HIGH SOLUTE SOLUBILITY AND EMULSION FORMATION IN SUPERCRITICAL HYDROFLUOROCARBON SOLVENTS

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Supercritical (sc) CO_2 is by far the most commonly used supercritical fluid. Reasons for this are that it is inexpensive, non-toxic, has low critical constants (T_c = 304.20 K, P_c = 72.8 bar) and is environmentally benign. The major problem encountered when using sc CO_2 is the low solubility of polar solutes. Hydrofluorocarbon (HFC) solvents such as difluoromethane (HFC 32) and 1,1,1,2-terafluoroethane (HFC 134a) are much more polar than scCO_2 and have easily accessible critical constants (HFC 32: T_c = 351.26 K, P_c = 57.82 bar; HFC 134a: T_c = 374.21 K, P_c = 40.59 bar). In addition HFCs are readily obtainable, non-toxic, non-ozone depleting, inert, non-flammable and highly compressible. These solvent properties indicate that they are idea solvents for supercritical applications. By altering temperature and pressure these solvents have been shown to be much more tuneable in terms of their ability to dissolve polar solutes than scCO_2. We present the solubility of a variety of solutes in HFC 32 and show how these can be modelled using various equations of state. At high solute concentrations these models break down and it has been found that solute-solute clustering may result in the formation of supercritical emulsions. The hydrogen bonding ability of these solvents is quantified for the first time as a function of temperature and pressure and it is shown that emulsion formation is prevalent when hydrogen bonding is significant.

INTRODUCTION

The use of supercritical fluids for extraction and as reaction media has received a large amount of attention over the last 30 years [1,2]. The majority of work has, however, focused on the use of carbon dioxide as a fluid, because of its readily accessible critical constants, environmental compatibility and low cost. The major problem that is encountered with the use of scCO_2 for extraction purposes is the low solubility of polar solutes. The “green” aspect of using scCO_2 as a solvent can be negated if large volumes or high pressures are required to solubilise the extract because of the large energy contribution associated with such processes. To circumvent these problems polar modifying agents have been added to CO_2 to increase the solvent polarity. Modifying fluids are often left as residues, which may be problematic if the extract is to be used for human consumption [3-4].

Recently we have highlighted that some hydrofluorocarbon fluids such as difluoromethane (HFC 32) and 1,1,1,2-tetrafluoroethane (HFC 134a) are relatively polar solvents, even in the supercritical state, and this allows them to be used as efficient extraction solvents either on their own or in conjunction with CO_2. [5-7] These solvents are also readily available in liquid form (they are used in the majority of refrigeration units) and are of low toxicity (HFC 134a is used as a solvent for oral drug inhalers). The dipolarity/polarisability parameter of these fluids has been determined over a wide range of temperature and pressure and shows that the polarity of scHFCs 32 and 134a can be similar to that for ethylacetate under ambient conditions. A knowledge of polarity alone is not enough to understand the solvency behaviour of a solvent medium and a significant problem associated with the wide spread use of these fluids in the supercritical state is the lack of solubility data. The current work describes the polarity of HFC 32 and solubility of a variety of substituted aromatic hydrocarbons.

