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# Cosolvent Effect of Methanol and Acetic Acid on Dibenzofuran Solubility in Supercritical Carbon Dioxide

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The experimental solubility of dibenzofuran in modified supercritical carbon dioxide is measured at (318.2, 328.2, and 338.2) K in the (9 to 21) MPa pressure range using a built-in-house static view cell apparatus. $CO_2$ is modified using methanol and acetic acid in the composition range of (3.5 to 5.5) mol %. Results are compared with those previously obtained for pure carbon dioxide, and the modifier effect is discussed. Solubility data obtained are correlated at each of the temperatures studied. The correlation equations may be used to predict the dibenzofuran solubility in methanol or acetic-acid-modified $CO_2$ within the composition and pressure intervals studied or at values close to the interval limits. Results show the feasibility of using modified supercritical $CO_2$ to extract dibenzofuran.

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## Introduction

Supercritical fluid extraction (SFE) has received increasing attention in the last decade as a technique for the treatment and remediation of solid matrixes contaminated with hazardous pollutants.[1] Carbon dioxide is the most used supercritical fluid because of its accessible critical parameters ($T_c = 304.2$ K, $P_c = 7.37$ MPa[2]), nontoxicity, low cost, and nonflammability. However, sometimes the solubility of certain compounds in $CO_2$ is low, and a small amount of an organic substance (modifier or cosolvent) is added to enhance this solubility. Either pure or modified carbon dioxide is increasingly used to separate organic pollutants from solid matrixes for analytical and cleanup purposes.[3−9] Recently, Kawashima et al.[10] studied the removal of similar compounds from fish oils using $CO_2$, and Gabarra et al.[11] studied the feasibility of using $CO_2$ and $CO_2$ modified with toluene to remove polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDBs) from fly ash in a solid-waste incineration facility. Methanol is a common cosolvent that has been proven to be effective for the extraction of pollutants from soils.[12,13] Methanol is also used for SFE of PCDDs and PCDBs from contaminated soils for analytical purposes.[14] There is always an interest in finding the optimum modifier for the extraction of these pollutants, so different substances are investigated for this purpose. Other examples are acetic acid,[13] benzene,[14] and water.[15]

The application of SFE requires the knowledge of accurate solubility information for all components in the system. For this reason, the high-pressure phase behavior of mixtures formed by carbon dioxide has been the subject of numerous investigations in the last years. Nevertheless, solubility data are still scarce for several classes of compounds.

Dibenzofuran (DB) is an aromatic compound that is solid under ambient conditions (melting point: 355 K[16]). Its structure is shown in Figure 1. It is a polar, flat molecule (dipole moment at 298.15 K is 0.88 D[17]), and because of the electrons of the oxygen, it is also a Lewis base. Critical parameters for DB were reported by Chirico et al.:[18] $T_c = 824$ K, $P_c = 3.64$ MPa, and the critical temperature is much higher than that of carbon dioxide. In a previous paper,[19] we investigated the high-pressure phase behavior of the $CO_2$ + DB system that may serve as a model for systems formed by carbon dioxide and the chlorinated DBs. Solubilities of DB in liquid and supercritical $CO_2$ at (301.3, 309.0, 319.2, 328.7, and 338.2) K as well as the solid−liquid−vapor (SLV) equilibrium line were determined using a static view cell apparatus.

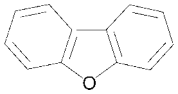

**Figure 1.** Structure of dibenzofuran.

In this article, the enhancement of DB solubility using $CO_2$ modified with methanol and acetic acid in the composition range of (3.5 to 5.5) mol % is investigated. Solubilities of DB in modified supercritical carbon dioxide are measured at (318.2, 328.2, and 338.2) K in the (9 to 21) MPa pressure range, and solubility correlation equations are obtained. These equations may be used to predict the DB solubility in methanol or acetic-acid-modified $CO_2$ within the composition and pressure intervals studied or at values close to the interval limits.

