J. of Supercritical Fluids 73 (2013) 63–69

Contents lists available at SciVerse ScienceDirect

The Journal of Supercritical Fluids

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

Measurement and correlation of quaternary solubilities of dihydroxybenzene isomers in supercritical carbon dioxide

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ARTICLE INFO

Article history:
Received 19 September 2012
Received in revised form 5 November 2012
Accepted 5 November 2012

Keywords:
Quaternary solubilities
Dihydroxybenzene isomers
Ternary systems
Wilson activity coefficient model

ABSTRACT

The equilibrium quaternary solubilities of dihydroxybenzene (resorcinol + pyrocatechol + hydroquinone + $SCCO_2$) isomers were experimentally determined at 308, 318 and 328 K over a pressure range of 9.8–15.7 MPa by using a saturation method. The effects of temperature, pressure and the components on each other have been thoroughly investigated. The selectivity of $SCCO_2$ for ternary (resorcinol + pyrocatechol + $SCCO_2$) and quaternary systems was discussed. A new model equation for quaternary solubilities of solids has been developed by accounting for non-idealities by combining the solution model with Wilson activity coefficient model. The model equation has five adjustable parameters and correlates the quaternary solubilities of current data along with two other quaternary data reported in the literature.

1. Introduction

Supercritical fluids find applications in many chemical processes [1–4] due to several advantages such as liquid like densities and gas like transport properties. The knowledge of solubility of a solid in a particular solvent is important in determining the feasibility of separation processes. The non-toxicity and ambient critical temperature of carbon dioxide makes it an often used supercritical fluid. The solute of interest is normally present along with multiple components, and the multi-component behavior of the solute differs from its pure component solubilities [5]. Thus the determination of multi-component solubilities in supercritical carbon dioxide ($SCCO_2$) is essential.

Depending upon the position of the functional groups, a large variation in the magnitude of solubilities of positional isomers (ortho-, meta-, and para-) in $SCCO_2$ is observed [6–8]. The difference in the component solubilities of individual isomers in $SCCO_2$ when present in a mixture indicates that solute–solute, solute–solvent interactions play a major role in determining the solute solubilities. The interactions between the molecules become more significant in determining the multi-component solubilities of solids in $SCCO_2$ [5]. To understand the existing interactions (solute–solute, solute-cosolutes, solute–solvent, cosolute–solvent) in the solution, the systems need to be investigated in detail. The increment or decrement in the solubilities of solute in the presence of the other components depends upon the interactions between the molecules.

Since experimental determination of solubilities of solids is expensive, models are used to correlate and correlate the solubilities at various conditions. Models based on equations of state [9,10] have been developed but these demand critical properties that require group contribution techniques. Therefore, several empirical models such as the solvate complex models [11–14], association models [15,16] and density-based models [17–19] have been developed. However, these models cannot be used to correlate solid mixtures because they do not account for the concentration of the cosolute.

The solubilities of binary systems (solute + $SCCO_2$) have been extensively investigated, as summarized in reviews [20–22] and several models have been developed. However, ternary solubilities (two solids + $SCCO_2$) have not been investigated extensively. To the best of our knowledge, the ternary solubilities of only 24 systems have been investigated. Further, there are very few models available for the solubilities of ternary systems [23–25]. There are only two systems for which quaternary (three solids + $SCCO_2$) solubilities have been reported [26,27] and no models are available for these systems.

The objective of this work is to investigate the ternary and quaternary mixture solubilities of dihydroxybenzene solid isomers in $SCCO_2$ at different temperatures and pressures. The effect of hydroquinone on quaternary solubilities of resorcinol and pyrocatechol along with the selectivity of $SCCO_2$ for this mixture has been studied. The solid mixture solubilities depend on the composition of other components and the interactions between the molecules. Our research objective is to develop a model equation which

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http://dx.doi.org/10.1016/j.supflu.2012.11.003

incorporates cosolutes composition and the interaction between the molecules. The mixture solubilities were correlated by using a model equation which has been derived based on solution model with activity coefficients. The performance of the model equation has been verified for the current quaternary system along with two other quaternary systems.

2. Experimental

2.1. Materials used

Carbon dioxide (CAS 124-34-9) with 99 wt% was obtained from Vinayaka Gases (India) was purified to 99.9% after passing it through silica bed. Dihydroxybenzene isomers (ortho-, CAS number 120-80-9, 98 wt%; meta-, CAS number 108-46-3, 99 wt%; and para-, CAS number 123-31-9, 99 wt%) and 1,4 dioxane (CAS number 123-91-1, 99 wt%) (HPLC grade) were purchased from Merck (India).

2.2. Solubility measurement

The flow apparatus with saturation method was employed to determine the solubilities of dihydroxybenzene isomers mixture in $SCCO_2$. A detailed description of the operation of the equipment has been presented in our previous work [23,24]. Carbon dioxide from cylinder was liquefied and pressurized by passing it through a pump (Jasco PU-1580). Pressurized CO_2 was passed through an oven, which was maintained at the desired temperature. This was then passed through the columns which were filled with the solid mixture alternatively with glass wool. The solid mixture with 1:1:1 mole ratio was finely grounded into fine powder of particle size less than 150 μm (~100 mesh) and the entrainment of the solid mixture from the columns was prevented by 2 μm filters which were fitted at the end of the columns. To ensure saturation, a flow rate of 0.2 cm^3/min was used and the experiments were run for 2 h. The stream was then expanded in the glass trap where the samples are collected and further analyzed by using HPLC. The experiments were conducted at a maximum temperature of 328 K, which is well below the melting point of the individual components (the melting points of the resorcinol, pyrocatechol and hydroquinone are 383, 378 and 445 K respectively). The temperature and pressure were controlled within ±0.1 K and ±0.2 MPa of operated temperature and pressure, respectively. The relative deviation in the mole fraction of the solubilities of the components was found to be ±4% of the reported data.

