

VOLUME EXPANSION COEFFICIENTS AND ACTIVITY COEFFICIENTS OF HIGH-PRESSURE CARBON DIOXIDE DISSOLUTION IN ORGANIC LIQUIDS AT 298 K

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The isothermal volume expansion coefficient and the liquid-phase composition of carbon dioxide dissolution in toluene, cyclohexanone, and butanol respectively at 298 K were measured using the high-pressure densitometer method with a liquid recirculating apparatus over a pressure range from 0.1 to 10 MPa. The solvent expansion behavior (expressed by the volume expansion coefficient) caused by the dissolution of carbon dioxide into the solvent was found to increase with the increase of pressure. The carbon dioxide-cyclohexanone system has the highest volume expansion coefficient in the range of pressure investigated. Experimental results obtained are analyzed by a thermodynamic procedure, and the nonidealities of vapor and liquid phases (i.e., fugacity coefficient and activity coefficient) are compared among these three systems.

Introduction

The study of vapor-liquid equilibria at high pressure has recently increased because of their theoretical interest and their practical importance in supercritical fluid extraction, oxidation, fractionation, etc.^{1,4,6,7,10-12,14-17} Gas anti-solvent recrystallization is a kind of crystallization occurring in the liquid phase with dissolution of an anti-solvent gas into the liquid. This process might assume an

important role in salting out valuable compounds from aqueous solution or in micronizing difficult-to-comminute materials.^{8,13} To understand such a process, phase equilibria for the system containing high-pressure carbon dioxide and a liquid solvent suitable for this application are necessary. When the liquid solvent is less volatile and the solubility of the solid in the liquid phase is low, the solubility of the high-pressure gas in the liquid solvent is the key point in triggering the process. However, a survey of the literature has revealed that data for the solubility of high-pressure carbon dioxide (or supercritical

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carbon dioxide) in liquid solvent are meager, and the analysis of such asymmetric solutions has not advanced.⁵⁾

In this work a new apparatus with liquid recirculation was devised for measuring the solvent expansion behavior, expressed by the volume expansion coefficient, and for investigating the solubility of compressed carbon dioxide in toluene, cyclohexanone, and butanol at 298 K. In these mixtures a Lewis-Randall rule was chosen as a reference state for the gas phase and a pure liquid was chosen as a reference state for the liquid phase. The fugacity coefficient in the vapor phase and the activity coefficient in the liquid phase were evaluated using thermodynamic relationships. It is also interesting to compare the butanol-carbon dioxide system involving a self-associated interaction, which may be formed by hydrogen bonding, with the other two systems, involving a Lewis acid-base interaction which may be formed by acidic carbon dioxide and basic aromatics.

1. Experimental

Figure 1 shows a schematic flow diagram for the measurement of solvent expansion behavior with liquid-phase recirculation. Liquid carbon dioxide (99.5+%), compressed by a high-pressure pump, flowed into two surge vessels, and attained the desired temperature and pressure. The compressed carbon dioxide was bubbled into a gas-absorption column from the bottom through a metering valve. An agitating device was provided for mixing of the gas with the liquid. A certain amount of solution was withdrawn from the bottom of the column and was circulated from the bottom to the top through a high-pressure circulation pump (Micropump, L-1130) and a high-pressure vibrating-tube densitometer (Anton-paar, DMA512), whose temperature was controlled by an ethylene glycol bath cascaded with the refrigeration system in pressurization. The temperature was controlled within 0.01 K. The approach of equilibrium was monitored by the stability of pressure, temperature, and density of the liquid phase. For the mixture studied, the equilibrium time usually required 15 minutes or longer near the liquefaction point of carbon dioxide. At each point of equilibrium the stable reading of the vibration, shown by a digital processor (Mettler Paar, DMA60), was recorded. The total amount of carbon dioxide charged could be measured at 0.1 MPa and 298 K with the use of a wet test meter for each individual experiment. An unknown density could be calculated using the following equation.²⁾

