Solubility of Substituted Aromatic Hydrocarbons in Supercritical Difluoromethane

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The solubilities of a variety of substituted phenols and benzoic acid derivatives is determined in supercritical difluoromethane (HFC-32) at 90 °C using a capacitative method, and they are presented as a function of pressure. The compounds are shown to be more soluble than they are in CO_2 under comparative conditions. The enhancement factor is used as a way of expressing solubility to remove the effect of vapor pressure; the observed trend is explained in terms of the polarity of the substituents. The solubility data are fitted to a Peng−Robinson equation of state for which a good correlation is observed.

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. A comprehensive review of the solute solubility in supercritical carbon dioxide ($scCO_2$) has recently been published.[3] 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 solubilize 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.[4−6]

Recently, we have highlighted that some hydrofluorocarbon (HFC) fluids such as difluoromethane (HFC-32) and 1,1,1,2-tetrafluoroethane (HFC-134a) are relatively polar solvents,[7−9] 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. These solvents are also readily available (they are used in the majority of refrigeration units) and nontoxic (they are also used as solvents for oral drug inhalers). The dipolarity/polarizability parameter has been determined over a wide range of temperature and pressure and shows that the polarities of scHFC-32 and scHFC-134a can be similar to that for ethyl acetate under ambient conditions.[8] Knowledge of polarity alone is not enough to understand the solvency behavior of a solvent medium, and a significant problem associated with the widespread use of these fluids in the sc state is the lack of solubility data.

The current work describes the solubilities of a variety of substituted aromatic hydrocarbons in HFC-32 at 90 °C. The data were determined using a capacitative method, which was first described by Hourri et al. for the determination of naphthalene solubility in $scCO_2$.[10] The technique is of limited use for $scCO_2$ because the low solubility of polar solutes means that the overall change in dielectric constant is relatively small. In the current work we demonstrate that the method is ideal for use with HFC fluids.

Experimental Section

The schematic diagram of the capacitance cell used for the measurement of the dielectric constants of a number of solutes (Table 1) in a supercritical medium as a function of pressure along an isotherm is shown in Figure 1. The cell was constructed from type-316 stainless steel and was rated to 1.5 kbar. The internal volume of the cell, lined with a layer of Teflon (about 1 mm thick) was approximately 25 cm^3. The electrical feedthroughs were sealed with Swagelok fittings. The capacitor consisted of two parallel rectangular stainless steel plates (attached to the electrical feedthroughs), with an area of 6.6 cm^2, held 1 mm apart by Teflon spacers, to give a cell geometrical capacitance of 14.6 pF. Prior to each experiment, the cell was purged with the appropriate gas at 1 bar of pressure. The pressure was then raised using a model 10-500 pump (Hydraulic Engineering Corp.; Los Angeles, CA), driven by compressed air, and held at a given value (±2 bar) using a UCC type PGE 1001.600 manometer. The temperature of the cell was measured using an iron−constantan thermocouple, the tip of which was in contact with the solvent close to the center of the cell. This was held at a given value (±0.5 K) using a CAL 9900 controlled heater. The solvents, difluoromethane [HFC-32] (Ineos Fluor, 99.99%) and CO_2 (BOC Limited, 99%), were used as received.

The dielectric constant, ϵ, was measured with capacitance C_0 such that the measured capacitance was given by

$$C = \epsilon C_0 \tag{1}$$

Cell capacitances, C, were measured at 65 kHz with a 20 mV ac voltage amplitude using a 1254 frequency response analyzer and a 1286 potentiostat (both Solatron Instruments), controlled by ZPLOT software. The acquired data were analyzed using ZVIEW software. C_0 was measured prior to each experimental run, and the uncertainty of each capacitance reading was 50 fF. The capacitor was tested with several pure solvents of known ϵ, including acetonitrile, dichloromethane, acetone, and toluene, where the

