

Influence of co-solvent on dye solubility in supercritical carbon dioxide

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Abstract -It is well known that the solubility of non-volatile solid such as disperse dye in a supercritical fluid is significantly increased by adding a small amount of co-solvent into the fluid. The phase equilibrium calculation for the ternary system composed of supercritical fluid, solute and co-solvent is established by using an expanded liquid model based on the regular solution coupled with Flory-Huggins theory. The solubility of non-volatile solid in ternary system including a co-solvent is correlated with the liquid model for activity coefficient with good accuracy. The model needs only the melting point and heat of fusion for the non-volatile solid that can be measured or available in literature. But the critical properties and the vapor pressure of the solid that are necessary to estimate the phase equilibrium by using a cubic equation of state are not required in this model.

Key words : supercritical fluid carbon dioxide, co-solvent, disperse dye, solubility, expanded liquid model

1. Introduction

Since early 1990s, supercritical fluid dyeing that uses the supercritical fluid as an alternate solvent instead of water in conventional dyeing process had been arousing much interest in textile industry because of wastewater treatment. Conventional dyeing process of polyester fiber discharges much wastewater that is contaminated by various kinds of dispersing agents, surfactants and unused dye. It is very difficult to treat the wastewater including many additives by the conventional process. The dyeing technique with supercritical fluid is an alternative one which has been developed without environmental contamination. Schollmeyer and coworkers [1-4] had established the pioneering works for the process. They reported on dyeing of

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synthetic fibers such as polyester, polypropylene, polyamide and triacetate etc. by the various disperse dyes and extended the supercritical dyeing to natural fibers such as cotton and wool. They investigated the effect on the polyester pretreatment by a heat-setting process before dyeing in supercritical carbon dioxide and also reported the results of experiences with UHDE pilot plant by supercritical carbon dioxide. Chang et al. [5], Bae et al. [6] and Lee et al. [7] carried out the experiment for dyeing the polyester fibers and films by C.I. disperse red 60, orange 3, blue 3 and blue 79 disperse dyes in supercritical carbon dioxide.

The supercritical condition of high temperature and pressure is necessary, at which the disperse dye can be much more solved and impregnated into the polymer fiber swelled by supercritical fluid. It is experienced that polyester fiber in supercritical carbon dioxide can be dyed over 373 K and 250 bars [5-7]. Bach et al. [8,9] had accomplished the pilot test of polyester dyeing in supercritical carbon dioxide at 393 K and 290 bars using a pilot plant. For more advanced development of the supercritical dyeing process, the dyeing process must be done possibly at lower pressure. Many investigators [5, 10-14] had reported that the solubility of solid with high-molecular weight such as disperse dye is remarkably increased by adding small amount of co-solvent.

In this work, the solubility of solute in a ternary supercritical fluid + solute + co-solvent mixture is estimated by using an expanded liquid model that is considered the supercritical fluid as a liquid phase. The effect of co-solvent concentration on the solubility of solute in supercritical carbon dioxide may be predicted by the model.

2. Theoretical background

The solubility of solute x_2 in mixed solvent of carbon dioxide at high pressure and a small amount of co-solvent is expressed as Eq. (1) [15].

$$\ln x_2 = \frac{\Delta H^f}{RT} \left(\frac{T}{T_m} - 1 \right) - \frac{1}{RT} \int_{T_m}^T \Delta C_p dT + \frac{1}{R} \int_{T_m}^T \frac{\Delta C_p}{T} dT + \int_{P_2^{sat}}^P \frac{\Delta v_2}{RT} dP - \ln \gamma_2 \quad (1)$$

The second to fourth term in the right hand side of Eq. (1) contribute slightly to the result and may be neglected.

The activity coefficient of species k in the mixed solvent with i and j components may be expressed, using the regular solution model coupled with Flory-Huggins theory as follow [16];

$$RT \ln \gamma_k = v_k \sum_i \sum_j \left(A_{ik} - \frac{1}{2} A_{ij} \right) \phi_i \phi_j + RT \left(\ln \frac{\phi_k}{x_k} + 1 - \frac{\phi_k}{x_k} \right) \quad (2)$$

The second term of right hand side of Eq. (2) represents Flory-Huggins mixing entropy of solution that is composed of the quite different size of molecules.

Applying Eq. (2) to the solute in ternary supercritical carbon dioxide, solute and co-solvent system,

$$RT \ln \gamma_2 = v_2 \{ A_{12} \phi_1^2 + A_{23} \phi_3^2 + (A_{12} - A_{13} + A_{23}) \phi_1 \phi_2 \} + RT \left(\ln \frac{\phi_2}{x_2} + 1 - \frac{\phi_2}{x_2} \right) \quad (3)$$

Subscripts 1, 2 and 3 stand for carbon dioxide, disperse dye and co-solvent respectively.

