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Solubilities of 4-Phenyltoluene, Phenylboric Acid, Biphenyl, and Iodobenzene in Carbon Dioxide from Measurements of the Relative Permittivity

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Solubility data were obtained for the first time for phenylboric acid, iodobenzene, and biphenyl in carbon dioxide at (353 and 383) K and between pressures of (100 to 300) bar. Data were obtained using a method that used the relative permittivity of the binary mixture. The technique was verified by comparison of solubility data for 4-phenyltoluene that had been determined previously by ourselves using a cloud point technique. The relative permittivity for CO_2 was also determined at (353 and 383) K between pressures of (100 to 300) bar.

Introduction

The synthesis of organic molecules in the absence of volatile organic solvents remains an important industrial and environmental goal. A promising alternative to such solvents is the use of supercritical carbon dioxide ($scCO_2$) as a solvent medium.[1−3] The Suzuki reaction is a well-established versatile tool in synthetic organic chemistry and has important applications in the pharmaceutical industry.[4] The reactants, an aryl halide and a boronic acid, cross couple in the presence of a palladium catalyst to form a new carbon−carbon bond. In previous work, we have carried out Suzuki reactions in $scCO_2$[5] and have detailed the component solubilities for a typical Suzuki reaction between *p*-tolylboronic acid + bromobenzene to form 4-phenyltoluene at (353 and 383) K and between pressures of (98 to 317) bar.[6] In this paper, we report the solubilities of the components for a second Suzuki reaction that couples phenylboric acid with iodobenzene to form biphenyl to enable further optimization to be undertaken. Vapor-phase data were obtained for phenylboric acid, iodobenzene, and biphenyl in carbon dioxide at (353 and 383) K from (100 to 300) bar. Solubility data have been previously reported for CO_2 + biphenyl by Zhao et al.,[7] McHugh and Paulaitis,[8] and Chung and Shing;[9] however, these data were up to 105 bar and 333 K, 484 bar and 331 K, and 271 bar and 328 K, respectively. In this work, data were obtained from the relative permittivity of the binary mixture at a particular pressure and temperature. This approach was first described by Hourri et al.,[10] who measured the solubility of naphthalene in $scCO_2$, and has since been used by several authors.[11,12] The reliability of the experimental procedure and results was ascertained by comparing the data obtained for 4-phenyltoluene using the relative permittivity approach to that obtained from a cloud point technique.[6] The relative permittivity for CO_2 was also determined at (353 and 383) K between pressures of (100 to 300) bar. Moriyoshi[13] has previously reported data at 353 K, and these are compared to the data obtained in this work. The structures of phenylboric acid, iodobenzene, biphenyl, and 4-phenyltoluene are shown in Figure 1.

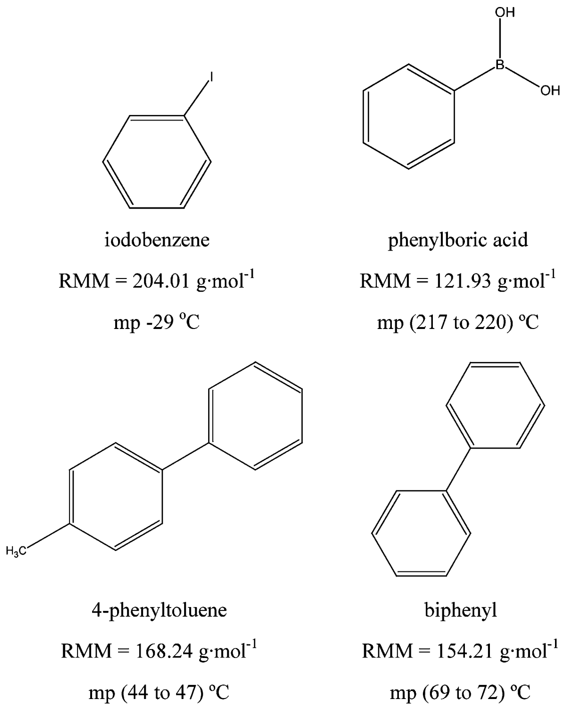

Figure 1. Structures of compounds.

