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# Vapor-liquid distribution coefficients of hops extract in high pressure CO<sub>2</sub> and ethanol mixtures and data correlation with entropy-based solubility parameters



FLUID PHASE

## Masaki Ota<sup>\*</sup>, Satoshi Sugahara, Yoshiyuki Sato, Richard Lee Smith Jr., Hiroshi Inomata

Research Center of Supercritical Fluid Technology, Tohoku University, 6-6-11-403, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

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#### ABSTRACT

Vapor-liquid distribution coefficients (*K*) of hops extract in high pressure  $CO_2$  and ethanol mixture solvents were measured with a flow apparatus at temperatures from 323 to 343 K, pressures from 8 to 10 MPa and feed concentrations of hops extract in ethanol solvent from 0.5 to 5 wt%. Distribution coefficients of  $\beta$ -myrcene, caryophyllene, humulene, cohumulone, humulone, colupulone and lupulone were found to be independent of feed concentration in ethanol solvent (from 0.5 to 5 wt%) for a given temperature and pressure. Thus, feed composition of hops extract was fixed at 0.5 wt% and both temperature and pressure effects were examined. Pressure dependence of the distribution coefficients could be clearly observed, while the temperature dependence of the distribution coefficients was relatively small. Data could be correlated with the entropy-based solubility parameter model to within 20% deviation in log *K*.

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#### 1. Introduction

The hops plant, *Humulus lupulus*, contains many resinous compounds, alpha- and beta-acids, and essential oils that give its extracts a characteristic taste [1]. The separation of compounds in hops is an active research area by food and beverage companies. One separation technique for hops is supercritical carbon dioxide extraction. Among the literature reported on hops extraction [2–8], Formato et al. demonstrated that supercritical carbon dioxide could extract both alpha- and beta-acids (bitter components) with ethanol entrainer [3]. Böhm et al. showed that hops extraction with supercritical carbon dioxide could be monitored online and that extracts could be used in particle formulations [8]. In general, however, separation of the many hops components, such as those associated with aroma and flavor, has not received as much attention as its general extraction [2,4–7].

For separation of hop components with sufficient yield and selectivity, one idea is to dissolve hops in ethanol and contact the solution with high-pressure carbon dioxide in a mixer-settler system in which vapor-liquid equilibria occurs and hops components

\* Corresponding author. E-mail address: masa@scf.che.tohoku.ac.jp (M. Ota). distribute between each phase in accordance with their fugacities. At equilibrium, the composition of each phase is determined based on vapor-liquid equilibrium data. In other words, knowledge of the distribution coefficients of compounds in hops could be used to separate CO<sub>2</sub>-philic and ethanol-philic constituents. The distribution coefficients of hops compounds depend on temperature and pressure, however, no fundamental data exist in the literature for hops–CO<sub>2</sub>–ethanol systems.

A mechanical mixer-settler system was developed for flow type VLE measurements in our previous work [9], which used coupled back-pressure regulators working in a given interval for separating equilibrium vapor and liquid samples. With the previous flow-type apparatus, it was possible to measure high pressure vapor-liquid equilibrium in a binary CO<sub>2</sub> and ethanol mixture, however, its application to food products was not discussed [9]. In this work, the measurement of the distribution coefficients of compounds typically found in hops between CO<sub>2</sub>-rich and ethanol-rich phases was studied. The objective of the research was to examine the selectivities of major compounds contained in hop extracts with the purpose to separate fractions of flavor and the bitter components. The measurements were conducted at temperatures from 323 to 343 K, pressures from 8 to 10 MPa and at feed concentrations of the hops extract in ethanol solvent from 0.5 to 5 wt%. An entropy-based solubility parameter (eSP) model reported for correlating solubility



data [10] was applied to the prediction of distribution coefficients of hops compounds in CO<sub>2</sub>-ethanol systems.

### 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.  $\beta$ -myrcene (95.0%) and humulene (96.0%) were obtained from Sigma-Aldrich Co. LLC. Ethyl pentadecanoate (97.0%) obtained from Tokyo Chemical Industry Co., Ltd. was used as internal standard for GC-FID analysis. Resin standard was obtained from the American Society of Brewing Chemists. Hops extract was donated by Suntory Holdings, Ltd. Its characterization is shown in Fig. 1 and the chemical structures of its major compounds are shown in Fig. 2 as discussed later. All chemicals were used as received.