If the solute is less soluble in the solvent mixed with small amount of co-solvent, Gurdial et al. [10, 18] proposed following Eq. (4) that is the similar one suggested by Myers and Prausnitz [19].

$$RT \ln \gamma_2 = v_2 [A_{12} \Phi_1^{*2} + A_{23} \Phi_3^{*2} + (A_{12} - A_{13} + A_{23}) \Phi_1^* \Phi_3^*] + RT \left(\ln \frac{\Phi_3^* v_2}{x_3^* v_3} + 1 - \frac{\Phi_3^* v_2}{x_3^* v_3} \right) \quad (4)$$

Where, Φ^* and x^* are effective volume fraction and mole fraction respectively and defined as;

$$\Phi_3^* = \frac{x_3^* v_3}{x_1^* v_1 + x_3^* v_3} \quad (5) \quad x_1^* + x_3^* = 1 \quad (6)$$

$$\text{And} \quad \frac{\Phi_1^*}{\Phi_3^*} = \frac{\Phi_1' (\delta_2 - \delta_3)^2}{\Phi_3' (\delta_2 - \delta_1)^2} \quad (7) \quad \Phi_1^* + \Phi_3^* = 1 \quad (8)$$

$$\text{Where,} \quad \Phi_1' = \frac{x_1 v_1}{x_1 v_1 + x_3 v_3} \quad (9) \quad \Phi_1' + \Phi_3' = 1 \quad (10)$$

The exchange energy densities A_{12} , A_{13} and A_{23} are represented as follows;

$$A_{12} = (\delta_{d1} - \delta_{d2})^2 + \delta_{p2}^2 + \delta_{h2}^2 - \beta_{12} \quad (11) \quad A_{13} = (\delta_{d1} - \delta_{d3})^2 + \delta_{p3}^2 + \delta_{h3}^2 - \beta_{13} \quad (12)$$

$$A_{23} = (\delta_{d2} - \delta_{d3})^2 + (\delta_{p2} - \delta_{p3})^2 + \delta_{h2}^2 + \delta_{h3}^2 - \beta_{23} \quad (13)$$

The dispersion, polar and hydrogen bonding components of the solubility parameter for species i are denoted by δ_{di} , δ_{pi} and δ_{hi} , respectively. Carbon dioxide is a non-polar component and, therefore, the dipole and hydrogen bonding forces are

negligible. δ_{d1} is the dispersion contribution of solubility parameter of carbon dioxide which is estimated by Giddings et al.[20]. For solute and co-solvent, the dipole-dipole forces and hydrogen bonding interactions need to be considered. However, the polarity and hydrogen bonding contributions of the solutes such as disperse dyes to solubility parameter are not considered in this study, because it is known that the polarity of disperse dyes in supercritical condition is very weak. Therefore, δ_d is equal to the total δ and evaluated by Eq. (14).

$$\delta = (\Delta E / v)^{1/2} \quad (14)$$

ΔE and v are estimated from the group contribution method supposed by Fedors [21]. δ_{d3} , δ_{h3} and δ_{p3} of the co-solvents are evaluated with considering the temperature effect [10]. The specific interaction parameters β_{12} and β_{23} can be easily obtained from each binary mixture consisting of ternary system. Conversely, there is no simple way of obtaining the parameter β_{13} . Since the molecular interactions between carbon dioxide and co-solvent are supposed weak compared to those between the solute and the co-solvent, it is assumed by Gurdial et al. [10] that the parameter is zero and omitted from the Eq. (12). But, in this work, it is regressed by the ternary data, using the determined β_{12} and β_{23} .

3. Result and Discussions

3-1. Determination of β_{12} from binary data

Applying Eq. (2) to the solute in supercritical carbon dioxide,

$$RT \ln \gamma_2 = v_2 [(\delta_1 - \delta_2)^2 - \beta_{12}] \phi_1^2 + RT \left(1 + \ln \frac{\phi_2}{x_2} - \frac{\phi_2}{x_2} \right) \quad (15)$$

is obtained. The solubility parameters δ_1 and δ_2 are evaluated by Giddings et al.[20] and by Eq.(14) respectively. ϕ_1 and ϕ_2 are volume fractions of solvent and solute respectively. β_{12} are regressed from the binary systems; supercritical carbon dioxide + C.I. disperse red 60[7], carbon dioxide + phenanthrene[22], carbon dioxide + fluorene[23] and carbon dioxide + acridine[23].