## Experimental Section

The apparatus used to perform the solubility measurements is a built-in-house static synthetic device similar to that described by McHugh and Krukonis.[20] It consists of a high-pressure cell made of stainless steel whose volume can be varied by a piston. The working volume is ∼ 15 $cm^3$. The cell is fitted with a sapphire window. Its contents can be illuminated and observed through this window using a boroscope and a digital camera connected to a computer. A schematic diagram is presented in Figure 2.

The cell can be heated up to 373 K by means of a silicone heating tape and is controlled by a PID temperature controller. A type J calibrated thermocouple is placed inside the cell, and it is used both as a control point and for measuring the temperature. The precision is ± 0.05 K, and the stability of the thermostat is estimated to be ± 0.2 K. The sample can be

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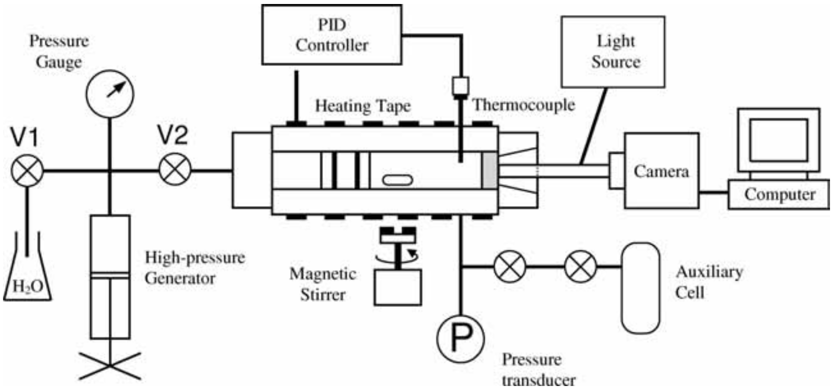

**Figure 2.** Schematic diagram of the static view cell apparatus used to perform phase equilibria measurements.

**Table 1. Dibenzofuran Solubility in the $CO_2$ ($y_1$) + DB ($y_2$) + Cosolvent ($y_3$) System at (318.2, 328.2, and 338.2) K**

| | | *P*/MPa | | |
|---|---|---|---|---|
| $10^3 \cdot y_2$ | $y_3$ | 318.2 K | 328.2 K | 338.2 K |
| | | $CO_2$ + DB + Methanol | | |
| 3.39 | 0.0460 | 9.3 | 10.87 | 12.47 |
| 4.59 | 0.0499 | 9.6 | 11.08 | 12.90 |
| 4.65 | 0.0401 | 10.1 | 11.52 | 13.39 |
| 6.71 | 0.0481 | 10.8 | 11.88 | 13.86 |
| 8.73 | 0.0439 | 12.9 | 13.01 | 15.11 |
| 10.3 | 0.0529 | 14.2 | 13.45 | 15.53 |
| 10.6 | 0.0432 | 15.3 | 13.94 | 16.08 |
| 12.0 | 0.0473 | 16.9 | 14.39 | 16.49 |
| 12.3 | 0.0394 | 18.5 | 15.23 | 17.40 |
| 14.1 | 0.0529 | 20.6 | 15.27 | 17.40 |
| 15.5 | 0.0459 | | 16.39 | 18.46 |
| | | $CO_2$ + DB + Acetic Acid | | |
| 5.05 | 0.0414 | | 10.75 | 12.63 |
| 6.41 | 0.0369 | 10.3 | 11.41 | 13.45 |
| 7.96 | 0.0482 | 10.6 | 11.40 | 13.50 |
| 8.03 | 0.0515 | | 11.00 | 13.01 |
| 8.89 | 0.0412 | 12.0 | 12.31 | 14.46 |
| 9.99 | 0.0534 | 11.7 | 11.65 | 13.83 |
| 10.5 | 0.0461 | 13.0 | 12.33 | 14.47 |
| 11.8 | 0.0431 | 15.6 | 13.04 | 15.33 |
| 12.1 | 0.0425 | 16.5 | 13.47 | 15.62 |
| 13.0 | 0.0549 | 15.0 | 12.47 | 14.67 |
| 13.3 | 0.0498 | 15.9 | 12.79 | 15.10 |
| 14.9 | 0.0480 | 20.5 | 13.90 | 16.07 |

