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Determination and calculation for solubility of *m*-nitroaniline and its mixture in supercritical carbon dioxide

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ABSTRACT

Equilibrium solubility of *m*-nitroaniline and *p*-nitroaniline in supercritical carbon dioxide ($SCCO_2$) is essential to design the process of $SCCO_2$ extraction and to investigate the effect of each solute on the solubility in $SCCO_2$ ternary system. However, the solubility data is not reported so far. We performed the solubility measurements at the temperatures of 308–328 K and in the pressure range of 11.0–21.0 MPa. The experimental results showed the solubility of *m*-nitroaniline and *p*-nitroaniline was enhanced in *m*-nitroaniline + *p*-nitroaniline + $SCCO_2$ ternary system. The improvement factor (i), separation factor (μ) and separation efficiency (*HE*) in the ternary system were defined and calculated, and the best separation result could be obtained at 21.0 MPa and 328 K using $SCCO_2$ extraction, where the separation efficiency was up to 90.9%. Based on the chemical association theory, a new model was developed to calculate the solubility of mixed solutes in $SCCO_2$. The correlation result of the new model was tested by about 500 solubility data from 15 kinds of two solutes mixtures in $SCCO_2$. The correlated result showed that the new model could achieve much better *AARD* (%) than those of frequently used Sovova and Sovova-T models.

Keywords: Solid mixture solubility; *m*-Nitroaniline; *p*-Nitroaniline; Supercritical carbon dioxide; Model

1. Introduction

m-Nitroaniline (*m*-NA) and *p*-Nitroaniline (*p*-NA) are all important intermediates for organic material synthesis and azoic dyes for the dye industry (Chung et al., 1997; Dubrow et al., 1996; Zhang et al., 2006). However, anilines have been listed as the priority pollutants by many countries due to their toxicity, potential carcinogenic and mutagenic effects (Suna et al., 2007), and are difficult to be eliminated (Nair et al., 1990). Because the nitro group in aromatic ring resists chemical and biological oxidation degradation, the two compounds are difficult to be degraded too. Unfortunately, the two compounds usually exist together in industrial wastewater and cause pollution. There may be ways to remove aniline compounds from wastewater (Gautam et al., 2005; Saupe, 1999; Spacek et al., 1995). However, to our best knowledge, few processes have been published to effectively and efficiently separate them.

Nowadays, different separation technologies are used in the industrial development to obtain high-purity products. As one of novel effective separation technologies, supercritical fluid technology has been paid more attention in different processes in recent 30 years. Supercritical fluid extraction technology plays an important role in separating solid mixtures (Lucien and Foster, 2000). Carbon dioxide (CO_2) has some unique properties, such as mild critical conditions, nontoxic, readily separated and inexpensive. Thus, CO_2 is usually used as a supercritical solvent in many supercritical fluid processes. Most of the solubility measurements in supercritical carbon dioxide ($SCCO_2$) were found in solid solute + solvent system and solute + solvent + cosolvent system; whereas solubility

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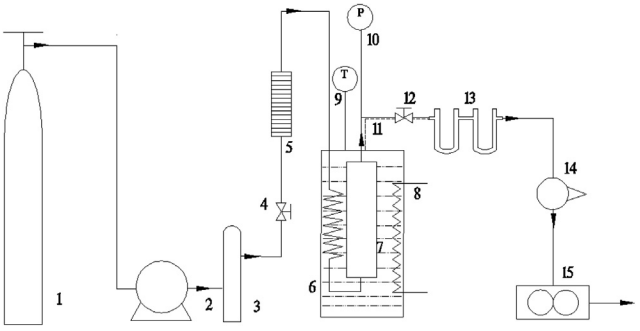

Fig. 1 – Schematic diagram of the experimental apparatus: 1, CO_2 high-pressure cylinder; 2, Nova compressor; 3, high-pressure surge flask; 4, pressure micrometering valve; 5, preheating cell; 6, constant-temperature stirred water bath; 7, high-pressure equilibrium cell; 8, preheating coils; 9, platinum resistance thermometer; 10, calibrated pressure gauge; 11, heating coils; 12, decompression sampling valve; 13, two U-shaped containers; 14, rotated flow meter; 15, wet gas flow meter.

research on mixed solid solutes in $SCCO_2$ has been rarely reported (Fonseca et al., 2011).

In order to separate *m*-NA and *p*-NA mixture with supercritical fluid extraction technology, the solubility of *m*-NA and *p*-NA should be measured firstly in $SCCO_2$ binary or ternary system. Recently, our team has reported the solubility of *p*-NA in $SCCO_2$ with and without cosolvent (Jin et al., 2013). However, the solubility of pure *m*-NA and its mixture with *p*-NA in $SCCO_2$ has not been found in previous literature.

