N*-methyl-2-nitro-4-toluidine, *N*,*N*-diethyl-4-nitroaniline and 4-(*N*,*N*-dimethylamino)benzophenone]. They showed that their average π^* decreased smoothly with decreasing density (at 309–315 K), from -0.12 at 860 kg m^{-3} through -0.22 at 680 kg m^{-3} and -0.46 at 460 kg m^{-3} to the vapor value of -1.08.[18] The second group[19] used a single probe, 2-nitroanisole, and data at 308 and 323 K and many densities, and obtained on the whole somewhat less negative values for π^* than the former group, as shown in Fig. 1. Yonker *et al.*[19] preferred to see a break in the curve, and drew two straight lines through the data, but this may not be a valid representation. The same probe, 2-nitroanisole, was used by O'Neill *et al.*[20] at densities of 650–940 kg m^{-3} and 306 K, and obtained even less negative, indeed positive, π^* values over most of the range. However, Maiwald and Schneider,[21] employing 2-nitroanisole, 4-nitroanisole and *N*,*N*-dimethyl-4-nitroaniline as probes, obtained at $T_r = T/T_c = 1.1$ results in better agreement with the earlier ones of Yonker *et al.*,[19] as shown in Fig. 1.

The positive π^* values above a reduced density $d_r = d/d_c = 1.9$ (890 kg m^{-3}) were confirmed, as were the very negative values at low densities.

Less conventional probes were also employed to obtain the dipolarity/polarizability of SCCD. Eberhardt *et al.*[22] used the pentakis(4-*tert*-butyl)-substituted betaine dye that Hyatt[16] had already used, but over a range of pressures and at 313, 333 and 353 K, finding negative values for E_T^N down to -0.068 at 313 K and 15 MPa, passing through zero near 30 MPa, and up to 0.053 at 55 MPa. Sun *et al.*[23] used the absorption and fluorescence of the probes 4-(*N*,*N*-dimethylamino)benzonitrile and ethyl 4-(*N*,*N*-dimethylamino)benzoate at reduced densities of 0.05–2.2 to obtain measures of the dipolarity/polarizability of SCCD. They found bathochromic shifts for both modes and both probes as the density increased, and modeled their findings in terms of clustering of the CO_2 molecules around the probes, even at reduced densities <0.5 (235 kg m^{-3}). Rice *et al.*[24] used anthracene and pyrene as probes in SCCD of densities 300–900 kg m^{-3}, observing bathochromic shifts as the density increased. Sigman and Leffler[25] studied the *cis–trans* transformation of 4-(*N*,*N*-diethylamino)-4′-nitro-azobenzene in SCCD of 340–1070 kg m^{-3}. They employed its *trans* configuration as a solvatochromic probe, but based the resulting π^* values (Fig. 1) on their earlier average values.[18] The agreement with more recent values[22] is, therefore, poor except at the lowest and highest densities. Ikushima and co-workers[26,27] measured the C=O stretching frequencies of cyclohexanone, acetone, *N*,*N*-dimethylformamide and methyl acetate as probes in SCCD and interpreted these data in terms of π^* values varying from -0.8 at 100 kg m^{-3} up to -0.1 at 800 kg m^{-3}. These π^* values were in fair agreement with those of Yonkers *et al.*[19] and of Maiwald and Schneider[21] and practically independent of temperature.

Attempts have been made to relate the solvatochromic π^* values to macroscopic properties of SCCD. Sigman and Leffler[28] found for the four different densities of SCCD studied previously[18] that

$$\pi^* = (-1.03 \pm 0.04) + (6.86 \pm 0.30)[(n^2 - 1)/(2n^2 + 1)] \quad (5)$$

where the first term represents the π^* value for the gas phase and n is the refractive index of the SCCD. A more sophisticated treatment was accorded this subject by Yonker *et al.*,[29] using the McRae and Bayliss model.[30] They replaced the term in square brackets in Eqn (5) by $F_0 = [(n^2 - 1)/(2n^2 + 2)]$ and plotted their π^* values against this variable. Their plots are substantially the same for 308 and 323 K and similar to the plot in Fig. 1 against the densities of the SCCD. Two straight lines were fitted to the data, one at $F_0 = 0.08$ and the other at higher F_0 values, but for no obvious reason. Bulgarevich *et al.*[31] used 4-nitroanisole as a probe and obtained π^* values parallel to those of Maiwald and Schneider[21] but shifted down by $\sim$0.13 units (Fig. 1). The solvation number of CO_2 in the cybotactic region around the probe molecule was estimated according to Kajimoto *et al.*[32] Out of the estimated eight molecules of CO_2 that could surround the 4-nitroanisole molecule, the actual number increased with the density (d/kg m^{-3}) from 1 at 33 to 6 at 640 kg m^{-3} in a second-degree curve: $0.69 + 0.0186d - (1.6 \times 10^{-5})d^2$. Sasaki *et al.*[33] used Phenol Blue (*N*,*N*-dimethylindoaniline) as the probe at densities of 300–820 kg m^{-3} and 313–343 K. They did not calculate π^* values but compared the transition energy E_T with the McRae and Bayliss[30] model and found lower values than expected. The deviations were explained by clustering of CO_2 molecules around the Phenol Blue molecule, the more so as the temperature was lowered at $d = 400$ kg m^{-3}: $\sim$60% at 313 K and $\sim$20% at 343 K. Nugent and Ladanyi[34] examined the clustering of CO_2 molecules around a solute in SCCD by means of molecular dynamics (MD) simulations, using bromine (Br_2) as a probe that underwent solvatochromic shifts in its absorption spectrum. The surroundings (solvation sphere within 0.64 nm of the center of a molecule) of both Br_2 and CO_2 molecules had practically the same number of solvent CO_2 molecules that increased with the density nearly linearly, reaching 17 at $2.8d_c \approx 1310$ kg m^{-3}. 1-(9-Anthryl)-3-(4-*N*,*N*-dimethylaniline)propane was used by Khajehpour and Kauffman[35] as a probe for the estimation of the clustering length scale of SCCD. They measured the fluorescence lifetimes of this probe relative to its analog devoid of the dimethylamino functionality, and concluded that this length was $\sim$0.12 nm.

