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Modified Solubility Parameter as an Index to Correlate the Solubility in Supercritical Fluids

Yutaka Ikushima,* Tomio Goto, and Masahiko Arai†
Government Industrial Research Institute, Tohoku, Nigatake 4-Chome, Sendai 983
†Chemical Research Institute of Non-Aqueous Solutions, Tohoku University,
Katahira, Sendai 980
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Synopsis. The conventional solubility parameter was modified so that it could be applied to supercritical fluids. It was found that the parameters could correlate the experimental solubility data of some hydrophobic solutes in carbon dioxide, ethylene, and carbon dioxide-entrainer systems.

Supercritical fluids have the capacity to dissolve nonvolatile and thermolabile materials without denaturalization by several orders of magnitude greater than gases in the standard state.[1–4] However, since the dissolving power is widely variable from one supercritical solvent to another, a supercritical fluid (SCF) method has been a considerable trial-and-error process and, consequently, has required much expenses and time. With the addition of a proper entrainer to supercritical solvents, the extraction efficiency can be enhanced compared to SCF alone in many extraction processes;[5–9] particular attention has been drawn to the effect of entrainer. However, the solubility significantly varies with the entrainer. Therefore, recently a parameter for representing the effect of the entrainer has been desired. The solubility parameter concept[10] has widely been used for many years for interpreting and predicting the thermodynamic behavior of a solution. In recent years, the SCF extraction method has been remarkably noted; for supercritical fluids a similar solubility parameter is expected to be presented.[11]

The purpose of this paper is to extend the conventional solubility parameter concept to SCF with an assumption of random mixing of the spieces present in the mixture and to examine its usefulness in selecting a suitable supercritical solvent and entrainer in the SCF extraction process.

Solubility Parameter for Supercritical State. The basic assumption in the solubility parameter concept is that there is a correlattion between the cohesive energy and mutual solubility. The definition of the solubility parameter δ is in terms of the square root of the molecular cohesive energy, $(-E)$, per unit volume.

$$\delta = (-E/V)^{1/2} \tag{1}$$

$-E$ is the energy of a liquid relative to its ideal vapor at the same temperature. It can, therefore, be considered that $-E$ consists of the energy required to vaporize the liquid to its saturated vapor and, then, to isothermally expand it to infinite volume.

$$-E = \Delta U_v + \int_{v=v}^{v=\infty} (\partial U/\partial V)_T \mathrm{d}V, \tag{2}$$

where ΔU_v is the energy to vaparize liquid to saturated vapor. At the critical temperature, the first term in Eq. 2 is zero, and $-E$ can be represented as

$$-E = \int_{v=v}^{v=\infty} (\partial U/\partial V)_T \mathrm{d}V. \tag{3}$$

Equation 3 can be modified to express δ more conveniently:

$$-E = (H^* - H) - RT(1-z) = \Delta H - RT(1-z) \tag{4}$$

and

$$\delta = [(\Delta H - RT(1-z))/V]^{1/2}, \tag{5}$$

where H^*, H, z, and R are the standard enthalpy, molar enthalpy, compressibility factor, and gas constant, respectively. ΔH is represented from the thermodynamic relations as follows:

$$\Delta H = RT_cT_r{}^2 \int_0^{P_r} (\partial z/\partial T_r)_{P_r} \mathrm{d}P_r/P_r. \tag{6}$$

ΔH can be also determined using:

$$\Delta E/T_c = \Delta H/T_c - (1-z)RT_r, \tag{7}$$

where T_c, T_r, and P_r are the critical temperature, reduced temperature, and reduced pressure, respectively. Here, the function $\Delta E/T_c$ is available in the literature as functions of T_r and P_r.[12] In addition, to make δ applicable to any solvent, the solubility parameter is expressed in terms of reduced parameters. Thus,

$$\delta_r = [P_r/z(T_r \int_0^{P_r} (\partial z/\partial T_r)_{P_r} \mathrm{d}P_r/P_r - 1 + z)]^{1/2}, \tag{8}$$

where δ_r is the modified solubility parameter, $(\delta/P_c{}^{1/2})$.

