

Development of a predictive Dimensionless Distribution coefficient (pDD) model for fractionation of Hops extracts

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Abstract

Measurements of vapor-liquid distribution coefficients (*K*-values) of compounds contained in hops-extract ethanol or ethanol aqueous solution in high pressure CO₂ system were carried out at temperatures of 313–373 K and pressures of 5–14 MPa with a continuous flow apparatus for fractionation of hops-extract with supercritical counter-current extraction process. Using available experimental data for maximum 322 *K*-values, a correlation equation for the vapor-liquid distribution coefficient of 7 solutes in hops-extract was constructed based on entropy-based solubility parameter (eSP). The constructed generalized form of predictive Dimensionless Distribution (pDD) model that takes into account the eSP concept, originally developed in the previous work (Fluid Phase Equilibria, 434, 44-48, 2017), was also applied to the available experimental data, which includes the re-fitted four universal parameters. Thus, the pDD model can be applied for counter-current extraction simulation based on chemical engineering thermodynamics and material balance.

Keywords

Peng-Robinson equation of state, Subcritical fluid separation, Partition coefficient

1. Introduction

Toward early achieving Sustainable Development Goals (SDGs), green solvents have gained much attention for producing lean products for both better earth-environment and more qualitative human-life. A promising functional solvent is supercritical carbon dioxide (scCO₂) which has been widely used so far for many chemical engineering processes. Especially, supercritical fluid extractions (SFE) with scCO₂ have assessed since 1980s, that have been examined for huge numbers of natural resources produced from all over the world. In the usual scCO₂ extractions, non-polar solutes are favorably extracted, while highly-polar chemicals are not extracted and need some entrainers (or modifiers) such as ethanol, ethanol aqueous solution or water etc. due to the non-polarity of the pure scCO₂ solvent.

Such a SFE process is usually operated in a homogeneous single phase such as supercritical phase or high-pressure liquid phase. On the other hand, subcritical-fluid solute separation (SFS) process proposed in this work are conducted in high-pressure vapor-liquid or liquid-liquid heterogeneous multi phases. For the SFS process, CO₂ - ethanol binary solvents [1] or CO₂ - ethanol - water ternary solvents [1] were used for separation of many kinds of biochemicals contained in plants, that were assessed in our previous studies [2]-[5]. Another CO₂ - water binary solvents can possibly be a good candidate for separation of extremely different polarities of solutes.

For now, there are many literatures focused on vapor-liquid equilibria (VLE) for the CO₂ - ethanol - water ternary systems [1], [6]-[14], that can be applied for alcohol dehydration processes [15]-[17]. However, there seems to be no literature except for our group, that focused on vapor-liquid equilibria in the solute-including systems (CO₂ - ethanol - water - solutes more than quaternary systems) for solute separation processes. Even in our previous work [2]-[5], only hops-extract ethanol solution was a model feed solution selected for quantitative evaluation of vapor-liquid equilibrium ratio of solute (so called *K*-value of solute) or counter-current extraction efficiency with pure scCO₂ solvent systems.

In this work, CO₂ - ethanol - water ternary solvent systems were adopted for an extended approaches of the previous work [2]-[5]. Hops-extract ethanol aqueous solution containing both flavor and resin components was treated as a model feed solution, which was quantitatively evaluated with the flow-type VLE measurement systems at different temperatures, pressures, feed compositions. The predictive Dimensionless Distribution coefficient model (pDD model) developed in our previous work [2] was adopted in the theoretical calculations that could re-adjust the universal parameters, that could be applied for counter-current extraction systems with pure scCO₂ solvent selected in this work.

2. Experimental

2.1. Materials

Carbon dioxide (99.5%) was supplied by Taiyo Nippon Sanso Corporation. Ethanol (99.5%) were obtained from Wako Pure Chemical Industries, Ltd. Ultrapure water was produced with ultrapure water maker (RFD250NB) by Toyo Roshi Kaisha, Ltd.

2.2 Experimental methods and procedures

The flow apparatus used in the measurements was developed in the previous studies [1]-[2] and consisted of a feed system, equilibrium cell and streams for vapor and liquid phases. The feed used was hops extract dissolved in ethanol aqueous solution, of which concentration was adjusted to be 0.5 wt%.