**Table 2. Fixed Parameters ($C_i$), Fitting Coefficients ($a_i$), and Standard Deviation ($\sigma$) for Correlations of Dibenzofuran Solubility in Modified $CO_2$ using Equation *1***

| temp | 318.2 K | | 328.2 K | | 338.2 K | |
|---|---|---|---|---|---|---|
| cosolvent | MeOH | AcH | MeOH | AcH | MeOH | AcH |
| $C_1/10^5 \cdot$MPa | 0.9367 | | 0.1559 | | −0.1384 | |
| $C_2/10^2 \cdot$MPa | 1.201 | | 4.571 | | 9.305 | |
| $C_3$/MPa | 9.501 | | 11.37 | | 10.54 | |
| $a_1/10^5 \cdot$MPa | 1.220 | 0.7445 | −1.074 | −3.418 | 3.702 | 2.253 |
| $a_2/10^2 \cdot$MPa | −158.8 | −194.1 | −39.95 | −13.68 | −107.0 | −101.1 |
| $a_3$/MPa | 20.16 | 24.58 | −34.79 | −65.88 | 9.303 | −9.923 |
| $\sigma$/MPa | 0.3 | 0.4 | 0.2 | 0.2 | 0.11 | 0.11 |

compressed (up to 30 MPa) or decompressed by displacing the piston using a high-pressure generator and water as hydrostatic fluid. The pressure is determined inside the cell by a relative transducer with an estimated error of ± (0.01 + 0.0015*P*) MPa. Further details of the apparatus as well as the procedure to validate it have been described elsewhere.[19]

Solubility data are measured following the synthetic method. A mixture of known composition is prepared in the cell, and its phase behavior is studied against pressure and temperature. Every component is separately loaded into the cell. DB is introduced first. Then, the cell is closed, and the liquid cosolvent is added using a syringe. After that, the cell is purged with $CO_2$ several times at low pressure. Finally, liquid carbon dioxide is gravimetrically transferred into the cell by means of an auxiliary cell. The amounts of every component are determined by weight. Because of the characteristics of this procedure, it is very difficult to have an accurate control of the amounts loaded a priori, which means that the relative concentration of the cosolvent/$CO_2$ cannot be kept constant. The overall composition can be determined very precisely with an estimated error of 0.1 %.

Once the sample is loaded, the cell is kept at constant temperature, and the sample is compressed to a single phase. The pressure is then slowly decreased until a condensed phase appears. The contents of the cell are agitated by a magnetic stirrer to ensure homogeneity in the single phase. If the characteristics of the system allow it, the sample can be alternatively solubilized and precipitated to obtain a precise pressure value. In this work, both ternary systems presented metastability phenomena at 318.2 K, and the solution was oversaturated when the pressure was decreased, thus preventing us from obtaining accurate measurements. To avoid this problem, we increased the pressure from a two-phase region instead. The pressure was raised in 0.1 MPa steps with enough time in between to ensure thermodynamic equilibrium. The value at which the last DB crystal disappeared was recorded. According to this procedure, the precision of the pressure measurements at 318.2 K is estimated to be ± 0.05 MPa.

The materials employed were $CO_2$ (Air Liquide, 99.98 mol % pure), DB (Fluka, ≥ 99 mol % pure), methanol (Carlo Erba, ≥ 99.7 mol % pure), and acetic acid (Probus (99 to 99.5) mol % pure). Commercial materials were used without further purification.