Experimental Section

Materials. Phenylboric acid (97%) [98-80-6], iodobenzene (98%) [591-50-4], biphenyl (99.5%) [92-52-4], and 4-phenyltoluene (98%) [644-08-06] were supplied by Sigma-Aldrich U.K., and all were used without further purification. Liquid carbon dioxide was obtained from BOC, CP grade, and had a given purity of 99.995%.

Equipment. High-pressure vapor-phase solubility data for 4-phenyltoluene, phenylboric acid, iodobenzene, and

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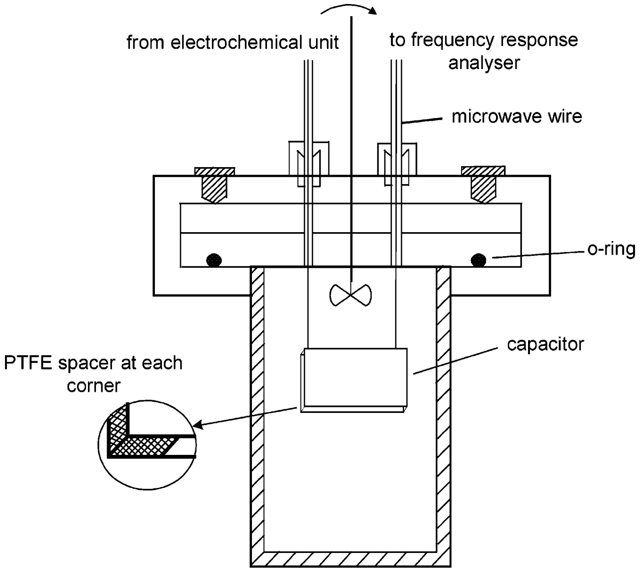

Figure 2. Details of the capacitance bridge.

biphenyl were measured using a capacitance method that enables the relative permittivity to be derived. Details of the capacitance bridge are shown in Figure 2. The high-pressure equilibrium cell used for the relative permittivity measurements (Parr Instruments, Moline, IL) had an internal volume of 100 cm^3 and was fitted with two sets of in-line sapphire windows. The cell was typically charged with (50 to 80) mg of phenylboric acid and up to 15 g of biphenyl and 4-phenyltoluene. For the liquid, up to 32 g of iodobenzene was used. The masses charged were in excess and ensured saturation of the vapor phase at the conditions studied. Liquid carbon dioxide was compressed by the use of a liquid piston pump (Haskel, model MCP-71, Haskel Europe, Sunderland, U.K.) and directed to the equilibrium cell. The temperature in the cell was increased to the desired isothermal condition, and the pressure was raised until dissolution of the compound occurred. This condition was verified by directing a color camera at the view cell and observing the image on a monitor. Dissolution was aided by the use of an impeller (Rushton turbine) coupled to an external magnetic drive (Parr Instruments, Moline, IL). Typically, the time required to achieve equilibrium was 2 h for the solids and 15 min for the liquid components.

The parallel plate capacitor was constructed in-house of stainless steel held apart by PTFE spacers at the corners to a distance of 0.75 mm and had an area of 6.27 cm^2. Each spacer was held in position by a PTFE nut and bolt (RS Components, U.K.) that passed through a hole in each of the plates and avoided the flexing of the spacer at the temperature conditions (mp of PTFE = 327 °C). One plate acted as the working electrode, and the other, as the counter. Two additional reference electrodes were employed. The capacitor was placed in the vapor phase of the mixture, and its location was verified by the camera. The pressure was recorded using a transducer (Druck PTX 1400; Druck Ltd, Leicester, U.K.) with dedicated display to within 0.1 bar. The temperature was controlled to within ±0.1 °C using a Watlow 93 temperature controller coupled to a J-type thermocouple (Watlow Ltd, Nottingham, U.K.). For safety reasons, upon depressurization any heavy component present in the expanded gas stream was trapped downstream in a glass collector maintained at approximately −80 °C in a dry ice/acetone slurry.

