G^E	excess Gibbs function, liquid phase
g	G^E/RT
P	total pressure
P_i^{sat}	vapor pressure of pure i
R	universal gas constant
T	absolute temperature
V_i^L	molar volume of pure liquid i
x	mole fraction, liquid phase

Greek Letters

λ_{ij}, λ_{ji}	parameters in eq 1
η_{ij}, η_{ji}	parameters in eq 1
Δ	signifies a difference

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Solubilities of Phenol and Chlorinated Phenols in Supercritical Carbon Dioxide

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Solubilities of phenol, *p*-chlorophenol, and 2,4-dichlorophenol in supercritical carbon dioxide were measured at 36 °C over a range of pressures from 80 to 250 atm. The solubility of phenol in supercritical carbon dioxide was also measured at 60 °C over the same pressure range. The data represent the effects of pressure and temperature on solubility as well as solubility trends in an homologous series of compounds.

Introduction

Recent applications in high-pressure dense-gas extraction processes—such as coffee decaffeination (*1*) and regeneration of activated carbon (*2*)—have led to an increasing interest in this separation process, which is based upon the ability to vary the solvent power of a fluid in the vicinity of its critical point with small changes in temperature and/or pressure. Supercritical carbon dioxide (T_c = 31 °C; P_c = 72.8 atm) appears to be the preferred solvent in the above processes, primarily because carbon dioxide is environmentally acceptable, inexpensive, and readily available. There are, however, very little experimental data for solubilities in supercritical carbon dioxide, especially as a function of temperature and pressure. Francis (*3*) has measured solubilities in liquid carbon dioxide for a large number of solutes but only at a single temperature and pressure—saturated carbon dioxide at 25 °C. Tsekhanskaya et al. (*4*) measured the solubility of solid naphthalene in supercritical carbon dioxide at three different temperatures and over a range of pressures. The data illustrate the large solubility enhancement, which results when compressing gaseous carbon dioxide to supercritical fluid densities, and the dramatic sensitivity of solubility as a function of temperature and pressure in the critical region of the solvent. As a preliminary study in our work investigating the use of supercritical carbon dioxide for regenerating activated carbon, we have measured the solubilities of three common waste-water pollutants—phenol, *p*-chlorophenol, and 2,4-dichlorophenol—in supercritical carbon dioxide as a function of pressure.

Experimental Section

A schematic diagram of the experimental apparatus for measuring solubilities is given in Figure 1. Liquid carbon dioxide (Linde "bone dry") at ambient temperatures is charged into a Milton Roy high-pressure liquid pump and compressed to the desired pressure. The pump is used to continuously deliver solvent at flow rates from 60 to 300 standard cm^3/min and at constant pressures up to 250 atm. Preliminary experiments were accomplished at flow rates up to 500 cm^3/min with no effect on the measured solubilities. After reaching thermal equilibrium within the constant-temperature bath (controlled by a Sargent-Welch Thermonitor), the solvent is fed into the first of two high-pressure equilibrium cells (High Pressure Equipment, Inc.) connected in series. The solvent migrates slowly through the column—packed with glass beads and the heavy solute—becoming saturated with the solute prior to exiting the second column. Entrainment of the solute is prevented by inserting glass wool plugs at the top of each packed column. Once the saturated solution exits the second cell, it is flashed to atmospheric pressure across a heated metering valve (Whitey Co.) and the heavy component is collected in a cold trap held at ice temperature. The amount collected is determined by weighing, and the corresponding volume of carbon dioxide is measured with a wet-test meter. The equilibrium pressure is measured at the exit of the second column with a Bourdon-type Heise pressure gauge (0–5000 psi range). Fluctuations in pressure due to the high-pressure liquid pump are less than ±25 psi over the entire pressure range. Temperature is measured to within 1 °C with

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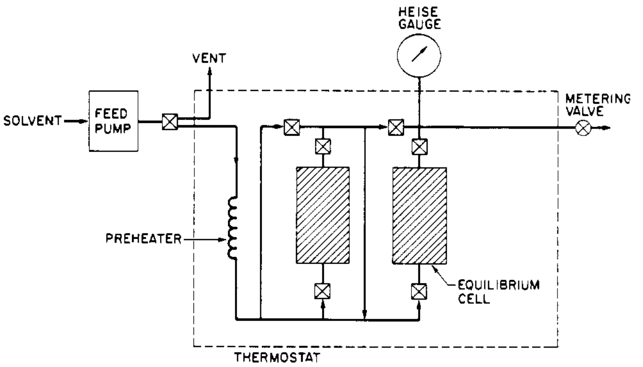

Figure 1. Schematic diagram of the experimental apparatus for measuring solubilities.