## Results and Discussion

The pressures at which the DB is solubilized into modified carbon dioxide are determined at (318.2, 328.2, and 338.2) K in the DB mole fraction range between $3 \cdot 10^{-3}$ and $15.5 \cdot 10^{-3}$. The concentration of either methanol or acetic acid in carbon dioxide lies within (3.5 to 5.5) mol %. Results are presented in Table 1. The experimental data were fitted to the following empirical equation:

$$P/\text{MPa} = (C_1 + a_1 y_C) y_{DB}^2 + (C_2 + a_2 y_C) y_{DB} + (C_3 + a_3 y_C) \tag{1}$$

where $P$ is the pressure in the P-y diagram, $y_{DB}$ is the dibenzofuran mole fraction, $y_C$ is the cosolvent mole fraction, and $C_1$, $C_2$, $C_3$, $a_1$, $a_2$, and $a_3$ are fitting coefficients. If the

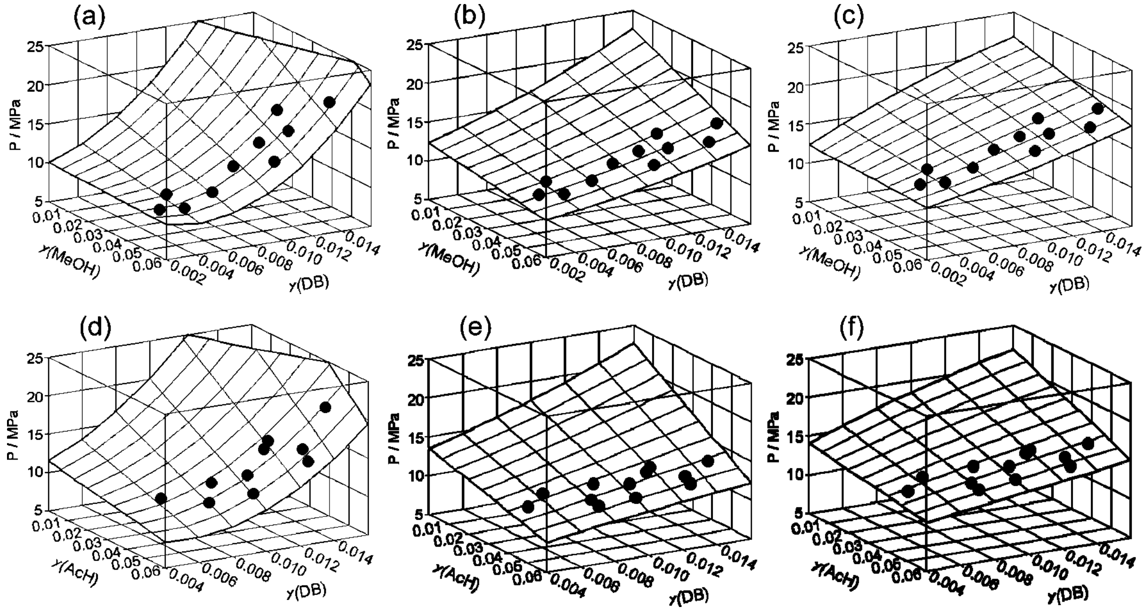

**Figure 3.** Solubilities for DB in modified $CO_2$ versus DB and cosolvent mole fraction. Cosolvents used are methanol (MeOH) and acetic acid (AcH). (a) methanol, 318.2 K; (b) methanol, 328.2 K; (c) methanol, 338.2 K; (d) acetic acid, 318.2 K; (e) acetic acid, 328.2 K; (f) acetic acid, 338.2 K.

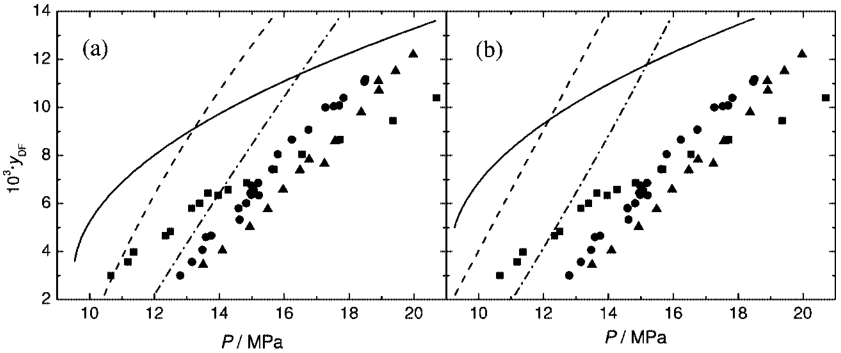

**Figure 4.** Solubility for (a) DB + $CO_2$ + methanol system and (b) DB + $CO_2$ + acetic acid system at the fixed cosolvent mole fraction of 0.045 at: —, 318.2 K; – – –, 328.2 K; •–•–•, 338.2 K. Comparison with the DB + $CO_2$ system: ■, 319.2 K; ●, 328.7 K; ▲, 338.2 K.