Relative Permittivity Procedure. Upon dissolution and equilibration of the compound in the vapor phase, the static relative permittivity ϵ of a binary mixture was determined from the capacitance C given by

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

The capacitance of the evacuated cell under vacuum C_0 was measured at the experimental temperatures prior to the experiments. Cell capacitances were determined at 65 kHz with an amplitude of 150 mV using a frequency response analyzer (Solartron 1250, Solartron Analytical, Farnborough, U.K.) coupled to an electrochemical interface (Solartron 1286). The impedance complex plane plots were gathered using ZPlot and analyzed by ZView software (Solartron). Measurements were made along each isotherm at pressure intervals between (100 to 300) bar at (353 and 383) K, and the mean values of ϵ were determined from three measurements. The variance of ϵ did not exceed 0.01%, and in the best case, measurements of the variance were less than 0.002%. A 0.01% variance in ϵ was obtained for the biphenyl data, and resulted in a maximum uncertainty of 6.2% in the calculated solubility value at the lowest pressure (100 bar); the error is a decreasing function of pressure.

Results and Discussion

Calculation of Solubility from the Relative Permittivity. The solubility of a component in supercritical fluids by measurement of the relative permittivity has been detailed by Hourri et al.[10] and more recently by Abbott et al.[11] They have shown that using the Clausius−Mosotti function

$$\frac{\mathrm{CM}}{\rho} = \frac{\epsilon - 1}{\epsilon + 2}\frac{1}{\rho} = A_\epsilon + \beta_\epsilon \rho + C_\epsilon \rho^2 + \ldots.. \tag{2}$$

where CM = $(\epsilon - 1)/(\epsilon + 2)$ and A_ϵ, β_ϵ, and C_ϵ are the first, second, and third dielectric virial coefficients, respectively, they could obtain

$$\mathrm{CM}' - \mathrm{CM}'' = A'_\epsilon \rho' - A''_\epsilon \rho'' + \beta \tag{3}$$

The primed quantities refer to the saturated supercritical solution density (i.e., ρ'), and the double primed, to the supercritical CO$_2$ solvent density (i.e., ρ''). For polar solutes, the first dielectric virial coefficient A_ϵ can be written as

$$A^{\mathrm{s}}_\epsilon = \frac{4}{3}\pi N_{\mathrm{A}}\left[\alpha + \frac{\mu^2}{3kT}\right] \tag{4}$$

where μ is the permanent dipole moment, α is the polarizability of the molecule, N_{A} is Avogadro's number, and k is the Boltzmann constant.[11] It is worthwhile to point out that to obtain A^{s}_ϵ in dm^3/mol, 4 needs to be divided by the permittivity in a vacuum, $4\pi\epsilon_0$. If the permanent dipole μ is 0, then 4 returns to that of A^{s}_ϵ for a nonpolar solute. Knowing that the solubility of the solute in the binary mixture $\rho^{\mathrm{s}} = \rho' - \rho''$, the solubility can then be determined using the following relation

$$\rho^{\mathrm{s}} = \frac{\mathrm{CM}' - \mathrm{CM}''}{A^{\mathrm{s}}_\epsilon} - \frac{\beta}{A^{\mathrm{s}}_\epsilon} \tag{5}$$

where $(\beta/A^{\mathrm{s}}_\epsilon)$ is the correction to the solubility arising from the difference (CM′ − CM″) and is relative to the higher-order terms in ρ' and ρ''. The quantity β was estimated by evaluating the expression (CM − $A_\epsilon \rho$) for both the solvent and supercritical solution. For pure CO$_2$, using density values from NIST,[14] the measured relative permittivity

Table 1. Data for Use in Equation 5

compound	μ/D	$10^{-26}\alpha$/dm^3
4-phenyltoluene	0.26	2.21
phenylboric acid	1.74	1.32
biphenyl	0.00	2.02
iodobenzene	1.27	1.55