The obtained β_{12} is almost independent of temperature, but strongly dependent of density of carbon dioxide as shown Figs. 1 and 2. Therefore, β_{12} is correlated to the carbon dioxide density. The density of carbon dioxide is estimated by the equation of state by Huang et al. [24].

3-2. Solubility of solute in co-solvent

The second to fourth term in the right hand side of Eq. (1) contribute only slightly

to the result and may be ignored. Hence, Eq. (1) may be expressed as

$$\ln x_2 = \frac{\Delta H_f}{RT} \left(\frac{T}{T_m} - 1 \right) - \ln \gamma_2 \quad (16)$$

The melting point (T_m) and heat of fusion at T_m (ΔH_f) are measured by using a differential scanning calorimeter and shown in Table 1. The activity coefficient of solute in co-solvent γ_2 is predicted by Eq. (2) that is applied to the binary solute + co-solvent system. The solubility of disperse dyes is measured in this work and the solubility of fluorene, phenanthrene and acridine are estimated by UNIFAC method [29]. Those are compared with the observed one in literature as shown in Table 2. Substituting the solubility in Table 2 to x_2 in Eq. (16), and replacing the obtained γ_2 , β_{23} in Eq. (13) can be determined by using the similar expression to the Eq. (15). The parameter β_{23} that is determined at low pressure may be used at high pressure. β_{23} is nearly independent of temperature as shown in Table 2. β_{23} for the solution of C.I. disperse red 60 in co-solvent is almost constant even though at the different temperatures of 283.2K, 305.2K and 333.3K. The similar results [29] are reported for the solubility of naphthalene in hexane and acetone, and anthracene in acetone, diethylether and ethanol.

3-3. Comparison of the estimated with the observed solubility

The obtained β_{12} , β_{13} and β_{23} from binary and ternary data are substituted to Eqs. (11) to (13) to calculate A_{12} , A_{13} and A_{23} . Those are replaced into Eq. (4) to predict γ_2 . Finally, the solubility of solute is evaluated from Eq. (16). The solubility comparison of the calculated with the observed in literature can be shown in Table 3 and Figs. 3 and 4.

AAD% in Table 3 may be enlarged, because the mole fraction of solute y_2^{exp} in denominator is extremely small value. The results for AAD% in Table 3 may be satisfied, considering the experimental error of solubility in supercritical fluids.

4. Conclusions

The solubility of non-volatile substance such as disperse dye in supercritical carbon dioxide is estimated by using an expanded liquid model to consider the supercritical fluid as a liquid phase. The results of the evaluated solubility for the supercritical carbon dioxide + solute + co-solvent ternary systems are summarized as follows;

- (1) β_{12} obtained from carbon dioxide and solute binary mixture is nearly independent of temperature, but strongly dependent of the density of carbon

dioxide.

(2) The solubility of C.I. disperse red 60 in co-solvent are measured at room temperature and atmospheric pressure, and the parameter β_{23} determined from the experimental solubility are nearly constant and almost independent of temperature.

(3) The solubility of non-volatile solutes such as C.I. disperse red 60, phenanthrene, fluorene and acridine can not be evaluated by the gas model using an equation of state, because the critical properties and sublimation pressure of the solutes can not be measured. But the solubility at any temperature, pressure and concentration of co-solvent can be satisfactory estimated by the expanded liquid model that needs not them.

Acknowledgement

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List of symbols

A : exchange energy density [cal/cm³]

C : cohesive energy density [cal/cm³]

ΔC_p : specific heat difference between gas and liquid [cal/mol]

ΔE : molar internal energy change [cal/mol]

ΔH^f : molar heat of fusion [cal/mol]

P : pressure [atm]

R : gas constant [1.987 cal/mol. K]

T : temperature [K]

v : molar volume [cm³/mol]

Δv : molar volume difference between gas and liquid [cm³/mol]

x : mole fraction [-]

x^* : effective mole fraction [-]

Greek Symbols

β : specific cohesive energy density [cal/cm³]

γ : activity coefficient [-]

δ : solubility parameter [cal/cm³]^{1/2}

ϕ : solute-free volume fraction [-]

ϕ^* : effective volume fraction [-]

Subscripts

1 : supercritical carbon dioxide
2 : solute
3 : cosolvent
d : dispersion
h : hydrogen bonding
i, j : components of i and j
m : melting point
mix : mixture
p : polar