#### 2.2. Experimental methods and procedures

The flow apparatus used in the measurements was developed in a previous study and consisted of a feed system, equilibrium cell and streams for vapor and liquid phases [9]. The feed used was hops extract dissolved in ethanol [9], of which the hops concentration was adjusted to be from 0.5 to 5 wt%.

An HPLC pump coupled with a cooling unit (Jasco Co., PU-2080-CO<sub>2</sub>) was used to deliver CO<sub>2</sub> to the equilibrium cell (3.2 cm<sup>3</sup>) at a constant flow rate. Another HPLC pump (Jasco Co., PU-2085) was used to supply the ethanol 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 (1/2" inch tube,  $\phi$  9.4 × 200 mm) that contained with Dixon packing ( $\phi$  1.5 mm) at constant pressure.



**Fig. 1.** Analyses of the hops extract used in this study: (a) GC-MS and (b) HPLC-UV chromatograms. Detected peaks were (1)  $\beta$ -myrcene, (2) caryophyllene, (3) humulene, (4) cohumulone, (5) humulone, (6) colupulone and (7) lupulone.



**Fig. 2.** Chemical structures of major compounds for the hops extract used in this work: (1)  $\beta$ -myrcene, (2) caryophyllene, (3) humulene, (4) cohumulone, (5) humulone, (6) colupulone and (7) lupulone.

Pressure was measured with a pressure gauge (Krone Co., KDM30) to within an uncertainty of  $\pm$ 87.5 kPa. The phase separation was visibly confirmed with the equilibrium cell, for which the temperature was controlled to within an uncertainty of  $\pm$ 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 gas burette, 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 bitter components, high-performance liquid chromatography with an ultra violet detector (HPLC-UV) was used. The experimental procedure followed was according to that suggested by Sahlstrom and Rostad [11]. 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 cm<sup>3</sup>/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:

$$K_{\text{solute}} = \frac{y_{\text{solute}}}{x_{\text{solute}}} \tag{1}$$

where  $y_{\text{solute}}$  and  $x_{\text{solute}}$  are mole fractions of the solute in vapor

phase and liquid phase, respectively.

#### 3. Results and discussion

#### 3.1. Distribution coefficients of hops extract in CO<sub>2</sub>-ethanol systems

Fig. 1 shows GC-FID and HPLC-UV analyses of the hops extract. From the GC-FID analysis (Fig. 1a), three major compounds in the hops extract could be identified as (1)  $\beta$ -myrcene, (2) caryophyllene, (3) humulene. From the HPLC-UV analysis (Fig. 1b), four major compounds including (4) cohumulone, (5) humulone, (6) colupulone and (7) lupulone could be identified by comparison with the literature [11]. The chemical structures of the seven identified components in hops extract are shown in Fig. 2. From the GC-FID and HPLC-UV analyses, the content of each component was quantified and is listed in Table 1 and Table S1. The weight fraction of compounds that could be identified in the hops extract was about 72%. For discussion, Hildebrand solubility parameters ( $\delta_{H, Solute}$ ) were calculated according to Fedors' method [12] as shown in Table 1.

Fig. 3 shows distribution coefficients of the major compounds of hops extract in  $CO_2$  + ethanol mixtures as a function of feed composition at 333 K and 10 MPa [9]. From Fig. 3, β-myrcene showed the highest K value (~ $10^{0}$ ) among the major hops extract components. The second highest K values were those of caryophyllene and humulene  $(\sim 10^{-1})$ . The others (cohumulone, humulone, colupulone and lupulone) had low K values ( $10^{-3}$ ~ $10^{-2}$ ). The K values were in order of their molecular weight and almost corresponded to the order of the Hildebrand solubility parameter of solute as listed in Table 1. From these results, it was concluded that the flavors ( $\beta$ -myrcene, caryophyllene and humulene) and the bitter components (cohumulone, humulone, colupulone and lupulone) could be separated according to their distribution between vapor and liquid phases at these conditions. Although the Kvalue for each component varied slightly with feed composition of hops extract in ethanol (Fig. 3), the K values were almost independent of feed composition. Thus, the feed composition of hops extract in ethanol was fixed at 0.5 wt% for further experiments.