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Table 1. Properties of the Solutes Employed in This Work

solute	company	$10^{30}\mu$/C·m	10^{30}(polarizability)/m^3	T_c/K P_c/MPa	melting point/°C
naphthalene	Fisons (98%)	0	16.5	748.4 4.05	80−82
anthracene	BDH Chemicals (97%)	0	25.4	869.3 3.243	216−218
o-hydroxybenzoic acid	Fisons (97%)	8.839	12.36	704.24 5.002	158−160
m-hydroxybenzoic acid	BDH Chemicals (98%)	7.972	11.15		201−203
p-hydroxybenzoic acid	BDH Chemicals (98%)	9.206	12.87		215−217
p-toluic acid	Aldrich (98%)	6.671	15.15	772.04 4.001	180−182
p-aminobenzoic acid	BDH Chemicals (98%)	10.34	15.8		187−189
p-chlorobenzoic acid	Aldrich (99%)	6.738	16.1		239−241
o-chlorobenzoic acid	Aldrich (98%)	8.172	16.3		138−140
p-aminophenol	BDH Chemicals (98%)	6.071	12.8	781.78 5.662	188−190
p-chlorophenol	BDH Chemicals (98%)	6.671	13.0	699.5 4.938	43−45

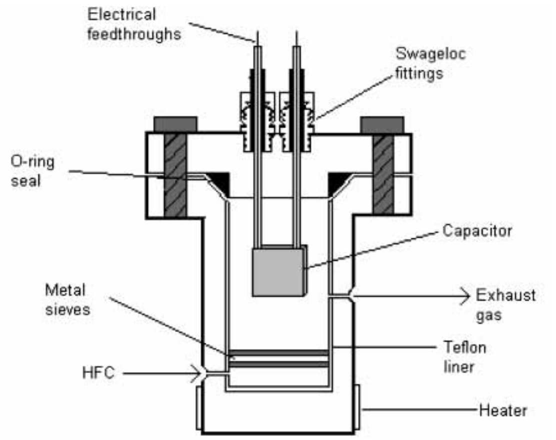


Figure 1. High-pressure capacitance cell.

dielectric constant was found to vary by no more than 1% from literature values.

The method to find the solubility of solid solutes in supercritical fluids by measurement of the dielectric constant has been described previously by Hourri et al.,[10] where it was shown that

$$\mathrm{CM}' - \mathrm{CM}'' = A_e^s\rho^s + \beta \qquad (2)$$

where **CM** = $(\epsilon - 1)/(\epsilon + 2)$ and the single and double primed quantities pertain to the saturated supercritical solution and the supercritical solvent, respectively. A_e^s is the first dielectric virial coefficient. For a nondipolar solute, this is given by

$$A_e^s = \frac{4\pi N_A}{3}\alpha \qquad (3)$$

where N_A is Avogadro's number and α is the molecular polarizability. For a polar solute, this equation was slightly modified so that the first dielectric virial coefficient was

$$A_e^s = \frac{4\pi N_A}{3}\left(\alpha + \frac{\mu^2}{3k_BT}\right) \qquad (4)$$

where μ is the permanent dipole moment, k_B is the Boltzmann constant, and α is the molecular polarizability. Equation 2 then gives us the working relation for the solubility determination, ρ^s, which is

$$\rho^s = \frac{\mathrm{CM}' - \mathrm{CM}''}{A_e^s} - \frac{\beta}{A_e^s} \qquad (5)$$

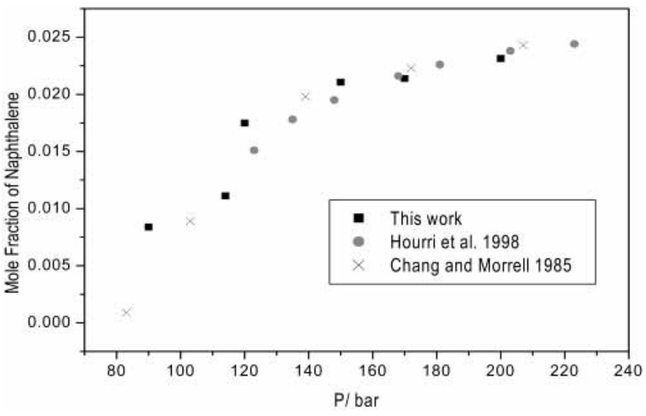


Figure 2. Comparison of the solubility of naphthalene as a function of pressure, *P*, measured in this work compared with published data in CO_2 at 318 K.