For the procedures described in detail in literature [2], an HPLC pump coupled with a cooling unit (Jasco Co., PU-2080-CO₂) was used to deliver CO₂ to the equilibrium cell (3.2 cm³) at a constant flow rate. Another HPLC pump (Jasco Co., PU-2085) was used to supply the ethanol aqueous solution of hops extract into the equilibrium cell. The feed was quantified volumetrically. After the feed materials were pressurized by the HPLC pumps, they were homogenized with a static mixer that contained with Dixon packing (ϕ 1.5 mm) at constant pressure. Pressure was measured with a pressure gauge (Krone Co., KDM30) to within an uncertainty of ± 87.5 kPa. The phase separation was visibly confirmed with the equilibrium cell, for which the temperature was controlled to within an uncertainty of ± 0.5 K via an oven (Toyo Roshi Kaisha, Ltd., DRM420DB). Steady-state was checked by confirming the constant flow rate of materials. The vapor and liquid phases were flowed out from top and bottom outlet nozzles separately and then collected in each sampling trap after being depressurized by two backpressure regulators (BP-2080-D). Liquid sample collected in a trap was quantified by mass with an electronic balance (Mettler-Toledo International Inc., AX-504), while the gas sample from the vapor and liquid phase was quantified with a dry gas flow meter (Shinagawa Co. Ltd., DC-2) and a wet gas flow meter (Shinagawa Co. Ltd., W-NK-0.5), respectively.

For analysis of the flavors contained in the hops extract, a gas chromatography coupled with a flame ionization detector (GC-FID; Agilent Co., GC-8A) was used. The carrier gas and the column used in the GC-FID system was He (99.995%) and a DB-5 (Agilent Technologies Japan, Ltd.), respectively. Column temperature was controlled at 593.2 K at the same injection temperature. For analysis of the resins, high-performance liquid chromatography with an ultra violet detector (HPLC-UV) was used. The mobile phase was a mixture of methanol/0.01 M phosphoric acid aqueous solution (70:30, v/v) at the start (0 min) and after a given time (90 min), the concentration was changed to final conditions of methanol/0.01 M phosphoric acid aqueous solution (100:0, v/v). Flow rate was controlled at 0.6 cm³/min. An ODS column (Shiseido Japan Co., Ltd., Capcell Pak UG120) having a size of 4.6mmID x 250 mm was used in the HPLC analysis. Column temperature was maintained

at 313 K.

Vapor-liquid distribution coefficient of solutes (K value) was defined on a molar basis as:

$$K_{\text{solute}} = \frac{y_{\text{solute}}}{x_{\text{solute}}} \quad (1)$$

where y_{solute} and x_{solute} are mole fractions of the solute in vapor phase and liquid phase, respectively.

3. The predictive Dimensionless Distribution (pDD) coefficient model [2]

For correlation of the K value data, the Hildebrand solubility parameter (δ_H) based on the regular solution concept can be used [18]. However, δ_H is usually obtained at ambient conditions (298.15 K and 101.3 kPa). For extending the δ_H in high pressure systems, an entropy-based solubility parameter (eSP, δ_s) proposed in a previous work [19] was used for the modeling. The eSP is expressed as:

$$\delta_s^2 \equiv \left(\frac{\partial P}{\partial T} \right)_v = \left(\frac{\partial s}{\partial v} \right)_T \quad (2)$$

where P , T , s and v are the pressure, temperature, entropy and volume. For the calculation of δ_s of vapor and liquid phases, the Peng-Robinson equation of state (EOS) with the van der Waals one fluid model (vdW1) [20] was applied to determine $(\partial P/\partial T)_v$ with the interaction parameter k_{ij} and the size parameter of l_{ij} set according to the vapor-liquid equilibrium data in CO₂ - ethanol - water ternary mixtures (solute-free) in Table 1. Using the PR-vdW1 EOS, a linear relationship between the eSP (δ_s) and the Hildebrand solubility parameter, δ_H at 298.15 K and 101.3 kPa could be determined as [19]:

$$\delta_s \cong 50 \delta_H \quad \text{at 298.15 K and 101.3 kPa} \quad (3)$$

Eq. (3) allows conversion from Hildebrand solubility parameters to eSP which was applied to the calculation of entropy-based solubility parameter of solute ($\delta_{s, \text{Solute}}$) as listed in Table 2.