In this work, the solubility of pure *m*-NA and its mixture with *p*-NA was measured in $SCCO_2$ binary and ternary systems by the dynamic method from 11.0 to 21.0 MPa at temperature of 308 K, 318 K and 328 K. Moreover, the improvement factor (*i*), separation factor (μ) and separation efficiency (*HE*) were defined and calculated. Based on the chemical associated theory, a new semi-empirical density model was developed to calculate the solubility of each solute in two solutes mixture for 15 kinds of systems in $SCCO_2$, and the correlated results of the new model were compared with Sovova (Sovova, 2001) and Sovova-T (Tang et al., 2010) models, respectively.

2. Experiment

2.1. Materials

m-NA and *p*-NA were supplied by Beijing Hengye Zhongyuan Co., Ltd., with mass fraction of more than 99.7% and 99.5%, respectively. The melting points of *m*-NA and *p*-NA are 387 K and 419 K, respectively. CO_2 with a purity of more than 99.9% (mass fraction) and nitrogen with a purity of 99.999% were both obtained from Beijing Praxair Industrial Gas Co. Ltd. The nitrogen gas was used as carrier gas of GC. Anhydrous ethanol (with mass purity of more than 99.7%) was obtained from Beijing Chemical Reagent Factory. All chemicals were used without further purification.

2.2. Apparatus and procedure

The schematic diagram of the solubility measurement apparatus is shown in Fig. 1, which has been described in detail previously (Tang et al., 2012; Tian et al., 2007a,b).

Approximately 8 g *m*-NA or 8 g solid solute mixture (*m*-NA and *p*-NA, mole fraction 1:1), which was ground to pulverized powder and distributed into three layers to prevent channeling, was charged into the high-pressure equilibrium cell of 150 mL effective volume at the beginning of experiment. Pure CO_2 from a cylinder firstly flowed into a high-pressure surge flask by the compressor (Nova, model 5542121). By controlling the pressure micrometering valve, CO_2 entered into a preheating cell with an electric coil so that its temperature and pressure could reach to the operating condition. Then $SCCO_2$ flowed into a high pressure equilibrium cell loaded by solute with glass beads and stainless steel sintered disks at both ends to prevent physical entrainment of undissolved solute. The cell was immersed into a constant-temperature stirred water bath (Chongqing Yinhe Experimental Instrument Corporation, model CS-530), and its temperature was controlled by a temperature controller with accuracy of ±0.5 K. The temperature and pressure of the equilibrium cell were measured by a calibrated internal platinum resistance thermometer (Beijing Chaoyang Automatic Instrument Factory, model, XMT) and a calibrated high precision pressure gauge (Heise, model CTUSA), with accuracy of ±0.1 K and ±0.05 MPa, respectively. After achievement of equilibrium in 40 min, the decompression sampling valve wrapped with heating coil was opened. Then CO_2 saturated with solute expanded into a two U-shaped tubes of normal pressure and temperature at a flow rate of 0.4 L/min. Close the decompression sampling valve in 20 min to ensure that the amount of dissolved solute is enough to be analyzed. The volume and flow rate of CO_2 were measured by a calibrated wet-gas flow meter (Changchun Instrument Factory, model LML-2) and a rotated flow meter, respectively. The total volume of CO_2 was measured with an uncertainty of 0.01 L at room temperature and atmospheric pressure during the experiment. The collected samples were dissolved by anhydrous ethanol and analyzed by the Gas Chromatography (Shimadzu, GC-2014C).

In order to determine the equilibrium time, the solubility was measured at different equilibrium time from 10 to 60 min. Experiment result showed that the solubility was constant and achieved a maximum value when the time was more than 30 min. Therefore, 40 min was chosen as the required equilibrium time. In order to determine the suitable flow rate of CO_2, the solubility was measured at the range from 0.3 to 1.0 L/min for CO_2, and it was found that the solubility did not change when the flow rate was less than 0.6 L/min. So, the flow rate of 0.4 L/min was adopted in this work.

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

2.3. Analytical method

The external standard method was adopted to analyze the mass concentration (c) of *m*-NA and *p*-NA in $SCCO_2$ by GC-2014C. In this work, the column used was GsBP-5 (30 m × 0.25 mm × 0.25 μm) and the column temperature was set at 175 °C; the injector temperature and detector temperature were set as 250 °C and 300 °C, respectively. The carrier flow rate was 0.3 L/min and the split ratio was chosen as 50:1. A standard curve was obtained with the regressed coefficient better than 0.9995. The solubility of each solute for the