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Binary and ternary solubility of amino- and nitro-benzoic acids in supercritical carbon dioxide

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ABSTRACT

In this paper, the solubility of 3-aminobenzoic acid (3-ABA) in supercritical carbon dioxide ($SCCO_2$) was measured in a flow-type apparatus at temperatures of 308, 318, and 328 K within the pressure range of 10.0–21.0 MPa. Moreover, the solubility of the mixture of 3-ABA and 3-nitrobenzoic acid (3-NBA) with mass ratio of 1:1 was also investigated under the same condition. Its solubility reduction factor (*SE*), separation efficiency (*HE*) and mixture separation factor (μ) were also studied. Furthermore, a modified Bartle model was proposed for correlating the solubility of the solid chemicals in $SCCO_2$ with solvent density and experimental temperature. The accuracy of the modified and the traditional Bartle model was compared by data from experiment and literature, in which 1106 solubility data points of two solutes in experiments and 49 solutes in literature were considered. The calculation results showed that the modified Bartle model can give a better prediction on the solubility of different solid solutes in $SCCO_2$ than the traditional one.

1. Introduction

In last few decades, supercritical fluid (SCF) technology has been growing rapidly and widely used in pharmaceutical industries, food processing, chemical reaction, and separation processes [1]. In the SCF applications, carbon dioxide is a good solvent because of its low cost, zero-pollution, high purity, and moderate critical constants (7.38 MPa and 304 K). Besides, supercritical carbon dioxide ($SCCO_2$) also provides a strong solvent ability, a high diffusivity and a low viscosity, for which it is usually used as an attractive solvent in many industrial processes, such as the pharmaceutical industry [2].

3-Aminobenzoic acid (3-ABA) and 3-nitrobenzoic acid (3-NBA) are important intermediates in organic synthesis, pharmaceuticals and dyestuffs. It is well known that 3-ABA is synthesized through the reaction of catalytic hydrogenation using 3-NBA as the raw material [3]. After the reaction, the unreacted 3-NBA should be separated to purify 3-ABA product. Therefore, it is necessary to investigate the separation of 3-ABA and 3-NBA.

The solubility of the chemicals is a very important parameter in $SCCO_2$ in the separation of organic compounds using $SCCO_2$ extraction technology. Thus, the solubility data of solid chemicals in $SCCO_2$ have been published in many recent literatures [4,5]. However, no solubility data of pure 3-ABA and its mixture with 3-NBA in $SCCO_2$ have been reported yet. In our previous work, the solubility of pure 3-NBA in $SCCO_2$ had been studied [6]. In this work, the binary solubility of pure 3-ABA and ternary solubility of mixed 3-ABA and 3-NBA in $SCCO_2$ was investigated.

The semi-empirical Bartle model was commonly used to correlate the solubility of chemicals in $SCCO_2$ [7]. However, it failed to reach the required prediction accuracy by traditional Bartle model, which is even lower than that by other semi-empirical models [8]. Therefore, a new semi-empirical model was proposed through the modification of traditional Bartle model.

In this paper, the binary solubility of pure 3-ABA and ternary solubility of mixed 3-ABA and 3-NBA in $SCCO_2$ were measured at temperatures of 308, 318, and 328 K within a pressure range from 10.0 to 21.0 MPa. Besides, the separation possibility of 3-ABA and 3-NBA using $SCCO_2$ extraction was investigated. The experimental solubility data were correlated by the traditional Bartle model and the modified Bartle model, respectively. Moreover, the correlation accuracy of the new model was evaluated by solubility calculation based on data of 49 different solid chemicals in the literature.

2. Experimental methods

2.1. Chemicals and raw materials

All the chemicals were used without further purification. Their detailed descriptions are listed in Table 1.

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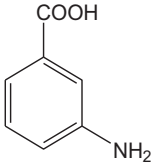
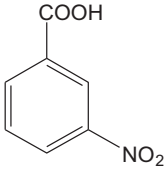
Table 1
Chemical structures of solid compounds.

Compound	Formula	Molecular structure	T_m (K)[a]	Source	Purity (%)[b]	Molar mass (g mol^{-1})
3-Aminobenzoic acid	$C_7H_7NO_2$		447.2	Beijing Hengye Zhongyuan Chemical Co., Ltd, China	99.0	137.14
3-Nitrobenzoic acid	$C_7H_5NO_4$		414.2	Beijing Hengye Zhongyuan Chemical Co., Ltd, China	99.0	167.13
Carbon dioxide	CO_2	–	–	Beijing Praxair Industrial Gas Co., Ltd, China	99.9	44.01

[a] T_m is the melting point of compound searching from the website of Chem.YQ.
[b] The purity percent is based on masses.