Table 2. Solubility Data for Naphthalene in CO_2 at 318 K

pressure/bar	molarity/mol·L^{-1}	mole fraction	density[a]/mol·L^{-1}
90	0.102 11	0.008 38	7.755
114	0.145 54	0.011 11	14.286
120	0.243 64	0.017 49	15.031
150	0.312 99	0.021 06	16.921
170	0.327 56	0.021 38	17.671
200	0.367 26	0.023 13	18.503

[a] *NIST Chemistry WebBook* (http://WebBook.nist.gov).

where (β/A_e^s) is the correction to the solubility arising from the difference (CM′ − CM″) and relative to the difference of the higher order terms in ρ' and ρ''.

Values of the dipole moment were taken from the literature,[11] and values for the molecular polarizability were either taken from the literature[12] or estimated via an additive method by Le Fevre.[13] These values are shown in Table 1. The uncertainties of these values of dipole moment and molecular polarizabilty are unknown. However, if a theoretical maximum uncertainty of 5% is assumed in the molecular polarizability values, then the mole fraction solubility is found to fluctuate by no more than ±0.5%. When looking at an uncertainty of 5% for the dipole moment values, this solubility fluctuation is found to increase to ±6%. When polar solutes are used, both of these properties have to be considered and this theoretical 5% uncertainty in both properties gives rise to errors in mole fraction solubility up to ±9%, which has to be taken as the maximum limit. Actual uncertainties are likely to be less and are mainly influenced by the uncertainty in the dipole moment value. Dielectric constant and density values of pure HFC-32 were taken from previously published data.[9]

Table 3. Solubility Data for Salicylic Acid in CO_2 at 318 K

pressure/bar	molarity/mol·L^{-1}	mole fraction	density^a/mol·L^{-1}
98	0.007 241	0.000 731	10.971
110	0.012 59	0.000 914	13.776
120	0.021 371	0.001 422	15.031
150	0.028 816	0.001 703	16.921
170	0.039 309	0.002 213	17.671
195	0.053 161	0.002 892	18.381

[a] *NIST Chemistry WebBook* (http://WebBook.nist.gov).

Table 4. Solubility Data for Salicylic Acid in HFC 32 at 363 K

pressure/bar	molarity/mol·L^{-1}	mole fraction	density^a/mol·L^{-1}
140	0.046 635	0.003 197	14.593
180	0.052 863	0.003 414	15.521
209	0.057 406	0.003 585	16.003
230	0.063 99	0.003 919	16.333
241	0.072 522	0.004 401	16.499

[a] *NIST Chemistry WebBook* (http://WebBook.nist.gov).

Table 5. Solubility Data for *m*-Hydroxybenzoic Acid in HFC 32 at 363 K

pressure/bar	molarity/mol·L^{-1}	mole fraction	density^a/mol·L^{-1}
89	0.004 838	0.000 399	12.091
106	0.005 753	0.000 432	13.282
130	0.008 569	0.000 611	14.287
198	0.011 215	0.000 708	15.745
252	0.013 083	0.000 787	16.606

[a] *NIST Chemistry WebBook* (http://WebBook.nist.gov).

Table 6. Solubility Data for *p*-Hydroxybenzoic Acid in HFC 32 at 363 K

pressure/bar	molarity/mol·L$_{-}^{1}$	mole fraction	density^a/mol·L^{-1}
89	0.002 107	0.000 174	12.091
100	0.004 667	0.000 361	12.953
159	0.006 178	0.000 409	15.003
170	0.007 021	0.000 458	15.321
200	0.008 36	0.000 526	15.878
240	0.008 899	0.000 549	16.469

[a] *NIST Chemistry WebBook* (http://WebBook.nist.gov).