$$\rho = \rho^{\circ} + K(\tau^2 - \tau^{\circ 2}) \quad (1)$$

The calibration constant, K , obtained from the

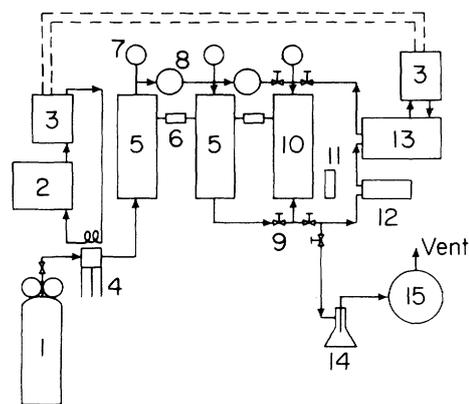


Fig. 1. Schematic flow diagram for measurement of liquid solvent expansion (1) carbon dioxide cylinder (2) cooler (3) constant temperature bath (4) metering pump (5) surge vessel (6) temperature controller (7) pressure indicator (8) pressure regulator (9) micro-metering valve (10) mini-absorption column (11) magnetic stirrer (12) recycle pump (13) densitometer (14) separation flask (15) wet test flow meter

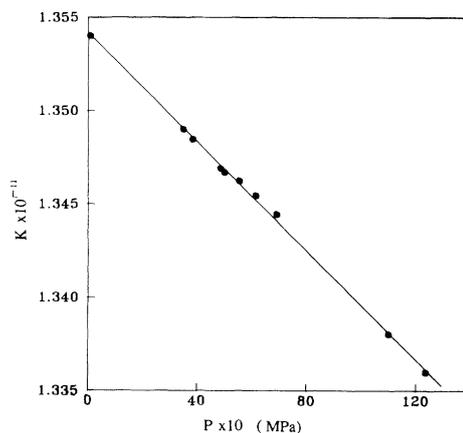


Fig. 2. Calibration constant versus pressure used for determination of density

calibration of distilled water and toluene, is shown in Fig. 2. Known literature densities of water and toluene were obtained from Chen's data³⁾ and Kashiwagi's data.⁹⁾ The expanded and unexpanded volumes were easily obtained, based on the density of carbon dioxide in the vapor phase, total amount of carbon dioxide charged, and measured density in the liquid phase according to Eq. (A1). The experimental solubility of carbon dioxide in the liquid phase could be obtained from the weight of CO_2 in the liquid phase, which is the difference between the weight of the liquid phase at each pressure and the weight of the liquid phase at unexpanded state according to Eq. (2).

$$(\rho V)^L - (\rho V)^{\circ L} = W_1^L \quad (2)$$

2. Results and Discussion

The experimental volume expansion coefficient, $\Delta V/V^{\circ}$, defined as the ratio of the volume being

expanded versus the original volume, was obtained from measurement of the density in the liquid phase and a mass balance around the whole system. The equation is shown in the Appendix. The only assumption is that the evaporation of solvents into the vapor phase is small enough to be neglected. The accuracy of the experimental data (i.e., mole fraction of CO₂ in the liquid phase) is within $\pm 10\%$, when compared with Fink's data (1990).⁵⁾ The solvent expansion behavior of toluene-carbon dioxide, butanol-carbon dioxide, and cyclohexanone-carbon dioxide mixtures is shown in Fig. 3. The cyclohexanone-carbon dioxide system has the highest volume expansion coefficient over the entire range of pressure investigated. Obviously, solvent expansion behavior did not occur strongly at low pressures below about 4 MPa, but changed linearly with total pressure. As the pressure approached the condensation pressure of carbon dioxide, the expansion coefficient increased markedly for all three systems. This result corresponds to the curvatures of the isothermal p - x phase diagram for these three systems, shown in Fig. 4. To obtain the predicted volume expansion coefficient, a rigorous Peng-Robinson equation of state with two adjustable parameters, r_{ij} , and k_{ij} , was used to correlate with the experimental solubility of carbon dioxide. Data of the volume expansion coefficient and isothermal p - x diagram are shown in Tables 1, 2, and 3 for the carbon dioxide-toluene, carbon dioxide-cyclohexanone, and carbon dioxide-butanol systems. The calculation procedure for the predicted volume expansion coefficient and the solubility of carbon dioxide in the liquid phase are shown in the Appendix.

