Solubility of Solid Aromatic Isomers in Carbon Dioxide

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The solubility of a family of disubstituted aromatic isomers, the hydroxybenzoic acids, was measured in supercritical carbon dioxide at 373 K over a pressure range of 200–400 bar; the solubility of another family, the dihydroxybenzenes, was measured at 328 K and at one pressure, 310 bar. The solubility within a family was found to be a function of the melting point of the isomer, the lower the melting point, the higher the solubility. The results suggest that supercritical solvents can be used to separate certain ortho and para isomers.

Introduction

During the past 10 years the use of supercritical fluids as solvents for extracting/separating chemicals, foods, and beverage products has been reported in the literature. Applications such as decaffeination of coffee (*1*), extraction of hops (*2*), spices (*3*), and seed oils (*4*, *5*), and separation of alcohol–water (*6–8*) have been described; additionally, the theoretical aspects of supercritical fluid solubility and phase phenomena have been presented in many papers (*9–11*) and comprehensive reviews (*12–14*). The properties of supercritical fluids, and especially of supercritical carbon dioxide, which are attractive for processing foods and beverage products can also be applied to other types of separations, and since the start of the 1980s processes which employ the pressure-dependent dissolving power characteristics for the fractionation of low vapor pressure oils (*14*), extraction of solvents and monomers from polymers (*14*, *15*), and redistribution of particle size of dyes and chemical intermediates (*14*) are being developed. Because of increasing performance demands being placed upon many polymers and fine chemicals supercritical fluid extraction with its ability to purify refractory or labile compounds is receiving increasing attention as a separation process for these materials.

A number of aromatic isomers serve as raw materials for a wide variety of chemical, pharmaceutical, and polymer products; in some cases the individual isomers are difficult to obtain in pure form, and frequently the separation involves an ortho–para pair. In order to evaluate the potential of employing supercritical solvents in some purification processes, the solubilities of two families of isomers, *o*-, and *m*-, and *p*-hydroxybenzoic acid and *o*-, *m*-, and *p*-dihydroxybenzene, were measured in carbon dioxide. (The *o*-hydroxybenzoic acid isomer is normally called salicylic acid and the *o*-, *m*-, and *p*-dihydroxybenzene isomers are normally called respectively catechol, resorcinol, and hydroquinone, but postional notation will be employed in discussing the results.)

Experimental Section

Measurements of the solubilities of *o*-, *m*-, and *p*-hydroxybenzoic acid were carried out in supercritical carbon dioxide at 373 K over a pressure range of 207–414 bar in a flow system shown schematically in Figure 1. Table I lists the melting points and other pertinent data of the isomers tested.

For each solubility test about 30 g of oven-dried, powdered solid was charged alternately between layers of glass wool to an extraction vessel, a 1.8 cm diameter × 30 cm long stainless steel tube (Autoclave Engineers, Inc.), and connected to the system shown in Figure 1; the glass wool served to keep the powder from compacting during passage of gas through the extractor. Carbon dioxide (Airco, Inc., Grade 2.8) was supplied at about 87 bar pressure and 313 K to the suction side of a double-end diaphragm compressor (Superpressure, Inc.) and was compressed to the measurement pressure. The pressure was controlled by a back-pressure regulator (Circle Seal, BPR) which diverted the bulk of the compressed gas from the surge tank back to the suction side of the compressor resulting in an almost pulse-free flow of gas to the extractor. The high-pressure gas passing downstream of the compressor was heated in a tube preheater to about 373 K and was passed through the extraction vessel which was maintained at 373 ± 2 K by a temperature indicator/controller which measured the temperature via an iron–constantan thermocouple (Superpressure, Inc.) positioned in the bed of powder and which regulated power to a heater (Glascol tapes) on the extractor.

Table I. Physical Properties of *o*-, *m*- and *p*-Hydroxybenzoic Acids

isomer	mp, °C	supplier, purity
ortho	158–160	Aldrich, 99+%
meta	201–203	Aldrich, 99%
para	214–215	Aldrich, 99+%

The solution (consisting of carbon dioxide and dissolved solid) leaving the extraction vessel was passed through a heated, flow-regulating, pressure let-down valve and was expanded to ambient pressure. The solid which was dissolved by the gas passing though the extraction vessel precipitated during the pressure-reduction step and was separated from the gas in the U-tube collector (Kimax, 200 mm) whose exit junction was fitted with a glass wool filter to prevent fine-particle solids from passing through the tube; a second U-tube with a more tightly packed glass wool filter was positioned downstream of the first collector and served to trap any fine particles which might have passed through the first filter; in all the solubility tests discussed subsequently at least 99% of the total solid dissolved was collected in the first U-tube.