References

1. Saus, W., Knittel, D. and Schollmeyer, E. : *Textile Res. J.*, 63, 135-142(1993).
2. Gebert, B., Saus, W., Knittel, D., Buschmann, H.-J. and Schollmeyer, E. : *Textile Res. J.*, 64, 371-374(1994).
3. Knittel, W. and Schollmeyer, E. : *Melliand Textilber.*, 76, 1092-1096(1995).
4. Bach, E, Cleve, E. and Schollmeyer, E. : in high pressure Chem. Eng., von Rohr, Ph. R. Trepp, Ch., Eds., Elsevier Science, Amsterdam, 581-586(1996).
5. Chang, K. H., Bae, H. K. and Shim, J. J. : *Korean J. Chem. Eng.*, 13, 310-316(1996).
6. Bae, H. K. and Hur, B. K. : *HWAHAK KONGHAK*, 34, 379-382(1996).
7. Lee, J. W., Min, J. M. and Bae, H. K. : *J. Chem. Eng. Data*, 44, 684-687(1999).
8. Bach, E., Cleve, E. and Schollmeyer, E. : *Melliand International* 2, 165(1999).
9. Bach, E., Cleve, E. and Schollmeyer, E. : *Melliand International* 3, 192(1998).
10. Guradial, G. S., Macnaughton, S. J, Tomasko. D. L. and Foster, N. R.: *Ind. Eng. Res.*, 32, 1488-1497 (1993).
11. Van Alsten, J. G. and Eckert, C. A.: *J. Chem. Eng. Data*, 38, 605-610(1993).
12. Guan, B., Han, B. and Yan, H. : *Fluid Phase Equilibria*, 149, 277-286(1998).
13. Catchpole, O. J., Grey, J. B. and Noermark, K. A. : *J. Chem. Eng. Data*, 43, 1091-1095(1998).
14. Iwai, Y., Yamamoto, M., Hata, Y., Koga, Y. and Arai, Y. : *J. Chem. Eng. Japan*, 29, 728-731(1996).
15. Prausnitz J. M., Lichtenthaler, R. N. and de Azevedo G. E.: "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice-Hall, Englewood Cliff, N.J, 1986.
16. Hildebrandt. J. H. and Scott, R. L.: "Regular Solutions", Prentice Hall, Englewood Cliff, New Jersey, 1962
17. Barton, A. F. M.: "CRC Handbook of Solubility Parameters and other

- Cohesive Parameters", CRC press. Ind, Boca. Raton, Florida. 1983.
18. Purkayastha, A. and Walkley, J. : Can. J. Chem., 50, 834(1972).
 19. Myers, A. L. and Prausnitz, J. M. : Ind. Eng. Chem. Fundam., 4, 209(1965).
 20. Giddings, J. C., Myers, M. N., McLaren, L. and Keller, R. A.: Science (Washington, D. C.), 162, 67-73(1968).
 21. Fedors, R. F.: Polym. Eng. Sci., 14, 472(1974).
 22. Kurnik, R. T., Holla, S. J. and Reid, R. C. : J. Chem. Eng. Data, 26, 47-51(1981).
 23. Schmitt, W. J. and Reid, R. C. : J. Chem. Eng. Data, 31, 204-212(1986).
 24. Huang, F.-H., Li, M.-H. and Lee, L.-L.: J. Chem. Eng. Japan, 18, 490(1985).
 25. Lee, J. W., Min, J. M. and Bae, H. K., Fluid Phase Equilibria, 179, 387(2001).
 26. Kramer, A. and Thodos, G. : J. Chem. Eng. Data, 34, 184-187(1989).
 27. Kramer, A. and Thodos, G. : Ind. Eng. Chem. Res., 27(8), 1506-1510(1988).
 28. Iwai, Y., Koga, Y., Fukuda, T. and Arai, Y. : J. Chem. Eng. Japan, 25, 757-760(1992).
 29. Gmehling, J. G., Anderson, T. F. and Prausnitz, J. M. : Ind. Eng. Chem. Fundam., 17(4), 269-273(1978).
 30. Lide, D. L.(Editor): "CRC Handbook of Chemistry and Physics", 71st Ed., CRC Press, 1990-1991.
 31. Barna, L., Blanchard, J.-M., Rauzy, E. and Berro, C. : J. Chem. Eng. Data, 41, 1466-1469(1996).
 32. Johnston, K. P., Ziger, D. H. and Eckert, C. A. : Ind. Eng. Chem. Fundam., 21, 191-197 (1982).
 33. Muthukumar, P., Gupta, R. B., Sung, H. D., Shim, J. J. and Bae, H. K.: Korean J. Chem. Eng., 16, 111-117(1999).

Figure Captions

Figure 1. β_{12} vs. density of carbon dioxide for carbon dioxide + C.I. disperse red 60 system[7].

Figure 2. β_{12} vs. density of carbon dioxide for carbon dioxide + phenanthrene system.

Figure 3. Experimental and calculated y_2 for carbon dioxide + C.I. disperse red 60 + acetone system at 333.2 K.

