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Solubilities of Benzene Derivatives in Supercritical Carbon Dioxide

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ABSTRACT: The solubilities of benzene derivatives in supercritical carbon dioxide was determined by the saturation method over the pressure range (9.5 to 14.5) MPa. The solubilities were determined at (308 and 313) K for 1-chloro-2,4-dinitrobenzene and (308, 318, and 328) K for *m*-dinitrobenzene. At 308 K, the solubility (in mole fraction) of 1-chloro-2,4-dinitrobenzene varied from $(2.83 \text{ to } 5.88) \cdot 10^{-3}$ while the solubility of *m*-dinitrobenzene increased from $(2.05 \text{ to } 5.54) \cdot 10^{-3}$ as the pressure increased from (9.5 to 14.5) MPa. However, the solubilities of both compounds decreased with increasing temperature. Models based on the solubility parameter and semiempirical models such as the Méndez-Santiago−Teja model, the Gordillo model, and the association model, were used to correlate the experimental solubility data for the benzene derivatives.

INTRODUCTION

Supercritical fluids (SCFs) are widely used in the food,[1,2] pharmaceutical,[3−5] environmental,[6,7] and material processing[8,9] industries. Their properties, such as liquidlike densities, gaslike diffusivities, low surface tension, and low viscosity, make them preferred solvents. Carbon dioxide, which is nontoxic and nonflammable and has a critical temperature close to the ambient temperature, is most commonly used as an SCF.[10] The design of processes such as extraction, separation, purification, synthesis, etc., requires knowledge of the solubility of the compounds in the solvent used in the process. The solubility of the solute depends on temperature and pressure, and therefore, the extraction efficiency of SCFs can be altered by tuning the temperature and pressure.

1-Chloro-2,4-dinitrobenzene and *m*-dinitrobenzene are derivatives of benzene and find their applications in the synthesis of many chemicals.[11−13] They are also used as intermediates in the synthesis of drugs. *m*-Dinitrobenzene is used as precursor to rubber, pesticides, dyes, and pharmaceuticals. It is used in the synthesis of the analgesic drug acetaminophen (paracetamol).[11] 1-Chloro-2,4-dinitrobenzene is a synthesis reagent in many alkyl and aryl reactions.[13]

The solubilities of a variety of benzene derivatives have been determined by various other studies. However, this is the first study of the solubilities of 1-chloro-2,4-dinitrobenzene and *m*-dinitrobenzene in supercritical carbon dioxide ($SCCO_2$). The solubilities were correlated using the Méndez-Santiago−Teja model, the Gordillo model, an association model, and models based on the solubility parameter.

MATERIALS AND METHODS

Materials. Carbon dioxide gas (CAS no. 124-38-9, 0.99 mass fraction) was purchased from Vinayaka Gases (India). It was then further purified to 0.999 mass fraction (as verified by GC−MS) by passing it through a bed of silica gel. 1-Chloro-2,4-dinitrobenzene (CAS no. 97-00-7, 0.99 mass fraction) and *m*-dinitrobenzene (CAS no. 99-65-0, 0.98 mass fraction) were obtained from Rolex Chemical Industries (India).

Experimental Procedure. The equilibrium solubility of each solute was determined with a flow apparatus using the saturation method. The method of operation has been described in earlier studies.[14] Carbon dioxide from a gas cylinder was pressurized using a pump (Jasco PU-1580-CO_2), which was operated in a constant-flow mode. A back-pressure regulator (Jasco PU-1580-81-BP) was used to maintain the pressure within ± 0.2 MPa of the operating pressure. Two columns (300 mm × 14 mm) packed with the desired solute were connected in series. Each column was filled with about 35 g of solute along with glass wool for every operating condition. This was placed in an oven where the temperature was controlled within ± 0.1 K of the operating temperature. CO_2 was pressurized using a syringe pump (Jasco model PU-1580-CO_2) and fed through the saturation columns from the bottom. $SCCO_2$ was then passed through the columns filled with the solute. To avoid the entrainment of solute, the column ends were fitted with 2 μm filters. After a sufficient amount of time to allow for saturation of the solute in $SCCO_2$, it was expanded in a glass trap and measured gravimetrically. All of the solubility experiments were carried out at a constant flow rate (based on the pump head), and the flow rates were chosen to ensure that saturation was attained.[14] The solubility of the compound in $SCCO_2$ was determined on basis of the total flow rate of $SCCO_2$. The mole fraction of the solute in $SCCO_2$ (y_2) is given by the following expression:

$$y_2 = \frac{n^{\text{solute}}}{n^{\text{solute}} + n^{\text{SCCO}_2}} \qquad (1)$$

where *n* represents the number of moles. Further details about the experimental procedure can be found elsewhere.[14] Each experiment was repeated three times, and the relative deviation was less than ± 5 %.

Models and Correlations. *Solubility Parameter Model.* The solubility parameter model[15] can be used to determine the solubility parameters of the solute and $SCCO_2$, and these can then be used to determine the equilibrium solubility of the solute. The equilibrium solubility of a solute in an SCF can be calculated

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by equating the fugacities of the pure solid solute (component 2) and the solute in the supercritical phase (component 1):

$$f_2^{\mathrm{s}} = f_2^{\mathrm{scf}} \tag{2}$$

From the regular solution model, the fugacity of the solute in the supercritical phase is expressed in terms of activity coefficient (γ_2) and saturation fugacity of the pure solute (f_2^{l}) as

$$f_2^{\mathrm{scf}} = y_2 \gamma_2 f_2^{\mathrm{l}} \tag{3}$$

For regular solutions, the solute activity coefficient γ_2 can be expressed in terms of solubility parameters (δ)[16] as

$$RT \ln \gamma_2 = V_2 {\phi_1}^2 (\delta_2 - \delta_1)^2 \tag{4}$$

where V_2 is the molar volume of the solute, δ_1 and δ_2 are the solubility parameters of the solvent and solute, respectively, and ϕ_1 is the volume fraction of the solvent, which is given by the following expression:

$$\phi_1 = \frac{y_1 V_1}{y_1 V_1 + y_2 V_2} \tag{5}$$

As the mole fraction of the solute in the SCF is very small, ϕ_1 approaches unity. Prausnitz et al.[17] derived the following expression for the ratio of the fugacities of a solute in solid and liquid phases by neglecting the heat capacities:

$$\ln \frac{f_2^s}{f_2^l} = \frac{\Delta_{\mathrm{f}} H}{RT}\left(\frac{T}{T_{2,\mathrm{m}}} - 1\right) \tag{6}$$

where $\Delta_{\mathrm{f}} H$ is the enthalpy of fusion of the solute and $T_{2,\mathrm{m}}$ is the melting temperature of the solute. Combining eqs 2 to 6 affords the following expression for the solubility of the solute:

$$\ln y_2 = \frac{\Delta_{\mathrm{f}} H}{RT}\left(\frac{T}{T_{2,\mathrm{m}}} - 1\right) - \frac{V_2}{RT}(\delta_2 - \delta_1)^2 \tag{7}$$

The molar volume of the solute can be estimated using standard techniques.[18] In eq 7, the solubility parameter of solute is unknown and is determined for each data point, as discussed below.

The expression for the solubility parameter of SCCO$_2$ obtained from the Peng−Robinson equation of state is[15]

$$\delta_1 = \left[\frac{a(T)}{V(V+b) + b(V-b)}\left(1 + m \cdot T_{\mathrm{r}}^{1/2}\right)\right]^{1/2} \tag{8}$$

in which V is the volume of SCCO$_2$ and

$$a(T) = a(T_{\mathrm{c}})\left[1 + m\left(1 - T_{\mathrm{r}}^{1/2}\right)\right]^2 \tag{8a}$$

$$a(T_{\mathrm{c}}) = 0.45724 \cdot R^2 \cdot {T_{\mathrm{c}}}^2 / P_{\mathrm{c}} \tag{8b}$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{8c}$$

$$b = 0.0778 \cdot R \cdot T_{\mathrm{c}} / P_{\mathrm{c}} \tag{8d}$$

$$T_{\mathrm{r}} = T / T_{\mathrm{c}} \tag{8e}$$

where P_{c}, T_{c}, and ω are the critical temperature, critical pressure, and acentric factor, respectively.