Table 7. Solubility Data for *p*-Toluic Acid in HFC 32 at 363 K

pressure/bar	molarity/mol·L^{-1}	mole fraction	density^a/mol·L^{-1}
90	0.095 731	0.007 815	12.185
118	0.153 864	0.011 099	13.862
139	0.201 735	0.013 852	14.521
162	0.215 366	0.014 217	15.172
180	0.222 893	0.014 353	15.521

[a] *NIST Chemistry WebBook* (http://WebBook.nist.gov).

Table 8. Solubility Data for *p*-Chlorobenzoic Acid in HFC 32 at 363 K

pressure/bar	molarity/mol·L^{-1}	mole fraction	density^a/mol·L^{-1}
135	0.118 53	0.008 196	14.445
170	0.130 444	0.008 514	15.321
200	0.145 446	0.009 161	15.878
221	0.149 951	0.009 247	16.199

[a] *NIST Chemistry WebBook* (http://WebBook.nist.gov).

Table 9. Solubility Data for *o*-Chlorobenzoic Acid in HFC 32 at 363 K

pressure/bar	molarity/mol·L^{-1}	mole fraction	density^a/mol·L^{-1}
100	0.135 554	0.010 471	12.953
134	0.151 476	0.010 499	14.411
170	0.177 51	0.011 585	15.321
190	0.181 629	0.011 555	15.706
219	0.189 153	0.011 688	16.182
248	0.223 325	0.013 473	16.564

[a] *NIST Chemistry WebBook* (http://WebBook.nist.gov).

Table 10. Solubility Data for *p*-Aminobenzoic Acid in HFC 32 at 363 K

pressure/bar	molarity/mol·L^{-1}	mole fraction	density^a/mol·L^{-1}
69	0.000 183	0.000 029 3	6.241
90	0.000 469	0.000 038 5	12.185
120	0.000 707	0.000 050 7	13.930
153	0.000 837	0.000 056	14.920
175	0.001 017	0.000 065 9	15.423
220	0.001 204	0.000 074 3	16.190

[a] *NIST Chemistry WebBook* (http://WebBook.nist.gov).

Table 11. Solubility Data for Anthracene in HFC 32 at 363 K

pressure/bar	molarity/mol·L^{-1}	mole fraction	density^a/mol·L^{-1}
79	0.004 485	0.000 422	10.579
125	0.005 686	0.000 403	14.116
148	0.006 97	0.000 471	14.817
175	0.008 15	0.000 528	15.423
220	0.009 642	0.000 596	16.190

[a] *NIST Chemistry WebBook* (http://WebBook.nist.gov).

Table 12. Solubility Data for *p*-Chlorophenol in HFC 32 at 363 K

pressure/bar	molarity/mol·L^{-1}	mole fraction	density^a/mol·L^{-1}
122	0.648 614	0.046 198	14.007
150	0.768 064	0.051 635	14.862
185	0.808 208	0.051 758	15.615
220	0.856 662	0.052 88	16.190
258	0.863 901	0.051 718	16.707

[a] *NIST Chemistry WebBook* (http://WebBook.nist.gov).

Table 13. Solubility Data for *p*-Aminophenol in HFC 32 at 363 K

pressure/bar	molarity/mol·L^{-1}	mole fraction	density^a/mol·L^{-1}
89	0.013 214	0.001 088	12.091
111	0.016 135	0.001 189	13.583
132	0.029 776	0.002 074	14.365
188	0.032 882	0.002 097	15.689

[a] *NIST Chemistry WebBook* (http://WebBook.nist.gov).

Results

Figure 2 and Table 2 show solubility results for naphthalene in CO_2 at 318 K and a variety of pressures for this work. In Figure 2, these results are compared to previously published solubility results using a dielectric[10] and a gravimetric method.[14] From this plot it can be seen that there is good agreement between the data from this work and other reported solubilities.