Maiwald and Schneider[21] used the solvatochromic comparison method with the probe pairs 4-nitroaniline–*N*,*N*-dimethyl-4-nitroaniline and 4-nitrophenol–4–nitroanisole to measure the hydrogen bond accepting (HBA)/electron pair donating (EPD) properties (β) of SCCD. They found no significant differences between the two members of each of the pairs, indicating a zero HBA/EPD ability for SCCD, as is, of course, expected. The latter pair of probes was also employed by Ikushima *et al.*,[27] who reached the same conclusion of $\beta \approx 0$ at pressures >10 MPa. Also, the hydrogen bond donating ability (HBD) (α) of SCCD was found to be zero,[27] although in their earlier paper[26] these authors used a roundabout method, involving correlations of results from several other probes with α values of liquid solvents, to estimate $\alpha \approx 0.2$ at a density of 250 to $\alpha \approx -0.1$ at 800 kg m^{-3}. Such values have no meaning, since SCCD as a solvent has no hydrogen bond donating ability at all, being aprotic and non-protogenic.

SOLVATOCHROMIC PROBES IN SUPERCRITICAL WATER (SCW)

SCW is distinguished by a high polarity and hydrogen bond donating (HBD) and accepting (HBA) abilities of its

individual molecules. On the other hand, SCW has a much lower structuredness, i.e. hydrogen-bonded network, than water has at ambient conditions, although by no means entirely negligible when its density is above $\sim 500\,\mathrm{kg\,m^{-3}}$.[36,37] SCW has a low[36,38] relative permittivity, ε_r, and can dissolve both organic solutes and ionic substances effectively. Even below the critical point of 647 K (see Table 1 for the critical constants), that is, in subcritical water, does the disruption of the hydrogen-bonded network make itself felt in this respect (solubility of organic solutes). Thus, at 548 K (reduced temperature $T_r = T/T_c = 0.85$) water has $\varepsilon_r = 23.5$.[38] In spite of its potential use for supercritical water oxidations with oxygen, in order to destroy obnoxious and toxic organic materials, that has already been the basis of technological processes, the solvation properties of SCW have only sparingly been studied so far by means of solvatochromic probes. One reason was the instability of the organic materials commonly employed as probes for studying such properties at the high temperatures involved. There are therefore no values of π^*, α and β available for SCW, although such values were obtained for subcritical water and solvatochromic shifts of other probe molecules, not generally employed for obtaining these solvatochromic parameters, were measured in SCW.

The polarity and hydrogen-bonding properties of subcritical water (saturated, i.e. in equilibrium with water vapor) were studied by Lu *et al.*[39] by means of solvatochromic probes up to 548 K, according to Eqn (4). It was assumed that the spectral shifts of the probes at the elevated temperature correspond to the π^*, α and β values established for the same shifts in solvents at ambient conditions, ignoring possible thermochromism. With 4-nitroanisole as the probe, the π^* values decreased gradually from 1.09 at 298 K to 0.70 at 548 K, at which temperature the dipolarity/polarizability of subcritical water corresponded to that of acetic acid at ambient temperature. The betaine dye probe 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinium-1-yl)phenolate was employed for measuring the HBD properties of subcritical water, instead of the more commonly used betaine dye yielding $E_T(30)$ values, since the former had a lower pK_a value, hence was less basic and less apt to be protonated by the water. The α values diminished initially more rapidly as the temperature was increased than the π^* values, but reached a relatively larger fraction of $\alpha = 1.17$ at 298 K, i.e. 71% at 548 K, than did π^*, 64%. In contrast, the HBA properties of subcritical water, measured by the probe pair 4-nitroaniline–*N*,*N*-dimethyl-4-nitroaniline yielding the β parameter, did not vary much with increasing temperatures from the 0.18 ascribed to monomeric water.[39]

Proper SCW was probed for its solvent power by Bennett and Johnston[40] and subsequently by Oka and Kajimoto.[41] Bennett and Johnston employed the spectral shifts of the π–π^* band of benzophenone and the n–π^* band of acetone to study the polarity and hydrogen-bonding properties of SCW. As the density decreased with increasing temperature from ambient to above T_c, a blue shift was observed for the band in benzophenone, as expected. The spectral shifts for SCW at 683 to 713 K lie on a single, nearly linear curve (slightly concave upwards) as a function of the reduced density $0.3 \le d_c \le 1.8$. At 653 K, near the critical point, i.e. $T_r = 1.009$, clustering of the water around the probe molecule was found with maximum clustering near $d_c = 1$, where some 50% enhancement of the density around the probe occurred. The n–π^* band of acetone was used by Bennett and Johnston[40] to explore the HBA ability of SCW. The band shifts to the red were corrected for thermochromism and compared with shifts in ordinary liquids in order to obtain the contribution from the HBD properties of SCW. As the reduced density $d_r = d/d_c$ decreased below 0.5, the HBD ability of SCW diminished rapidly (see also Ref. 37). However, for subcritical water at $0.5 \le d_r \le 1.5$ there was a near plateau in the band shift, indicating that only slight variations in the HBD ability of water occurred.