The solute solubility parameter was correlated to the density (ρ, in mol·mL^{-1} or kmol·dm^{-3}) as

$$\delta_2 = A_0 + A_1 \rho^{A_2} \tag{9}$$

where the A_j are constants.

Semiempirical Models. Many semiempirical models are available in the literature,[19−21] and most of these models relate the solubilities to the density of the SCF. The most widely used semiempirical model is the Méndez-Santiago−Teja (MT) model,[20] which was developed on the basis of the theory of dilute solutions. This model correlates the solubility of the solute to the density of SCCO$_2$ and temperature and can be used as a test for self-consistency of the data:

$$\left(\frac{T}{\mathrm{K}}\right) \ln\left(\frac{y_2 P}{P^*}\right) = \left(\frac{M}{\mathrm{K}}\right) + \left(\frac{N}{\mathrm{K \cdot mL \cdot mol^{-1}}}\right)\left(\frac{\rho}{\mathrm{mol \cdot mL^{-1}}}\right) + O\left(\frac{T}{\mathrm{K}}\right) \tag{10}$$

where M, N, and O are temperature-independent constants, ρ is the density of SCCO$_2$, and P^* is the reference pressure of 0.1 MPa.

The solubilities of the solutes follow a curvilinear variation with pressure under isothermal conditions, and a similar trend is followed with temperature under isobaric conditions.[22] Tabernero et al.[23] extensively studied the various empirical relationships and concluded that the model suggested by Gordillo et al.[24] provides the best correlation. The expression that relates solubility to pressure (MPa) and temperature (K) is

$$\ln y_2 = A + B \cdot P + C \cdot P^2 + D \cdot P \cdot T + E \cdot T + F \cdot T^2 \tag{11}$$

Recently, a four parameter model correlating the solubility with temperature, pressure, and density that is based on the association of the solute with the SCCO$_2$ was developed:[25]

$$y_2 = \left(\frac{P}{P^*}\right)^{(\kappa - 1)} \exp\left(\frac{a}{T} + b\rho + c\right) \tag{12}$$

where κ represents the association number and a, b, and c are constants (a and b have units of K and mL·mol^{-1}, respectively). It has been reported that the above association model[25] is better than other existing models in correlating the solubilities of drugs in SCCO$_2$. We used this association model[25] in this study to model the solubility data.

■ RESULTS AND DISCUSSION

The experiments were conducted at (308 and 313) K for 1-chloro-2,4-dinitrobenzene and at (308, 318, and 328) K for *m*-dinitrobenzene over the pressure range (9.5 to 14.5) MPa. The solubility of 1-chloro-2,4-dinitrobenzene was not measured at higher temperatures because the melting point of the compound is 325 K. The solubility data for the compounds are reported in Table 1. The crossover pressure was observed between (13.5 and 14.5) MPa for 1-chloro-2,4-dinitrobenzene, but a crossover pressure was not observed in the operating pressure range for *m*-dinitrobenzene.

The solubilities of chlorophenols were compared with nitrophenols, and it was found that chlorophenols exhibit higher solubilities than nitrophenols.[26,27] Substitution of either the

Table 1. Solubilities ($y_2 \cdot 10^3$) of 1-Chloro-2,4-dinitrobenzene and *m*-Dinitrobenzene in Mole Fraction in $SCCO_2$ at Temperatures of (308 and 313) K and (308, 318, and 328) K, Respectively, over the Pressure Range (9.5 to 14.5) MPa

	$y_2 \cdot 10^3$				
	1-chloro-2,4-dinitrobenzene		*m*-dinitrobenzene		
P/ MPa	308 K	313 K	308 K	318 K	328 K
9.5	2.83	1.78	2.05	0.57	0.19
10.5	3.55	2.52	2.93	1.32	0.45
11.5	4.21	3.23	3.42	2.25	0.94
12.5	4.99	4.26	4.09	2.83	1.42
13.5	5.47	5.17	4.61	3.53	1.98
14.5	5.88	6.19	5.54	4.12	2.33