Figure 4. Experimental and calculated y_2 for carbon dioxide + C.I. disperse red 60 + ethanol system at 333.2 K.

Table 1. Physical properties of solutes and co-solvent at 298.2 K.

Solute or Co-solvent	T_m [K]	H_f [cal/mol]	ΔU [cal/mol]	v [cm ³ /mol]	Solubility parameter [cal/cm ³] ^{1/2}			
					δ	δ_d	δ_p	δ_h
C.I. Disperse Red 60	459.2 ^{b)}	5392 ^{b)}	35270 ^{c)}	388.9 ^{c)}	14.8 ^{f)}	14.8	0	0
Phenanthrene	369.5 ^{a)}	4455 ^{a)}	17970 ^{c)}	145.6 ^{c)}	11.1 ^{f)}	11.1	0	0
Fluorene	388 ^{a)}	4678.5 ^{a)}	16690 ^{c)}	136.9 ^{c)}	11.0 ^{f)}	11.0	0	0
Acridine	384.2 ^{a)}	4707.6 ^{a)}	19740 ^{c)}	137.1 ^{c)}	12.0 ^{f)}	12.0	0	0
Acetone	–	–	–	74.0 ^{d)}	9.77 ^{d)}	7.58 ^{d)}	5.08 ^{d)}	3.42 ^{d)}
Methanol	–	–	–	40.7 ^{d)}	14.47 ^{d)}	7.38 ^{f)}	6.01 ^{d)}	10.90 ^{d)}
Ethanol	–	–	–	58.73 ^{e)}	12.76 ^{e)}	6.16 ^{e)}	5.47 ^{e)}	9.77 ^{e)}

a) : from ref. (30) b) : Measured in this work c) : Estimated from Fedors group contribution method [21]

d) : from ref. (10) e) : from ref. [17] f) : Calculated by Eq. (14)

Table. 2 Estimated and experimental solubility of solute in co-solvent.

Solute	Co-solvent	Temp. [K]	Solubility [mole fraction]		β_{23}
			Estimated by UNIFAC	Measured	
C. I. Disperse	Acetone	305.8	-	2.357×10^{-3} ^{a)}	32.3
Red 60	Ethanol	305.8	-	2.485×10^{-4} ^{a)}	120.3
C. I. Disperse	Acetone	333.3	-	5.220×10^{-3} ^{a)}	31.9
Red 60	Ethanol	333.3	-	5.159×10^{-4} ^{a)}	111.6
C. I. Disperse Red 60	Acetone	283.3	-	1.478×10^{-3} ^{a)}	33.2
	Ethanol	283.3	-	923×10^{-4} ^{a)}	128.5
	Acetone	293.2	0.0971	0.115 ^{b)}	44.3
Phenanthrene	Acetone	323.2	0.3475	-	45.3
	Methanol	293.2	0.0091	0.0064 ^{b)}	150.8
	Methanol	323.2	0.0231	-	139.3
Fluorene	Acetone	293.2	0.0479	-	42.9
	Acetone	323.2	0.1684	-	43.6
Acridine	Acetone	323.2	0.1856	-	51.2
	Methanol	323.2	0.0274	-	148.4

^{a)} : Measured in this work ^{b)} : from ref. [29]

Table. 3 Comparison of the estimated solubility of solute with the observed one.