The later study by Oka and Kajimoto[41] employed 4-nitroaniline as the probe. With this probe, too, clustering of the water around the probe was observed at 653 K, i.e. $T_r = 1.009$, but clustering being limited to $T_r = 1.05$, this no longer occurred significantly at 683 K. The probes *N*,*N*-dimethyl-4-nitroaniline and 4-nitroanisole were studied only at 683 K, i.e. in the region were no clustering took place. Quinoline was used as a probe by Osada *et al.*[42] to investigate the HBD ability of subcritical water and SCW. Blue shifts of the absorption band were observed in SCW at $0.2 \le d_r \le 1.5$ that were considerably lower than at higher d_r values, corresponding to subcritical water. This was interpreted as showing that SCW had a *lower* local density around the probe than the bulk density. Solvatochromic shifts of the β-naphtholate anion were used by Xiang and Johnston[43] to study again the hydrogen-bonding ability of SCW.

SOLVATOCHROMIC PROBES IN SUPERCRITICAL FLUOROCARBONS

Supercritical fluorocarbons that have found practical uses have critical temperatures somewhat but not much above ambient (see Table 1). The substances of which the solvation properties have been studied by means of solvatochromic probes include difluoromethane, trifluoromethane (fluoroform), chlorotrifluoromethane and several fluoroethanes. These are as a rule much more polar than SCCD, have lower T_c values than SCW and some have good HBD properties, so that they are able to dissolve both non-polar and polar and even highly hydrophilic organic substances.

The earliest characterization of a supercritical fluoro (halo)carbon appears to be that of chlorotrifluoromethane, $CClF_3$ (Freon13), by Yonker *et al.*[19] (note the misprint in the abstract, where CCl_3F is written). The probe employed

was 2-nitroanisole and $\pi^* = -0.29 \pm 0.03$ was assigned to it at $T_r = 1.0033$ and $d_r = 1.5$, which became gradually less negative as the reduced density was increased from 1.3 to 2.1. Phenol Blue (*N*,*N*-dimethylindoaniline) was used by Kim and Johnston[44] and it was concluded that $CClF_3$ had significantly lower solvent power than, say, *n*-hexane. Although $CClF_3$ has a small dipole moment (0.50 D, 1 D = 3.335×10^{-30} C m), it has lower polarizability per unit volume than *n*-hexane. A more detailed investigation of the dipolarity/polarizability of $CClF_3$, as measured with 2-nitroanisole yielding π^* values, was made by Maiwald and Schneider.[21] At a reduced temperature $T_r \approx 1.1$ and over a reduced density range from 0.1 to 2.4, $CClF_3$ had more negative π^* values than SCCD (Fig. 1), but also a somewhat more negative value, -0.37 at $d_r = 1.5$, than assigned by Yonker *et al.*[19]

Fluoroform (trifluoromethane, CHF_3) was the next fluorocarbon to be studied with respect to solvatochromic shifts of the light absorption or fluorescence probe molecules. The shift of the absorption band of 4-(*N*,*N*-dimethylamino)benzonitrile in supercritical fluoroform with increasing density was employed by Kajimoto *et al.*[32] for the estimation of the aggregation of the solvent around the probe molecule. The bathochromic shifts of this probe deviated considerably from what was expected from the polarity of the supercritical CHF_3 in terms of the linear dependence of the shifts on $[(\varepsilon_r - 1)/(\varepsilon_r + 2) - (n^2 - 1)/(n^2 + 2)]$ established with the solutes bromobenzene, tetrahydrofuran, butyronitrile, 1-chlorobutane, ethanol and cyclohexanol. These deviations were then used for the estimation of the solvation number of the fluoroform around the probe, varying from 1 at a gas-like density of 20 kg m^{-3} to 6 at 750 kg m^{-3}. The implication of this finding is that a solvatochromic probe in a supercritical fluid of varying densities may measure a property specific for the probe + fluid pair and has not a more general prediction power as to the solvation properties of the SCF against other solutes! Only if several dissimilar probes yield converging values for this property of the given SCF can it be said that the magnitude of this property has been established for use with any arbitrary solute.

Two related but different probes, 4-(*N*,*N*-dimethylamino)benzonitrile and ethyl 4-(*N*,*N*-dimethylamino)benzoate, were used by Sun *et al.*[23] in supercritical fluoroform. The shifts $\Delta\nu$ of the absorption bands at 332.8 K are plotted against the reduced density d_r in Fig. 2. The shifts depend somewhat on the temperature (they are larger at 303 K), but are more or less parallel, the benzoate curve being 10% higher than the benzonitrile curve (at $d_r = 0.5$). At liquid-like densities proper normalization could, therefore, permit the use of these shifts as indicating a more general property of the SCF, whereas at gas-like densities a more specific aggregation of the CHF_3 around the probe took place.