2.3. Analysis of dihydroxybenzene mixtures

The dihydroxybenzene isomers mixture was analyzed by using high performance liquid chromatograph (HPLC) (Waters 2407) with variable wavelength UV detector set at 280 nm. A reverse phase C18 column was used for the separation of isomers. 4 vol% of dioxane in deionized water was used as the eluent [28]. A flow rate of 0.2 cm^3/min was maintained to ensure separation of isomers and distinct peaks at 2, 5.9 and 7.4 min were obtained for hydroquinone, resorcinol and pyrocatechol, respectively. Pure samples of these compounds were injected initially and a calibration curve for each compound was obtained.

3. Theoretical model

The solubility of solid solute either increases or decreases to a greater extent in the presence of other components. In our previous studies on solid mixture solubilities, a new semi-empirical model equation has been derived with the solution model in combination with activity coefficients for ternary systems [23]. The same has been extended for quaternary systems studied here. At equilibrium, the fugacity of the solute in solid phase (sp) is equal to the fugacity of solute in $SCCO_2$.

$$f_2^{\mathrm{sp}} = f_2^{\mathrm{SCCO_2}} \tag{1}$$

From regular solution model [29], the fugacity of the solute in $SCCO_2$ is expressed as

$$f_2^{\mathrm{SCCO_2}} = x_2 \gamma_2 f_2^{\mathrm{l}} \tag{2}$$

where f_2^{l} represent fugacity of solute in liquid phase. Substituting Eq. (2) in Eq. (1) and applying logarithm

$$\ln \frac{f_2^{\mathrm{sp}}}{f_2^{\mathrm{l}}} = \ln\ x_2 + \ln \gamma_2 \tag{3}$$

The ratio of fugacities of a component in solid to liquid was obtained in terms of heat of fusion (ΔH_2^{f}) and melting temperature of the solute ($T_{2,\mathrm{m}}$) by neglecting heat capacities of the components as [29]

$$\ln \frac{f_2^{\mathrm{s}}}{f_2^{\mathrm{l}}} = \frac{\Delta H_2^{\mathrm{f}}}{R} \left(\frac{1}{T_{2,\mathrm{m}}} - \frac{1}{T} \right) \tag{4}$$

Eq. (4), when substituted in Eq. (3), results in

$$\ln\ x_2 = \frac{\Delta H_2^{\mathrm{f}}}{R} \left(\frac{1}{T_{2,\mathrm{m}}} - \frac{1}{T} \right) - \ln\ \gamma_2 \tag{5}$$

The activity coefficient in Eq. (5) was obtained by using Wilson activity coefficient model [30],

$$\ln\ \gamma_i = 1 - \ln \left(\sum_j x_j \lambda_{ij} \right) - \sum_k \frac{x_k \lambda_{ki}}{\sum_j x_j \lambda_{kj}} \tag{6}$$

where $\lambda_{ij} = 1$ for $i = j$, $\lambda_{ij} \neq \lambda_{ji}$ and $\lambda_{ij} = (V_j/V_i)\exp(-a_{ij}/RT)$, where V_j, V_i are molar volumes of the components and a_{ij} is the interaction potential between the components i and j, respectively. In order to know the effect of the other components on the solubilities of solute, the infinite dilute activity coefficient of solute is expressed in terms of other solid components. Because the solubilities of solid solute in $SCCO_2$ is small, the infinite dilute activity coefficient model can be applied

$$\begin{aligned} \ln\ \gamma_2^{\infty} = {} & 1 - \ln(x_1\lambda_{21}) - \ln\left(1 + \frac{x_3\lambda_{23} + x_4\lambda_{24}}{x_1\lambda_{21}}\right) \\ & \times \left(\frac{x_1\lambda_{12}}{x_1 + x_3\lambda_{13} + x_4\lambda_{14}} + \frac{x_3\lambda_{32}}{x_1\lambda_{31} + x_3 + x_4\lambda_{34}} \right. \\ & \left. + \frac{x_4\lambda_{42}}{x_1\lambda_{41} + x_3\lambda_{43} + x_4} \right) \end{aligned} \tag{7}$$

The logarithm term was expanded by neglecting the higher order terms as

$$\ln\left(1 + \frac{x_3\lambda_{23} + x_4\lambda_{24}}{x_1\lambda_{21}}\right) \approx \frac{x_3\lambda_{23} + x_4\lambda_{24}}{x_1\lambda_{21}} \tag{8a}$$

The following inequalities are assumed to be valid for the solid mixture solubilities in $SCCO_2$,

$$x_1 \gg (x_3\lambda_{13} + x_4\lambda_{14}) \tag{8b}$$

$$x_1\lambda_{31} \gg (x_3 + x_4\lambda_{34}) \tag{8c}$$

$$x_1\lambda_{41} \gg (x_3\lambda_{43} + x_4) \tag{8d}$$

The mole fraction of carbon dioxide is represented by x_1 and is simply equal to $1 - x_2 - x_3 - x_4$. Therefore, the above inequalities can be rewritten as

$$(x_3\lambda_{13} + x_4\lambda_{14}) + x_2 + x_3 + x_4 \ll 1 \tag{8e}$$