Table 2. Relative Permittivity of CO_2

nominal P/bar	ϵ_r, t = 80 °C	ϵ_r, t = 110 °C
100	1.1125	1.0783
150	1.2327	1.1717
200	1.3318	1.2519
250	1.4140	1.3166
300	1.4632	1.3632

values, and $A_\epsilon'' = 7.35$ dm^3/mol,[15] we found that the deviation in the value of $(CM'' - A_\epsilon''\rho'')$ over the range of pressures was no greater than 7.25% CM″ and is similar in value to the work of Hourri et al.,[10] who recorded a value of 4.25%. This maximum deviation was obtained at the lower end of the pressure range. For the saturated solution, the average deviation of the second- and higher-order contributions $(CM' - A_\epsilon'\rho')$ to the supercritical solution quantity CM′ were approximated as being equal to that for pure CO_2, relative at the same given pressures and temperatures. A detailed evaluation of β/A_ϵ^s is given by Hourri et al.[10]

The permanent dipole (μ) and polarizability (α) values for each component for use in 4 are given in Table 1. The permanent dipole values were obtained from McCellan,[16] and the polarizability values were determined using ChemSketch software. The uncertainties of the dipole moments are not available; however, if a manner similar to that of Abbot et al.[11] is adopted where a theoretical maximum uncertainty of 5% is assumed, then the solubility is found to vary by a maximum of ±5.8%. In addition, the calculated solubility is dependent on the CO_2 density and hence fluctuations in the temperature. Temperature control of ±0.1 °C can lead to an uncertainty in the calculated solubility values of up to 0.0007%.

Relative Permittivity of CO_2. The relative permittivities (ϵ_r) of CO_2 were obtained at (353 and 383) K and are shown in Table 2. The data obtained at 353 K are compared in Figure 3 to that of Moriyoshi[13] and provide verification of the experimental technique. The largest relative error in the relative permittivity for coinciding pressures was no greater than 1.3%.

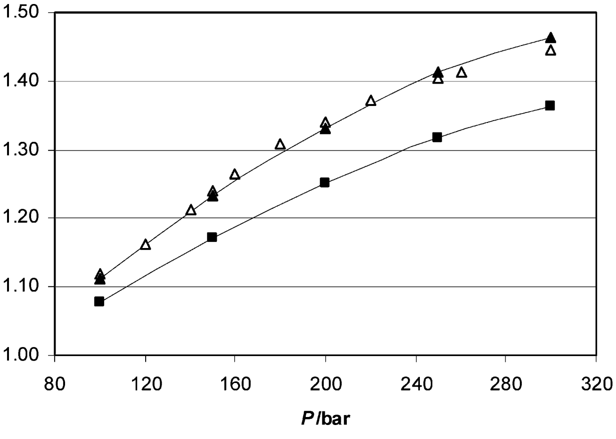

Figure 3. Relative permittivity of CO_2: ▲, this work, 80 °C; ■, this work, 110 °C; △, Moriyoshi et al.[13]

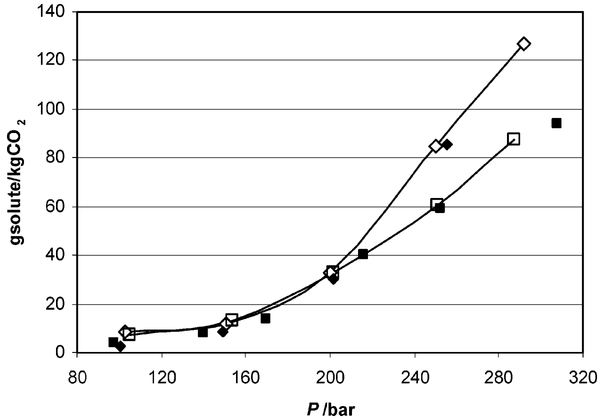

Figure 4. Comparison of solubility data measured using the relative permittivity and cloud point techniques: ◇, relative permittivity, this work, 80 °C; □, relative permittivity, this work, 110 °C; ◆, Leeke et al.,[6] cloud point, 80 °C; ■, Leeke et al.,[6] cloud point, 110 °C.