Three further supercritical fluorocarbons, difluoromethane (HFC32), 1,1,1,2-tetrafluoroethane (HFC134a)

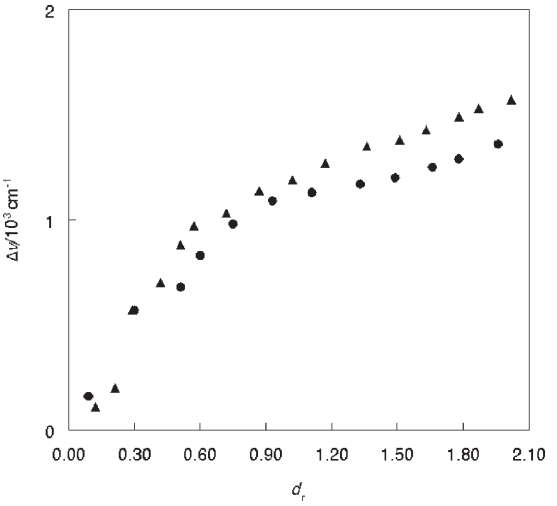

Figure 2. Solvatochromic shifts $\Delta\nu/10^3\,cm^{-1}$ of 4-(*N*,*N*-dimethylamino)benzonitrile (●) and ethyl 4-(*N*,*N*-dimethylamino)benzoate (▲) in supercritical fluoroform (CHF_3) as a function of the reduced density, d_r, at 332.8 K[23]

and pentafluoroethane (HFC125), were studied by Abbott and Eardley[45,46] with respect to their dipolarity/polarizability by means of the solvatochromic probe Nile Red. This probe had previously been shown[47] to yield π^* values. These three polar SCFs, in common with supercritical fluoroform and in contrast to chlorotrifluoromethane and carbon dioxide, which have low polarities, show plots of π^* against the reduced density that vary with the temperature at low reduced densities d_r and at temperatures near T_c. At higher d_r and T_r, the π^* values converge towards a common curve against d_r, of the S-shaped type shown in Fig. 2. At any given d_r the order among the SCF π^* values is HFC32 > HFC134a > HFC125, which does not agree with the order of the dipole moments. At sufficiently high densities, $d_r \approx 2$, π^* may reach a value as high as 0.40 for each of the three supercritical fluorocarbons studied.

These fluoroethanes (R134a≡HFC134a and R125≡HFC125) together with four others, hexafluoroethane (R116), 1,1,1-trifluoroethane (R143a), 1,1-difluoroethane (R152a) and fluoroethane (R161), were studied by Lagalante *et al.*[48] with respect to both their dipolarity/polarizability (π^*) and HBA/EPD ability (β) by means of solvatochromic probes. Except for the hexafluoroethane, all these SCFs are polar with dipole moments $\mu > 1.5$ D. The probe 4-nitroanisole was used for π^* measurement and the pair 4-nitrophenol and 4-nitroanisole was used for β measurements in the solvatochromic comparison mode. The π^* and β values were plotted against the concentration c of the SCF (in kmol m^{-3}) so that quantitative comparison with the data of the previous authors is difficult, since the pressure was not specified, and the data spanned a range of temperatures. The non-dipolar R116 had π^* values lower than those for ethane (see below) but the dipolar fluorocarbons showed π^* values rising from the gas-like very negative $\pi^* \approx -1$ to a

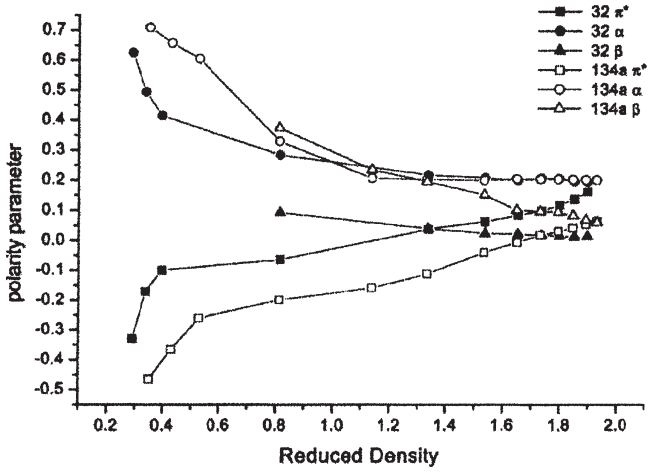

Figure 3. Solvatochromic parameters α, β and π^* for difluoromethane (HFC32, closed symbols) and 1,1,1,2-tetrafluoroethane (HFC134a, open symbols) as functions of the reduced density, d_r, at a reduced temperature $T_r = 1.128$. Reprinted with permission from Ref. 49. Copyright (2003) American Chemical Society

plateau of $\pi^* \approx -0.1$ at concentrations between 6 and 9 kmol m^{-3} and rising further up to a maximum of $\pi^* \approx 0.4$ at higher c values. Monofluoroethane, R161, is an exception, in having generally more negative π^* values, reaching zero only at 12 kmol m^{-3}. The general shape of the π^* vs c curves was very similar to the π^* vs d_r curves in Fig. 2. The β values, however, did not vary much from the gas-like to the liquid-like concentrations, and were best described as average values over the entire range: -0.25 ± 0.03 for R116, -0.11 ± 0.04 for R125, -0.12 ± 0.02 for R134a, -0.14 ± 0.04 for R143a and -0.01 ± 0.04 for R152a.