Tables 4−13 show the first solubility measurements in scHFC-32 at 363 K over a range of pressures for the solutes shown in Table 1. Table 3 is included for comparison of solubilities in scHFC-32 and $scCO_2$, where it is seen that the solubility of salicylic acid in this HFC solvent is approximately double its solubility in the most commonly used sc solvent CO_2. Figures 3 and 4 are compiled from the data given in Tables 4−13, comparing the effect of substituent on para-substituted benzoic acids and phenols, respectively. From these plots, it can be seen that mole fraction solubility increases with increasing pressure for all the solutes studied and that solubility is greatly affected by the polarity of the substituent present. For both the benzoic acids and the phenols, it can be seen that solubility decreases with increasing polarity of the substituent. It has been noted previously that the presence of a carboxy group causes a decrease in the solubility.[15] This is illustrated by comparison of Figures 3 and 4, where it can be observed

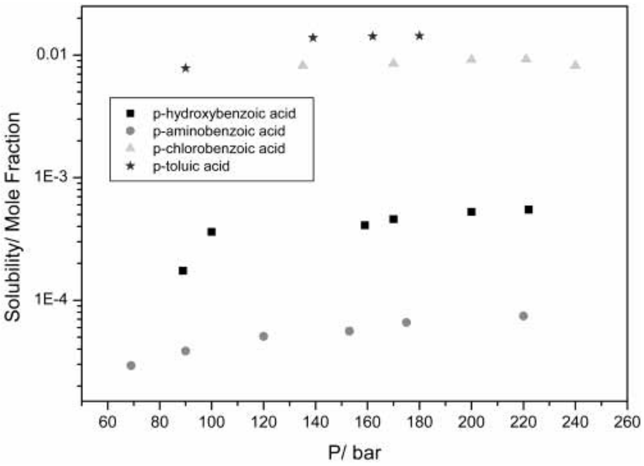


Figure 3. Effect of substituent on benzoic acid solubility in HFC-32 as a function of pressure at 363 K.

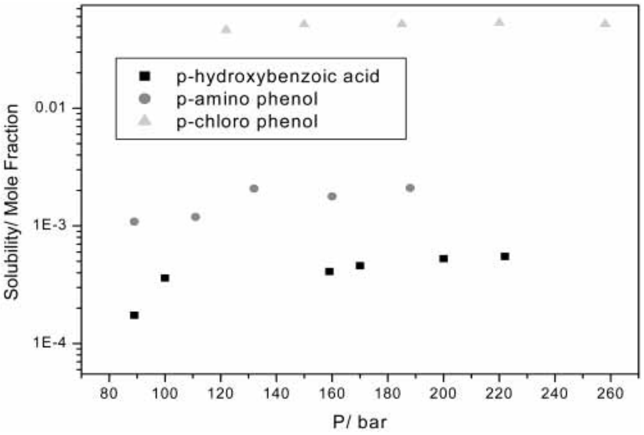


Figure 4. Effect of substituent on phenol solubility in HFC-32 as a function of pressure at 363 K.

that the solubilities of the phenols are approximately 2 orders of magnitude greater than those of the corresponding benzoic acid.

Figure 5 is compiled from the results given in Tables 4−6 and those from Krukonis et al.[16] for the same solutes in supercritical CO_2 at similar temperatures and pressures. These results are also displayed as a function of reduced pressure and shown on a different axis in Figure 5. The solubility of each corresponding solute is found to be greater in scHFC-32. The increase in solubility in this medium is to some extent what would be expected for a polar solute in this more polar solvent. For these systems, a dipole−dipole interaction between the polar solute and HFC-32 exists which would tend to enhance solubility relative to that with the dipole−quadrupole interaction present with the polar solutes and $scCO_2$ system.