Table 3. Experimental Data for CO_2 + 4-Phenyltoluene

relative permittivity method				cloud point method[6]	
P/bar	ϵ_r	$y2$	solubility g/kg CO_2	P/bar	solubility g/kg CO_2
			t = 80 °C		
102.9	1.1147	0.0022	8.4	100.8	2.53
151.0	1.2390	0.0032	12.1	148.9	8.28
200.1	1.3570	0.0086	33.1	201.6	30.23
250.1	1.4933	0.0216	84.5	255.3	85.22
292.2	1.5964	0.0320	126.5		
			t = 110 °C		
105.1	1.0798	0.0019	7.4	97.3	4.17
153.6	1.1764	0.0035	13.4	140.2	8.14
201.3	1.2691	0.0085	32.8	169.5	14.00
250.8	1.3577	0.0156	60.4	215.8	40.01
287.4	1.4314	0.0223	87.3	253.3	59.00
				307.6	94.14

Comparison of Solubility Data. Vapor-phase solubility data for the CO_2 + 4-phenyltoluene system were previously measured using a cloud point apparatus at (353 and 383) K[6] and are compared in Figure 4 and Table 3 with data from the relative permittivity technique. The solubility is expressed in g of solute/kg of CO_2 and in mole fraction of solute ($y2$). In the Figure, as in all of the Figures, the lines are used to show trends in the data. The experimental values are in good agreement with data from our earlier work at high pressures. At low pressures, comparison of the data is less than satisfactory. The errors between the two sets of data are compared where the pressures coincide. If a comparison is made with the data from the cloud point at 102.9 bar, 80 °C with those from the relative permittivity method at 100.8 bar, 80 °C, then a relative error of over 230% exists. At 200.1 bar, 80 °C (cloud point) and 201.6, 80 °C (relative permittivity), this error has decreased to 9.5%, and at 250.8 bar, 110 °C (cloud point) and 253.3 bar, 110 °C (relative permittivity), the error has fallen to 2.4%. At the lower pressures, the solubility is small, and errors are enhanced. This error decreases with pressure. There is a difference of 2.1 bar between the pressures being compared at 100 bar, 80 °C, but this cannot be the sole cause of the large error. Obtaining data at high pressure is always erroneous, and both the cloud point and relative permittivity have their own sources of error. The sources of errors and uncertainties associated with the relative permittivity method have been discussed above. Moreover, the solubility data shown throughout the paper are expressed to one decimal place for values over 1 g of solute/kg of CO_2 and to two decimal places for data under 1 g of solute/kg of CO_2 to warn the reader of possible errors. The largest source of error with cloud point method is the

Table 4. Experimental Data for CO_2 + Phenylboric Acid

P/bar	ϵ_r	solubility g/kg CO_2	*y*2
		t = 80 °C	
100.2	1.1127	0.29	0.00010
149.5	1.2330	0.29	0.00010
199.8	1.3323	0.29	0.00010
253.7	1.4146	0.30	0.00011
297.2	1.4639	0.31	0.00011
		t = 110 °C	
99.3	1.0785	0.57	0.00021
146.3	1.1720	0.57	0.00020
202.0	1.2525	0.57	0.00021
251.4	1.3174	0.57	0.00021
300.4	1.3641	0.60	0.00022

Table 5. Experimental Data for CO_2 + Iodobenzene

P/bar	ϵ_r	solubility g/kg CO_2	*y*2
		t = 80 °C	
101.3	1.1187	25.4	0.0055
150.6	1.2883	109.1	0.0230
176.8	1.4023	177.7	0.0369
200.6	1.5313	256.2	0.0524
220.7	1.6998	365.8	0.0731
		t = 110 °C	
102.3	1.0861	42.0	0.0090
150.8	1.2052	100.9	0.0213
201.1	1.3444	178.9	0.0374
220.3	1.4287	251.6	0.0515
248.5	1.5919	396.8	0.0788

Table 6. Experimental Data for CO_2 + Biphenyl

P/bar	ϵ_r	solubility g/kg CO_2	*y*2
		t = 80 °C	
102.2	1.1143	4.2	0.0012
150.7	1.2434	12.3	0.0035
200.4	1.3856	41.5	0.0117
251.1	1.5569	88.5	0.0246
293.5	1.7058	132.4	0.0364
		t = 110 °C	
101.8	1.0800	5.6	0.0016
151.0	1.1792	13.6	0.0039
200.6	1.2789	32.2	0.0091
250.8	1.3841	61.3	0.0172
295.4	1.4870	95.4	0.0265

subjective visualization by the operator of the cloud at the cloud point. At pressures where a component has low solubility, this ability deteriorates because the cloud does not visually form completely because of the small mass of the component at the onset of precipitation from solution. These rationales would help to explain the large discrepancy between the two sets of data observed at lower pressures.

