Effect of Solutes on the Viscosity of Supercritical Solutions

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Received: October 9, 2006; In Final Form: January 18, 2007

This study shows that solutes can impart significant structure to supercritical solutions, resulting in unexpectedly high solution viscosity at pressures close to the critical value. The viscosity passes through a minimum as the pressure is increased, and this is accounted for by a solvation of the solutes leading to a decrease in solute−solute interactions. At high pressure, the solution viscosity is similar to that of the pure solvent as solvent−solvent interactions dominate. The increase in relative viscosity is modeled using a modified Dole−Jones equation, and it is shown that the change in relative viscosity is related to the volume fraction occupied by the solute. A general model is presented for simple solutes whereby the viscosity of a supercritical solution can be calculated from the molecular volume of the solute and the viscosity of the pure fluid. The higher than expected viscosity observed at low pressures is used to explain the variation of reaction rate constant with pressure.

Introduction

Supercritical (sc) fluids have found use in extraction, chromatography, and catalysis because of the marked changes that can occur in physical properties as a result of modest changes in temperature or pressure.[1−5] Among the most frequently cited advantages of using sc fluids is that they have low viscosities and hence result in high mass transport for solutes. Comparatively little data has been reported for the viscosity of sc solutions, and most of the data are presented for sc CO_2. A number of research groups have examined the changes in viscosity of sc fluids upon the addition of cosolvents or modifiers.[6,7] They found that in dilute solutions viscosities and densities increase with size, polarity, and concentration of the cosolvent.

The majority of high-pressure viscosity studies have been concerned with the dissolution of biomolecules or polymers and have been carried out at subcritical pressures. The reason for this is the experimental difficulties faced with working at both high temperatures and pressures. The studies that have been conducted report only modest increases in viscosity in sc CO_2. This is not surprising because the sc fluids and solutes employed were nonpolar.[8−10] As a result, only moderate ordering in the sc solution would be expected.

Recently, it was shown that a modified quartz crystal resonator could be used to characterize the viscosity of sc solutions.[11] The technique was used to investigate the effect of quaternary ammonium salts upon the viscosity of sc difluoromethane. It was found that the solvation of ionic aggregates leads to considerable structuring of the solution, and this results in an appreciable increase in solution viscosity. The experimental viscosities were confirmed by measuring the diffusion coefficient of ferrocene using voltammetry.

In this work, a modified quartz crystal resonator is used for the first investigation into the effect of solute polarity on the viscosity of a sc fluid at constant solute concentration. The data will provide useful information about solute clustering in sc fluids.

Experimental Section

Before performing viscosity measurements, the piezoelectric quartz crystal was modified to prevent adsorption of the aromatic solutes to the gold electrode. A layer of butanethiol was adsorbed onto the gold electrode surface of a quartz crystal. To do this, a quartz crystal was first cleaned with dilute HNO_3 solution. The crystal was then placed in a solution of 0.02 mol dm^{-3} 1-butanethiol in ethanol for 36 h. On removal from the solution, the crystal was rinsed with ethanol. The resonant frequency of the crystal was measured prior to and after the thiolation process. The shift in oscillating frequency was calculated and related to the mass deposited onto the electrode surface by the Sauerbrey equation and was calculated to be equivalent to an approximate coverage of 2 monolayers.

Before conducting the high-pressure measurements, the quartz crystal was calibrated from known viscosity and density data.[12−14] The cell used for the viscosity measurements under sc conditions was the same as that described previously.[11] Prior to each experiment, the cell was purged with difluoromethane (Ineosfluor, 99.99%, used as received). 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 high-pressure cell was loaded with the appropriate quantity of solute and subsequently heated and pressurized to the desired conditions. The system was allowed to equilibrate until steady oscillation of the quartz crystal was observed at which point the spectra were taken. The oscillation frequency maximum was calculated from an average of three spectra. Measurements were made using a E5061A Network Analyzer (Aligent Technologies) at an oscillating frequency of 10 MHz and 20 kHz range. Variations in both admittance and oscillating frequency were observed. Variations in oscillating frequency were related to the density-viscosity product of the solution by an extension to the Sauerbrey equation described elsewhere.[11] The solutes employed were *o*-hydroxybenzoic acid (salicylic acid) (Fison, 97%), naphthalene (Fison, 98%), and

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p-methylbenzoic acid (*p*-toluic acid) (Aldrich, 98%). Each solute was used as received.