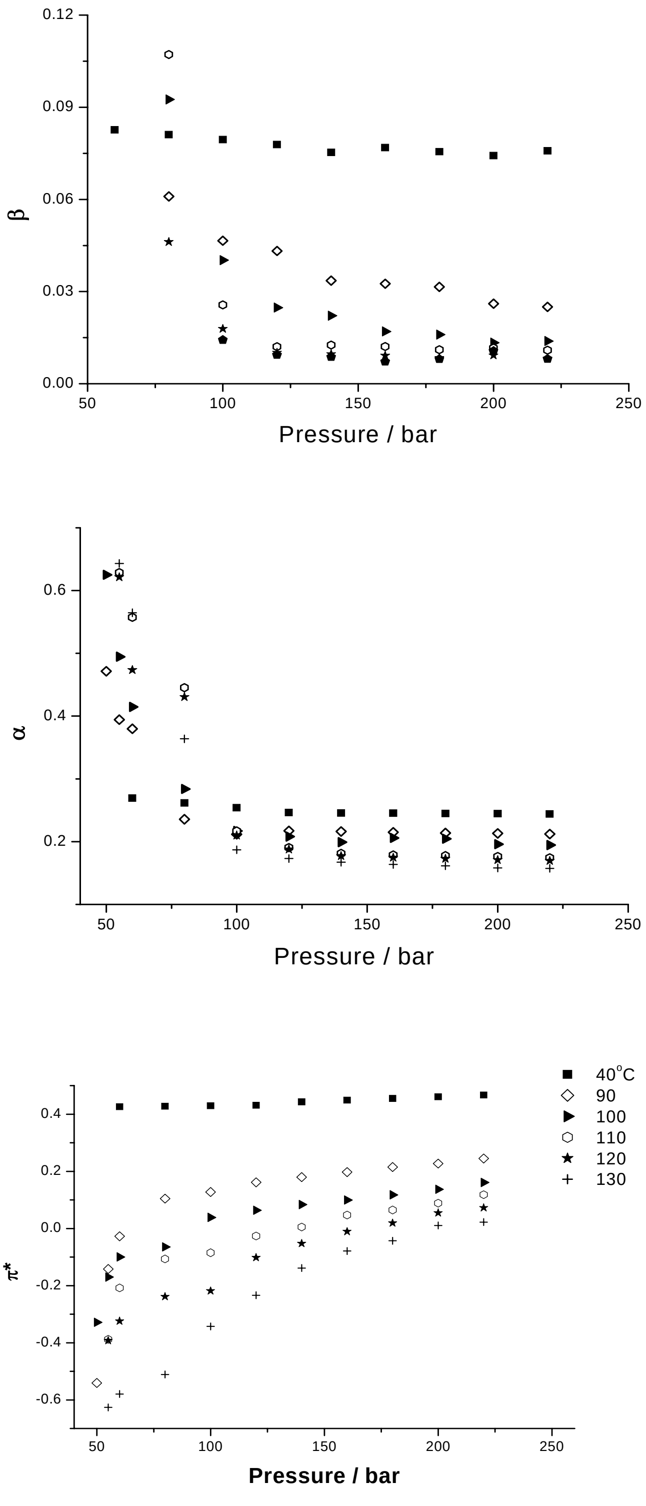

Figure 1: α, β and π* values for HFC 32 as a function of pressure and temperature.

MATERIALS AND METHODS

The solvents; difluoromethane [HFC 32] (Ineos Fluor, 99.99%) and CO_2 (BOC Limited, 99%) were used as received. Details of the experimental procedures are given elsewhere. [8,9]

RESULTS AND DISCUSSION

Most studies of solvent polarity in sc fluids have used the parameters introduced by Abboud, Kamlet and Taft. [10] They showed that a variety of solution properties such as reaction rates, equilibrium constants or Gibbs Energies of solvation could be related via simple solvatochromic parameters through a schematic equation of the form

$$\boldsymbol{XYZ = XYZ_o + s\pi^* + a\alpha + b\beta} \qquad \textbf{(1)}$$

where XYZ is the solvent property, XYZ_o is the solvent property in a reference solvent, π^* is the dipolarity/ polarisability 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 shift absorption maxima of a variety of indicator solutes in a range of solvents, such that

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

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 most commonly used to quantify the α, β and π^* values. To obtain the α, β and π^* values for HFC 32 the susceptibility constants a, b and s values for the three indicator dyes used in the current study were first obtained by measuring their absorption spectra in 16 solvents of different polarity and solvent type i.e. HBD, HBA and NHB. **Figures 1** shows the α, β and π^* values for HFC 32 at a variety of temperatures and pressures. The π^* values are similar to those reported previously, confirming the accuracy of the fit parameters for the indicator solutes.