Fig. 4 and Table S2 show vapor-liquid distribution coefficients of hops extract in  $CO_2$  + ethanol mixtures as a function of temperature. Fig. 4a showed that two phases existed over the range of temperatures at 8 MPa whereas measurements were not possible at 10 MPa at the lowest temperature (Fig. 4b) because the conditions resulted in a single phase system. In Fig. 4a and b, the distribution coefficients of the hops extract components depended very weakly on temperature. On the other hand, at constant temperature (Fig. 5a–b), the distribution coefficients exhibited noticeable pressure dependence. For  $\beta$ -myrcene, *K* values decreased with increasing pressure, while for the other compounds, *K* values increased with increasing pressure. These results imply that  $\beta$ myrcene can be separated efficiently in the vapor phase at



**Fig. 3.** Vapor-liquid distribution coefficients of hops extract in CO<sub>2</sub> + ethanol mixtures as a function of feed composition in ethanol at 333 K and 10 MPa for a flow rate of CO<sub>2</sub> and ethanol mixtures (solute-free) of 0.07 mol/min. Feed concentrations of the hops extract in ethanol solvent were adjusted from 0.5 to 5 wt%. Symbols are: black squares ( $\beta$ -myrcene), open squares (caryophyllene), black triangles (humulene), open triangles (cohumulone), black circles (humulone), open circles (colupulone) and X-marks (lupulone).

relatively low pressures (ca. 8 MPa).

For correlation of the distribution coefficients, the  $K_{\text{solute}}$  should be related to the distribution coefficient of CO<sub>2</sub> ( $K_1 = y_1/x_1$ ) and ethanol ( $K_2 = y_2/x_2$ ) and their ratio ( $\alpha_{12} = K_1/K_2$  or  $\alpha_{21} = K_2/K_1$ ), however, it was difficult to find a generalized form ( $K_1$ ,  $K_2$ ,  $\alpha_{12}$  or  $\alpha_{21}$ ) as shown in Fig. S1. Detailed information on all components and their state properties are necessary for prediction of the  $K_{\text{solute}}$ data are given in supplementary materials (Table S2).

For correlation of the *K* value data, the Hildebrand solubility parameter ( $\delta_H$ ) based on the regular solution concept can be used [13]. However,  $\delta_H$  is usually obtained at ambient conditions (298.15 K and 101.3 kPa) and its definition for high pressure systems is not clear. Therefore, an entropy-based solubility parameter (eSP,  $\delta_S$ ), which was proposed in a previous work [10], was used for the modeling. The eSP is expressed as:

$$\delta_{S}^{2} \equiv \left(\frac{\partial P}{\partial T}\right)_{V} = \left(\frac{\partial S}{\partial V}\right)_{T}$$
<sup>(2)</sup>

where *P*, *T*, *S* and *V* are the pressure, temperature, entropy and volume. For the calculation of  $\delta_S$  of vapor and liquid phases, the Peng-Robinson equation of state [14] was applied to determine

 $\left( rac{\partial P}{\partial T} 
ight)_V$  with the interaction parameter being  $k_{
m ij}$  being set equal to

0.08 at temperatures from 323 to 343 K and the size parameter of  $l_{ij}$  being set equal to 0 according to the vapor-liquid equilibrium data of CO<sub>2</sub> + ethanol binary mixtures (solute-free) [15]. Using the Peng-Robinson equation of state, a linear relationship between the eSP ( $\delta_S$ ) and the enthalpy-based solubility parameter,  $\delta_H$  (Hildebrand

Table 1

Solubility parameter ( $\delta_{H, \text{ Solute}}$ ) of each solute contained in hop extracts estimated by Fedors' method [12]. Entropy-based solubility parameter ( $\delta_{S, \text{ Solute}}$ ) was calculated according to reference [10]. A relationship ( $\delta_{S, \text{ Solute}}$ ) [10] was applied to the calculation at 298.15 K and 101.3 kPa.

Component	Content in hops extract [wt%]	Molecular weight [g/mol]	$\delta_{H, \text{ Solute}} [\text{MPa}^{0.5}]$	$\delta_{S, \text{ Solute}} \left[ (\text{Pa/K})^{0.5} \right]$
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 ± 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. 4.** Vapor-liquid distribution coefficients of hops extract in  $CO_2$  + ethanol mixtures as a function of temperature at (a) 8 MPa and (b) 10 MPa for a feed composition of hop extracts in ethanol of 0.5 wt% and a flow rate of  $CO_2$  and ethanol mixutres (solute-free) of 0.07 mol/min. Symbols are: black squares ( $\beta$ -myrcene), open squares (caryophyllene), black triangles (humulene), open triangles (cohumulone), black circles (humulone), open circles (colupulone) and X-marks (lupulone).

solubility parameter) at 298.15 K and 101.3 kPa could be determined as [10]:

$$\delta_s \cong 50 \ \delta_H$$
 at 298.15 K and 101.3 kPa (3)