To describe nonidealities of the vapor and liquid phases for these three systems containing carbon dioxide, two auxiliary functions have been used in the work: the vapor-phase fugacity coefficient, ϕ , and the liquid-phase activity coefficient, γ . The phase equilibria may be described conveniently by choosing

a Lewis-Randall rule as a reference state for the gas phase and a pure liquid as a reference state for the liquid phase. The vapor-phase fugacity for each component, i , is written as

$$f_i^V = y_i \phi_i P \quad (3)$$

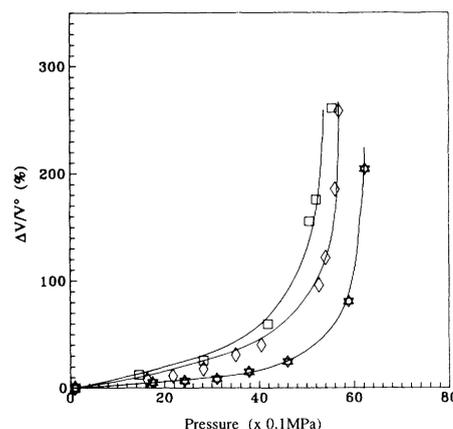


Fig. 3. Solvent expansion coefficient of toluene, cyclohexanone, and butanol absorbed with carbon dioxide (\diamond : toluene; \square : cyclohexanone; \star : butanol; —: calculated using Eq. A3)

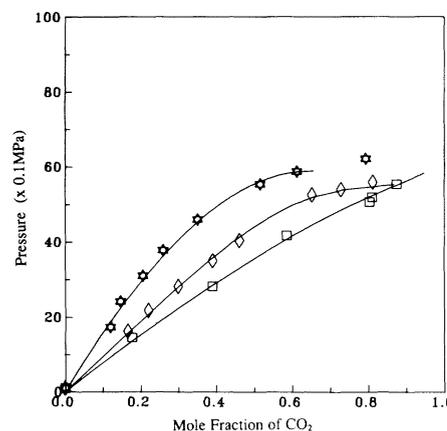


Fig. 4. Isothermal p - x phase diagram at 298 K (\diamond : toluene; \square : cyclohexanone; \star : butanol; —: calculated using Peng-Robinson equation of state)

Table 1. Volume expansion coefficient and liquid-phase composition for toluene and carbon dioxide system at 298 K

Experimental data			Calculated data	
Pressure (0.1 MPa) P	Liquid composition x_1	Expansion coefficient $\Delta V/V^\circ$ (%)	Pressure (0.1 MPa) P	Expansion coefficient $\Delta V/V^\circ$ (%)
1.0	0.000	0.00	1.0	0.00
16.3	0.166	7.70	27.5	22.22
21.8	0.220	11.22	28.2	22.95
28.2	0.299	17.63	34.3	33.06
35.0	0.390	30.72	36.4	36.50
40.4	0.460	40.00	46.5	60.85
52.6	0.651	95.50	52.6	99.06
54.0	0.727	121.11	54.0	118.01
56.0	0.810	185.00	56.0	172.10
56.8	—	258.11	56.8	264.32

Table 2. Volume expansion coefficient and liquid-phase composition for cyclohexanone and carbon dioxide system at 298 K

Experimental data			Calculated data	
Pressure (0.1 MPa) <i>P</i>	Liquid composition <i>x</i> ₁	Expansion coefficient $\Delta V/V^\circ$ (%)	Pressure (0.1 MPa) <i>P</i>	Expansion coefficient $\Delta V/V^\circ$ (%)
1.0	0.000	0.00	1.0	0.00
14.6	0.178	12.48	14.6	15.56
28.2	0.390	25.52	28.2	30.71
41.8	0.586	59.55	41.8	61.12
50.7	0.802	155.30	43.2	67.52
52.0	0.809	175.30	45.2	75.61
55.4	0.874	260.73	50.7	125.30
			52.0	165.30
			55.4	275.44

Table 3. Volume expansion coefficient and liquid-phase composition for butanol and carbon dioxide system at 298 K