Table I. Experimental Solubilites for Phenol in Supercritical Carbon Dioxide

$T = 36$ °C		$T = 60$ °C	
pressure, atm	phenol mole fraction	pressure, atm	phenol mole fraction
78.25	0.003 488	112.11	0.006 496
79.86	0.007 314	125.31	0.012 33
85.40	0.009 581	143.82	0.018 59
95.50	0.011 27	144.16	0.018 72
104.44	0.012 43	150.56	0.018 04
109.53	0.012 80	158.19	0.021 95
117.58	0.013 67	166.05	0.022 09
121.99	0.013 90	175.16	0.028 30
131.05	0.014 86	180.57	0.029 01
144.42	0.015 02	184.35	0.030 65
144.79	0.015 15	190.01	0.031 58
153.67	0.015 89	201.29	0.031 46
159.39	0.016 04	208.36	0.038 90
161.30	0.016 36	218.91	0.036 44
169.50	0.015 90	229.90	0.044 60
180.22	0.016 71	238.63	0.046 60
180.59	0.016 51		
191.37	0.016 70		
193.83	0.016 86		
204.88	0.017 55		
210.94	0.017 88		
213.09	0.017 93		
218.84	0.018 22		
231.13	0.018 34		
246.17	0.018 16		

Table II. Experimental Solubilities for *p*-Chlorophenol in Supercritical Carbon Dioxide at 36 °C

pressure, atm	phenol mole fraction	pressure, atm	phenol mole fraction
79.90	0.005 96	141.02	0.017 48
89.08	0.009 73	150.92	0.020 31
99.88	0.010 99	167.67	0.020 47
109.76	0.013 03	200.62	0.027 89
120.12	0.014 06	236.70	0.032 89
129.56	0.015 83		

a calibrated copper–constantan thermocouple referenced to an ice bath.

The phenol is obtained from Fischer (reagent grade) and both chlorinated phenols are obtained from Aldrich (99+% purity). All chemicals are used without further purification.

Results

The experimental solubility data for phenol in supercritical carbon dioxide at 36 and 60 °C are presented in Table I. The data for *p*-chlorophenol and 2,4-dichlorophenol at 36 °C are given in Tables II and III, respectively. Each mole fraction in these tables represents the average value of at least three samples—the standard deviation in each case is generally less than 5% and is typically about 1 or 2%. The experimental data are also plotted in Figures 2 and 3. The two isotherms in Figure 2 represent distinctly different solubility behavior for phenol (normal melting temperature = 41 °C) in supercritical carbon dioxide as a function of pressure. At 36 °C, experimental solubilities are for solid phenol in supercritical carbon dioxide. The pressure dependence is similar to that for other solid–supercritical fluid systems, such as solid naphthalene–supercritical carbon dioxide at 35 °C (*4*, *5*). At 60 °C, however, phenol is a liquid and thus carbon dioxide will be mutually soluble in the condensed phase—the solubilities depicted are for phenol in the supercritical-fluid phase. The 36 °C isotherms in Figure 3 for *p*-chlorophenol (normal melting temperature = 43 °C) and 2,4-dichlorophenol (normal melting temperature = 45 °C) are characteristic of liquid–supercritical fluid systems, such as the phenol–carbon dioxide system at 60 °C, where the solubility continues to increase at elevated pressures. This behavior is consistent with the experimental data of Francis (*3*) who observed significant freezing point depressions and two mutually soluble liquid phases for *p*-chlorophenol and 2,4-dichlorophenol

Table III. Experimental Solubilities for 2,4-Dichlorophenol in Supercritical Carbon Dioxide at 36 °C

pressure, atm	phenol mole fraction	pressure, atm	phenol mole fraction
79.27	0.020 84	148.11	0.061 72
85.10	0.033 84	160.01	0.069 74
111.12	0.046 52	168.80	0.085 97
124.01	0.045 93	203.55	0.108 1

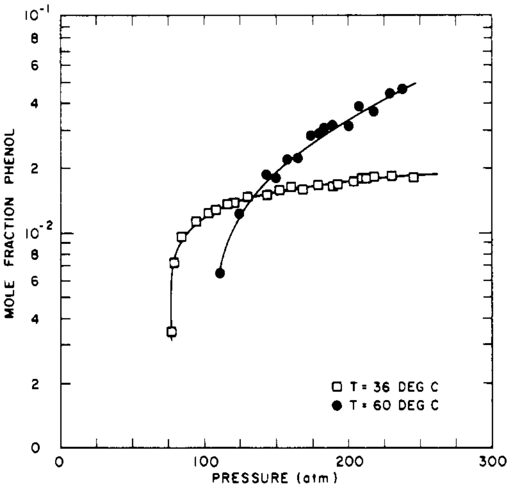

Figure 2. Experimental solubilities for phenol in supercritical carbon dioxide at 36 and 60 °C.

