Solubility of polyvinyl alcohol in supercritical carbon dioxide and subcritical 1,1,1,2-tetrafluoroethane

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A B S T R A C T

To understand the phase behavior of polyvinyl alcohol (PVA) in supercritical and subcritical fluids, the solubility in supercritical carbon dioxide ($SCCO_2$) and subcritical 1,1,1,2-tetrafluoroethane (sub-R134a) was determined for a couple of PVA which differ in their molecular weights. At temperatures of 313, 323 and 333 K, the solubility of PVA was measured in $SCCO_2$ with the dynamic method in the pressure range of 9.0–18.0 MPa and in sub-R134a with the static method from 7.0 to 15.0 MPa. The solubility parameters (δ) of $SCCO_2$ and sub-R134a at the experimental condition were calculated with Huang's equation of state and Giddings's equation, respectively. The effects of pressure, temperature, solute molecular weight, and solvent type on solute solubility were analyzed from the view of solvent density, solvent polarity, interaction between solvent and solute, solubility enhancement factor (*SE*), and solubility parameter. Five semi-empirical models (Chrastil, K-J, M-S-T, S-S, and Bartle models) were used to correlate the solubility data of PVA in $SCCO_2$ and sub-R134a, and satisfactory correlation results were obtained.

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1. Introduction

Supercritical fluids (SCFs) have been widely applied in the field of extraction [1], reaction [2], dye [3], nanometer material [4] and so on, due to their unique characteristics of high diffusivity, large density, low viscosity, and low surface tension. In recent decades, researches show that SCFs could significantly lower the glass transition temperature, melting point, viscosity, and surface tension of polymer materials [5–8], which results in the diffusivity capacity enhancement of micro-molecule in polymer materials. Therefore, SCFs are also often used in the process of modification [9], synthesis [10], particle formation [11], and foaming of polymer materials [12,13].

As a green solvent, supercritical carbon dioxide ($SCCO_2$) is the most popular solvent among SCFs due to its moderate critical condition (T_c = 304.2 K, P_c = 7.38 MPa). Nevertheless, $SCCO_2$ is an aprotic solvent with low polarizability, low dielectric constant, and low cohesive energy density, which makes its dissolving capacity for polar solute weak [14]. As one of the most used solvent of HFCs, 1,1,1,2-tetrafluoroethane (R134a) has attracted much attention in recent years [15]. The dipole moment of R134a is 2.1 D which is

much more than that of CO_2 (0 D) [16]; meanwhile, R134a presents high dissolving capacity at its subcritical condition [17] when the operational pressure is more than its critical pressure (P_c = 4.06 MPa). Then there comes the question that whether and what degree the dissolving capacity of subcritical R134a (sub-R134a) is higher than that of $SCCO_2$. However, the comparison of dissolving capacity between sub-R134a and $SCCO_2$ is rarely reported in the published literature [18,19,20].

Polyvinyl alcohol (PVA) is one of the most important industrial chemical materials. As a biodegradable high polymer, PVA is mainly used for the production of binder, emulsifier, dispersant, glue water, and composite material [21,22]. In addition, PVA foaming material has attracted more and more attention [23–25] due to their characters of high polarity, material compatibility, heat resistance, and antistatic property. As a novel technology, the supercritical or subcritical fluid technology plays important role in the process of foaming materials [26–28] in recent years. To our best knowledge, the solute phase behavior in supercritical and subcritical fluids is the foundation of the foaming technology for polymer. However, the solubility of PVA in $SCCO_2$ or sub-R134a has never been reported so far.

In this work, the solubility of PVA with molecular weight 16,000, 47,000, and 74,800 was measured in $SCCO_2$ and sub-R134a. To compare the dissolving capacity of $SCCO_2$ and sub-R134a, the solubility enhancement factor (*SE*) and solvent solubility

Nomenclature

y	Mole fraction of PVA in SCCO$_2$ or sub-R134a, mol mol^{-1}
S_c	Mass fraction of PVA in SCCO$_2$ or sub-R134a, g L^{-1}
M_1	Molecular weight of CO$_2$ or R134a, g mol^{-1}
M_2	Molecular weight of PVA, g mol^{-1}
M_n	Number-average molecular weight, g mol^{-1}
M_w	Weight-average molecular weight, g mol^{-1}
M_w/M_n	Polydispersivity index
T_c	Critical temperature, K
P_o	Operational pressure, MPa
P_c	Critical pressure, MPa
$P^{ref.}$	Reference pressure, 0.1 MPa
ΔE	Energy of vaporization to the gas at zero pressure
V	Volume, m^3
$\left(\frac{\partial E}{\partial V}\right)_T$	The internal pressure
$\left(\frac{\Delta E}{V}\right)_T$	The cohesive energy density
m	Specific parameter
n	Number of data points
$AARD$	Average absolute relative deviation, %
SE	Solubility enhancement factor
k_1, a_1, b_1	Parameters in Chrastil equation
k_2, a_2, b_2	Parameters in K-J equation
k_3, a_3, b_3	Parameters in M-S-T equation
k_0, k_4, a_4, b_4	Parameters in S-S equation
k_5, a_5, b_5	Parameters in Bartle equation