Table 2. Thermodynamic Properties of the Solutes

	$\Delta_f H$	$T_{2,m}$	V_2
	$J \cdot mol^{-1}$	K	$cm^3 \cdot mol^{-1}$
1-chloro-2,4-dinitrobenzene	20200[a]	325[a]	119.15[c]
m-dinitrobenzene	24200[b]	362[b]	105.6[c]

[a] Adapted from Gilbert.[35] [b] Adapted from Gupta and Singh.[36] [c] Estimated by the method of Immirizi and Perini.[18]

chloro or nitro group in the ortho position of the phenol increases the solubility because of intramolecular hydrogen bonding.[28] The solubilities of the benzene derivatives studied were compared with those of benzene, nitrobenzene, and chlorobenzene. The solubilities of benzene and chlorobenzene at 313 K around 7.75 MPa are $6.73 \cdot 10^{-2}$ and $6.6 \cdot 10^{-3}$, respectively.[29,30] The dew-point pressure of nitrobenzene[31] at 310 K for a mole fraction of $3.55 \cdot 10^{-2}$ is 8.86 MPa. This indicates that nitrobenzene has a higher solubility than chlorobenzene, 1-chloro-2,4- dinitrobenzene, and *m*-dinitrobenzene. The addition of nitro groups to aromatic compounds decreases the solubility,[28] and therefore, nitrobenzenes show lower solubilities than benzene. The solubility of benzene and its other derivatives thus follows the order benzene > nitrobenzene > chlorobenzene >1-chloro-2,4-dinitrobenzene > *m*-dinitrobenzene. The solubilities of these compounds follow the order of solute vapor pressures.

In eq 7, the heat of fusion and the melting temperature were taken from the literature, while the molar volume of the solute was estimated by the group-contribution method.[18] The thermodynamic properties of the solutes studied are presented in Table 2. The dependence of the molar volume of the solute on temperature and pressure is not known. In this work, the molar volume of the solute was assumed to be constant, and the solubility parameter was determined. A similar kind of approach was followed by Guigard et al.,[32] who calculated the solubility parameters of the solute by assuming the molar volume of the solute to be constant.

δ_1 and δ_2 are the solubility parameters of solvent and solute, respectively, and they were determined from eqs 8 and 9, respectively. Plots of the obtained solubility parameters of the solute and $SCCO_2$ against the density of $SCCO_2$ are shown in Figure 1. The density of $SCCO_2$ was determined using the Span−Wagner equation of state.[33]

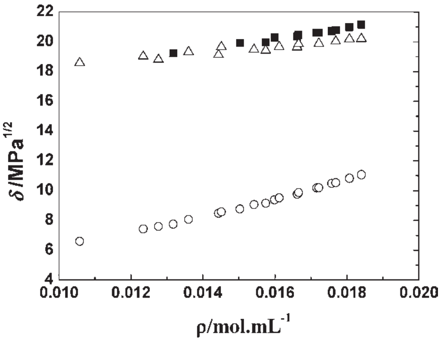

Figure 1. Variation of the solubility parameters (δ) with the density of $SCCO_2$ (ρ): ■, 1-chloro-2,4-dinitrobenzene; △, *m*-dinitrobenzene; ○, $SCCO_2$.

The solubility of the solute in $SCCO_2$ was obtained from eq 7 by substituting the solubility parameters. The optimization procedure reduced the absolute average relative deviation [AARD, defined as AARD = $N^{-1}(\sum_{i=1}^{N}|y_2^{\text{calcd}} - y_2^{\text{exptl}}|/y_2^{\text{exptl}}) \cdot$ (100 %), where N represents the number of data points and y_2^{calcd} and y_2^{exptl} represent the calculated and experimental solubilities of the solute, respectively]. The parameters obtained by reducing the AARD between the solubility of the solute determined experimentally and that calculated from the model are shown in Table 3.