Recently, Abbott *et al.*[49] returned to the subject of using solvatochromic probes for studying the properties of fluorocarbon SCFs. They employed Nile Red for probing the HBD properties (α), the probe pair 4-nitroaniline and *N*,*N*-dimethyl-4-nitroaniline for probing the HBA/EPD properties (β) and the latter solute for probing the dipolarity/polarizability (π^*) of the SCFs difluoromethane (HFC32) and 1,1,1,2-tetrafluoroethane (HFC134a). At a constant $T_r = 1.128$ and at $0.3 \leq d_r \leq 1.9$, the trends were found to be common for the two SCFs: α decreased strongly from near 0.7 to $\alpha \approx 0.3$ with d_r increasing up to $\sim$0.8 and then only slightly, β decreased moderately from $\sim$0.4 for HFC134a and $\sim$0.1 for HFC32 at $d_r = 0.8$, and π^* increased in nearly parallel S-shaped curves up to 0.15 for HFC32 and 0.05 for HFC134a (Fig. 3).

SOLVATOCHROMIC PROBES IN OTHER SUPERCRITICAL FLUIDS

There are several other SCFs that have been studied with respect to the use of solvatochromic probes to obtain their solvation properties, but they have received much less attention than SCCD, SCW and supercritical fluorocarbons. They can be grouped into polar SCFs (ammonia, methanol, ethanol) and non-polar SCFs (xenon, ethane, ethene, dinitrogen oxide, sulfur hexafluoride), to be discussed in turn.

Supercritical ammonia featured in the studies of Maiwald and Schneider[21] and of Yonker *et al.*,[19] though in the latter only incidentally. The π^* parameter was obtained by Maiwald and Schneider[21] with 2-nitroanisole as the probe and showed the familiar S-shaped curve when plotted against the reduced density d_r at $T_r \approx 1.1$, reaching $\pi^* = 0$ at $d_r = 0.85$ and $\pi^* = 0.45$ at $d_r = 1.9$. Somewhat higher values, obtained with the same probe, were reported by Yonker *et al.*,[19] according to whom $\pi^* = 0.55$ already at $d_r = 1.4$, albeit with large uncertainties, ± 0.2, in π^*. As expected, and contrary to other SCFs that showed negative or near zero β values, supercritical ammonia had the sizable value of $\beta = 0.5 \pm 0.1$ for $0.9 \leq d_r \leq 2.1$ at 413 K. These β values were measured by the solvatochromic comparison method with the probe pair 4-nitroaniline–*N*,*N*-dimethyl-4-nitroaniline.[21] At lower temperatures (293 and 333 K) and higher reduced densities ($d_r = 2.4$) the β values were even higher, reaching 0.8 at 293 K and $d_r = 2.5$, but decreasing somewhat thereafter.

Supercritical methanol was studied by means of solvatochromic probes by Bulgarevich *et al.*[50] The probe employed for measuring π^* was ethyl 4-(*N*,*N*-dimethylamino)benzoate (4-nitroanisole being unstable in methanol at $T = 493$ K), and at 523 K showed steadily increasing values of π^* as d_r increased. However, the values reported for the very low $d_r = 0.3$, namely < -1.1, were more negative than generally accepted for vacuum, hence the π^* scale employed by Bulgarevich *et al.*[50] was incompatible with the commonly used one. The value $\pi^* = 0$ was reached at $d_r = 1.6$ and $\pi^* = 0.6$ was reached at $d_r = 2.9$ at 523 K, whereas the π^* vs d_r curve at 563 K was more or less parallel to that at 523 K but $\sim$0.1 units lower. The α values could not be measured in supercritical methanol, since the probes employed, 4-nitroaniline and Reichardt's betaine dye used to obtain $E_T(30)$ values, were unstable in it. In subcritical methanol these probes gave concordant results for α as a function of temperature and density:

$$\alpha = [1.57 + 0.00305T - (9.04 \times 10^{-6})T^2] - [0.24 - 0.00764T + (1.317 \times 10^{-5}T^2)] \times 10^{-3}(d/kg\,m^{-3}) \quad (6)$$

valid up to 453 K. At this temperature α has decreased from its value of 0.98 at ambient conditions to $\sim$0.8, comparable to that of ethane-1,2-diol under ambient conditions. The UV absorption spectrum of anthracene in supercritical methanol at 563 K was used[50] to study the local density augmentation of the SCF near the solute. The local density had a maximum of about twice that of the bulk at $d_r \approx 0.25$ and decreased steadily as d_r increased up to 2, where no enhanced density was found

any longer. The enhanced density near the anthracene molecules could also be described by a Langmuir adsorption model.

The application of solvatochromic probes to supercritical ethanol was studied by Lu *et al.*[51] The probes employed were 4-nitroanisole for π^*, the probe pair 4-nitroaniline and *N*,*N*-dimethyl-4-nitroaniline for β and the betaine dye 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridino) phenolate for α. The results at 523 K were plotted against d_r in a small-scale figure, so that quantitative comparisons with results for other SCFs cannot be readily made. The trends, however, are clear. In the subcritical region π^* increases, reaches ~ -0.1 at $d_r = 1$, and increases moderately at higher densities up to 0.1. The β parameter is practically constant and near zero, ± 0.1, over the entire range $0.1 \leq d_r \leq 1.7$, whereas α was measured only in the supercritical range and decreased from ~ 0.6 to ~ 0.5 as the density increased.

