Fluid Phase Equilibria 409 (2016) 271–279

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Measurement and modeling for solubility of 3-hydroxybenzaldehyde and its mixture with 4-hydroxybenzaldehyde in supercritical carbon dioxide

Hao Wu, Jing Zhu, Yiwei Wang, Chengwei Chang, Junsu Jin*

Advanced Materials Research Institute of Changzhou, Beijing Key Laboratory of Membrane Science and Technology, Beijing University of Chemical Technology, Beijing, 100029, China

ARTICLE INFO

Article history:
Received 15 July 2015
Received in revised form
1 October 2015
Accepted 6 October 2015
Available online 14 October 2015

Keywords:
Solubility
3-Hydroxybenzaldehyde
4-Hydroxybenzaldehyde
Supercritical carbon dioxide
Semi-empirical model

ABSTRACT

To understand the phase behavior of 3-hydroxybenzaldehyde (3-HBA) and the solubility effect of 3-HBA and 4-hydroxybenzaldehyde (4-HBA) on each other in supercritical carbon dioxide ($SCCO_2$), the equilibrium solubility of 3-HBA and its mixture with 4-HBA, was measured in $SCCO_2$ binary system (comprising of a solute and $SCCO_2$) and ternary system (comprising of two solutes and $SCCO_2$) at temperature and pressure given in range of 308–328 K and 11.0–21.0 MPa respectively. Comparing the solubility of 3-HBA and 4-HBA between in the binary system and ternary system, it was found that the equilibrium solubility of both 3-HBA and 4-HBA was enhanced in the ternary system due to the molecular interaction. The experimental data were correlated by Chrastil, Mendez-Santiago and Teja (M-S-T), Sovova, their modified models, and Zhu et al. model. Also a new model was deduced and established based on the Chemistry Association Theory and was verified by 636 groups of solubility data. The correlated results indicated that the new model obtained a less deviation than other models, including the modified Chrastil model, the modified M-S-T model, the modified Sovova model, and Zhu et al. model, all of which have same adjustable parameters.

1. Introduction

As one of the promising technologies, supercritical fluid technology (SFT) has extensive application in the field of pharmaceuticals, cosmetics, agriculture and food, semiconductors, waste water and so on. Supercritical carbon dioxide ($SCCO_2$) is the most widely used supercritical fluid (SCF) for its temperate critical conditions, low cost, nonflammability, nontoxicity, quick diffusion, and excellent dissolving capacity [1]. Supercritical fluid extraction (SFE) is the most frequently used SFT, and its main application includes the extraction of effective compounds from a variety of complex mixtures due to its high efficiency and steady robustness [2–6]. Therefore, the solubility study on each solute of the multicomponent systems in $SCCO_2$ is essential to design the $SCCO_2$ extraction process. Furthermore, the solubility of each component in mixture is usually different from that in their respective binary system due to the factors such as hydrogen bonding and relative position of functional groups of solute molecules [7,8]. Each solute may behave as a solid cosolvent resulting to the solubility enhancement of the other [8–10]. However, currently, most of the investigations on solid solubility have been concerned with the binary system consisting of one solute in SCF [11]. Therefore, the solubility research of multiple system is important. To the best of our knowledge, the equilibrium solubility of 4-hydroxybenzaldehyde (4-HBA) in $SCCO_2$ was found in our previous work [12]; however, there is no solubility data of 3-hydroxybenzaldehyde (3-HBA) and its mixture with 4-HBA in $SCCO_2$ reported so far.

In this work, the solubility of 3-HBA in $SCCO_2$ binary system and each solute in 3-HBA + 4-HBA + $SCCO_2$ ternary system was measured with the dynamic method in the temperature and pressure range of 308–328 K and 11.0–21.0 Mpa respectively. 3-HBA and 4-HBA isomers with high purity are important chemical materials and intermediate to industrial chemistry, which are widely used in medicine manufacturing and perfume industry [13,14], so it is necessary to propose the optimal separation or purification operation condition of its isomeric mixtures by the $SCCO_2$ extraction process. The effect of a solute on other's solubility in the ternary system was investigated from the aspect of molecular

* Corresponding author.
E-mail address: jinjs@mail.buct.edu.cn (J. Jin).

http://dx.doi.org/10.1016/j.fluid.2015.10.012
0378-3812/

interaction and the relative position between formyl (−CHO) and hydroxyl (−OH). In addition, the experimental solubility in the ternary system was correlated with seven semi-empirical models which were already published. Furthermore, based on the Chemistry Association Theory, a new semi-empirical model was established for correlating the solubility of two solutes mixture in $SCCO_2$, and the correlated results of the new model were compared with other four models having same number of adjustable parameters.

2. Experiments

2.1. Materials

The basic information on chemicals used in this work is listed in Table 1, including the CAS number, provenance, and purity. All of these reagents were used without further purification.

2.2. Apparatus and procedure

Fig. 1 shows the schematic diagram of experimental apparatus. The detailed experimental procedure description on how to measure the equilibrium solubility of solutes mixture in $SCCO_2$ has been reported in our previous work [15,16].

