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Solubility of flavone, 6-methoxyflavone and anthracene in supercritical CO₂ with/without a co-solvent of ethanol correlated by using a newly proposed entropy-based solubility parameter



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ABSTRACT

Solubility of flavone, 6-methoxyflavone and anthracene in supercritical CO₂ with an ethanol co-solvent ranging from 0.05 to 0.40 were measured at 333 K and 22.0 MPa. Solubility of each compound increased with increasing mole fraction of ethanol. Solubility data were correlated with Chrastil equation considering a relationship between fluid density and solubility and compared with newly proposed relations that use an entropy-based solubility parameter (SSP). Among proposed relations, one relation taking temperature dependence into consideration, that included two fitting parameters had absolute relative deviation (ARD) of 3.9% compared to the experimental data and were much more reliable than a relation not taking temperature dependence into consideration within ARD of 7.6%. The expression similar to Chrastil model that included three fitting parameters and considered SSP was the best ARD within 3.6% among the proposed relations. From these correlation results, the SSP can be applied to determine the solubility of substances at high pressure with multicomponent solvent mixtures.

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1. Introduction

Supercritical carbon dioxide extractions with ethanol co-solvent have been widely studied for attention for pharmaceutical [1], natural food [2], agricultural science and applications [3] because carbon dioxide is cheap and safe solvent for organic and biochemical components and ethanol is a common and relatively safe polar modifier [4]. Extractions with supercritical carbon dioxide has the advantage of mild operating conditions that make it highly versatile for processing biochemical for use in health food, supplements and medicines [5].

As one of the secondary metabolites, flavonoids have more than 4000 species of their chemical structures in nature [6] and the solubility and processing for these compounds in supercritical CO_2 is important for future development. Among the many of flavonoids, 6 types were chosen for evaluation. Uchiyama et al. measured solubility of flavone and 3-hydroxyflavone in supercritical CO_2 [7]. Solubility of 7,8-dihydroxyflavone and 3,3',4',5,7-

* Corresponding author. E-mail address: masa@scf.che.tohoku.ac.jp (M. Ota). pentahydroxyflavone (quercetin) were measured in supercritical CO_2 by Matsuyama et al. [8] Sato et al. measured solubility of flavone and 6-methoxyflavone in supercritical CO_2 [9]. Each measurement was based on a flow-type apparatus. In supercritical CO_2 with ethanol co-solvent, Chafer et al. measured quercetin [10]. Using the same system, solubility of catechin [11] was measured by Berna et al. However, compared to the existence of flavonoids in nature, solubility data of flavonoids are greatly lacking in the literature.

Correlation of solubility data has also been assessed by many researchers with the Chrastil model being one of the main methods to correlate solubility data [12]. From temperature and fluid density dependence on solubility, enthalpy of solvation and number of solvated molecules to the solute can be evaluated [12]. Mendez-Santiago and Teja proposed a model for correlating the solubility of compounds in supercritical CO₂ systems [13] and in supercritical CO₂ with and without co-solvent addition [14]. The method was successively applied to many solutes.

The solubility parameter of solutes is a characteristic property of a solute and has been used to correlate solubility in supercritical CO_2 [9,15]. However, few literature reports have attempted in correlations for systems that include ethanol as co-solvent. One of the

reasons for this is that the solubility parameter is generally not directly applicable to polar substances at high temperature and pressure conditions.

In this work, a newly developed correlation method is proposed that uses the solubility parameter estimated from an equation of state for the binary CO₂-ethanol mixture. The most commonly-used solubility parameter at ambient temperature and pressure is based on the concept of cohesive energy density that can be expressed by enthalpy of vaporization and molar volume, as proposed by Hildebrand [16]. However, limitations of this method exist because the solubility parameter of a liquid for a pure component is unambiguously calculated under conditions of the vapor-liquid region. At high pressures including single phase conditions or for multicomponent fluid mixtures, some difficulties occur in the determination of the solubility parameters according to its original [16] or later definition [17]. Therefore, an entropy-based solubility parameter (SSP) for correlation of solubility of solutes in the high pressure region and for multicomponent fluid mixtures is proposed. The solubilities of flavone, 6-methoxyfavone and anthracene in supercritical carbon dioxide with and without ethanol co-solvent are measured and correlated.