Among the non-polar SCFs, the monoatomic xenon is the simplest, and only π^* (expressing polarizability) is relevant to it. The probe 2-nitroanisole was employed by Smith *et al.*[52] to establish that xenon was less polarizable than SCCD, having at $T_r \approx 1.02$ (299 K) and critical density $d_r = 1$ a π^* value of -0.4, compared with -0.2 for CO_2. The π^* values for supercritical xenon hardly vary at higher densities, remaining near -0.4 up to $d_r = 1.6$.

The application of Phenol Blue as a solvatochromic probe in supercritical ethene was reported by Kim and Johnston.[44] A large bathochromic shift was noted as the density increased in the range $0.85 \leq d_r \leq 2.2$, with inappreciable temperature dependence at 283 and 298 K. The relevant quantity here is the polarizability per unit volume that increases with the density. The local density of ethene around the probe molecules is linearly related to the compressibility of the SCF.

Much more attention was paid to supercritical ethane in this respect. The π^* values measured by Smith *et al.*[52] at $T_r \approx 1.02$ (308 K) with 2-nitroanisole increased from the gas value to -0.45 at the critical density, $d_r = 1$ and reached -0.25 at $d_r = 2.4$, ethane therefore being considerably more polarizable than, say, supercritical xenon. A further study by Yonker and Smith[29] reported π^* values with the same probe at $T_r \approx 1.06$ (323 K) plotted against the Onsager reaction field $F_0 = 2(n^2 - 1)/(2n^2 + 1)$ and found for ethane considerably more negative π^* values than for SCCD at the same F_0 and T_r. Sun *et al.*[23] employed ethyl 4-(*N*,*N*-dimethylamino)benzoate in supercritical ethane but found only small bathochromic shifts for the absorption band and practically none for the emission band on increasing the density from $d_r < 0.4$ to $d_r > 1.8$. Ethane was the reference SCF for fluorinated ethanes in the study of Lagalante *et al.*[48] Supercritical ethane, propane (non-dipolar) and dimethyl ether (dipolar) featured in the study by Lemert and DeSimone[53] over the pressure range 3.5–30 MPa and temperature range 298–428 K. They used the dye 9-(α-perfluoroheptyl-β,β-dicyanovinyl)julolidine as the solvatochromic probe and found the solvent molecules to cluster around the probe.

SOLVATOCHROMIC PROBES IN SCF MIXTURES AND EXPANDED FLUIDS

Since SCCD is an inexpensive solvent with convenient density, temperature and pressure ranges and is also environmentally benign and safe, it has, as said, found extensive use. Its main drawback is its pronounced non-polar and non-polarizable nature (negative or slightly positive π^* values), so that its solvation power for polar solutes is small. This situation can be ameliorated by the use of polar co-solvents in the SCCD. With small additions of the co-solvent the polarity increases appreciable but the fluid can still be considered an SCF. Of course, the co-solvent must be chosen so as to retain the advantages of the SCCD in terms of environmental effects and ease of removal from a reaction or separation mixture. On the other hand, it is possible to provide an ordinary liquid solvent with properties more like those of an SCF by dissolving in it a gas, say carbon dioxide, at a temperature and pressure making it a sub- or near-critical fluid, where it is strongly expanded and its compressibility is much enhanced. Such a liquid can then be called an expanded fluid, the density, hence solvation power, of which can be readily tuned advantageously.[49–54] SCCD was again the most widely studied modified SCF with respect to the use of solvatochromic probes to trace the effects of the co-solvents. Yonker *et al.*[19] determined the spectral shifts of 2-nitroanisole in SCCD at 323 K with the addition of 5.6 and 9.5 wt% methanol as a function of the pressure. Above ~ 20 MPa the pressure had little effect but a considerable bathochromic effect of the methanol was noted, although less than proportional to the methanol content. Deye *et al.*[55] studied SCCD modified with methanol at $T_r = 0.99$, i.e. at near-critical conditions with Nile Red as the probe, and again found a bathochromic effect with 1–4% methanol (by volume). At higher methanol contents the temperature employed was 298 K, i.e. $T_r = 0.98$, and the trend continued smoothly with higher methanol contents (5, 10, 20, ..., 100%). At 318 K, $T_r = 1.046$, where the mixture can be considered supercritical, the effect of 1–10 vol% persisted, but was smaller than at the lower temperature. In a subsequent paper, Berger and Deye[56] studied methanol-modified SCCD at 313 K to ascertain the pressure–density relationships with up to 11.5 mol% methanol. The pressure required to achieve a given density decreased with increasing methanol content, as expected. However, the critical point changed with composition, hence the values were not valid for $T_r = 1.03$ as in pure carbon dioxide. In near-critical SCCD ($T_r = 1.01$) with up to 4.5 mol% methanol the fluorescence of 7-azaindole was shifted considerably towards the red, increasingly with increasing

density, as measured by Tomasko *et al.*[61] The results indicated that the fluorescence by the exciplex formed dominated the observed shift. Kelley and Lemert[57] studied several solvents (cyclohexane, toluene, tetrahydrofuran, acetone and methanol) expanded with carbon dioxide at 308 and 329 K by means of Phenol Blue as the probe. As the pressure, and hence the CO_2 content, increased, a hypsochromic shift of the absorption band of the probe was noted. The polarity of the fluid decreased and the polar solvent clustered around the probe molecules.