The ambient gas leaving the collection system passed through a rotameter, (Fischer-Porter, Inc., Series 10A 35) for flow rate measurement and through a dry test meter (Singer, Inc., DTM-200) for flow volume integration. The flow rate of the carbon dioxide through the extractor was maintained at 3 SLPM (standard liters per minute); that flow rate was found satisfactory to ensure that solubility equilibrium was achieved in the gas at the exit of the extractor. (Flow rate effects on the solubility measurements were tested very briefly, and it was found that flow rates as high as 20 SLPM could be used without compacting the fine particle solid and still achieve an equilibrium concentration; however, a 3 SLPM flow rate was an easy one to maintain constant.) Gravimetric determinations of the amount of solid collected coupled with the integrated volume of gas passing through the system during a solubility test allowed concentration levels of the isomer in the gas to be calculated.

Results and Discussion

The solubility values (mole fraction) of the hydroxybenzoic acid isomers in carbon dioxide are listed in Table II, and the values are plotted in Figure 2. Each value is the average of four measurements; for the meta and para isomers the maximum spread in the values was 6%, and for the ortho isomer 11%.

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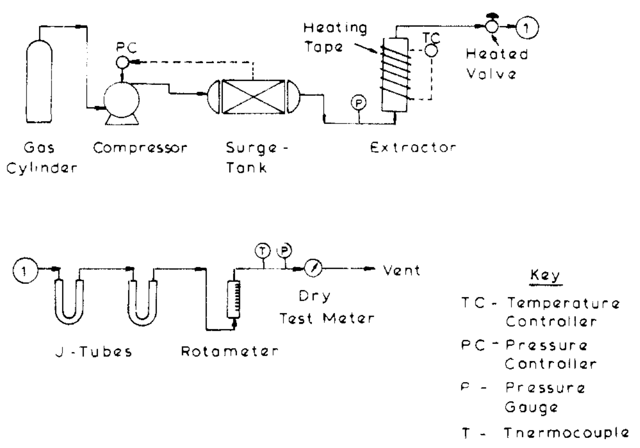

Figure 1. Schematic diagram of experimental setup for measuring solubilities in supercritical carbon dioxide.

Table II. Solubility, y (Mole Fraction), of o-, m-, and p-Hydroxybenzoic Acids in Supercritical Carbon Dioxide at 373 K

press., bar	$10^3 y$(ortho)	y(meta)	$10^5 y$(para)
207	2.07	2.71×10^{-5}	1.33
276	2.99	5.35×10^{-5}	3.57
345	3.53	7.54×10^{-5}	5.77
414	6.99	1.12×10^{-4}	7.49

As can be determined from an examination of the values and the curves and as was anticipated from information available about the behavior of these materials in liquid organic solvents, the lowest melting isomer, *o*-hydroxybenzoic acid, exhibits the highest solubility in carbon dioxide; its solubility is almost 2 orders of magnitude higher than the solubilities of the meta and para isomers. The solubilities of the meta and para isomers are reasonably close to each other as might be a priori inferred from their close melting points.

Another group of workers has carried out measurements of the solubilities of two of the isomers, *o*- and *p*-hydroxybenzoic acid, in carbon dioxide at a temperature of 313 K over a pressure range of about 50–200 bar (*16*). Although the solubility levels for the isomers are reported to be much less (because of the lower pressure level tested) than the values reported in this work, a similar 2 orders of magnitude difference between the solubility levels of the *o*- and *p*-hydroxybenzoic acids was observed; for example, at 150 bar, the solubility of the ortho isomer was found to be 0.0003 (mole fraction), and that of the para isomer 0.000 002.

The reasons for the inverse relationship between the solubility in liquid organic solvents of aromatic isomers of an isomer family and their melting points have been discussed elsewhere (*17*). Briefly, among disubstituted benzenes the para isomer melts considerably higher than the other two because of its symmetry and thus its more facile accommodation into a crystal lattice, and since dissolution, like melting, involves overcoming intermolecular forces of a crystal, a lower solubility of the para isomer in a given solvent would be expected. For the particular case of the *o*-hydroxybenzoic acid internal (intramolecular) hydrogen bonding may occur and may be additionally responsible for the lower melting point (*18*) and, thus, the higher solubility of the isomer in carbon dioxide. It is of interest to point out, then, that supercritical-carbon dioxide acts in a manner similar to organic liquid solvents in its dissolving characteristics for the ortho and para isomers. It exhibits, however, the additional feature of a pressure-dependent dissolving power at constant temperature as Figure 1 shows.