Correlation of Solubility Behavior. It has been shown that the solubility of solid solutes in supercritical CO_2 can be correlated using a cubic equation of state.[17] We have used the Peng−Robinson equation to attempt to correlate the solubilities in scHFC-32 of a number of the solutes in this study. Details of the pure solute data used as input to the Peng−Robinson equation are summarized in Table 1. When no critical data were available from the literature, the solute critical temperature and pressure were estimated using Joback's modification of the Lydersen group additivity method.[18] The resulting solubility estimation curves from the Peng−Robinson equation for salicylic acid and *p*-aminophenol are shown in Figures 6 and 7, respectively.

In terms of understanding the effects of the supercritical solvent on the solubility of a range of solutes, it is generally more profitable to examine the solubility enhancement caused by the solvent rather than the absolute solute solubility. This solubility enhancement is simply the ratio of the measured solute concentration in the supercritical solvent to the concentration of the pure solute as a result of its own vapor pressure at the temperature of interest. The solubility enhancement for a number of the solutes is shown in Figure 8. If Figure 8 is compared to Figures 3 and 4, which show pressure versus observed solubility, it can be seen that the order of solute solubility has now been reversed. Anthracene, the least polar of the solutes, shows the lowest solubility enhancement while increasing the solute polarity, and the number of polar substituents appears to increase the degree of enhancement. It is interesting to compare the results for salicylic acid (*o*-hydroxybenzoic acid) with those for the isomeric *p*-hydroxybenzoic acid. Despite its higher dipole moment and higher absolute solubility in scHFC-32, salicylic acid shows

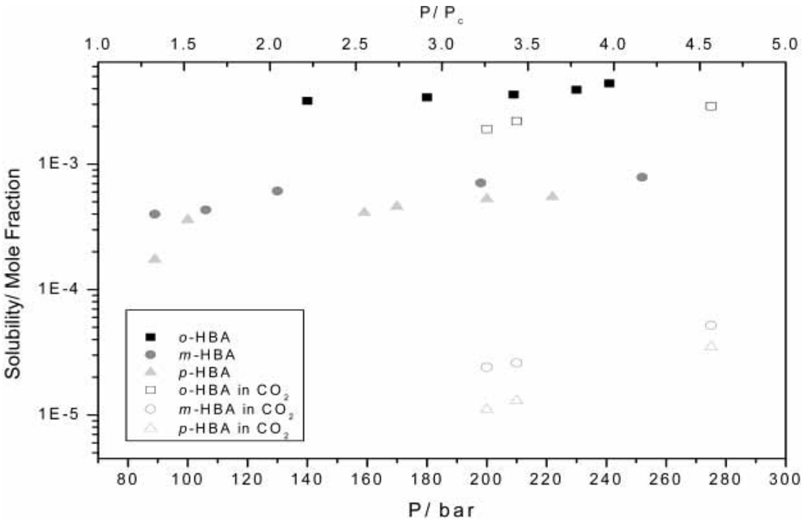


Figure 5. Comparison of the solubilities of *o*-, *m*-, and *p*-hydroxybenzoic acids (HBA) in HFC-32 at 363 K and CO_2 at 373 K as a function of pressure and reduced pressure.

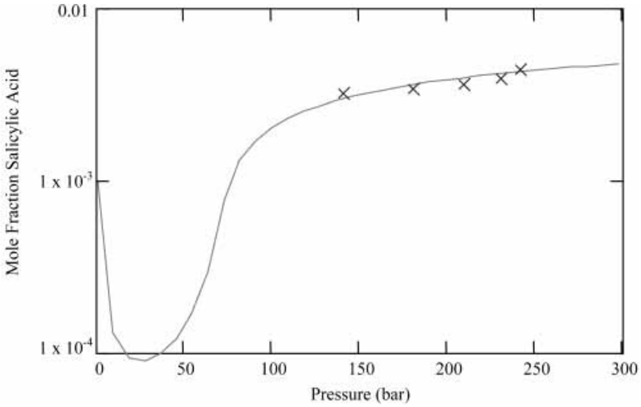


Figure 6. Solubility of salicylic acid in HFC-32 at 363 K: ×, experimental data; solid line, fitted data.