The β values for both solvents are small but positive. For HFC 32 the β value is almost invariant with either temperature or pressure in the liquid state (i.e. below 78 ^{o}C). At $T \geq T_c$ a decrease in β with increasing temperature and pressure is observed. The β values for both fluids are similar to those reported recently for sc ethanol by Lu *et al.* [11]. HFC 32 would be expected to be a relatively good HBD. The magnitude of the α values are comparable with related compounds e.g. methylene chloride at ambient conditions where $\alpha = 0.3$. The decrease in α with increasing pressure in the sc state is consistent with the data presented recently for ethanol. [11] The α values are shown to be almost constant with increasing pressure in the liquid state and decrease with increasing pressure in the supercritical state.

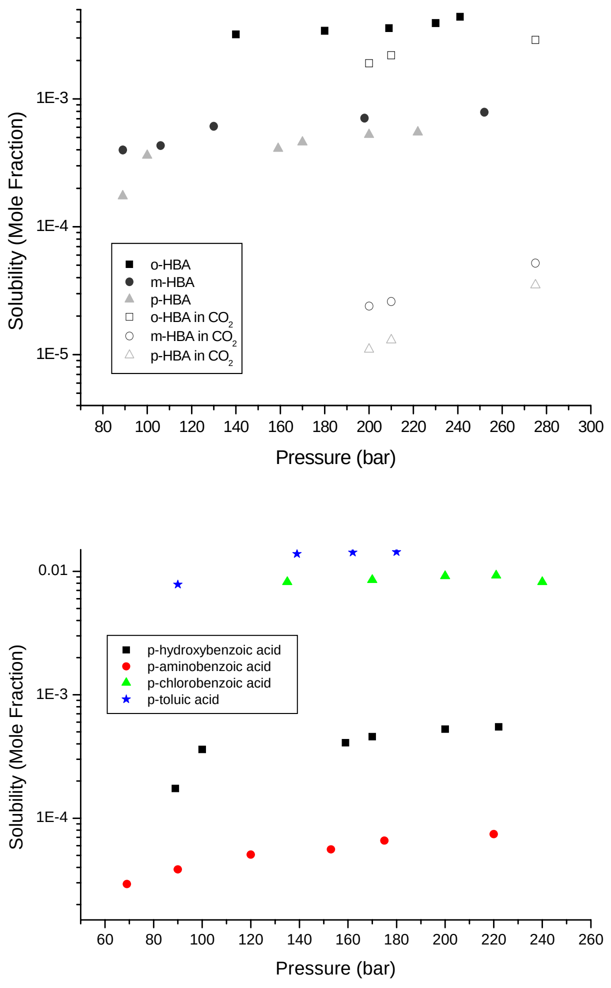

Figure 2: Solubility of various solutes in HFC32 at 90^{o}C as a function of pressure.

The hydrogen bond donor properties of the solvents decrease with increasing pressure and this trend is suggested to be due to a decrease in solvent-solvent interactions and an increase in the preferential solvation around the polar moieties as the local solvent density decreases. A strong correlation is observed between the polarisability/

dipolarity parameter, π^* and the hydrogen bond donor character, α and the relation changes significantly at the conditions where the solvent-solvent interactions decrease. [8]

The strong hydrogen bond character and the large polarisability/ dipolarity make HFC 32 a good solvent for non-volatile polar solutes. The solubility of a range of substituted aromatic compounds has been characterized using dielectometry [9]. The solubility of a particular solute was affected by pressure, solvent polarity, number of polar interaction sites and their relative substitution position. The solubility of polar solutes in medium was found to be approximately an order of magnitude higher than in the most commonly used supercritical solvent, CO_2 under comparable conditions. **Figure 2** shows examples of solubility in HFC 32 at 90°C as a function of pressure. An additional point of interest with scHFCs is that high concentrations of polar solutes lead to clustering in solution, particularly at pressures close to p_c. This causes large density fluctuations and ultimately a supercritical emulsion is formed. These systems are characteristically black to transmitted light and can lead to unusual solution effects. [12]

CONCLUSIONS

HFC32 is shown to be a polarisable solvent with strong hydrogen bond forming capability. The polarity is strongly pressure dependent and can be interpreted in terms of the change in solvent clustering around the solute. The high solvent polarity leads to high solubility for polar solutes and this in turn can produce supercritical emulsions.

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