Application of Solubility Parameter. Next, we turn to the application of δ_r and examine how δ_r values fit experimental data well. Kurnik[13] has

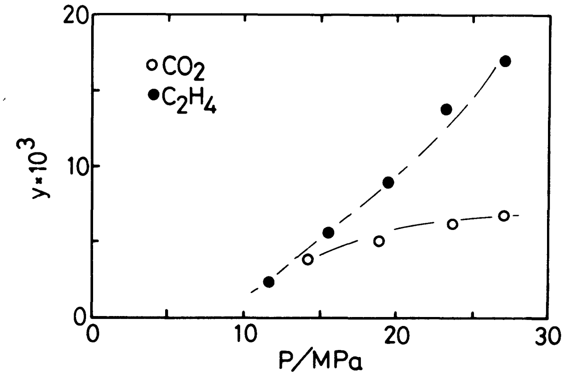

Fig. 1. Experimental solubilities for 2,6-dimethylnaphthalene in supercritical carbon dioxide and ethylene at 318 K.[13]

studied the solubility of 2,6-dimethylnaphthalene in different kinds of supercritical fluids at the same temperature. Figure 1 shows its solubility in supercritical carbon dioxide and ethylene at pressures of 11.6—27.0 MPa and 318 K. This reveals a great difference between carbon dioxide and ethylene in the power of dissolving the solute. The solubility curves for carbon dioxide and ethylene are separated over the range of the pressures examined. The solubility for ethylene increases more rapidly with the pressure than does that for carbon dioxide. These two curves scarcely imply a similarlity to each other.

Figure 2 shows the same solubility data using the modified solubility parameter (δ_r). The data for these two solvents fall on a single line. We have obtained a good correlation between the experimental data and the δ_r. The δ_r was found to be a good parameter for the solubility of 2,6-dimethylnaphthalene.

Recently, higher fatty acids have been noted in terms of their medicinal purposes and their utility as precursors of prostaglandins.[14,15] Therefore, we have examined the extration efficiency of *dl*-α-tocopherol,[16] triolein,[7,8] mixtures of triglycerides,[7,8] higher fatty acid methyl esters[17] on the addition of entrainers to the CO_2. Further, Sako et al. reported[9] the extraction of lipid, which contained γ-linolenic acid(γ-C_{18-3}), from fungi using hexane as an entrainer. Table 1 indicates the enhancement factors in the solubility on the extraction of *dl*-α-tocopherol, triolein, lipid in fungi, mixtures of tristearin and triolein, and stearic-(C_{18-0}), oleic-(C_{18-1}), linoleic-(C_{18-2}), and linolenic (C_{18-3}) acid methyl esters with the addition of several entrainers to the CO_2 at 19.6 MPa. The enhancement factor α is definited as

$$\alpha = C_2/C_2^*, \tag{9}$$

where C_2 and C_2^* are the solubility on the extraction with and without entrainer, respectively. The concentrations of each entrainer in CO_2 are 4 or 10 per cent by weight. As entrainers, ethyl acetate, ethanol, aceone, ether, dichloromethane, and hexane were sued. On the extraction of lipid such as glycerides and fatty acid methyl esters with supercritical carbon dioxide (SC-CO_2), the addition of ethanol and ether decrease the extraction efficiency, but ethyl acetate, hexane, and dichloromethane enhance it.

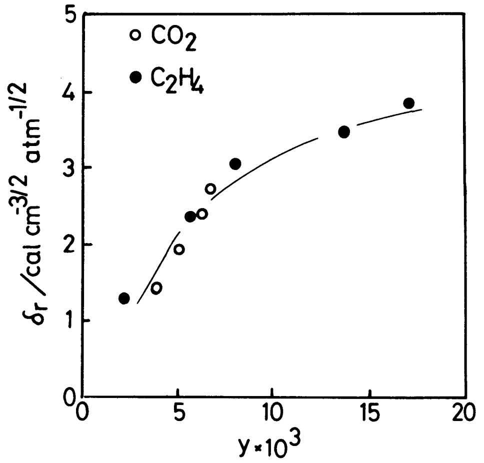

Fig. 2. Correlation of modified solubility parameters of supercritical carbon dioxide and ethylene with solubility of 2,6-dimethylnaphthalene.

We think that these effects of the entrainer could be due to a difference in the cohesive energy before and after mixing the CO_2 with the entrainer. The difference is given as energy of dissolution, ΔE_M, using the solubility parameter:

$$\Delta E_M = n_1V_1n_2V_2(\delta_1-\delta_2)^2/(n_1V_1+n_2V), \tag{10}$$

where subscripts of 1 and 2 indicate the solvent and entrainer, respectively, and n is the amount of them fed into the extractor. Furthermore, we modify ΔE_M to make it applicable to any entrainer in the following way. Thus,

$$\Delta E_M' = [n_1V_1n_2V_2/(n_1V_1+n_2V_2)][(\delta_1-\delta_2)^2/(P_{1c}P_{2c})^{1/2}]. \tag{11}$$

The energy per mole of an entrainer is given as $\Delta E_2'$.

$$(\partial\Delta E_M'/\partial n_2) = \Delta E_2' = V_2\phi_1^2(\delta_1-\delta_2)^2/(P_{1c}P_{2c})^{1/2}, \tag{12}$$

where ϕ_1 stands for the volume fraction of solvent. The concentration of an entrainer in the CO_2 is low, and $\phi_1 \simeq 1$.