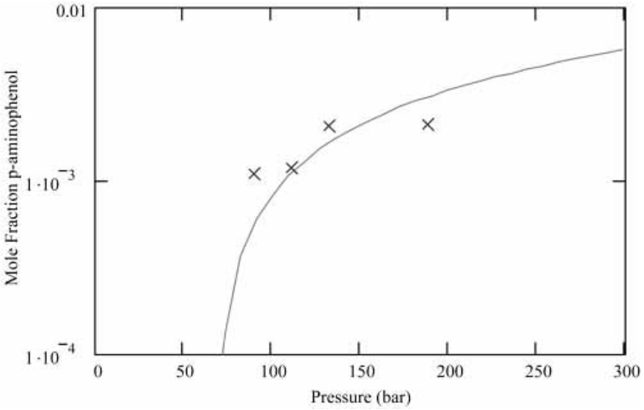
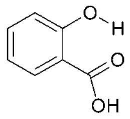
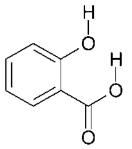


Figure 7. Solubility of *p*-aminophenol in HFC-32 at 363 K: ×, experimental data; solid line, fitted data.

a lower solubility enhancement than *p*-hydroxybenzoic acid, only slightly greater than that for anthracene. This behavior may be explained on the basis of a degree of intramolecular H-bonding in salicylic acid.





This could act to limit the availability or strength of solvation sites for interaction with the HFC-32. This ortho-interaction is not available for the *para*-isomer and is reflected in the lower melting point of the salicylic acid in comparison to that for either the meta- or para-isomer.

Since scHFC-32 is a relatively polar solvent, it can solvate polar solutes without the need for the addition of polar modifiers as with CO_2, which has been shown for the first time in this work.

Conclusions

These results show the first solubility measurements of a variety of substituted phenols and benzoic acid derivatives in the environmentally acceptable refrigerant HFC-32 at 363 K and pressures ranging from 60 to 260 bar. The results suggest that the dielectric constant method is capable of quickly and accurately determining the solubility of a range of solutes in this medium. Pressure, solvent polarity, number of polar interaction sites, and their relative substitution position affect the solubility of a particular solute. The solubility of polar solutes in this medium was found to be higher than that in the most commonly used supercritical solvent, CO_2.

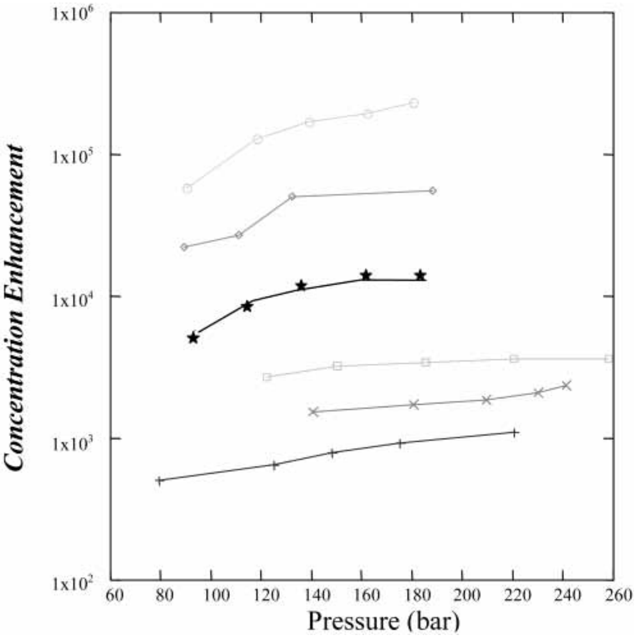


Figure 8. Concentration enhancement in difluoromethane at 363 K: ×, salicylic acid; +, anthracene; □, *p*-chlorophenol; ◇, *p*-aminophenol; ○, *p*-hydroxybenzoic acid; ★, *p*-toluic acid.

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