Results and Discussion

Figure 1 shows how the viscosity of pure CH_2F_2 varies with increasing pressure. As with all solvents under sc conditions, the viscosity values are relatively low compared to the liquid state. The values increase significantly above the critical pressure as the density of the liquid increases. To determine the effect of solute polarity on clustering, three different types of solutes were chosen; *o*-hydroxybenzoic acid (salicylic acid), naphthalene, and *p*-methylbenzoic acid (*p*-toluic acid). These solutes were selected on the basis that they would produce a range of solute−solute and solute−solvent interactions that could be explored, but they all had similar molecular volumes and melting points. Salicylic acid is known to be capable of forming hydrogen bonds, whereas naphthalene is nonpolar. Toluic acid was chosen as an intermediate between these two compounds. The solubility of each solute in sc CH_2F_2 has been characterized previously,[15] and to check that the solutions were all monophasic the solutions were observed in a tubular high-pressure cell with sapphire windows at either end such that the entire volume could be viewed. The solute (0.01 mol dm^{-3}) was loaded into the 10 mL cell, heated to 90 °C, and the pressure of CH_2F_2 was varied from 15 to 300 bar. The solute remained as a solid on the base of the cell until the critical point was reached whereupon the solute dissolved and a transparent homogeneous solution was formed. Pressurizing the system to 300 bar did not induce any phase changes, so it was concluded that each solution was homogeneous in the pressure range to be investigated.

The data for CH_2F_2 solutions containing 0.01 mol dm^{-3} of each solute as a function of pressure is shown in Figure 1. It is clear that the addition of a solute to a sc fluid alters the viscosity of the system significantly. Most strikingly, it is noted that all three solutes cause a significant increase in solution viscosity close to the critical pressure and the viscosity decreases through a minimum as the pressure is increased. The viscosity of the solution approaches that of the pure solvent at high pressures.

At pressures close to the critical pressure ($T_c = 78$ °C; $p_c = 57.8$ bar), the solution viscosity is significantly larger than that for the pure sc fluid, and this must arise from solute−solute−solvent interaction resulting in short-range solute−solvent clusters. We have shown recently that in this pressure region hydrogen-bond donor and acceptor properties dominate the interactions between solvents and solutes and the solvation sphere is incomplete.[16−18] It should be expected, therefore, that solutes such as salicylic acid should impart significant structure to the solution.

The number of solvent molecules in a fixed volume increases as the pressure increases. These solvent molecules will solvate the solute−solute clusters completing the solvation sheath around the solute molecules and breaking up the interactions between solute molecules. This is known to occur in the same pressure region as the viscosity minimum.[18] Figure 1 shows that it is in this region that the viscosity of the system decreases and reaches a minimum located around 80 bar. It is known that in this region the full solvation of solute molecules due to enhanced attractive solute−solvent interactions causes the local solvent density around a solute to be higher than the bulk solution density. The effect of enhanced local density about a solute is called local density augmentation, and is, in addition to the fluctuations of the properties in sc fluids, normally observed near the critical point.[19] As a consequence of these
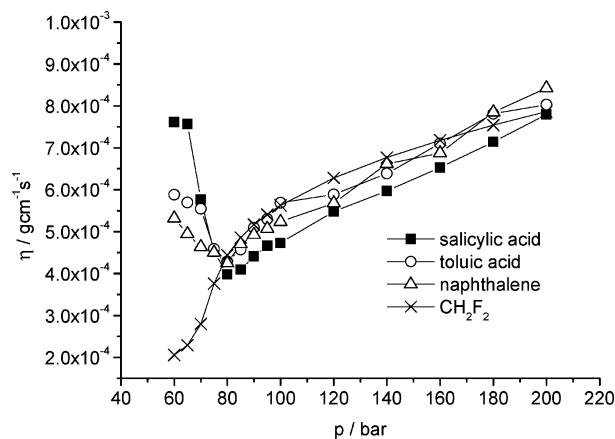

Figure 1. CH_2F_2 solution viscosity at 90 °C as a function of pressure with 0.01 mol dm^{-3} solute.
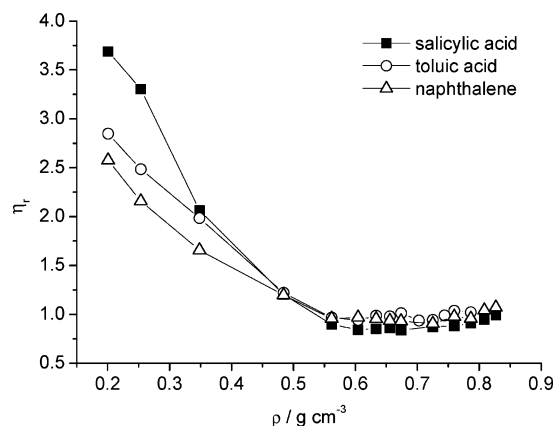