The solubility parameters for various solutes were correlated to the density by using linear and power relations, and it was found that the power fit of the solubility parameter to the density was able to correlate the experimental solubilities of the solutes more accurately than the linear fit.[34] The solute solubility parameter δ_2 was determined using the power fit. The parameters A_0, A_1, and A_2 for the power fits and the corresponding AARD values were determined and are reported in Table 3. The AARD for 1-chloro-2,4-dinitrobenzene was 4.31 %, and that for *m*-dinitrobenzene was 10.12 %. When A_2 is assumed to be unity, the power law fit is simply a linear fit. However, the AARD values for this case were not significantly different from the AARD values obtained by the power relationship fit. This indicates that the experimental solubilities were well-correlated by the linear fit in these cases.

The experimental solubility data were correlated using various semiempirical models. The temperature-independent parameters of the empirical models used in this study are presented in Table 3 along with the corresponding AARDs. The solubilities obtained from MT model (eq 10) and the experimental solubilities of the solute were plotted against the density of $SCCO_2$, as shown in Figure 2. The experimental solubilities at different temperatures for both solutes fall on a straight line, indicating the consistency of the data.

The usual semiempirical models correlate solubility to density, but the Gordillo model[24] (eq 11) correlates solubility with temperature and pressure and correlates the solubilities of many solutes more accurately than the other models.[23] A good agreement was observed between the experimental solubilities and the solubilities calculated from Gordillo model[24] for the benzene derivatives. Plots of solubility against pressure for the two solutes are shown in Figure 3. The model predicted the crossover pressure between (13.5 and 14.5) MPa for 1-chloro-2,4-dinitrobenzene. The AARDs for 1-chloro-2,4-dinitrobenzene and *m*-dinitrobenzene are 1.27 % and 8.52 %, respectively. The model

Table 3. Correlation Parameters of Various Models for the Solubilities of 1-Chloro-2,4-dinitrobenzene and *m*-Dinitrobenzene

compound	model	correlation parameters	AARD/%
1-chloro-2,4-dinitrobenzene	solubility parameter model		
	power fit	$A_0 = 15.7$, $A_1 = 1399.4$, $A_2 = 1.4$	4.31
	linear fit	$A_0 = 14.2$, $A_1 = 324.71$	4.37
	MT model	$M = -8487$, $N = 123000$, $O = 19.99$	7.25
	Gordillo model	$A = -22.86$, $B = -5.62$, $C = -0.0192$, $D = 0.0202$, $E = 0.367$, $F = -10.41 \cdot 10^{-4}$	1.27
	Association model	$\kappa = 1.14$, $a = -3830$, $b = 288.16$, $c = 1.3$	4.40
m-dinitrobenzene	solubility parameter model		
	power fit	$A_0 = 18.2$, $A_1 = 1363.8$, $A_2 = 1.6$	10.12
	linear fit	$A_0 = 17.5$, $A_1 = 168.2$	11.35
	MT model	$M = -6234$, $N = 116000$, $O = 12.92$	11.50
	Gordillo model	$A = -60.24$, $B = -3.03$, $C = -0.0645$, $D = 0.0155$, $E = 0.512$, $F = -12.06 \cdot 10^{-4}$	8.52
	association model	$\kappa = 1.73$, $a = -916.5$, $b = 231.7$, $c = -10.13$	8.10