Ternary system	Cosolvent Conc. [mole %]	Data No.	Temp. [K]	Pressure Range[bar]	AAD* [%]	Data source
CO ₂ (1)+ Red 60(2)+ Acetone(3)	4.12	4	333.2	142-326	2.0	[33]
CO ₂ (1)+ Red 60(2)+ Acetone(3)	0.0-4.56	3	333.2	253.2	17.7	[33]
CO ₂ (1)+ Red 60(2)+ Acetone(3)	4.12	1	333.2	253.2	2.4	[33]
CO ₂ (1)+ Red 60(2)+ Acetone(3)	4.56	1	333.2	253.2	32.0	[33]
CO ₂ (1)+ Red 60(2)+ Ethanol(3)	4.12	4	313.2	148-306	22.7	[33]
CO ₂ (1)+ Red 60(2)+ Ethanol(3)	4.12	5	333.2	135-337	22.1	[33]
CO ₂ (1)+ Red 60(2)+ Ethanol(3)	0.0-8.2	4	313.2	253.2	20.5	[33]
CO ₂ (1)+ Red 60(2)+ Ethanol(3)	0.0-7.7	4	333.2	253.2	25.2	[33]
CO ₂ (1)+ Red 60(2)+ Ethanol(3)	0.0	5	323.7	103-306	24.2	[7]
CO ₂ (1)+ Red 60(2)+ Ethanol(3)	0.0	5	353.7	102-306	44.7	[7]
CO ₂ (1)+ Red 60(2)+ Ethanol(3)	0.0	5	383.7	106-300	33.5	[7]
CO ₂ (1)+ Red 60(2)+ Ethanol(3)	0.0	5	413.7	102-302	26.9	[7]
CO ₂ (1)+ phenanthrene(2)+ Acetone(3)	0.0	6	323.2	105-415	16.3	[32]
CO ₂ (1)+ phenanthrene(2)+ Acetone(3)	1.0	8	323.2	105-449	22.3	[11]
CO ₂ (1)+ phenanthrene(2)+ Acetone(3)	2.5	6	323.2	118-346	22.8	[11]
CO ₂ (1)+ phenanthrene(2)+ Methanol(3)	0.0	6	323.2	104-415	16.3	[14]
CO ₂ (1)+ phenanthrene(2)+ Methanol(3)	1.0	7	323.2	104-346	5.5	[11]
CO ₂ (1)+ phenanthrene(2)+ Methanol(3)	2.5	7	323.2	104-346	11.8	[11]
CO ₂ (1)+ phenanthrene(2)+ Methanol(3)	3.9	9	323.2	104-346	34.8	[11]
CO ₂ (1)+ Fluorene(2)+ Acetone(3)	0.0	9	323.2	70-415	12.7	[32]
CO ₂ (1)+ Fluorene(2)+ Acetone(3)	1.0	7	323.2	104-346	19.7	[11]
CO ₂ (1)+ Fluorene(2)+ Acetone(3)	2.5	6	323.2	118-346	14.4	[11]
CO ₂ (1)+ Acridine(2)+ Acetone(3)	0.0	6	308.3	103-350	15.4	[14]
CO ₂ (1)+ Acridine(2)+ Acetone(3)	1.0	8	323.2	104-346	20.5	[11]
CO ₂ (1)+ Acridine(2)+ Acetone(3)	2.5	8	323.2	104-380	27.2	[11]
CO ₂ (1)+ Acridine(2)+ Methanol(3)	0.0	6	308.3	102-350	15.4	[14]
CO ₂ (1)+ Acridine(2)+ Methanol(3)	1.0	9	323.2	94-346	25.3	[11]
CO ₂ (1)+ Acridine(2)+ Methanol(3)	2.5	6	323.2	104-346	27.6	[11]
CO ₂ (1)+ Acridine(2)+ Methanol(3)	2.5	8	343.2	118-415	21.8	[11]
CO ₂ (1)+ Acridine(2)+ Methanol(3)	3.9	6	323.2	104-346	33.4	[11]

$$* : AAD \% = \sum_{i=1}^N \left| \frac{y_2^{\text{exp } i} - y_2^{\text{cold}}}{y_2^{\text{exp } i}} \right| \times 100$$

