Fluid Phase Equilibria 307 (2011) 11–15

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Measurement and correlation of solubility of benzamide in supercritical carbon dioxide with and without cosolvent

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ARTICLE INFO

Article history:
Received 28 January 2011
Received in revised form 21 April 2011
Accepted 26 April 2011
Available online 4 May 2011

Keywords:
Solubility
Benzamide
Supercritical carbon dioxide
Cosolvent

ABSTRACT

The experimental equilibrium solubility of benzamide in supercritical carbon dioxide was measured at temperatures between 308 K and 328 K and for pressures from 11.0 MPa to 21.0 MPa using a dynamic flow method. The effects of three cosolvents – ethanol, acetone and ethylene glycol, were investigated at a cosolvent molar concentration of 3.5%. The results showed that the solubility was enhanced by the presence of the three cosolvents, and ethanol exhibited the highest cosolvent effect. The solubility data in the absence and presence of cosolvents were correlated by two density-based models. The calculated results showed satisfactory agreement with the experimental data.

1. Introduction

Supercritical fluids (SCFs) have the potential to offer large improvements in many extraction, fractionation, reaction, crystal growth and preparation of new materials [1–4]. Compared to conventional organic solvents, SCFs have several interesting properties like high diffusivity, low viscosity and low surface tension. A particularly attractive solvent is carbon dioxide (CO_2), which is widely used in supercritical fluid applications as a "green solvent". Because CO_2 is inexpensive, non-flammable, non-toxic, and environmentally benign, and has mild critical conditions (T_c = 304.2 K, P_c = 7.38 MPa). Moreover, CO_2 is generally recovered and purified from a relatively CO_2-rich gas stream which is created as an unavoidable byproduct of a large-scale chemical production process or some form of biological process.

Compounds of dissimilar chemical structures usually have large variations in the magnitude of solubility in supercritical CO_2 (SC CO_2). Therefore much attention has been paid to receiving reliable phase equilibrium data and understanding the relationship between chemical structure and solubility of organic compounds [5,6]. In the binary system, despite the similar structure and almost the same molecular weight of *p*-toluenesulfonamide (*p*-TSA, containing the group $-CH_3$) and sulfanilamide (SNA, containing the group $-NH_2$), the solubility of *p*-TSA in SC CO_2 was around two orders of magnitude higher than that of SNA [7], which showed a different group-contribution. In the system involving cosolvent, the strong attractive molecular interactions between aspirin and methanol enhanced solubility in SC CO_2 by up to 14 times [8]. It is believed that solubility could be strongly affected by the solute's ability in participating in hydrogen bonding with the cosolvents.

Benzamide is extensively used as intermediate for the synthesis of pharmaceuticals and dyes. However, the solubility data of benzamide in SC CO_2 has not been reported in the literature. In this work, solubility data of benzamide in supercritical carbon dioxide were measured from (11.0 to 21.0) MPa at (308, 318 and 328) K using a dynamic flow method. The determination of solubility is essential to know the property of the functional group $-CONH_2$, which is a typical functional group in some antibiotic drugs. The cosolvent effects of ethanol, acetone and ethylene glycol at a same molar concentration were studied and compared. Two density-based models, the Chrastil model and the Méndez-Santiago and Teja equation [9,10], were employed to correlate the solubility data.

2. Experiment

2.1. Materials

High purity CO_2 (>99.9%) was supplied by Beijing Praxair Industrial Gas Co. Ltd. Benzamide (>99.0% in mass fraction) was obtained from Aldrich. Basic information about benzamide is given in Table 1. Analytical grade ethanol, acetone and ethylene glycol were purchased from Beijing Chemical Reagent Factory, with a minimum purity of 99.7%, 99.9% and 99.5% by mass, respectively. All the samples were used without further purification.

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doi:10.1016/j.fluid.2011.04.021

Table 1
Properties of benzamide.

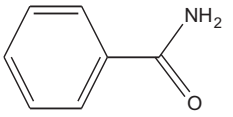
Solute	Formula	CAS	MW (g mol^{-1})	T_m (K)	Structure
Benzamide	C_7H_7NO	55-21-0	121.14	405.7[11]	

Table 2
Experimental solubility for benzamide in supercritical carbon dioxide.

