

CORRELATION OF SOLUBILITIES OF COAL LIQUEFACTION PRODUCTS IN SUPERCRITICAL ETHYLENE AND ETHANE USING AN EQUATION OF STATE

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Introduction

Separation methods for coal liquefaction products have received considerable attention recently in connection with the use of such products as the raw

materials for fine chemicals. Supercritical fluid extraction is showing promise as a separation method. Correlation methods for solubilities are important in the design of a supercritical extraction process. A number of approaches are already available in the literature to predict or correlate the solubilities of solid components in supercritical fluids. Many of them are

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based on equations of state (EOS) and the binary parameters needed in the EOS must be optimized by using the experimental data of solubilities to give good agreement between the correlated values and the experimental data. Therefore, it seems very useful if the binary parameters can be obtained without experimental solubility data. In a previous work,⁴⁾ the cubic equation of state proposed by Yu *et al.*^{10,11)} was applied to correlate the solubilities of coal liquefaction products (solid components) in supercritical carbon dioxide and solubility enhancements by entrainers. The binary parameters required in the EOS to give the best fit with the experimental solubility data were correlated using pure-component properties. In the present work, the same method has been applied to correlate the solubilities of coal liquefaction products in supercritical ethylene and ethane.

1. Equation of State

The solubilities of solid component in supercritical fluid, y_i , can be calculated by the following equation.

$$y_i = \frac{p_i^{\text{sat}}}{p} \cdot \frac{1}{\phi_i^G} \exp \left\{ \frac{v_i^S(p - p_i^{\text{sat}})}{RT} \right\} \quad (1)$$

where p is the pressure, T is the temperature, p_i^{sat} and v_i^S are the saturated vapor pressure and solid-state molar volume of solid component, respectively, and ϕ_i^G is the fugacity coefficient of solid component in supercritical fluid. To evaluate ϕ_i^G , the following cubic equation of state proposed by Yu *et al.*^{10,11)} was adopted.

$$p = \frac{RT}{v-b} - \frac{a}{v(v+c) + b(3v+c)} \quad (2)$$

where a , b , and c are pure-component parameters which can be calculated by using the values of critical pressure, critical temperature, and Pitzer's acentric factor as shown in the previous paper¹⁾.

To apply Eq. (2) to a mixture, the following mixing rules for constants a , b , and c were used.

$$a = \sum \sum y_i y_j a_{ij}, \quad a_{ij} = (1 - k_{ij})(a_i a_j)^{0.5} \quad (3)$$

$$b = \sum \sum y_i y_j b_{ij}, \quad b_{ij} = (1 - l_{ij})(b_i + b_j)/2 \quad (4)$$

$$c = \sum \sum y_i y_j c_{ij}, \quad c_{ij} = (1 - l_{ij})(c_i + c_j)/2 \quad (5)$$

where k_{ij} and l_{ij} denote the characteristic parameters between unlike molecules i and j . From Eqs. (2) to (5), the fugacity coefficient ϕ_i^G can be thermodynamically derived.

As discussed previously³⁾, the conventional mixing rules with k_{ij} and l_{ij} introduced into both attraction and size terms are suitable to give good correlation because the solubilities of solid component in supercritical fluid are quite small in general.

2. Correlation of Binary Parameters and Results

In the previous paper⁴⁾, the binary parameters k_{12} and l_{12} (i.e., cross parameters a_{12} , b_{12} and c_{12}) were determined to give good representation for the solubility data of solid components (2) in supercritical CO₂(1). Further, it was found that the binary parameters could be correlated with pure-component properties as follows.

The binary parameters k_{12} contained in attraction term a_{12} can be expressed as

$$k_{12} = k_{12}(308) - \alpha(T - 308) \quad (6)$$

where

$$k_{12}(308) = 1 - [a_{12}(308)/\{a_1(308)a_2(308)\}^{0.5}] \quad (7)$$

and

$$a_{12}(308) = a_{12}^{\text{NP}}(308) + a_{12}^{\text{PH}}(308) \quad (8)$$

$$a_{12}^{\text{NP}}(308) = \beta \{C_n (v_2^S)^{2/3}\}^\gamma \quad (9)$$

$$a_{12}^{\text{PH}}(308) = \varepsilon (\delta_2^{\text{PH}} v_2^S)^\zeta \quad (10)$$