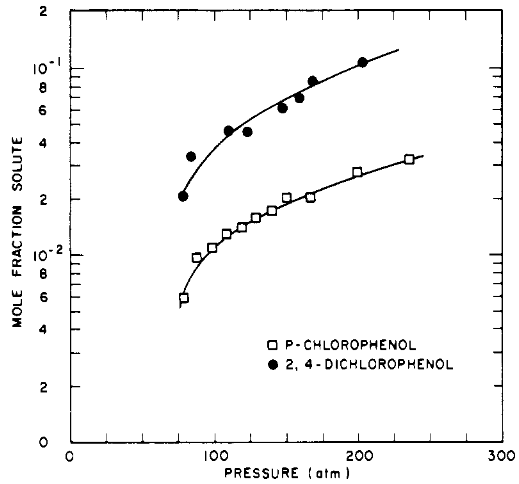

Figure 3. Experimental solubilities for *p*-chlorophenol and 2,4-dichlorophenol in supercritical carbon dioxide at 36 °C.

in the presence of liquid carbon dioxide at 25 °C. The experimental data in Figure 3 also suggest that solubilities in supercritical carbon dioxide increase as the number of chlorine groups on the solute increases. This is in agreement with the experimental results of Francis and is probably a consequence of the decreased hydrogen bonding in the condensed phase with the addition of chlorine groups.

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Thermodynamic and Physical Properties of Binary Mixtures Involving Sulfolane. Excess Volumes and Dielectric Constants of Benzonitrile–Sulfolane and Acetonitrile–Sulfolane Systems

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Excess volumes and dielectric constants were measured for sulfolane + acetonitrile and sulfolane + benzonitrile mixtures over the entire composition range, $0 \leq x \leq 1$, at several temperatures, ranging between 283.13 and 333.16 K. The observed low deviations from ideality are indicative of only moderate interactions of all kinds; nevertheless the experimental data supply evidence for the supposition that interactions between unlike molecules predominate in acetonitrile–sulfolane mixtures, whereas these interactions are relatively weak if compared with the average of the energies of interaction between benzonitrile pairs of molecules, in benzonitrile–sulfolane mixtures.

Introduction

These measurements were carried out as a part of a long term study (*1*) of the thermodynamic and physical properties of binary mixtures involving sulfolane. The aim of the research was to study the nature and the entity of molecular interactions in these systems and, for this particular work, to provide further experimental data for a comparison of the behavior of the -CN group in aromatic and aliphatic molecules.

In spite of their fairly high dipole moments, ranging between 3.4 and 4.8 D, both nitrile and sulfolane are not good proton acceptors (*2*) even if the negative ends of their dipoles are at the exterior of the molecules; on the other hand, they cannot act as proton donors (*3*) (their donicity numbers range between 11.9 (C_6H_5CN) and 14.8 (CH_3CN) (*4*)). Furthermore the sulfolane, owing to the steric hindrance of its globular molecule, does not easily interact with any kind of ions or molecules.

Therefore the presence of only moderate interactions of all kind is expected in the systems benzonitrile-sulfolane and acetonitrile–sulfolane. A previous study on the nitrobenzene–sulfolane system (nitrobenzene and benzonitrile molecules possess similar shape, quite equal volumes, and dipole moments (*1*)) was consistent with this supposition; the observed very low deviations from ideality were interpreted in terms of moderate interactions between nitrobenzene pairs of molecules, competitive in strength with the interactions between unlike molecules. In the case of acetonitrile (μ = 3.5 D) a reduced self-association is expected because of the lacking of mesomeric forms, which enhance the polarity of molecules; on the contrary they are present in benzonitrile as well as in nitrobenzene.

Therefore the study of acetonitrile–sulfolane and benzonitrile–sulfolane systems should provide a sharper differentiation of the effects, arising from interactions between like and unlike molecules, on excess properties.

Experimental Section

Materials. Sulfolane, kindly supplied by Shell Italia, was purified carefully and dried (*5*); the melting point of the final product was 301.61 K, in close agreement with the most reliable literature data (*6*). Fluka high-purity benzonitrile was fractionally distilled three times through a 60-cm column in accordance with the recommendations of Brown and Ives (*7*) for dielectric constant measurements; bp 464 K. Fluka high-purity acetonitrile was purified in the way reported in ref 8. The specific conductance of the purified sample was less than $2 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$. Solutions were made by weight (reduced to mass) in a drybox and then stored in dark containers and protected from moisture as far as possible. For the sake of uniformity with our previous works (*1*), the sulfolane is identified as component 2 and the other substance as component 1, and compositions are stated as mole fractions, x_2, of sulfolane in the case of volumes and as volume fractions, ϕ_2, in the case of dielectric constants.

Apparatus and Procedure. Measurements of density and dielectric constant were made in the temperature range 283.16–333.16 K and over the entire composition range.

Densities of solutions were measured with an Anton Paar DMA 60 digital density meter thermostated by a Lauda ultrathermostat, which controlled the temperature to within 0.005 K. The density was determined by measuring the period of oscillation of a vibrating U-shaped tube filled with liquid samples. A calibration was made with standard pure liquids for each temperature. The maximum error in density was estimated to be 3×10^{-5} g cm^{-3}.

Dielectric constants were measured, at 2 MHz, with the heterodyne beat method, using a DM 01 dipolmeter (Wissen-

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