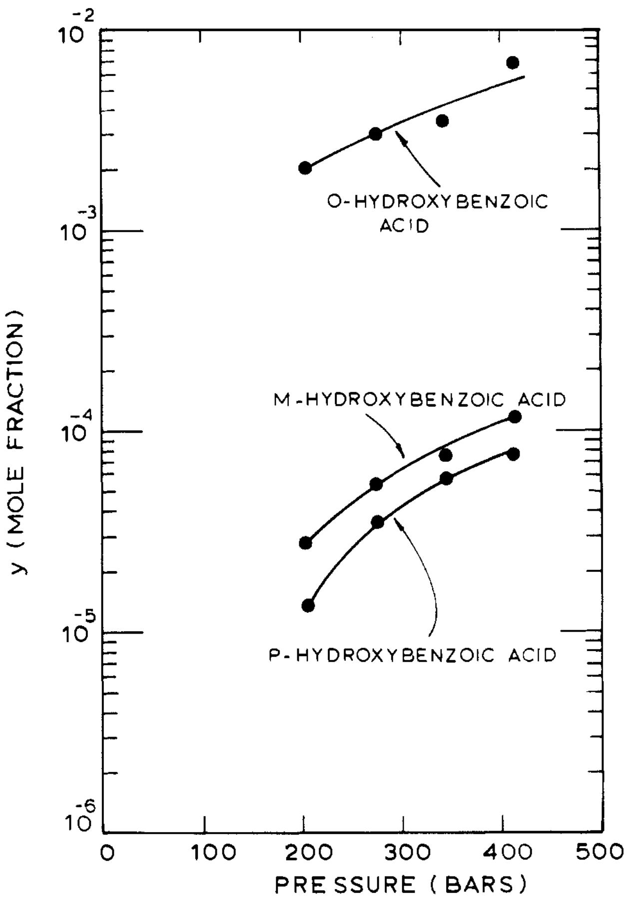

Figure 2. Solubility of *o*-, *m*-, and *p*-hydroxybenzoic acids in supercritical carbon dioxide.

Table III. Solubility, y (Mole Fraction), of the Dihydroxybenzenes in Supercritical Carbon Dioxide at 328 K and 310 bar

isomer	y	mp, °C	supplier, purity
ortho	1.8×10^{-3}	104–106	Aldrich, 99+%
meta	4.85×10^{-4}	109–110	Aldrich, 98
para	2.05×10^{-5}	172–173	Aldrich, 99+

To evaluate further the solubility behavior of solid aromatic isomers another isomer family, the dihydroxybenzenes, catechol, resorcinol, hydroquinone, was tested at 328 K and at a single pressure level, 310 bar. The measured solubility values for the isomers are given in Table III along with the respective melting points and purities; each solubility value is the average of three determinations with an 8% maximum spread. As the data in the table show, the ortho isomer (with the lowest melting point) exhibits the highest solubility in carbon dioxide with the solubilities of the meta and para isomers decreasing with increasing melting point. As found for the hydroxybenzoic acids an almost 2 orders of magnitude difference in solubility between the ortho and para dihydroxybenzene isomers was measured. (Incidentally, the 328 K temperature level, and not 373 K, which was the test temperature for the hydroxybenzoic acids, was chosen for the brief study of dihydroxybenzene solubility in order to stay well below the normal melting point of the lowest melting (ortho) isomer. Additionally, it was felt that the 328 K level would also be well below any melting point depression temperature, thus ensuring that solid isomer solubilities were being measured; the melting point depression which can result from an interaction of high-pressure carbon dioxide with a solid has been discussed by other authors (*19*). In the tests carried out with the *o*-dihydroxybenzene and with all the other isomers no melting of the solid was observed. In another unrelated but interesting aside, the resorcinol (*m*-dihydroxybenzene), whose purity was stated as 98%, was obtained as a pale brown powder; the extracted solid precipitated in the collector tube was a white powder of, presumably, higher purity, such color

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change, and purity increase, often being seen in supercritical fluid extraction testing.)