The binary parameter l_{12} introduced into the size terms b_{12} and c_{12} can be correlated with

$$l_{12} = 1 - 2\{b_{12}/(b_1 + b_2)\} \quad (11)$$

where

$$b_{12} = \eta + \theta (v_2^S/v_{C,1}) \quad (12)$$

In the above equations, $k_{12}(308)$ is the parameter k_{12} at 308 K, $a_{12}(308)$ is the parameter a_{12} at 308 K, $a_{12}^{\text{NP}}(308)$ is the contribution of dispersion forces and $a_{12}^{\text{PH}}(308)$ is the contribution of polar and hydrogen bonding forces, where 308 K is chosen as a standard temperature because the temperature was chosen as that for the supercritical CO₂-solid component systems previously⁴⁾, and many data are available for the ethylene and ethane systems. Further, C_n is the number of atoms except for hydrogen for solid component, δ_2^{PH} is the contribution of polar and hydrogen bonding forces to the solubility parameter calculated by van Krevelen's method¹²⁾, $v^S = v^S$ except for benzoic acid ($v^S = 2v^S$ for benzoic acid), and $v_{C,1}$ is the critical molar volume of supercritical fluid. The pure component properties were cited from the literature¹⁾. The values of coefficients were determined based on the experimental solubility data and they could be adopted commonly for the supercritical CO₂-coal liquefaction product systems.

The same approach has been applied to correlate the binary parameters k_{12} and l_{12} for the ethylene(1)-solid component(2) and the ethane(1)-solid component(2) systems. The values of the coefficients α through θ determined here for the ethylene and ethane binary systems are listed in **Table 1** together with those for the carbon dioxide binary systems for comparison.

Table 1. Parameters for supercritical fluid (1)-solid component (2) system

Supercritical fluid	$\alpha \times 10^4$	β	γ	$\varepsilon \times 10^2$	ζ	$\eta \times 10^5$	$\theta \times 10^5$
Carbon dioxide ⁴⁾	3.656	1.0659	0.5184	3.0712	3.7645	3.097	4.388
Ethylene	6.674	1.3243	0.5290	3.0712	3.7645	3.443	7.317
Ethane	6.989	1.2719	0.5955	3.0712	3.7645	1.159	10.16

Table 2. Correlation performance for solubilities of solids in supercritical ethylene(1)

Solid (2)	Temp. (°C)	N^*	Dev**	Ref.
Anthracene	50–85	29	42.3	5)
Benzoic acid	45–65	15	10.6	7)
2,3-Dimethyl-naphthalene	35–55	18	26.5	7)
2,6-Dimethyl-naphthalene	35–55	18	29.0	7)
Fluorene	25–70	24	29.2	6)
Hexamethylbenzene	25–70	24	49.5	6)
Naphthalene	12–50	137	22.4	2, 5, 9)
Phenanthrene	25–70	45	20.9	5, 7)
Pyrene	45–75	15	16.8	6)

* Number of data.

** $(100/N)(\sum |y_2(\text{calc}) - y_2(\text{exp})|/y_2(\text{exp}))$.**Table 3.** Correlation performance for solubilities of solids in supercritical ethane (1)

Solid (2)	Temp. (°C)	N^*	Dev**	Ref.
Acridine	35–70	32	35.7	8)
Anthracene	35–70	21	28.0	6)
Benzoic acid	35–70	30	15.9	8)
Biphenyl	35–45	10	11.0	8)
Naphthalene	35–55	55	17.3	6, 8)
2-Naphthol	35–70	28	84.7	8)
Phenanthrene	40–60	23	23.5	6, 8)

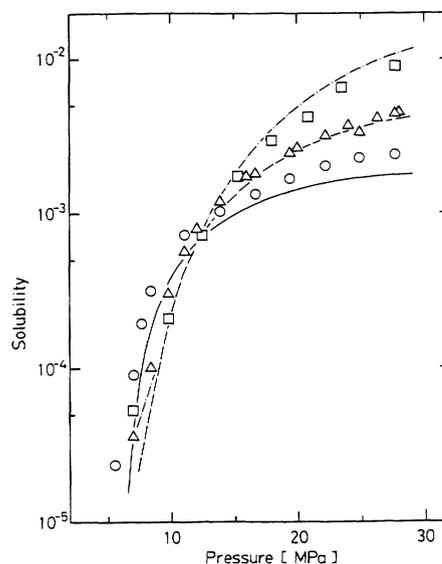
* Number of data.

