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Determination and modelling of solubility of *o*-aminobenzamide and its mixture with *o*-nitrobenzoic acid in supercritical carbon dioxide

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ABSTRACT

To research functional group effect on the solubility of *o*-aminobenzamide (*o*-AB) and *o*-nitrobenzoic acid (*o*-NBA) for each other, solubility of *o*-AB and its mixture with *o*-NBA in supercritical carbon dioxide ($SCCO_2$) was measured with dynamic method at temperatures ranging from 308 to 328 K and pressures ranging from 10.0 to 21.0 MPa. Then solubility of *o*-AB and *o*-NBA was correlated with four commonly used expanded liquid models. In addition, 2365 solubility data of 90 kinds of solid solute, coupled with solubility of *o*-AB and *o*-NBA in this work (2425 data points in total), were used to compare the correlation accuracy of the four expanded liquid models, and the best correlation accuracy was obtained by $\delta_2 \sim \delta_1/v_1$ model.

To evaluate the effect of heat capacity terms that is usually ignored during the derivational process of expanded liquid models, a new expanded liquid method (M-δ_1/v_1 model) was proposed based on $\delta_2 \sim \delta_1/v_1$ model and tested by the above mentioned 2425 groups of solubility data. The correlated results showed that M-δ_1/v_1 model achieved the minimum average absolute relative deviation (AARD, %) 9.72% among the five models of 30.05%, 14.22%, 13.91%, 15.07% for $\delta_2 \sim \rho$, $\delta_2 \sim \rho^d$, $\delta_2 \sim \delta_1/v_1$, and $\beta_{12} \sim \rho^2$ models, respectively. Furthermore, the result of statistical tests of $\delta_2 \sim \delta_1/v_1$ and M-δ_1/v_1 models indicated that the best correlation accuracy of M-δ_1/v_1 model could be attributed to the additional consideration of the heat capacity terms, rather than the more adjustable parameters.

1. Introduction

With efficient and broad spectrum biological activity and friendly environmental compatibility, *o*-aminobenzamide (*o*-AB) has received more attention. *o*-AB is the fluorescence label of oligosaccharide materials [1]. It is used in the discovery of a stable macrocyclic *o*-AB Hsp90 inhibitor [2], as well as in the development of nanoscale liquid chromatography-mass spectrometry of *o*-AB-labeled oligosaccharides at low femtomole sensitivity [3]. Moreover, *o*-AB is a part of microwave activated synthesis of quinazolin-4(3H)-one derivatives [4], and participates in the synthesis of new histone deacetylase inhibitors [5]. As known to all, *o*-AB can be synthesized by *o*-nitrobenzoic acid (*o*-NBA), thionyl chloride, ammonium hydroxide, and reductant; in addition, both *o*-AB [6] and *o*-NBA [7] are important intermediate for organic synthesis. Therefore, the separation of *o*-AB and *o*-NBA is important and necessary for accelerating the synthetic reaction, and purifying or recycling the two compounds in laboratorial and industrial application. However, the melting points of *o*-AB (384.4 K) [8] and *o*-NBA (419 K) [9] are so close that it is difficult to separate them with methods of melting and crystallization; what's worse, *o*-AB and *o*-NBA are all organic compounds that it is difficult to separate them with traditional solvent extraction, which might introduce impurity during the separation process. Until now, there is no effective method for separation of *o*-AB and *o*-NBA. Thus, a novel separation method should be proposed.

As a green environmental protection technique, supercritical fluid technology (SFT) has attracted much more attention due to the specific character of supercritical fluid in recent years [10–14], such as small viscosity, high diffusivity, strong dissolving capacity, and good selectivity. Although supercritical carbon dioxide ($SCCO_2$) has modest or even very reduced solvent power in the case of polar compounds, $SCCO_2$ is still the most commonly used supercritical fluid (SCF) because of many unique characters such as mild critical conditions, nonflammable, non-explosive and non-toxic; and especially it is readily separated, easy to be obtained and recycled, and inexpensive. Using $SCCO_2$ extraction process, many mixed solutes were separated and purified for field of food, medicine, health products, chemical application and so on [15,16]. Thus, $SCCO_2$ was used as solvent in this work.

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Nomenclature

y_1	Mole fraction of solvent (mol mol^{-1})
y_2	Solubility of solute in supercritical fluid (mol mol^{-1})
y_b	Mole fraction of solute in $SCCO_2$ binary system (mol mol^{-1})
y_t	Mole fraction of solute in $SCCO_2$ ternary system (mol mol^{-1})
$y_{exp.}$	Experimental solute solubility (mol mol^{-1})
$y_{cal.}$	Calculated solute solubility (mol mol^{-1})
N	Number of solubility data per system
Z	Number of adjustable parameters
EF	Enhancement factor
SF	Separation factor
SE	Separation efficiency
SD	Standard deviation
AARD	Average absolute relative deviation (%)
AARD′	New average absolute relative deviation (%)
γ_2	Activity coefficient of solute
γ_2^∞	Infinite dilution activity coefficient of solute
f_2^s	Fugacity of solute in solid phase (MPa)
f_2^l	Fugacity of solute in liquid phase (MPa)
ΔH_m	Melting enthalpy of solute (kJ/mol)
E	Cohesive energy (J)
T_m	Melting point of solute (K)
T	Operational temperature (K)
P	Operational pressure (MPa)
ρ	Density of supercritical solvent (g/L)
R	Gas constant 8.314 J/(mol K)
Δc_p	Difference of heat capacity of solute between the liquid and solid phase J/(kg·K)
V	Volume of solvent (m^3)
v_1	Molar volume of solvent (m^3/mol)
v_2^l	Molar volume of solute (m^3/mol)
ϕ_1	Volume fraction of the solvent
δ_1	Solubility parameters of solvent (MPa$^{0.5}$)
δ_2	Solubility parameters of solute (MPa$^{0.5}$)
β_{12}	Binary interaction parameter
a^0-a^3,b^0-b^3, c^3,d,k,n	Adjustable parameters