Greek letters

δ	Solubility parameter, MPa$^{1/2}$
ρ	Density of SCCO$_2$ or sub-R134a, g L^{-1}
ρ_c	Critical density, g L^{-1}
ρ_r	Reduced density, ρ/ρ_c
$\rho_r(liq)$	Reduced density, 2.66
$\rho_{ref.}$	Reference density, 700 g L^{-1}

Subscript

c	Critical condition
cal.	Calculated value
exp.	Experimental value

parameter (δ) were calculated; meanwhile, the experimental results were analyzed and discussed from the view of solvent density, solvent polarity, interaction between solvent and solute, solubility enhancement factor (*SE*), and solvent solubility parameter (δ). Five semi-empirical models, including Chrastil [29], K-J [30], M-S-T [31], S-S [32], and Bartle [33] models, were adopted to correlate the experimental solubility data of PVA in SCCO$_2$ and sub-R134a.

2. Experiment

2.1. Materials

PVA (M_n = 16000, 47,000, 74,800) were obtained from Aladdin Chemistry Co., Ltd., and Sinopharm Chemical Reagent Beijing Co., Ltd. The melting point and glass transition temperature of PVA are about 503 K [34,35] and 333–358 K [36], respectively. The physiochemical properties of PVA are depicted in Table 1. The boric acid (H$_3$BO$_3$), iodine (I$_2$), and potassium iodide (KI) were purchased from Beijing Hengye Zhongyuan Co., Ltd., with mass fraction of more than 99.5%, 99.8%, and 99.5%, respectively. CO$_2$ with mass purity of more than 99.9% was obtained from Beijing Praxair Industrial Gas Co., Ltd., and R134a with purity of 99.999% was purchased from DuPont Company. The deionized water was used in the experiment. All chemicals were used without further purification.

2.2. Apparatus and procedure

In this paper, the dynamic method was used for solubility measurement of PVA in SCCO$_2$, while the static method for PVA+ sub-R134a system. The main reason is that the volume of equilibrium cell for system R134a + PVA in this work is as small as 10 mL, which is more appropriate for the static method; while that for system CO$_2$ + PVA is 150 mL and more suitable for the dynamic method. Furthermore, it is found that most of the solubility measurements for solutes in SCCO$_2$ have been carried out using the dynamic method [37–40]; while the static method has been widely used in systems containing sub-R134a [18,19,41]. Both methods are reliable when applying the right experimental procedure.

2.2.1. Apparatus and procedure for SCCO$_2$ system

The solubility of PVA in SCCO$_2$ was measured with the dynamic method which had been described in our published works [42,43] in detail. The schematic diagram of the solubility measurement apparatus was shown in Fig. 1, and the reliability of this apparatus had been tested in our previous work [44].

About 30–40 g solid solute mixed with glass beads was packed in the equilibrium cell with an available volume of 150 mL. The stainless steel sintered disks at both ends of the equilibrium cell was used to prevent physical entrainment of the undissolved solute. Before the experiment, the valves between the high-pressure surge flask and two U-shaped tubes were opened for air removal with the high pressure CO$_2$.

The pure CO$_2$ from CO$_2$ cylinder was pressurized into the high-pressure surge flask by the compressor (Nova, model 5542121), and then the high pressure CO$_2$ was put into the preheating cell heated with electrical heating band. SCCO$_2$ entered into the high-pressure equilibrium cell, which was immersed in the constant-temperature stirred water bath (Chongqing Yinhe Experimental Instrument Co., model CS-503) with its accuracy of temperature ±0.01 K. In the high-pressure equilibrium cell, the solvent and solute reached equilibrium after 40 min. Then, solute mixed with CO$_2$ was discharged from the equilibrium cell into the two connected U-shaped tubes. We started the measurements at CO$_2$

Table 1
Physiochemical properties of PVA.

Compound	CAS number	M_n	M_w/M_n	Supplier	Purity
PVA	9002-89-5	16000	1.21	Aladdin Chemistry Co., Ltd., Beijing	≥98%
		47000	1.28	Sinopharm Chemical Reagent Beijing Co., Ltd.	≥98%
		74800	1.25	Aladdin Chemistry Co., Ltd., Beijing	≥98%