** $(100/N)(\sum |y_2(\text{calc}) - y_2(\text{exp})|/y_2(\text{exp}))$.

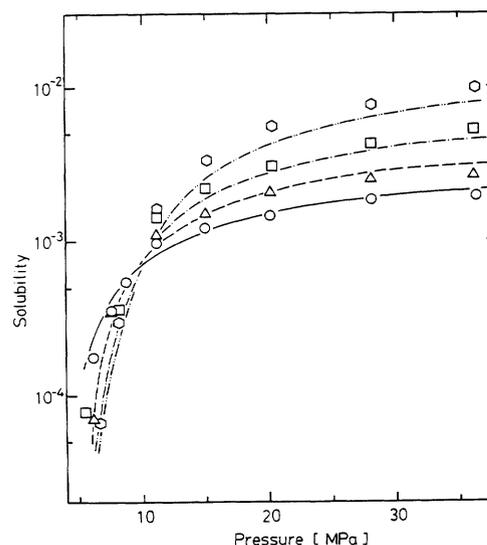
The calculated results by the parameters listed in Table 1 are good as shown in **Tables 2** and **3**, and **Figs. 1** and **2**. However, somewhat large discrepancies are shown for the ethylene-anthracene and the ethylene-hexamethylbenzene systems and the discrepancy for the ethane-2-naphthol system is remarkable.

Conclusion

The binary parameters k_{12} and l_{12} contained in the attraction and size cross terms of the equation of state proposed by Yu *et al.* could be generally expressed by pure-component properties. By using the generalized expression, the solubilities of coal liquefaction products in supercritical ethylene and ethane can be calculated with fair accuracy even if no experimental solubility data are available.

**Fig. 1.** Correlation of solubility data⁵⁾ of phenanthrene in supercritical ethylene

(○), data at 298.15 K; (△), 318.15 K; (□), 343.15 K; (—), correlation at 298.15 K; (---), 318.15 K; (— · —), 343.15 K

**Fig. 2.** Correlation of solubility data⁸⁾ of benzoic acid in supercritical ethane

(○), data at 308.23 K; (△), 318.19 K; (□), 328.21 K; (◇), 343.21 K; (—), correlation at 308.23 K; (---), 318.19 K; (— · —), 328.21 K; (— · · —), 343.21 K

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Nomenclature

a	= parameter of EOS	$[\text{J} \cdot \text{m}^3 \cdot \text{mol}^{-2}]$
b, c	= parameters of EOS	$[\text{m}^3 \cdot \text{mol}^{-1}]$
C_n	= number of atoms except for hydrogen in solid molecule	[—]
k, l	= binary parameters	[—]
N	= number of data	[—]
p	= pressure	[Pa]
p^{sat}	= saturated vapor pressure	[Pa]
R	= gas constant	$[\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}]$
T	= temperature	[K]
v	= molar volume	$[\text{m}^3 \cdot \text{mol}^{-1}]$
y	= mole fraction in gas phase	[—]
δ	= solubility parameter	$[\text{J}^{0.5} \cdot \text{m}^{-1.5}]$
α	= parameter in Eq. (6)	
β, γ	= parameters in Eq. (9)	
ε, ζ	= parameters in Eq. (10)	
η, θ	= parameters in Eq. (12)	
ϕ^{G}	= fugacity coefficient in gas phase	[—]
<Subscripts>		
C	= critical property	
i, j	= components i and j	
1	= supercritical fluid	
2	= solid component	
<Superscripts>		
NP	= contribution of dispersion forces	

PH	= contribution of polar and hydrogen bonding forces
S	= solid state

Literature Cited

- 1) Arai, Y., Y. Iwai, T. Shimizu and T. Fukuda: *J. Fuel Soc. Japan*, **69**, 281 (1990).
- 2) Diepen, G. A. M. and F. E. C. Scheffer: *J. Amer. Chem. Soc.*, **70**, 4085 (1948).
- 3) Iwai, Y., B. C.-Y. Lu, H. Yamamoto and Y. Arai: *Kagaku Kagaku Ronbunshu*, **15**, 676 (1989).
- 4) Iwai, Y., H. Yamamoto, T. Shimizu and Y. Arai: "Proceedings of the International Solvent Extraction Conference (ISEC), Kyoto, Japan", Elsevier (1991): in press.
- 5) Johnston, K. P. and C. A. Eckert: *AIChE J.*, **27**, 773 (1981).
- 6) Johnston, K. P., D. H. Ziger and C. A. Eckert: *Ind. Eng. Chem. Fundam.*, **21**, 191 (1982).
- 7) Kurnik, R. T., S. J. Holla and R. C. Reid: *J. Chem. Eng. Data*, **26**, 47 (1981).
- 8) Schmitt, W. J. and R. C. Reid: *J. Chem. Eng. Data*, **31**, 204 (1986).
- 9) Tsekhanskaya, Yu. V., M. B. Iomtev and E. V. Mushkina: *Russ. J. Phys. Chem.*, **38**, 1173 (1964).
- 10) Yu, J.-M. and B. C.-Y. Lu: *Fluid Phase Equil.*, **34**, 1 (1987).
- 11) Yu, J.-M., B. C.-Y. Lu and Y. Iwai: *Fluid Phase Equil.*, **37**, 207 (1987).
- 12) van Krevelen, D. W.: "Properties of Polymers", Elsevier, (1976).