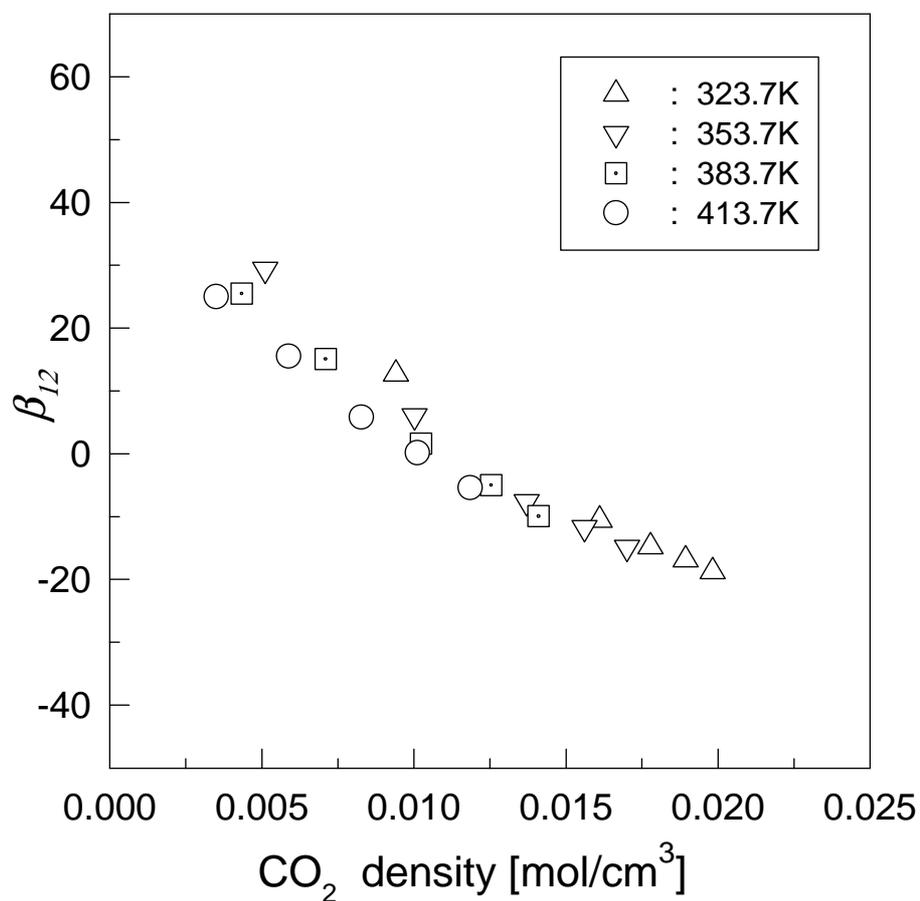


Fig. 1. β_{12} vs. density of carbon dioxide for carbon dioxide+C.I.disperse red 60 system[7].

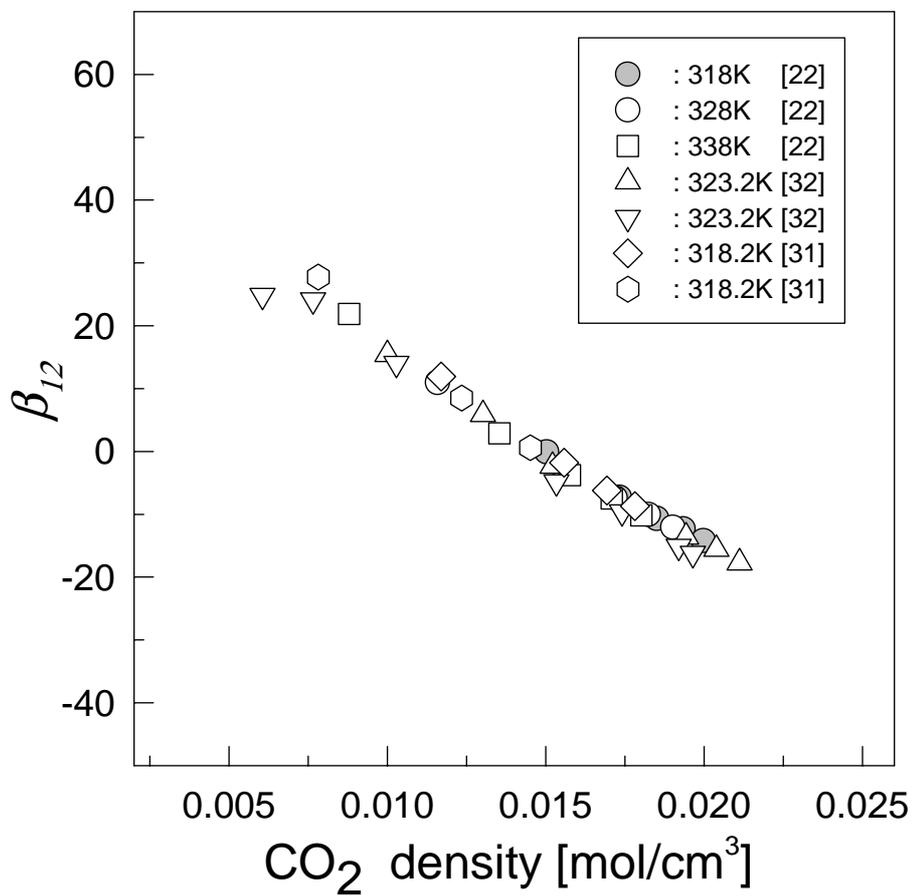


Fig. 2. β_{12} vs. density of carbon dioxide for carbon dioxide+phenanthrene system.