Figure 2. Relative viscosity of 0.01 mol dm^{-3} CH_2F_2 solute solutions at 90 °C as a function of density ($\rho_c = 0.424$ g cm^{-3}).

local density enhancements, the unoccupied volume between the solvated solute molecules will decrease compared to the solvent without solute. The observed decrease in solution viscosity is perceived to be a direct result of this effect, and it also explains why the viscosity of the solution is below that of the pure solvent at intermediate pressures.

Increasing the pressure above 80 bar leads to an increase in density and the molar free volume becomes similar to that of the pure sc fluid. Solvent−solvent interactions will govern this region because the mole fraction of solute has a negligible contribution to the viscosity of the solution. As a result, solution viscosity becomes the same as that of the pure sc solvent, that is solvent−solvent interactions dominate over solvent−solute interactions.

Figure 2 shows the values of relative viscosity for the same systems. These values are higher than those in studies of polymers or fatty acids in sc CO_2. This is not surprising because both solute−solute and solute−solvent interactions will be limited between these nonpolar solutes and nonpolar fluids, therefore not causing significant structuring of the fluid. As expected, the relative viscosities in Figure 2 decrease to a value of one as the pressure and density are increased and the viscosities become similar to that of the pure fluid. This indicates that at high pressures and densities the solute molecules do not impart any structure to the fluid. In contrast, in the low-pressure region the solute molecules have a role in ordering the fluid and causing the system to have structure.

The effect of a dissolved solute on viscosity has commonly been analyzed using the Dole−Jones equation[20]

$$\eta_r = 1 + Ac^{1/2} + Bc \tag{1}$$

where η_r is the relative viscosity ($\eta_r = \eta/\eta_0$), c is concentration, and A and B are constants. The A coefficient arises from ion–ion interactions and for nonelectrolytes will have a value of zero.[21] The B coefficient is related to the size and shape of solute molecules and describes the effect of the solute on the solvent structure. Negative B values result from the breaking up of the solvent structure, whereas positive values imply that the solution is more ordered than the pure solvent. For nonelectrolyte systems, eq 1 can be simplified to

$$\eta_r = 1 + Bc \tag{2}$$

There have been relatively few studies that analyze the effect of nonelectrolytes using the Dole–Jones relationship, and none have employed solvents under sc conditions. The studies that have been conducted have examined the effect of solutes in aqueous, polar, and nonpolar solvents.[22–28] The majority of high-pressure viscosity investigations have focused on modeling the phase behavior and viscosity.[29,30] In addition, activation volumes for high-pressure polymer solutions have commonly been estimated from viscosity data.[31,32]

For nonelectrolyte molecules, the B coefficient has commonly been related to the partial molar volume of solute, V_m, by an extension to the Einstein equation[33–39]

$$B = 2.5V_m \tag{3}$$

The constant 2.5 arises from the assumption that the solute molecules are spherical. The relationship between the size of the solute molecule and its B coefficient has been used to estimate the relative solvation numbers. In the liquid state, the structure of a solution is influenced by both the size of solvated species and the solute aggregation, which in turn rely on the strength of the intermolecular forces. Table 1 shows the dipole moment and molecular volume of the three solutes under investigation and the CH_2F_2 solvent molecule.
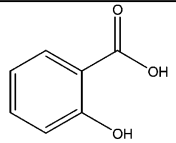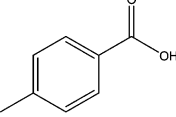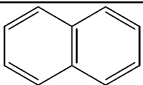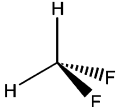
The assumptions used in eqs 2 and 3 are slightly different in supercritical fluids because the concentration of the solute remains constant and it is the concentration of solvent that changes; hence, an analogous form of eq 2 can be written

$$\eta_r = 1 + B'x \tag{4}$$

Figure 3 shows how the specific viscosity, η_s, (where $\eta_s = (\eta - \eta_0)/\eta_0 = \eta_r - 1$) varies with the mole fraction of solute, x. It can be seen that there are clearly two pressure regimes: At high mole fractions, corresponding to the low-pressure region, positive slopes are observed, which fit well to eq 4 indicating that the fluid is more ordered than the pure solvent. Below 0.001 mole fraction, the slopes are approximately zero, which suggests that the solute no longer has any significant influence on the overall structure of the fluid and the viscosity is similar that of the pure solvent. Hence, it can be concluded that there are two types of pressure regime above and below a critical mole fraction whereby at high solute mole fractions the solute–solute interactions dominate and at low mole fractions solvent–solvent interactions dominate. It would appear from Figure 3 that the critical mole fraction is solute-independent and must be controlled by solvent–solvent interactions.