Eq. (3) allows conversion from Hildebrand solubility parameters to eSP which was applied to the calculation of entropy-based solubility parameter of the solutes ( $\delta_{S, Solute}$ ) as listed in Table 1. The obtained entropy-based solubility parameter for vapor ( $\delta_{S, V}$ ) and liquid ( $\delta_{S, L}$ ) phases is shown in Table 2, respectively. Entropy-based solubility parameters of vapor ( $\delta_{S, V}$ ), liquid ( $\delta_{S, L}$ ) and solute ( $\delta_{S, Solute}$ ) did not show a simple relationship against all *K* value data (Fig. S2). Therefore, a new expression was considered to correlate the *K* value data.

According to the regular solution theory, two substances having close solubility parameters are well-soluble [13]. 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 a Gaussian waveform was satisfactory [16]. However, in some cases, the empirical relationship is better expressed as an asymmetric Gaussian waveform [16]. According to the system and its temperature and pressure trends, an asymmetric form was assumed between solubility of one solute in vapor (*y*'<sub>Solute</sub>) and liquid phase (*x*'<sub>Solute</sub>) at high pressure conditions so that the functional form used was:



**Fig. 5.** Vapor-liquid distribution coefficients of hops extract in  $CO_2$  + ethanol mixtures as a function of pressure at (a) 333 K and (b) 343 K for a feed composition of hop extracts in ethanol of 0.5 wt% and a flow rate of  $CO_2$  and ethanol mixtures (solute-free) of 0.07 mol/min. Symbols are: black squares ( $\beta$ -myrcene), open squares (caryophyllene), black triangles (humulene), open triangles (cohumulone), black circles (humulone), open circles (colupulone) and X-marks (lupulone).

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

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

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

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

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

Therefore, *K*<sup>'</sup> value can be calculated as follows:

$$K_{\text{solute}}' = \frac{y_{\text{solute}}'}{x_{\text{solute}}'} = \frac{\exp\left(-\frac{\left(\delta_{S,L} - \delta_{S,Solute}\right)^2}{2\sigma_y^2}\right)}{\exp\left(-\frac{\left(\delta_{S,L} - \delta_{S,Solute}\right)^2}{2\sigma_x^2}\right)} \quad \delta_{S,V} < \delta_{S,Solute} < \delta_{S,L}$$

$$\tag{8}$$

#### Table 2

Entropy-based solubility parameter of vapor  $(\delta_{S,V})$  or liquid phase  $(\delta_{S,l})$  in high pressure  $CO_2$  + ethanol mixutres calculated according to reference [10].

Temperature [K]	Pressure [MPa]	$\delta_{S,V}  [(Pa/K)^{0.5}]$	$\delta_{S, L} [(Pa/K)^{0.5}]$
323	8	274	975
333	8	247	995
	10	357	880
343	8	231	985
	10	306	915



**Fig. 6.** Logarithmic vapor-liquid distribution coefficient of major compounds in hops extract in  $CO_2$  + ethanol mixtures calculated from Eq. (10) for all data measured at temperatures from 323 to 343 K and at pressures from 8 to 10 MPa.

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

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

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

In the calculation, four parameters ( $\sigma_y$ ,  $\sigma_x$ , A and B) are determined by fitting. Least-squares method applied to the data (Fig. 6) shows that logarithmic vapor-liquid distribution coefficients of the major compounds in hops extract in CO<sub>2</sub> + ethanol mixtures could be correlated by Eqs. (8)–(10). The obtained  $\sigma_y$ ,  $\sigma_x$ , A and B were 308, 168, 16.6 and –7.10, respectively. From Fig. 6, logarithmic  $K_{sol$  $lute, calc}$  agreed well with a logarithmic  $K_{solute, exp}$  being within a deviation of 20%. Consequently, the model can be used to predict vapor-liquid distribution coefficients of hops extract in CO<sub>2</sub>+ethanol mixture solvent systems at other conditions.

#### 4. Conclusions

Vapor-liquid distribution coefficient data of hops extract,  $\beta$ -myrcene, caryophyllene, humulene, cohumulone, humulone,

colupulone and lupulone, in  $CO_2$ -ethanol systems are reported. The distribution coefficient data were insensitive to changes in temperature but were sensitive ot changes in pressure. An entropy-based solubility parameter model used in the framework of an asymmetric Gauss waveform function was found to be effective for correlating the data.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.fluid.2016.11.011.

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