CO_2 flowed into the surge flask from CO_2 cylinder by a high-pressure syringe pump (Nova, model 5542121) with constant pressure operating capability for pure CO_2. Using a pressure regulating valve, the fluid was compressed into a preheating cell wrapped with heating bands and then it was injected into the high-pressure equilibrium cell (volume 150 mL). The equilibrium cell was loaded with 8.0 g solute or solute mixture (mass ration 1:1 for 3-HBA and 4-HBA) and immersed in the constant-temperature stirred water bath (Chongqing Yinhe Experimental Instrument Corporation, model CS-530, accuracy ±0.01 K). Under the experimental temperature and pressure, the $SCCO_2$ and solute acquired equilibrium after 30 min when the solubility did not increase with longer equilibrium time. After phase equilibrium, the $SCCO_2$ flowed out from the top of the equilibrium cell through a decompression sampling valve (wrapped with heating coils), and the solid compound was separated from CO_2 and collected by two U-shaped tubes in turn. The volume of CO_2 was measured by the wet-gas flow meter.

The flow rate of CO_2 was optimized from 0.1 to 1.5 L/min, and 0.4 L/min was kept in all the experimental measurements because the solubility of solute was found to be maintained at all the values of CO_2 flow rate less than 0.4 L/min. The experimental temperature and pressure was measured by a resistance thermometer (Beijing Chaoyang Automatic Instrument Factory, model XMT, uncertainty ±0.1 K) and a pressure gauge (Heise, model CTUSA, uncertainty ±0.05 MPa).

In this work, each reported data was an average of three or more repeated measurements and the solubility data obtained was found to be reproducible within ±5%.

2.3. Analytical method

The solute collected in the U-shape tube was analyzed by gas chromatography (Shimadzu, model GC-2014C). The type of gas chromatographic column used in this work was Rtx-1 (30 m, 0.25 mm, 0.25 μm). The calibration curves of both 3-HBA and 4-HBA were determined with regression coefficients more than 0.9990. The temperatures of the sample injector and detector compartment were set at 533 K, and the temperature in column was 423 K. High-purity nitrogen, as the carrier gas, was regulated at flow rate of 1.2 mL/min. The solute collected in the clean U-shape tube was dissolved in anhydrous ethanol and to be analyzed at least five times for each experimental condition.

2.4. Correlation models

In this work, Chrastil [17], M-S-T [18], and Sovova [19] models were used for solubility correlation. Some researchers analyzed the influence of the molecular interaction of solutes on the equilibrium solubility and pointed out the modified models could make the solubility correlation more accurate. Therefore, the modified Chrastil [20], the modified M-S-T [21] and the modified Sovova [22] models were also introduced in this work to correlate the mixture solubility of each solute in $SCCO_2$. Zhu et al. model [7], another semi-empirical model with four adjustable parameters, was also adopted for comparing the correlation results of semi-empirical models with the same adjustable parameters.

3. Results and discussion

3.1. Solubility in the binary system

The equilibrium solubility of 3-HBA (y_{b1}) in pure $SCCO_2$ under all operating conditions are listed in Table 2 and plotted in Fig. 2. The value range of y_{b1} is from 2.51×10^{-5} to 60.11×10^{-5} mol mol^{-1}, which is more than that of 4-HBA (from 0.73×10^{-5} to 13.77×10^{-5} mol mol^{-1}) at the same operating condition also listed in Table 2. Fig. 2 describes that y_{b1} increases with the increasing pressure at each temperature. The increment of solubility is mainly caused by the increase of $SCCO_2$ density, which is dominated by the operation pressure. The high pressure causes the molecular interaction between CO_2 and 3-HBA being in an intense situation. However, the effect of temperature on solubility is more complicated than that of pressure because the temperature affects not only the density of $SCCO_2$ but also the vapor pressure of solute. With increasing temperature, the vapor pressure of solute increases with the reduced density of $SCCO_2$, which results in a crossover pressure region between (11.8 and 12.8) MPa. When the pressure is higher than the crossover region, the vapor pressure of solute dominates the solubility rising with increasing temperature; when the pressure is lower than the crossover region, the solubility is mainly influenced by the density of $SCCO_2$, which decreases with increasing temperature.

3.2. Solubility in the ternary system

The equilibrium solubility data of 3-HBA and 4-HBA in the ternary system (3-HBA + 4-HBA + $SCCO_2$), is also summarized in Table 2. As shown in Table 2, the trend for the effect of pressure and temperature on the solubility of each solute in the ternary system is

Table 1
Specification of chemicals.

Chemicals	CAS no.	Provenance	Mass fraction purity
3-Hydroxybenzaldehyde	100-83-4	Aladdin Chemistry Co. Ltd.	>97.0%
4-Hydroxybenzaldehyde	123-08-0	Aladdin Chemistry Co. Ltd.	>98.0%
Carbon dioxide	124-38-9	Beijing Praxair Industrial Gas Co. Ltd., China	>99.9%
Nitrogen	7727-37-9	Beijing Praxair Industrial Gas Co. Ltd., China	>99.999%
Anhydrous ethanol	64-17-5	Beijing Chemical Reagent Factory, China	>97.0%