Bulgarevich *et al.*[31] employed 4-nitroanisole to study the microscopic solvent structure of SCCD modified with methanol (up to 0.055 mole fraction) at 318 K ($T_r = 1.046$) in the cybotactic region of the probe. That is, the preferential clustering or aggregation of the solvent molecules in the immediate surroundings of the probe was investigated. The polar methanol was indeed preferentially present in these surroundings, but with increasing pressure it was pressed out from there by the more abundant carbon dioxide. The maximum enhancement of the local mole fraction of methanol over its bulk mole fraction, x_{MeOH}, about 4.5-fold, was attained near 10 MPa. In a subsequent study, Bulgarevich *et al.*[58] confirmed these findings and also studied the HBA/EPD properties of the mixtures by using the probe pair 4-nitrophenol–4-nitroanisole to obtain β values. These were rather independent of the pressure (at $1.0 \leq d_r \leq 1.8$) and changed from nearly zero for pure SCCD up to nearly those of pure methanol at $x_{MeOH} = 0.05$.

SCCD modified by ethanol was studied by Ikushima *et al.*[26] at an 8.9 mol% content and 318 K by means of cyclohexanone to measure π^*, the probe pair 4-nitrophenol–4-nitroanisole to measure β, and the probe pair 1-ethyl-4-(methoxycarbonyl)pyridinium iodide (Kosower's *Z*-probe)–4-nitroanisole for α. In these experiments the content of the modifier was kept constant so that the increasing pressures ($\sim$10 to $\sim$30 MPa) applied did not dilute the ethanol further with CO_2. Hence the values of all three solvatochromic parameters increased towards the value of liquid ethanol. For 2,2,2-trifluoroethanol (TFE) as the modifier, Ikushima *et al.*[26] found qualitatively similar results, but a larger enhancement of π^* with pressure than for ethanol, but the α values were much below that of pure TFE, more so than for the ethanol mixtures. TFE and its mixture with SCCD are devoid of appreciable HBA/EPD properties.

The fluorescence of bis[4,4′-(dimethylamino)phenyl]-sulfone and its decay were used by Schulte and Kauffman[59] to probe the local polarity of supercritical mixtures of carbon dioxide and ethanol at 328 K and at a mole fraction of ethanol = 0.1. The clustering of the ethanol around the probe enhanced its local concentration to at least fourfold but possibly up to 10-fold, the enhancement decreasing as the bulk concentration of the co-solvent increased.

Yonker and Smith[60] used 2-nitroanisole as a probe in solutions of 2-propanol in SCCD at mole fractions x_{iPrOH} of 0.051, 0.106 and 0.132 at three temperatures, 317, 335 and 395 K, and various pressures in the range 7–41 MPa. Both polarity and hydrogen bonding were measured in a combined manner with this probe, but it was possible to obtain the enhancement of the local composition of the solvent around the probe molecules in these experiments. At $x_{iPrOH} = 0.051$, up to threefold enhancement was obtained at the lower temperatures and even higher at 395 K, where the mixtures were supercritical. At 317 and 335 K at the higher x_{iPrOH} the mixtures were subcritical and a smaller enhancement was obtained at the lower pressures.

A summarizing paper by Bulgarevich *et al.*[58] explored several *n*-alkanols (ROH, up to hexanol) as modifiers of SCCD at low mole fractions ($x_{ROH} = 0.05$) at 318 K as a function of the pressure. At the lowest mole fraction studied, $x_{ROH} = 0.01$, the increase in π^* with pressure/density was almost the same for all alkanols, but the β values increased systematically from methanol to hexanol, being rather independent of the density (at $1.0 \leq d_r \leq 1.8$), although increasing somewhat as the density is diminished below $d_r = 1$, i.e. to subcritical regions.

Few polar co-solvents other than the alcohols were used as modifiers with SCCD and were also studied with solvatochromic probes. Dimethyl sulfoxide at 8.9 mol% and 318 K was studied by Ikushima *et al.*[26] as described above for ethanol-modified SCCD. The HBA/EPD ability as measured by β was fairly high, β increasing from 0.47 at $\sim$10 MPa to 0.52 at 25 MPa, and the π^* value remained near 0.12 in this pressure range. Water in SCCD, up to 0.3 mol%, caused at $T_r = 1.01$ only small spectral changes in the emission from 2-naphthol or 5-cyanonaphthol, as found by Tomasko *et al.*[61] The effect of acetone as a modifier of SCCD was studied by Lu *et al.*[62] Deye *et al.*[55] studied acetonitrile, dichloromethane and tetrahydrofuran expanded by carbon dioxide at 298 K by means of Nile Red as the probe. A red shift was noted, approximately the same for all three co-solvents, as their content increased, somewhat smaller than that observed for methanol co-solvent discussed above. Fluorinated co-solvents of SCCD were studied by Abbott *et al.*[63] and by Kho *et al.*[64] The former group employed 1,1,1,2-tetrafluoroethane (HFC134a) as the co-solvent and Nile Red as the solvatochromic probe. At 30 mol% HFC134a the mixture had a critical temperature $T_c = 332$ K that was more convenient than the higher one, 374 K, of pure HFC134a, but the polarity of the mixture was near that of the latter SCF. Clustering of the polar component near the probe molecules was observed, yielding up to fourfold enhanced concentrations.[63] The latter group studied fluorocompounds expanded by carbon dioxide: methyl nonafluorobutyl ether, ethyl nonafluorobutyl ether and decafluoropentane. In CO_2-expanded ethyl nonafluorobutyl ether, the π^* values measured with 2-nitroaniline and *N*-methyl-2-nitroaniline decreased gradually from 0.17 and 0.14 to 0.11 and 0.09, respectively, as the pressure, and with it the CO_2