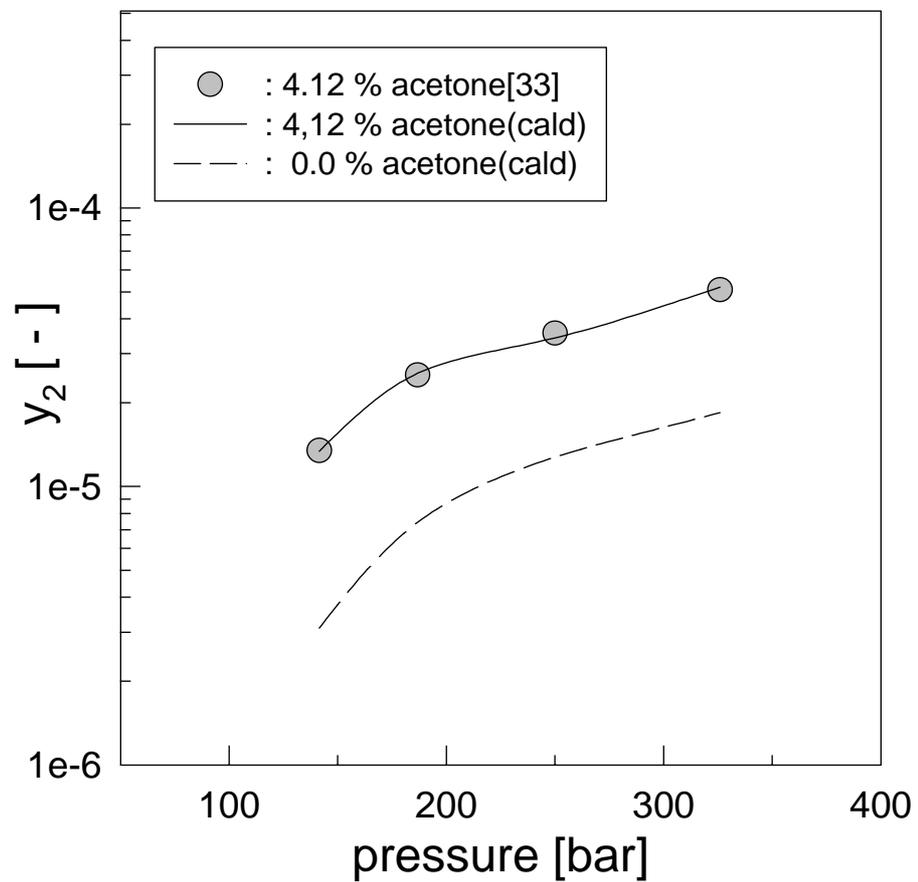


Fig. 3. Eperimental and calculated y_2 for carbon dioxide+C.I. disperse red 60+ acetone system at 333.2 K.

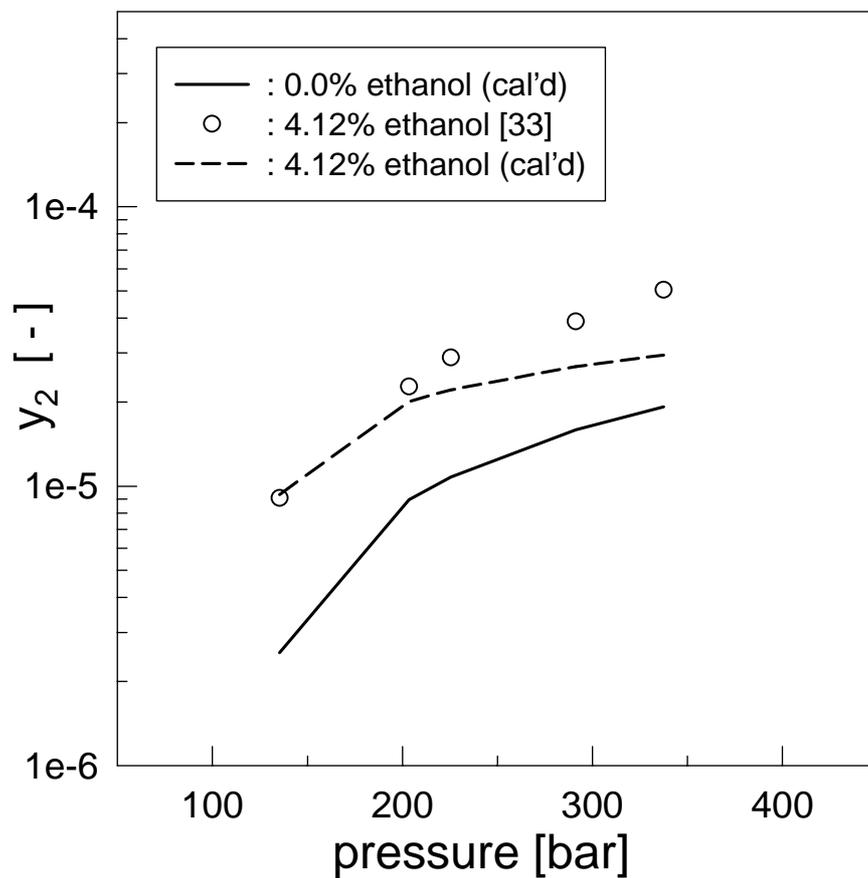


Fig. 4. Experimental and calculated y_2 for carbon dioxide +C.I. disperse red 60 +ethanol system at 333.2 K.