Experimental data			Calculated data	
Pressure (0.1 MPa) <i>P</i>	Liquid composition <i>x</i> ₁	Expansion coefficient $\Delta V/V^\circ$ (%)	Pressure (0.1 MPa) <i>P</i>	Expansion coefficient $\Delta V/V^\circ$ (%)
1.0	0.000	0.00	1.0	0.00
17.4	0.120	5.33	18.0	6.16
24.2	0.146	6.63	28.2	8.20
31.0	0.205	8.50	43.2	18.96
37.8	0.259	15.04	48.6	26.42
46.0	0.350	24.42	53.7	41.32
55.4	0.515	—	55.4	47.23
58.8	0.612	80.51	56.1	49.83
62.6	0.792	203.90	58.8	77.96
			62.2	213.83

The fugacity coefficient, ϕ_i , is calculated from the Peng–Robinson Equation of State (PREOS) with two adjustable parameters.¹⁰⁾ The interacting parameters in PREOS, r_{ij} and k_{ij} , were correlated by fitting the equation with the experimental solubility of carbon dioxide in the liquid phase for each system at 298 K. The values of r_{ij} and k_{ij} , obtained for the toluene-carbon dioxide, cyclohexanone-carbon dioxide, and butanol-carbon dioxide systems, were 0.120 and 0.000, 0.035 and -0.020 , 0.100 and -0.035 , respectively. The liquid-phase fugacity for each component, i , can be written as

$$f_i^L = x_i \gamma_i(T, x; P_i^{\text{sat}}, x_i = 1) \times f_i^\circ(T; P_i^{\text{sat}}, x_i = 1) \exp \left\{ \int_{P_i^{\text{sat}}}^P \frac{\bar{v}_i}{RT} dP \right\} \quad (4)$$

In Eq. 4, f_i° , the fugacity of pure component at reference pressure, is based on the following relation.¹⁸⁾

$$f_i^\circ(T; P_i^{\text{sat}}, x_i = 1) = \phi_i^{\text{sat}}(T) P_i^{\text{sat}}(T) \quad (5)$$

The fugacity coefficient of pure component at the saturated vapor pressure, $\phi_i^{\text{sat}}(T)$, which is also a function of temperature, could be calculated from

Table 4. Physical properties of carbon dioxide and liquid solvents used in this study

	Toluene	Cyclohexanone	Butanol	Carbon Dioxide
<i>A</i> *	16.0137	—	17.2160	22.5898
<i>B</i> *	3096.52	—	3137.02	3103.39
<i>C</i> *	-53.67	—	-94.43	-0.160
<i>T</i> _b	383.8	428.8	390.9	194.7
<i>T</i> _c	591.7	629.0	562.9	304.2
<i>P</i> _c	40.6	38.0	43.6	72.8
ω	0.257	0.443	0.590	0.225

PREOS for each component. The Antoine vapor-pressure correlation at 298 K was used for toluene, butanol, and carbon dioxide. The Thek–Stiel vapor-pressure equation was used for cyclohexanone. **Table 4** shows the physical property used in thermodynamic calculation. The exponential term is the so-called Poynting correction and represents the pressure correction from P_i^{sat} to P . The partial molar volumes of carbon dioxide in the liquid phase are approximately the same in all three systems over the entire range of pressure investigated. These values were calculated by using an analytical differentiation of the Peng–Robinson equation of state.²⁰⁾ The

calculated partial molar volumes of the three organic solvents are invariantly as much as that of carbon dioxide at low pressure, but partial molar volumes decrease significantly at high pressure because of an increase in the solubility of carbon dioxide in the solvent, shown in Fig. 5. The carbon dioxide molecules may surround the solvent molecules to reduce the partial molar volume of the solvent. This phenomenon is similar to the aggregation of carbon dioxide molecules on the surface of toluene molecules in the work of Shim *et al.* (1991).¹⁷⁾

By equating Eqs. 3 and 4, the calculated activity coefficient for each component was obtained for each system, as shown in Fig. 6. The calculated fugacity coefficient for each component is shown in Fig. 7. The nonideality in the liquid phase, which means deviation from the ideal solution, is very large in the system containing butanol. It is possible that self-association in the liquid phase at high pressure (i.e., hydrogen bonding among butanol molecules) may contribute to the highest nonideality in this system. Cyclohexanone has not only larger positive deviation due to stronger polarity but also larger negative deviation due to stronger solvation as shown in Fig. 3. This double effect results in lower nonideality in the system containing cyclohexanone than in the system containing toluene. Cyclohexanone, which is the least volatile component, gives the lowest fugacity coefficient over the entire range of pressure. In other words, nonideality in the vapor phase is greatest in the system containing cyclohexanone.