According to the regular solution theory, two substances having close solubility parameters are well-soluble [18]. From a previous study examined on organic solvent extractions from *Citrus* peels, the relationship between extraction yield of a solute and its solubility parameters of solvents showed that the Gauss waveform was satisfactory in many cases [21]. However, in some cases, the empirical relationship is better expressed as an asymmetric Gauss waveform [21]. According to the system and its temperature and pressure trends, an asymmetric form was assumed between solubility of one solute in vapor (y'_{Solute}) and liquid phase (x'_{Solute}) at high pressure conditions so that the functional form used was:

$$y'_{\text{solute}} = a \exp \left(- \frac{(\delta_{s,V} - \delta_{s,\text{Solute}})^2}{2\sigma_y^2} \right) \quad \delta_{s,V} < \delta_{s,\text{Solute}} \quad (4)$$

$$x'_{\text{solute}} = a \exp\left(-\frac{(\delta_{S,L}-\delta_{S,\text{Solute}})^2}{2\sigma_x^2}\right) \quad \delta_{S,\text{Solute}} < \delta_{S,L} \quad (5)$$

where a , σ_y and σ_x are constants. The relations (eq. (4) and (5)) are true for $\delta_{S,V} < \delta_{S,\text{Solute}} < \delta_{S,L}$. When $\delta_{S,V} < \delta_{S,L} < \delta_{S,\text{Solute}}$, the functions are expressed as follows:

$$y'_{\text{solute}} = a \exp\left(-\frac{(\delta_{S,V}-\delta_{S,\text{Solute}})^2}{2\sigma_y^2}\right) \quad \delta_{S,V} < \delta_{S,\text{Solute}} \quad (6)$$

$$x'_{\text{solute}} = a \exp\left(-\frac{(\delta_{S,L}-\delta_{S,\text{Solute}})^2}{2\sigma_y^2}\right) \quad \delta_{S,L} < \delta_{S,\text{Solute}} \quad (7)$$

Therefore, K' value can be calculated as follows:

$$K'_{\text{solute}} = \frac{y'_{\text{solute}}}{x'_{\text{solute}}} = \frac{\exp\left(-\frac{(\delta_{S,V}-\delta_{S,\text{Solute}})^2}{2\sigma_y^2}\right)}{\exp\left(-\frac{(\delta_{S,L}-\delta_{S,\text{Solute}})^2}{2\sigma_x^2}\right)} \quad \delta_{S,V} < \delta_{S,\text{Solute}} < \delta_{S,L} \quad (8)$$

$$K'_{\text{solute}} = \frac{y'_{\text{solute}}}{x'_{\text{solute}}} = \frac{\exp\left(-\frac{(\delta_{S,V}-\delta_{S,\text{Solute}})^2}{2\sigma_y^2}\right)}{\exp\left(-\frac{(\delta_{S,L}-\delta_{S,\text{Solute}})^2}{2\sigma_y^2}\right)} \quad \delta_{S,V} < \delta_{S,L} < \delta_{S,\text{Solute}} \quad (9)$$

in which it is assumed that eq. (10) can be used to calculate K values from the theory.

$$\ln K_{\text{solute,calc}} = A K'_{\text{solute}} + B \quad (10)$$

In Eqs. (8)-(10), the four fitting parameters (σ_y , σ_x , A , B) were re-adjusted in this work for the extended conditions including CO₂ - ethanol - water ternary solvent systems (217 experimental data obtained in this work) in addition to CO₂ - ethanol binary solvent systems (105 experimental data) [2].