2. Material and methods

2.1. Material

Carbon dioxide (99.5%) was supplied by Taiyo Nippon Sanso Corporation. Ethanol (99.5%) was obtained from Wako Pure Chemical Industries, Ltd. Flavone (99.5%), 6-methoxyflavone (99.0%) and anthracene (99.5%) were supplied by Wako Pure Chemical Industries, Ltd. Chemical structures were shown in Fig. 1. All chemicals were used as received.

2.2. Experimental methods and procedures

Apparatus designed and constructed for the measurements is shown in Fig. 2. A HPLC pump coupled with cooling unit (Jasco Co.,SCF-Get) was used to deliver CO₂ at a constant flow rate through the equilibrium cell (6.2 cm^3) packed the targeted solute. Another HPLC pump (Jasco Co., PU-2085) was used to supply ethanol at a constant flow rate. Temperature of the equilibrium cell was controlled by an oven (GL Science Inc., GC353B) to within an uncertainty of ± 0.5 K. After the fluids introduced by the HPLC pumps were mixed with a mixer at a given pressure measured with a pressure gauge (GE measurement and control, DPS 8200) within an uncertainty of 0.001 MPa, a six-way valve was switched to the equilibrium cell and the solvent was passed through the equilibrium cell. The obtained sample was depressurized with a backpressure regulator (Jasco Co., BP-2080-M). After a given time, the solute was collected from a trap and analyzed with a UV-vis spectrometer (Jasco Co., V-530). The CO₂ gas volume was quantified with a dry gas flow meter (Shinagawa Co. Ltd., DC-2) and the amount of solute obtained for the given amount of CO₂ was used to determine the equilibrium solubility. Solubility data were



Fig. 1. Chemical structure of flvavone, 6-methoxyflavone and anthracene targeted in this work.



Fig. 2. Experimental apparatus for measurements of solubility data used in this work. 1.CO₂ cylinder, 2.dryer, 3.pump, 4.chiller, 5, 6, 14, 15.valve, 7.oven, 8.mixer, 9.six way valve, 10.jacket, 11.equilibrium cell, 12.ethanol, 13.HPLC pump, 16.back pressure regulator, 17.trap, 18.dry gas flow meter.

measured for three times at the same temperature, pressure and mole fraction of ethanol and the average values were quantitatively evaluated.

3. Models

The Hildebrand solubility parameter (δ_H) [16] is given by eq. (1):

$$\delta_H = \sqrt{\frac{\Delta U_{\rm vp}}{\nu}} = \sqrt{\frac{\Delta H_{\rm vp} - RT}{\nu}} \tag{1}$$

where $\Delta U_{\rm vp}$, $\Delta H_{\rm vp}$, v, R and T are the internal energy of vaporization, enthalpy of vaporization, molar volume, gas constant and temperature, respectively. The $\Delta H_{\rm vp}$ is typically calculated from the Clausius-Clapeyron equation that is expressed with eq. (2) when $dP_{\rm vp}/dT$, T and volume change of vaporization ($\Delta V_{\rm vp}$) are available.

$$\frac{dP_{\rm vp}}{dT} = \frac{\Delta S_{\rm vp}}{\Delta V_{\rm vp}} = \frac{\Delta H_{\rm vp}}{T \,\Delta V_{\rm vp}} \tag{2}$$

The vapor pressure (P_{vp}) of a pure component is calculated by Antoine equation, eq. (3) and the differential form, dP_{vp}/dT is calculated by eq. (4).

$$\log_{10}(P_{\rm vp}) = A - \frac{B}{(T + C - 273.15)}$$
(3)

$$\frac{dP_{\rm vp}}{dT} = \frac{(\ln 10) P_{\rm vp} B}{(T+C-273.15)^2}$$
(4)

For the calculation using eq. (2), vapor molar volume was predicted by equation of states of ideal gas at 298.15 and 0.1013 MPa and liquid molar volume used in this work was literature value [18], which was listed in Table S1 with Antoine parameters [19]. Thus, ΔV_{vp} was calculated and obtained δ_H for some pure chemicals at 298.15 K are available in Table S1. From Table S1, the calculated δ_H values agreed well with the literature values [20].

In mixed-solvent systems or those at high pressure systems, the procedure for calculating solubility parameter for pure components is not valid because the Clausius-Clapeyron equation is not strictly applicable at the system conditions. An alternative method can be developed based on entropy as shown below.

For a binary mixed-solvent system, the differential form of the Gibbs energy is given by eqs. (5) and (6).

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