The B' coefficient in eq 4 is not the partial molar volume, but rather it must be related to the fraction of the volume occupied by the solute in the vessel. Figure 3 and Table 1 show that the larger solutes cause a proportionately smaller effect upon

TABLE 1: Dipole Moments and Molecular Volumes Calculated Using Commercially Available Solftware[50] [a]

Molecule	μ / Cm	V / Å^3	B' [b]	B' (calc)
(salicylic acid structure)	7.37×10^{-30}	149.37	1749	1115
(toluic acid structure)	9.32×10^{-30}	161.65	1145	1028
(naphthalene structure)	0	159.12	950	1045
(CH$_2$F$_2$ structure)	6.60×10^{-30}	51.79	-	-

[a] B' coefficients were obtained from Figure 3 and calculated using eq 5. [b] Multiple regression of data in Figure 3 ($R > 0.98$).
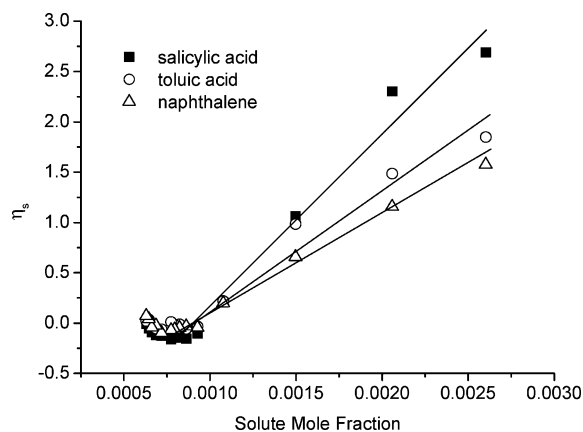

Figure 3. Specific viscosity of CH_2F_2 solute solutions at 90 °C as a function of solute mole fraction.

viscosity in the lower pressure region. One explanation for this could be that the larger solutes require more solvent molecules to solvate them, and thus they decrease the solvent density between the solute molecules. This would mean that the solute would have a smaller effect of the solute upon the solution viscosity. It could therefore be argued that the B' parameter is inversely proportional to the size of the solute, that is

$$B' = 1/(VN_A c) \tag{5}$$

where V is the molecular volume and N_A is the Avogadro constant. Table 1 shows that for the three solutes studied in this work very good agreement is obtained between the values calculated using eq 5 and those obtained experimentally from Figure 3. The slight discrepancy observed for salicylic acid is probably due to the dimerization of the solute through hydrogen bonding and the change in solvation of the dimer. Similar trends are found when the solute concentration is reduced to 0.001 mol dm^{-3} (not shown).[40] This indicates that even at relatively low concentrations the solute plays an important role in imparting structure to the solution at low pressures.

The fact that supercritical solutions are relatively viscous close to the critical pressure could be used to explain many observa-
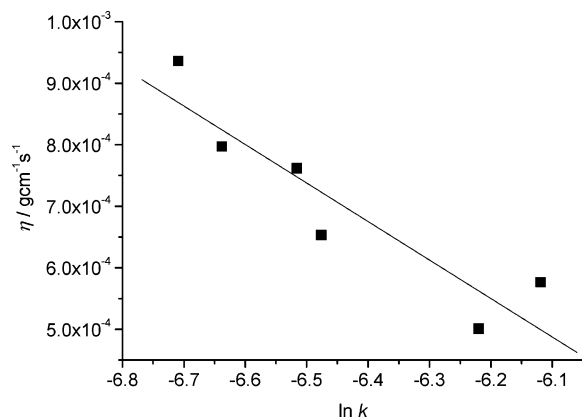
Figure 4. Plot of viscosity data from Figure 1 vs the reaction rate constant reaction of anisole with *t*-butylchloride in sc CH_2F_2 (data taken from ref 36).