Although the amount of solubility data on the dihydroxybenzenes is by no means as extensive as for the hydroxybenzoic acids, the solubility behavior given in Table III does lend credence to the statement that the solubility in supercritical carbon dioxide of isomers in a family is related to the melting point, the solubility decreasing with increasing melting point.

The hydroxybenzoic acids are frequently desired in relatively pure ortho and para forms for subsequent conversion to other compounds, and they most commonly must be separated from each other in a mixture not usually containing the meta isomer. The two isomers can be separated by other methods, by crystallization, for example, promoted by lowering the pH of a solution (of high pH) containing both compounds (in ionic form), advantage being taken of the fact that the p*K* for the para acid is higher than that of the ortho acid, resulting in a preferential precipitation of the para acid form. A relatively pure para isomer fraction can usually be prepared by such a process, but the remaining ortho isomer is usually contaminated with some previously unprecipitated para isomer as the pH is lowered further (*17*). Other studies which are to be carried out will test the ability of supercritical carbon dioxide to separate mixtures of *o*- and *p*-hydroxybenzoic acids.

Conclusions

With two families of disubstituted aromatic isomers, it has been demonstrated that solubility in supercritical carbon dioxide is related to the melting point; at a constant pressure and temperature of the carbon dioxide the solubility decreases with increasing melting point. The large difference in solubility between the ortho and para isomers suggests that supercritical fluid extraction might prove to be an effective way to separate a mixture of these isomers.

Registry No. CO_2, 124-38-9; *o*-hydroxybenzoic acid, 69-72-7; *m*-hydroxybenzoic acid, 99-06-9; *p*-hydroxybenzoic acid, 99-96-7; *o*-dihydroxybenzene, 120-80-9; *m*-dihydroxybenzene, 108-46-3; *p*-dihydroxybenzene, 123-31-9.

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Vapor–Liquid Equilibria for the Binary Systems Formed by Hexamethyldisiloxane, 1-Pentanol, and 2-Methyl-4-butanol

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The total vapor pressure was determined at 293.15 K, and liquid–vapor equilibria have been studied under isobaric conditions for binary systems hexamethyldisiloxane (HMDS)–1-pentanol and HMDS–2-methyl-4-butanol. In both systems a large positive deviation from the ideal behavior was observed, as evidenced by the vapor pressure maximum on the isotherm and the boiling point minimum under isobaric conditions.

In continuation of our studies (*1-4*), liquid-vapor phase equilibria have been studied in systems containing hexamethyldisiloxane (HMDS) and two alcohols. The nature of deviations from the ideal behavior could be estimated by measuring total vapor pressures under isothermic conditions and boiling points under isobaric conditions.

Introduction

HMDS can widely be used as a nonpolar solvent, owing to its physicochemical properties. It is a nontoxic and poorly reactive solvent (*5, 6*). Therefore, HMDS can replace a variety of common solvents such as benzene or toluene. This is the reason that prompted us to study the liquid–liquid and liquid–vapor equilibria of systems formed by HMDS. The information about the equilibria is useful in the application and separation of HMDS in technological processes.

Experimental Section

Reagents. Hexamethyldisiloxane (HMDS) was commercial product. After purification it had bp 100.8–101 °C, $d^{20}{}_4$ 0.7634 g cm^{-3}, and $n^{20}{}_D$ 1.3777. 1-Pentanol had bp 137 °C, $d^{20}{}_4$ 0.8133 g cm^{-3}, and $n^{20}{}_D$ 1.4103. 2-Methyl-4-butanol boiled at 130.5–131 °C, and had $d^{20}{}_4$ 0.8120 g cm^{-3} and $n^{20}{}_D$ 1.4076.

Measurements. Total vapor pressure over the whole concentration range of the system was measured in the previously described apparatus (*1*). Before carrying out the measurements, we checked the apparatus by using two-component benzene–toluene mixtures. Measurements of the total vapor pressure were carried out at 20 ± 0.05 °C.

Isobaric experiments were carried out by using the modified Swietoslawski ebulliometer (*7, 8*). The values of the total vapor pressure and outside pressure were measured with a precision of ±0.006 kPa and the temperature was measured with a precision of ±0.05 °C. Tables I and II contain the mean values of the measurements run in triplicate. The composition of the liquid and of the condensate was determined refracto-

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