T (K)	P (MPa)	ρ (kg m^{-3})	10^5y
308	11.0	745.54	1.91 ± 0.08
	13.0	786.89	3.14 ± 0.11
	16.0	828.10	4.36 ± 0.10
	18.0	848.87	5.26 ± 0.18
	21.0	874.40	6.19 ± 0.23
318	11.0	605.92	2.10 ± 0.06
	13.0	695.25	4.53 ± 0.15
	16.0	761.07	6.83 ± 0.26
	18.0	790.18	8.80 ± 0.17
	21.0	823.71	10.54 ± 0.32
328	11.0	417.06	2.23 ± 0.08
	13.0	573.33	5.21 ± 0.12
	16.0	682.39	9.83 ± 0.43
	18.0	724.13	12.82 ± 0.38
	21.0	768.74	16.05 ± 0.47

2.2. Apparatus and procedure

Solubility measurements were made using a flow-type apparatus as shown schematically in Fig. 1. A detailed description of the apparatus and operating procedure is given elsewhere [12,13]. Liquid CO_2 was compressed to the desired operating pressure using a high pressure syringe pump. The flow rates of cosolvents were controlled using the other high pressure pump. An equilibrium cell was immersed in a constant-temperature stirred water bath that maintained a constant temperature to within ±0.01 K. The accuracy of the temperature measurement is ±0.1 K, and the pressure fluctuation was controlled within ±0.05 MPa. Approximately 40 g of benzamide mixed with 2 mm glass beads was charged into the high-pressure equilibrium cell to guarantee the saturation conditions during each experiment.

After achievement of equilibrium in the cell, the saturated SCF stream was depressurized through a metering valve. The solute finally precipitated in the two connected U-shape tubes, and the total volume of CO_2 released during the experiment was measured by the calibrated wet gas flow meter with an accuracy of ±0.1% at room temperature and atmospheric pressure.

A model 2100 Unico UV–vis spectrophotometer was used to determine the mass of benzamide collected in the two U-type tubes. The solubility was determined from the mass of the solute and the corresponding volume of CO_2 released. Each reported datum was an average of at least three experimental runs with a relative standard deviation of 5% or less.

3. Results and discussion

3.1. Solubility of benzamide in pure SC CO_2

The experimental equilibrium solubility data for benzamide in SC CO_2 together with the density of carbon dioxide at each operating condition are shown in Table 2. Pure CO_2 density values were obtained from the NIST on-line chemistry web book [14]. The solubility is expressed in terms of benzamide mole fraction (y). It is readily seen that the solubility increases with increasing pressure at a constant temperature, and the higher the temperature, the higher the solubility. The influence of pressure on solubility is more pronounced at higher temperatures. The solute vapor pressure, solvent density, and intermolecular interactions in the fluid phase are influenced by the system temperature, and their contributions to the solubility of benzamide vary with the temperature. The nearly same solubility at 11.0 MPa for the three temperatures investigated is mainly due to the combined effects of increasing solute's vapor pressure and decreasing solvent's density as an increase of temperature. It is believed that the solubility isotherms would exhibit a crossover region near 11.0 MPa.

The experimental results were modeled using two density-based equations (Chrastil and Méndez-Santiago and Teja). The Chrastil equation [9], which correlates the solubility of a solute, in a supercritical solvent, to the density and temperature, is expressed as follows:

$$\ln S = k \ln \rho + \frac{a}{T} + b \tag{1}$$

This commonly used model is based on the supposition that each molecule of a solute associates with k molecules of supercritical solvent to form a solvato-complex. In this expression, S (kg m^{-3}) is the solubility of the solute in the supercritical phase, ρ (kg m^{-3}) is the density of the pure supercritical fluid, and T (K) is the operating temperature.

Méndez-Santiago and Teja presented a semi-empirical model based on the theory of dilute solutions [10]. They demonstrated that the solubility plotted as $T \ln E$ against the density of the solvent could yield a single line. The resulting expression (denoted as the M–T model) contains three adjustable parameters:

$$T \ln \left(\frac{yP}{P^{\text{std}}} \right) = A + B\rho + CT \tag{2}$$

where y is the solute mole fraction, P^{std} is the standard pressure (atmospheric pressure equal to 101,325 Pa), ρ (kg m^{-3}) is the density of the pure supercritical fluid, and T (K) and P (Pa) are the operating temperature and pressure.

The objective function used was the average absolute relative deviation (AARD), as shown in Eq. (3). Here y_{exp} are the experimental data, y_{cal} are the predicted values and n is the total number of data points.

$$\text{AARD}(\%) = \frac{100}{n} \sum_{1}^{n} \frac{\left| y_{\text{cal}} - y_{\text{exp}} \right|}{y_{\text{exp}}} \tag{3}$$

The values of calculated parameters for the correlation are tabulated in Table 3, together with the AARD between experimental and calculated solubility. The correlation by the two equations received the acceptable values of AARD less than 14%. Fig. 2 compares the calculated results using the Chrastil equation for benzamide with the experimental solubility values. For the M–T correlation, all the mole fraction solubility at different temperatures will coincide to a single straight line when plotting $T \ln (yP/P^{\text{std}}) - CT$ versus ρ. Fig. 3 shows the comparison of experimental solubility data and the calculated results using the M–T equation. The plots clearly show that solubility of benzamide in SC CO_2 increase with increasing density.