We use the $\Delta E_2'$ as a parameter for expressing the effect of the entrainer. Figure 3 shows the relation between the enhancement factor α and the $\Delta E_2'$. The values of the α and $\Delta E_2'$ are indicated in Tables 1 and 2, respectively. The $\Delta E_2'$ of these entrainers is found to conveniently express the solubility data under conditions examined. The less $\Delta E_2'$ an entrainer has, the more it can enhance the extraction efficiency. Namely, when the solubility parameter of an entrainer is closed to that of the CO_2, the $\Delta E_2'$ is decreased and the solubility is increased.

On the extraction of lipid such as glycerides or fatty acids with SC-CO_2 under constant experimental

Table 1. Effects of Entrainers on Extraction Efficiency

Solute	Enhancement factor α					
	$CH_3COOC_2H_5$	CH_2Cl_2	$(CH_3)_2CO$	C_2H_5OH	$C_2H_5OC_2H_5$	C_6H_{14}
Triolein[7,8]	1.83	1.43	0.75	0.54	0.71	
Tristearin and triolein[7,8]	2.17					
Lipid containing γ-C_{18-3}[9]						4.0, 2.3
C_{18-0}, C_{18-1}, C_{18-2}, and C_{18-3}[17]	1.85	1.40	1.06			
dl-α-Tocopherol[16]	1.89	1.38				

Table 2. Values of $\Delta E_2'$

	$\Delta E_2'$/cal mol^{-1} atm^{-1}
C_6H_{14}	1.6
$CH_3COOC_2H_5$	10.5
CH_2Cl_2	16.9
$(CH_3)_2CO$	20.1
C_2H_5OH	30.1
$C_2H_5OC_2H_5$	3.7

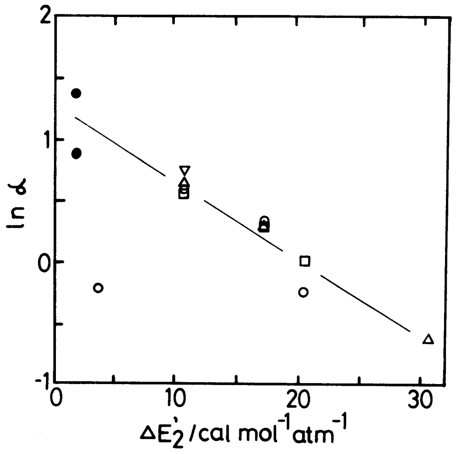

Fig. 3. Relationship between $\Delta E_2'$ and solubilities of lipids and *dl*-α-tocopherol with carbon dioxide-entrainer.[7–9,16,17] (□): A mixture of C_{18-0}, C_{18-1}, C_{18-2}, and C_{18-3} acid methyl esters, (●): lipid containing γ-C_{18-3} acid, (○): triolein, (▽): a mixture of tristearin and triolein, (△): *dl*-α-tocopherol.

conditions, if only we calculate the $\Delta E_2'$ value of the entrainer used, we can determine how much entrainer can enhance the extraction efficiency compared to the CO_2 alone. Furthermore, as shown in Table 1, in such a case that *dl*-α-tocopherol is extracted with the CO_2-ethyl acetate or CO_2-dichloromethane, the extraction efficiency is increased similarly to that of the lipid; a plot of the α against the $\Delta E_2'$ of ethyl acetate or dichloromethane is in agreement with that of the lipid. Therefore, parameter $\Delta E_2'$ might be applicable to the solubility data of not only the lipid but, also other hydrophobic materials. However, at present, the number of the solubility data using entrainers is few; we do not have any distinct evidence whether $\Delta E_2'$ could represent the solubility data using other materials as solutes or in the ranges of other pressures and temperatures. Further, on using ether as an entrainer for the extraction of triolein (Fig. 3), the $\Delta E_2'$ of ether can not represent the solubility data well. A possible reason for this is that there may be some association between ethyl ether and methyl ester molecules, causing the random-mixing assumption to be invalid in this case. We are further examining the adaptability of the parameters for the other extraction systems.

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