tions. In the low-pressure region, between 60 and 80 bar, this work shows that appreciable changes in solution viscosity occur with small variations in pressure. The viscosity is first observed to be at a maximum and rapidly decreases to a minimum as the pressure is increased. This suggests that the velocity of solutes will also vary; therefore, it is expected that solution properties such as reaction kinetics would be significantly altered around this region. Several authors have examined reactions in sc fluids and found enhanced reaction rates at pressures just above the critical point. Most of these investigations have involved the use of nonpolar sc fluids such as CO_2 although a number of authors have investigated more polar fluids. The only reaction carried out in CH_2F_2 for which kinetic data are available is the Friedel−Crafts alkylation reaction of anisole with *t*-butylchloride in sc CH_2F_2 and sc CO_2.[41] It was found that reaction rates were greater in sc CH_2F_2 due to the increased solvent polarity. Rate constants were observed to reach a maximum at ca. 80 bar that corresponds to the minimum solution viscosity in Figure 1. It was concluded that it was the dielectric constant of the solution that was the controlling influence on the reaction. Figure 4 shows a plot of the solution viscosity data from Figure 1 versus the reaction rate constant for the reaction of anisole ($\mu = 1.25$ D) with *t*-butylchloride ($\mu = 2.15$ D) in sc CH_2F_2. Very good correlation is obtained, showing that the solution viscosity is affecting the reaction rate. Although the solutes used in the Friedel Crafts reaction are clearly different from salicylic acid ($\mu = 2.21$ D), the dipole moments were similar and hence the dipole−dipole interactions would be comparable.

Many other groups have observed a maximum in reaction rate constant close to the critical pressure. Rhodes et al. compared the reaction kinetics of a Michael addition in nonpolar sc ethane to the more polar sc fluoroform.[42] Near the critical point, the reaction rate in sc ethane was observed to increase as a result of solute−solute clustering. It was thought that this increase could not be due to solvent−solute clustering because solvent density had little effect on the kinetics of the reaction. In sc fluoroform, solvent−solute clustering was proposed to be the reason for the changes in rate constant near the critical point. However, below the critical density solute−solute clustering was thought to dominate.

Ellington et al. have conducted a number of investigations into the effect of local density reaction rates.[43,44] Apparent bimolecular rate constants were calculated and found to exhibit a remarkable 25-fold increase with a decrease in pressure. It was argued that the local concentration of reactants exceeded the average bulk and this could account for the enhanced rate

constants at low pressures. Measurements of local composition and density showed this to be true.

More recently, Hou and co-workers calculated the apparent equilibrium constant for an esterification reaction in sc CO_2.[45] The results showed that at low pressures it increased with pressure, reaching a maximum in the critical region. This observed increase at low pressures was explained with respect to the degree of clustering these pressures. At high pressures, where clustering is insignificant, the equilibrium constant was found to be close to that of the reaction in the absence of CO_2.

The Diels−Alder reaction has also been the focus for a number of investigators.[46−48] The clustering of solvent molecules with reactants and the activated complex was proposed to be the reason for the enhanced reaction rates around the critical region.

Pronounced solvent effects have also been observed for hydrogen-bonding interactions in sc SF_6. The equilibrium for methanol−triethylamine association increased as the pressure decreased toward the critical point. The complex was stabilized at lower densities where the degree of hydrogen bonding is enhanced due to solute−solute clustering.[49]

Conclusions

In conclusion, the work presented here demonstrates the first investigation into the solute effects on the viscosity of sc solutions. It has been shown that the viscosity varies significantly from that of the pure sc fluid. In the region of low pressure, the viscosity is significantly larger than that of the pure fluid, and this is attributed to the enhanced degree of solute−solute clustering via hydrogen-bonding interactions. As the pressure is increased, the solvation sheath becomes complete and the molar free volume of the system increases. This region is characterized by a decrease in solution viscosity. Above this point, the molar volume increases further and the solute mole fraction becomes negligible. The viscosity in this region is shown to increase and at sufficiently high pressures become the same as that of the pure sc fluid. Although the levels of solute−solute interactions are only speculated, it is obvious that they play a role in structuring the sc fluid and influence the bulk viscosity. The data presented here is also consistent with our previous investigation into the effects of electrolytes on the viscosity of sc CH_2F_2 where the ion−ion interactions led to significant increases in solution viscosity. A modification of the Dole−Jones equation can be used to model the viscosity of supercritical solutions, and it is shown that the volume fraction of the solute is the key factor in affecting solution viscosity.

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