Solubility data of solute with SCF in multicomponent system is the the key property for application of SFT. Therefore, solubility measurement of *o*-AB and *o*-NBA in ternary system (solute mixture + $SCCO_2$) is important for *o*-AB and *o*-NBA separation; the solubility of *o*-AB and *o*-NBA in binary system is also necessary for solubility comparison between in binary and ternary system to evaluate the effect of one solute on solubility of the other. Moreover, nitro group (—NO_2) and carboxylic acid group (-COOH) of *o*-NBA are both electron-withdrawing group [17,18], while amino group (-NH_2) of *o*-AB is electron-donating group [18] that intermolecular hydrogen bonding may be formed between molecules of *o*-NBA and *o*-AB. Therefore, analysis of functional group effect on solubility of *o*-NBA and *o*-AB in $SCCO_2$ is also significant and efficient.

To the best of our knowledge, solubility of *o*-NBA in $SCCO_2$ binary system has been measured in our previous work [17]. In this work, solubility of *o*-AB and its mixture with *o*-NBA in $SCCO_2$ was measured at temperatures of 308, 318, 328 K and pressure range from 10.0 to 21.0 MPa. The enhancement factor (EF), separation factor (SF) and separation efficiency (SE) were also defined and calculated to decide whether $SCCO_2$ extraction technology could be used to separate and purify the mixture of *o*-AB and *o*-NBA.

Experimental determination of solute solubility with SFT at high pressures is time-consuming and high cost. Therefore, modelling of solubility data in $SCCO_2$ is helpful to predict solubility at supercritical condition. Expanded liquid models are theoretically deduced and property parameters needed are easily obtained; therefore, the expanded liquid models are widely used for solubility correlation and prediction. In this work, the solubility of *o*-AB and *o*-NBA was correlated with four common expanded liquid models, including $\delta_2 \sim \rho$ model, $\delta_2 \sim \rho^d$ model, $\delta_2 \sim \delta_1/v_1$ model, and $\beta_{12} \sim \rho^2$ model. For $\delta_2 \sim \rho$ model, solubility parameter of solute (δ_2) and solvent density (ρ) is linear relation; for $\delta_2 \sim \rho^d$model, δ_2 is power function of ρ; for $\delta_2 \sim \delta_1/v_1$ model, δ_2 is linear fit of the ratio of the solvent's solubility parameter (δ_1) and its molar volume (v_1); for $\beta_{12} \sim \rho^2$ model, variable β_{12} is quadratic function of ρ with δ_1 and δ_2 are both constants. To investigate the effect of heat capacity terms on correlation accuracy of expanded liquid model, a new expanded liquid model (M-δ_1/v_1 model) was proposed based on $\delta_2 \sim \delta_1/v_1$ model and verified by 2425 solubility data (from 92 kinds of solid solute), and the calculation result was compared with those of above four expanded liquid models.

2. Experiment

2.1. Materials

o-AB (with mass purity of more than 98%) and *o*-NBA (with mass purity of more than 99%) were obtained from Aladdin Chemistry Co., Ltd and Sinopharm Chemical Reagent Beijing Co., Ltd., respectively. The physicochemical properties [8,9,19] of the two solutes are given in Table 1. Carbon dioxide (CO_2) with mass fraction more than 99.9% was obtained from Beijing HuaNeng Gas Co., Ltd. The 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

In this work, solubility of *o*-AB and *o*-NBA in $SCCO_2$ was measured with dynamic method. The schematic diagram of solubility measurement apparatus, which has been described in our previous work [20,21], is shown in Fig. 1. The reliability of this apparatus has also been tested [22].

The main equipment of this experiment was the high-pressure equilibrium cell. Before the solubility measurement, about 10 g solid solute (mole ratio 1:1 for solutes mixture) mixed with glass beads was loaded and distributed for 3 layers in the high-pressure equilibrium cell to avoid channeling and dead volume; and the stainless steel sintered disks at both ends of the cell were used to prevent entrainment. Firstly, pure CO_2 from CO_2 cylinder was pressurized into the high-pressure surge flask by the compressor (Nova, model 5542121, Switzerland) with constant pressure operating capability for pure CO_2. The high pressure CO_2 was then introduced into the preheating cell heated with electrical heating band in order to reach to the experimental temperature and pressure in advance. Secondly, $SCCO_2$ entered into the high-pressure equilibrium cell with uncertainty of ±0.1 K for temperature and ±0.05 MPa for pressure, which was immersed in the constant-temperature stirred water bath (Chongqing Hongrui Experimental Instrument Co., model CS503F, China) with uncertainty of ±0.01 K. At last, solvent and solute reached equilibrium after 40 min when solubility would not increase with increasing