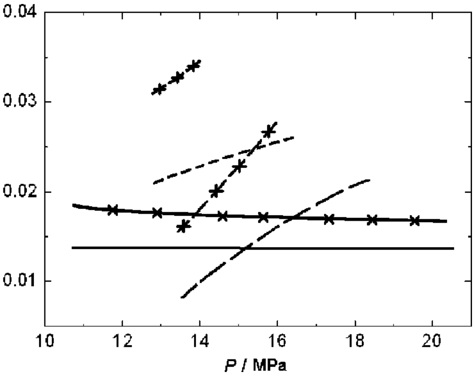

**Figure 5.** Increments of DB solubility, Δ*s*, for the ternary systems at 0.045 cosolvent mole fraction with respect to the binary system. —, methanol, 318.2 K; ---, methanol, 328.2 K; – – –, methanol, 338.2 K. The crossed lines correspond to values for acetic acid at the same temperatures indicated for methanol.

cosolvent concentration is zero, then eq 1 corresponds to a quadratic polynomial of the solubility for the DB + $CO_2$ system.

To fit eq 1 to the experimental data, the coefficients ($C_i$) remain fixed; their values were previously obtained by fitting a quadratic expression to data for the DB + $CO_2$ system taken from ref 19. The experimental temperatures for the binary system (319.2, 323.3, and 328.2) K are slightly different from those for the ternary system presented in this work; nevertheless, for fitting purposes, this difference is considered to be negligible. After the $C_i$ coefficients were determined, the other three parameters, $a_1$, $a_2$, and $a_3$, were fit to our data by a least-squares procedure. All of the coefficients, fixed and fitted, and the standard deviations between experimental and calculated data are gathered in Table 2. The experimental solubilities for the DB + $CO_2$ + cosolvent systems along with the calculated surfaces are represented in Figure 3. Equation 1 can therefore be used to interpolate data at cosolvent concentrations between 0 and 0.055 cosolvent mole fraction. Previously, Van Alster and Eckert measured the solubility of DB in $CO_2$ + methanol at 323.2 K and (1 and 2.5) mol % methanol concentration in carbon dioxide.[21] Unfortunately, neither the temperature nor the cosolvent concentrations are the same as those for solubility data presented in this work, so a direct comparison is not possible. However, a comparison between Van Alster and Eckert data and those obtained using eq 1 for (1 and 2.5) mol % methanol concentration in $CO_2$ at (318.2 and 328.2) K indicates good agreement for a given concentration between the three sets of data at (318.2, 323.2, and 328.15) K.

To appreciate the cosolvent effect of the substances, we compared solubility data for the DB + $CO_2$ system to data for the ternary systems at a fixed cosolvent mole fraction. Equation 1 was used to interpolate solubility data of DB in modified $CO_2$ at 0.045 cosolvent mole fraction. In Figure 4, the interpolated curves are compared with the solubility data for the binary system obtained from ref 19.

The solubility of DB in $CO_2$ is largely enhanced by the presence of either methanol or acetic acid, but the latter has a stronger cosolvent effect. As can be seen from Figure 4, the mole fraction solubility of DB in $CO_2$ at 15 MPa and 319.2 K is $7 \cdot 10^{-3}$. The DB mole fraction solubility in $CO_2$ modified with methanol at the same pressure and 318.3 K is $10 \cdot 10^{-3}$, whereas if the cosolvent is acetic acid, the DB mole fraction solubility is $12 \cdot 10^{-3}$.