content, increased from 0.1 to 5.5 MPa at 308 K, but the exact CO_2 content was not reported (>80 mol% at 4.93 MPa). Note, however, that the 'π^*' is not the same when measured by the two probes, although the curves are fairly parallel. Further modification of the solvation power was achieved by using another co-solvent with the CO_2-expanded fluoro ether. Thus, 10 mol% 2,2,2-trifluoroethanol enhanced the HBD properties (α) rather independently of the pressure (CO_2 content), whereas 10 mol% *N*-methylpyrrolidin-2-one yielded sizable HBA/EPD properties (β), but these decreased somewhat with increasing pressure (CO_2 content).[64] The solvation power of an unusual solvent, a room temperature ionic liquid (RTIL) expanded by SCCD, was studied by Lu *et al.*[65] employing a solvatochromic probe. It was expected to gain the benefits of a non-volatile and environmentally benign solvent such as an RTIL together with the advantages of SCCD in terms of tunability and reduction of the viscosity of the resulting fluid. Specifically, Lu *et al.*[65] used 1-butyl-3-methylimidazolium hexafluorophosphate as the RTIL and *N*,*N*-dimethyl-4-nitroaniline as the solvatochromic probe, and measurements were made at 308–323 K and pressures up to 22 MPa. The expansion by CO_2 had little effect (a minimal diminution) on π^*, since the RTIL ion pairs clustered around the probe molecules. However, the composition of the expanded solvent was not reported, but the volume expansion, up to 40% at 20 MPa and 308 K, showed a smooth dependence on the pressure through the critical value.

Not many studies of mixed SCFs that do not involve SCCD have been reported. Deye *et al.*[55] studied trifluoromethane (fluoroform, Freon 23) and chlorotrifluoromethane (Freon 13) modified with methanol by means of Nile Red and the betaine dye used to obtain $E_T(30)$ values as the solvatochromic probes. Whereas the absorption band of the former probe in Freon 13 was considerably affected by addition of methanol above 1% (the probe is insoluble in supercritical pure Freon 13), that of the latter already attained values close to that of pure methanol at 1% modifier. The emission maximum of 7-azaindole in supercritical fluoroform modified with 0.3, 1.2 and 3.0 mol% ethanol was studied by Tomasko *et al.*[61] The bathochromic effect found was not proportional to the ethanol content (the results for the two lower values practically coincided). Supercritical ethane modified by various basic co-solvents was studied with solvatochromic probes by Tomasko *et al.*[61] and by Hafner *et al.*[66] The former group used ethanol as the modifier and 7-azaindole as the probe, and they also studied ethene modified with ethanol with the same probe. The latter group[66] used 4-nitrophenol as the probe and propionitrile, acetone, triethylamine and *N*,*N*-dimethylacetamide as the co-solvents at 308 K. They found a bathochromic effect of the co-solvents increasing in the above order but only a slight dependence (increase) on the density. With 4-nitroanisole the effect was smaller (only propionitrile and triethylamine were tested) but the dependence on the density was somewhat larger.

CONCLUSIONS

The use of solvatochromic probes for the estimation of the solvation properties of SCFs is now well established. Nevertheless, some problems with this practice have not been solved satisfactorily. The main problem is the specific interaction of the probe molecule with the molecules of the SCF, so that its ability to represent the solvation properties of the SCF towards any other solute can be questioned. The above review of what has been achieved to date shows only a few cases where results, say in terms of π^*, for several dissimilar probes converge towards common values. This was more or less the case for SCCD at $d_r = 1.5$, where liquid-like conditions prevail. For other SCFs mainly a single probe was employed, so that no assurance has been obtained that the results are generally meaningful.

At lower reduced densities and near the critical point where the SCF has more gas-like properties and is highly compressible, the clustering of the SCF around the probe is well established, but this could well differ for different solutes, hence the resulting π^* or β values for the SCF have little general validity. This problem is exacerbated when mixtures of an SCF and a polar modifier are used. Little confidence can be placed in the solvatochromic parameters even at substantial densities, owing to the preferential solvation (clustering) around the necessarily polar probe molecules by the more polar component of the mixture (whether an SCF or an expanded liquid solvent).

Another problem that has not so far found a satisfactory solution is the transfer of numerical π^* or β values from liquid solvents under ambient conditions, obtained for given solvatochromic spectral shifts of the probes, to SCFs at different pressures but mainly different temperatures. For some SCFs the temperature of application of the probes, 323 K, is sufficiently near to ambient that the established thermochromism of the probes can be ignored as an approximation. For other SCFs, say SCW, difluoromethane or 1,1,1,2-tetrafluoroethane, the temperatures involved should not allow this simplification, and if analogy with ordinary liquid solvents is to be sought, the thermochromic shifts of the probes have to be taken into account.

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