4. Results and Discussion

Table 3 shows experimental K -value ($K_{\text{Solute, exp}}$) for 7 components in hops-extract in CO₂ - ethanol - water ternary solvent systems. In Table 3, total 217 experimental data were recorded in this work. Finally, total 322 experimental data including these 217 experimental data for CO₂ - ethanol - water ternary solvent systems in addition to 105 experimental data for

Table 1 Temperature dependence of both interaction parameter k_{ij} and size parameter of l_{ij} in the Peng-Robinson EOS with the van der Waals one fluid model [20] obtained in this work.

k_{ij}	l_{ij}
$k_{12} = 0.2206 - 0.0004793 T$	$l_{12} = 0.4535 - 0.001318 T$
$k_{13} = -0.4807 + 0.001580 T$	$l_{13} = -0.3214 + 0.001116 T$
$k_{23} = -0.3289 + 0.0007281 T$	$l_{23} = -0.01355 + 0.0002127 T$

CO₂ - ethanol binary solvent systems [16] were applied to the above-mentioned pDD theory described in Eqs. (8)-(10). The four fitting parameters (σ_y , σ_x , A, B) in Eqs. (8)-(10) re-adjusted in this work were given to (17068.9, 18536.5, 3875.4, -3875.4).

Table 2 Hildebrand solubility parameter ($\delta_{H, \text{Solute}}$) of each solute contained in hop extracts estimated by Fedors' method [22]. Entropy-based solubility parameter ($\delta_{S, \text{Solute}}$) was calculated according to reference [19]. A relationship ($\delta_{S, \text{Solute}} = 50 \delta_{H, \text{Solute}}$) [2], [19] was applied to the calculation at 298.15 K and 101.3 kPa.

Component	Content in hops extract [wt%]	Molecular weight [g/mol]	$\delta_{H, \text{Solute}}$ [MPa ^{0.5}]	$\delta_{S, \text{Solute}}$ [(Pa/K) ^{0.5}]
β -myrcene	4.60 \pm 0.23	136.23	15.7	785
caryophyllene	0.989 \pm 0.050	204.35	17.5	875
humulene	3.13 \pm 0.16	204.35	17.6	880
cohumulone	12.1 \pm 0.61	348.43	26.7	1335
humulone	28.5 \pm 1.43	362.47	26.3	1315
colupulone	11.9 \pm 0.60	400.55	23.6	1180
lupulone	10.5 \pm 0.53	414.58	23.3	1165
Ohters	28.2 \pm 1.41	-	-	-

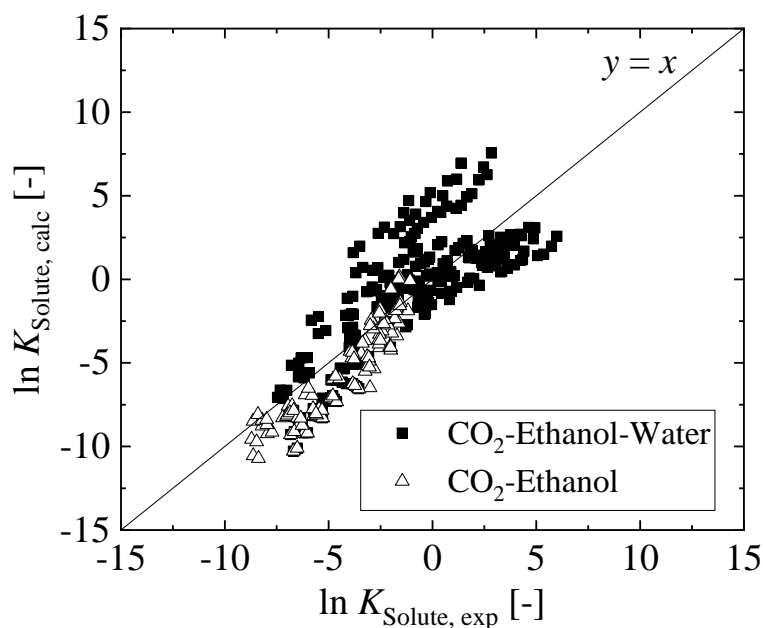


Fig. 1 Correlation between experimental data and calculation with the pDD model [2]

Table 3 Experimental K -value ($K_{\text{Solute, exp}}$) for 7 components in hops-extract in CO₂ - ethanol - water ternary solvent systems.