The temperature also plays an important role in the enhancement of the DB solubility. An inspection of Figure 4 reveals that the solubility curves in modified $CO_2$ at 318.2 K cross those at (328.2 and 338.2) K; however, these two are almost parallel to each other. This tendency is also observed for the binary system.[19]

Figure 5 shows the increment of solubility that is due to the effect of the modifier. Differences in DB solubility (expressed in grams of solute per gram of solvent) between the ternary system at 0.045 cosolvent mole fraction and the binary system,[19] $\Delta s$, are plotted against pressure. The Figure shows some interesting phenomena. First, the shape of the curves is different depending on the temperature. At 318.2 K, the solubility increment is almost constant with pressure; however, at (328.2 and 338.2) K, the effect of the cosolvent is greater as the pressure increases. Another interesting feature is that both the highest DB solubility and the highest solubility increment are obtained when acetic acid is used at 328.2 K (the intermediate temperature of those studied). Within the range of temperature considered, the maximum extraction efficiency at a given pressure will occur at an intermediate temperature. The knowledge of the phase behavior of these systems is therefore essential for establishing the optimum conditions in an SFE process.

To understand the variation of solubility with temperature in the ternary system, we need to study the entire phase diagram of the system and the possible occurrence of multiphase regions. According to the shape of the SLV line for DB + $CO_2$, this system presents a liquid−gas type III diagram[19] in the classification of Scott and van Konynenburg.[22] Isotherms at temperatures lower than those of the SLV line (up to 328.7 K for the DB + $CO_2$ system) would correspond to an SV equilibrium, whereas those at higher temperatures would show LV equilibrium.[19] The importance of the SLV lies in the fact that at temperatures close to this line, there is a solid solubility enhancement that is currently exploited in SFE experiments.[20]

No experimental data about the SLV line for the ternary systems DB + $CO_2$ + methanol and DB + $CO_2$ + acetic acid are available. However, it has been observed that a small amount of a cosolvent can lower the SLV line of this kind of system. This behavior has been observed for naphthol + $CO_2$ when methanol is added as cosolvent and for naphthalene + $CO_2$ when pentane is added.[23] If we assume a moderate decrease in the SLV line because of the presence of the cosolvent, the isotherms at 328.2 K as well as those at 338.2 K could be an LV equilibrium. At 318.2 K, however, crystals of DB were clearly observed to appear, which undoubtedly pointed to an SV equilibrium. It seems that the different behaviors of the curves observed in Figure 4 may be related to the state in which the solute precipitates. The higher values of DB solubility at 328.2 K that were also observed in Figure 4 indicate the proximity to the SLV line; apparently, it is also around this region where the maximum solubility increments due to the cosolvent effect are found.

The solubility enhancement due to the presence of a cosolvent in $CO_2$ usually increases with the modifier concentration because the density of the solvent is higher, which leads to higher solubilities. Nevertheless, sometimes the nature of the solvent and cosolvent can play an important role due to specific interactions between them,[21] leading to further increments in solute solubility. Both methanol and acetic acid have acidic groups that can interact with the oxygen of DB. Because the hydrogen of the acid group in the acetic acid is more acidic than that of the alcohol group in the methanol, a stronger cosolvent effect may be expected for acetic acid at a given temperature and cosolvent concentration.

## Conclusions

The solubility behavior of DB in $CO_2$ that was modified with methanol and acetic acid was investigated at (318.2, 328.2, and 338.2) K in the (9 to 21) MPa pressure interval for cosolvent concentrations in the ternary system lying within (3.5 to 5.5) mol %.

The data obtained in this paper are correlated using an empirical equation. By the use of this equation, the solubility of DB for other cosolvent concentrations may be interpolated.

These results show that both methanol and acetic acid are suitable cosolvents because they enhance the solubility of DB in $CO_2$. The effect of acetic acid is, however, greater. This behavior can be explained in terms of specific solute−cosolvent interactions. A significant dependence on the temperature and therefore on the state of the solute is also found. The largest solubility values as well as the largest solubility increment with respect to the binary system are obtained when acetic acid is used at 328.2 K.

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