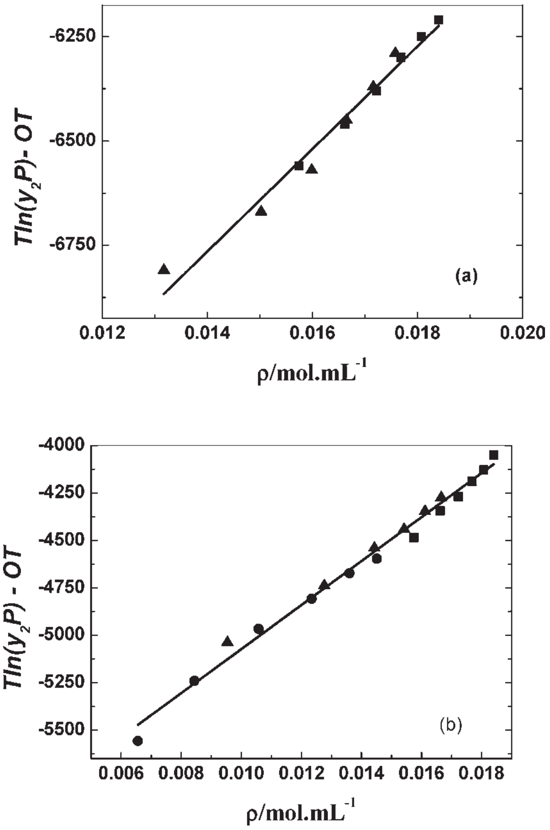

Figure 2. Solubilities (y_2) of (a) 1-chloro-2,4-dinitrobenzene (■, 308 K; ▼, 313 K) and (b) *m*-dinitrobenzene (■, 308 K; ▼, 318 K; ●, 328 K) as functions of the density of $SCCO_2$ (ρ). The lines were calculated using the MT model (eq 10).

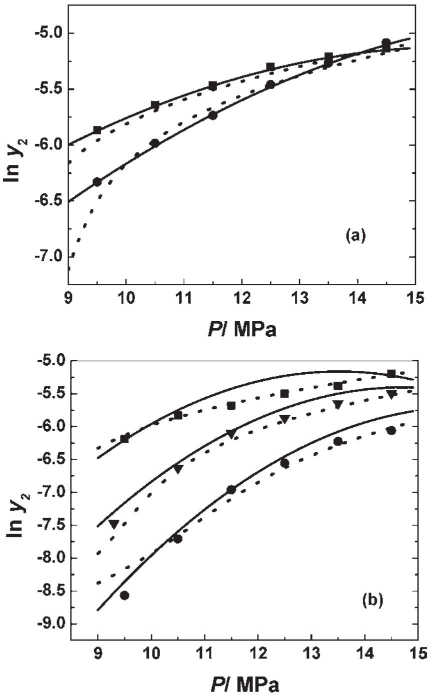

Figure 3. Solubilities (y_2) of (a) 1-chloro-2,4-dinitrobenzene (■, 308 K; ●, 313 K) and (b) *m*-dinitrobenzene (■, 308 K; ▼, 318 K, ●, 328 K) in $SCCO_2$ as functions of pressure (P). The solid lines were calculated using the Gordillo model (eq 11) and the dotted lines using the association model (eq 12).

correlated the solubilities of both solutes better than the MT model and the solubility parameter model.

Figure 3 also shows the correlation obtained using the association model (eq 12) for the solubilities of the two solutes. The association model assumes that the solvent molecules, free solute molecules, and solvent−solute clusters are at chemical equilibrium in the supercritical fluid phase and that a cluster consists of one solute associated with several solvent molecules. The number of associated solvent molecules is the association number, κ. This average association number is considered to be a constant for each binary system over a small temperature range. Because it is an average value for all possible clusters with different association numbers, the association number is usually not an integer and can even be less than unity.[34] From the model, it was observed that 1.14 molecules of $SCCO_2$ are required to form a complex for 1-chloro-2,4-dinitrobenzene, while *m*-dinitrobenzene needs 1.73 molecules. The AARDs of 1-chloro-2,4-dinitrobenzene and *m*-dinitrobenzene obtained from the model are 4.40 % and 8.10 %, respectively.

The AARDs of the models for the solutes indicate that this association model correlated the experimental solubilities more accurately than the MT model. The association model correlated the solubilities of *m*-dinitrobenzene better than any other model investigated in this study. The solubilities of *m*-dinitrobenzene were correlated better by the new association model than the Gordillo model, though the latter has six adjustable parameters while the former has only four adjustable parameters.

■ CONCLUSIONS

The equilibrium solubilities of benzene derivatives were measured by the saturation method at (308 and 313) K for 1-chloro-2,4-dinitrobenzene and at (308, 318, and 328) K for *m*-dinitrobenzene over the pressure range (9.5 to 14.5) MPa. The solubilities decreased with increasing temperature, and the solubility of 1-chloro-2,4-dinitrobenzene was higher than that of *m*-dinitrobenzene at the same temperature and pressure. The solubilities of the benzene derivatives were correlated by several models, including the solubility parameter model and semiempirical models.

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