T [K]	P [MPa]	H ₂ O/Ethanol in Feed [-]	K - value							
			F hep	F myr	F car	F hum	B coh	B hum	B col	B lup
313.2	10.03	1.01	0.156	1.55	2.28	2.81	0.199	0.215	0.276	0.303
	12.04	1.03	0.277	1.92	3.61	4.09	0.319	0.348	0.463	0.515
	16.06	1.00	0.556	2.35	4.34	5.02	0.588	0.648	0.894	0.997
	20.08	1.01	0.631	3.08	4.91	5.81	0.814	0.899	1.28	1.45
333.2	10.09	1.01	0.0186	0.297	0.132	0.123	0.00289	0.00272	0.00212	0.00194
	12.06	1.01	0.0961	1.03	1.24	1.20	0.0546	0.0569	0.0753	0.0794
	16.07	1.01	0.319	2.21	3.49	3.67	0.343	0.370	0.536	0.583
	19.97	1.01	0.644	3.29	4.18	5.17	0.721	0.794	1.23	1.35
353.2	10.02	1.01	0.0176	0.219	0.0650	0.0579	0.000858	0.000798	0.000806	0.000677
	12.05	1.01	0.0322	0.432	0.213	0.188	0.00357	0.00346	0.00489	0.00472
	16.06	1.01	0.123	1.08	1.55	1.60	0.117	0.123	0.180	0.189
	19.99	1.01	0.359	2.06	3.60	3.78	0.496	0.538	0.878	0.957
313.2	10.06	1.87	0.464	4.11	9.13	7.63	0.594	0.678	1.24	1.48
	12.08	1.88	0.625	4.52	13.51	14.76	1.13	1.31	2.55	3.04
	16.02	1.88	1.79	7.25	-	22.36	2.18	2.54	5.57	6.54
	20.03	1.87	3.04	13.15	-	21.73	3.20	3.77	8.55	10.12
333.2	10.03	1.87	0.0158	0.705	0.489	0.476	0.00360	0.00366	0.00622	0.00629
	11.98	1.87	0.0522	1.62	3.67	4.21	0.115	0.127	0.239	0.268
	15.99	1.88	1.13	5.39	8.01	12.40	1.11	1.28	2.83	3.28
	19.99	1.87	2.58	11.19	11.19	14.45	2.73	3.27	7.92	9.49
353.2	10.04	1.87	0.0231	0.613	0.249	0.216	0.00133	0.00131	0.00241	0.00236
	12.08	1.88	0.0267	0.851	0.947	0.889	0.00900	0.00918	0.0174	0.0178
	16.08	1.89	0.221	2.60	5.51	5.96	0.323	0.362	0.805	0.905
	20.08	1.87	1.41	8.53	7.89	13.35	1.72	2.00	5.11	6.20
313.2	10.08	4.04	-	-	-	-	8.83	12.58	69.50	83.32
	12.07	4.06	-	-	-	-	21.00	29.89	138.51	168.17
	16.08	4.02	-	-	-	-	40.26	58.24	382.53	823.62
	20.00	4.06	-	-	-	-	54.31	79.85	524.62	1919.9
333.2	10.06	4.04	0.0376	3.28	-	-	0.0388	0.0463	0.191	0.241
	12.04	4.05	-	-	-	-	1.47	2.03	9.36	15.52
	16.06	4.05	-	-	-	-	15.38	23.33	147.91	359.67
	20.06	4.04	-	-	-	-	33.67	49.37	395.36	1030.9
353.2	10.02	4.04	0.117	2.60	-	-	0.00585	0.00663	0.0294	0.0351
	12.06	4.04	0.146	4.75	-	-	0.0869	0.107	0.477	0.625
	16.08	4.05	-	-	-	-	4.89	7.29	53.38	111.07
	20.06	4.04	-	-	-	-	15.56	22.58	104.58	177.88

From the obtained results in Figure 1, Average Absolute Relative Deviation (AARD) was calculated to be 251.5 for the CO₂ - ethanol – water ternary solvent systems and 130.6 for the CO₂ - ethanol binary solvent systems, respectively. Thus, good correlation between experimental data and the pDD calculation in Fig. 1 was observed and the pDD model was promisingly applied for prediction of K -value of solutes with the known eSP values.

5. Conclusions

Using available experimental data for 322 K -values (K_{Solute}), a correlation equation [2] based on eSP concept was applied and four universal constants were re-determined. From the established calculation methods, the K_{Solute} could be applied to the counter-current extraction systems with supercritical CO₂ solvent (Subcritical-Fluid solute Separation: SFS)

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