Binary Mixtures. Vapor-phase solubility data were determined at (353 and 383) K for the three binary systems containing carbon dioxide + phenylboric acid, carbon dioxide + iodobenzene, and carbon dioxide + biphenyl. The data are shown in Tables 4 to 6 and Figures 5 to 7, respectively. Again, in all Figures the lines are used to show trends in the data. In the case of the iodobenzene system, the data obtained at the highest recorded pressure should be treated with a degree of caution. The position of the capacitor was such that it was close to the expanded liquid phase within the high-pressure cell. The solubilities of 4-phenyltoluene and iodobenzene show crossover pressures at 195 bar and 135 bar, respectively. These crossover pressures compare well to the crossover pressure for 4-phenyltoluene established in the cloud point technique (187.1 bar) and to the homologous aryl halide, bromobenzene (138.0 bar). Biphenyl also displays a crossover pressure at 156.3 bar. A deeper discussion of the crossover pressure is given by Foster et al.[17] and by ourselves in Leeke et al.[6]

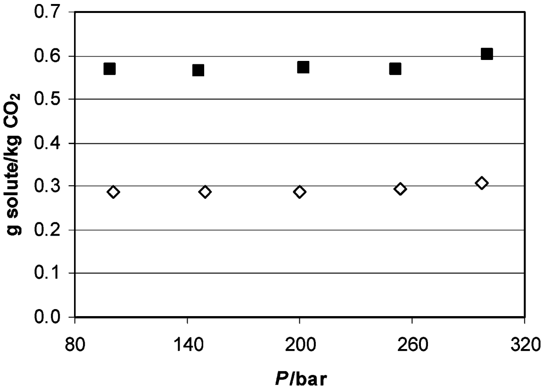

Figure 5. Solubility of phenylboric acid in CO_2: ◇, 80 °C; ■, 110 °C.

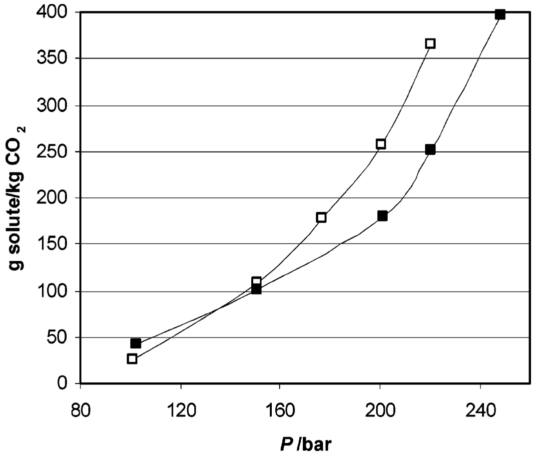

Figure 6. Solubility of iodobenzene in CO_2: □, 80 °C; ■, 110 °C.

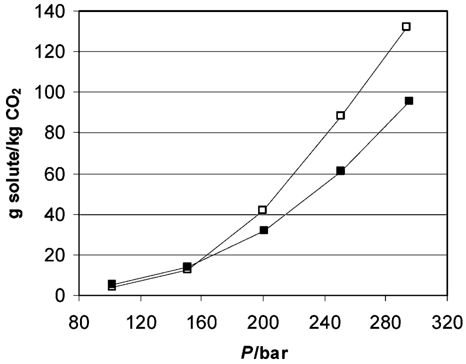

Figure 7. Solubility of biphenyl in CO_2: □, 80 °C; ■, 110 °C.

Conclusions

The solubilities of the organic compounds studied in this work can be determined from the static relative permittivity of the binary mixture in supercritical carbon dioxide. The technique is simple, allows data to be obtained in situ, and gives results that are comparable to those obtained from conventional solubility techniques.

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