2.2. Experimental procedure

The solubility of 3-ABA and its mixture with 3-NBA in $SCCO_2$ was measured using a dynamic flow technique in an experimental apparatus as shown in Fig. 1. CO_2 was first introduced from a cylinder into a high-pressure surge flask and was compressed (Nova, model 5542121). Then, the high-compressed CO_2 was charged into a preheating and mixing cell with a heating electric coil, in which the temperature and pressure of CO_2 were increased to the preset operating condition. Then, $SCCO_2$ was introduced into a high-pressure equilibrium cell from the bottom consecutively. The available volume of the equilibrium cell was 150 mL. 40 or 50 g packed solute mixed with the glass beads were loaded into the cell before experiment. At both ends of the cell, stainless steel sintered disks were installed in order to prevent the physical entrainment of undissolved chemicals. The temperature of the high-pressure equilibrium cell was controlled by a constant-temperature stirred water bath (Chongqing Yinhe Experimental Instrument Corporation, model CS-530) with a temperature controller (±0.5 K). The temperature in the cell was measured by a calibrated internal platinum resistance thermometer (Beijing Chaoyang Automatic Instrument Factory, model XMT, uncertainty of ±0.1 K), and the pressure was measured by a calibrated pressure gauge (Heise, model CTUSA, uncertainty of ±0.05 MPa). $SCCO_2$ was discharged from the top of the equilibrium cell through a decompression sampling valve (wrapped with heating coils). Then, the solid sample was separated from CO_2 and collected by two U-shaped containers in turn. It was observed that nearly most of the solute was collected in the first U-shaped container and a very little sample was found in the second U-shaped one. As both 3-ABA and 3-NBA are soluble in water, the U-shaped containers were washed with deionized water. A calibrated wet gas flow meter (Changchun Instrument Factory, model LML-2, uncertainty of ±0.01 L) was used to determine the total volume of CO_2 released from the equilibrium cell at room temperature and atmospheric pressure.

In this work, the time to reach equilibrium and the suitable flow rate of CO_2 was determined respectively to ensure the reliability of the experimental procedure. The flow rate was obtained with a rotated flow meter and the results revealed that the equilibrium of system was reached at the flow rate of CO_2 of 0.3–1.0 L min^{-1}. Thus, the average flow rate of 0.6 L min^{-1} was adopted thereafter. With the suitable flow rate of CO_2, the solubility of the chemicals was measured at 20th, 30th, 40th, 50th, and 60th min, respectively. The results revealed that the system had reached equilibrium after 30 min.

2.3. Analytical methods and solubility measurements

The amount of the solutes collected in the U-shaped containers was determined with an UV spectrophotometer (UNICO, model UV-2100) with deionized water as the reference solution. The maximum UV absorption of 3-ABA was 229 nm, and that of 3-NBA was 268 nm. A calibration curve of the concentration of solute was established with the regression coefficient better than 0.9995. The mole solubility of solute in $SCCO_2$ was calculated as follows:

$$y = \frac{S \times M_1}{S \times M_1 + \rho \times M_2} \quad (1)$$

where y is the mole fraction solubility of the solute, S is the solubility of solute (g L^{-1}), M_1 and M_2 are the molecular weights of CO_2 and solute (g mol^{-1}), respectively, and ρ is the density of CO_2 at room temperature and normal atmospheric pressure (g L^{-1}).

In case of the mixed 3-ABA and 3-NBA in $SCCO_2$, the cumulative absorbance was observed in the measurements resulting from the comprehensive contribution of both 3-ABA and 3-NBA. Using UV spectrophotometer, each composition of solutes was measured in the ternary system (3-ABA + 3-NBA + $SCCO_2$) at both wavelengths of 229 nm for 3-ABA and 268 nm for 3-NBA.

In our previous papers, the reliability of the experimental apparatus had been verified by measuring the solubility of solid solutes [6,8]. Each data point listed in this paper was the average value of three replicated measurements. The uncertainty of each measurement was within ±5%.

3. Theoretical section

3.1. Empirical models

Bartle et al. correlated the enhancement factor (ratio of the actual solubility to the ideal solubility) of the solute and the density of the solvent [7]:

$$\ln\left(y_2 \frac{P}{P_2^{sub.}}\right) = a\rho_1 + b' \quad (2)$$

In Eq. (2), y_2 is the mole fraction solubility of the solute in $SCCO_2$; P is pressure (MPa); the parameter a is related to the solvation of the solute; ρ_1 is the density of $SCCO_2$ at the operating temperature and pressure (g L^{-1}); and b' comes from the vapor pressure of the solute. To solve the inconveniences of sublimation pressure $P_2^{sub.}$ estimation, Bartle et al. changed the sublimation pressure by