Conclusion

In this study both the solvent expansion behavior and the isothermal p - x phase diagram for toluene, cyclohexanone, and butanol with carbon dioxide systems were measured using a high-pressure densitometer together with a liquid-phase recirculating device. Thermodynamic analysis for these three nonideal solutions was made by using the activity coefficient and fugacity coefficient. Solvent expansion behavior in the presence of compressed carbon dioxide may be predicted from 0.1 to 8 MPa using an appropriate equation of state. At low pressure the volume expansion coefficient is relatively low and the solubility of carbon dioxide increases linearly with partial pressure. As the system pressure approaches the vapor pressure of carbon dioxide the expansion increases dramatically, so that the solubility of carbon dioxide increases nonlinearly. This is another manifestation of the significant change of partial molar volumes of solvents which occurs in the high-pressure region. The results of the thermodynamic analysis indicate that the solvent, which can form association due to hydrogen bonding, may not show greater expansion behavior, but could end with

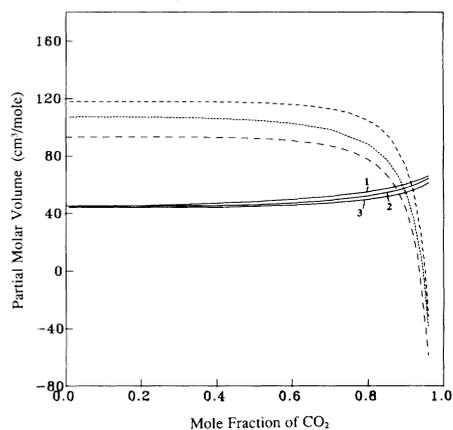


Fig. 5. Calculated partial molar volume of carbon dioxide and liquid solvents in the expansion study (1: CO₂ in butanol; 2: CO₂ in toluene; 3: CO₂ in cyclohexanone; —: toluene; - -: cyclohexanone; —: butanol)

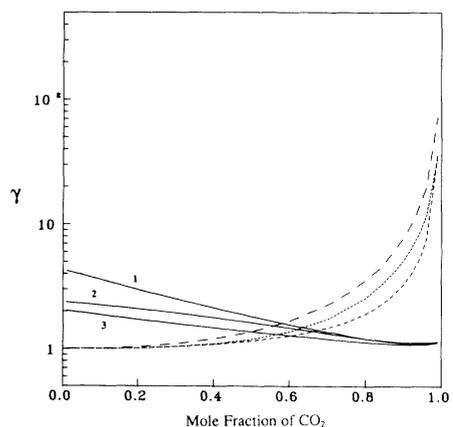


Fig. 6. Calculated activity coefficient of each component in liquid phase (1: CO₂ in butanol; 2: CO₂ in toluene; 3: CO₂ in cyclohexanone; —: toluene; - -: cyclohexanone; —: butanol)

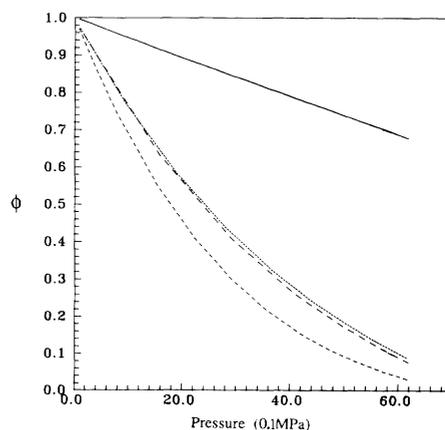


Fig. 7. Calculated fugacity coefficient of each component in vapor phase (—: CO₂ in butanol or toluene or cyclohexanone; —: toluene; - -: cyclohexanone; —: butanol)

a highly nonideal solution. The volume expansion coefficients of these three solvents seem to go further if the pressure continues to increase, because it is

possible that complete miscibility might exist between carbon dioxide and the solvent.

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Appendix

Volume expansion coefficient

By assuming a small evaporation of liquid solvents into the vapor phase, the experimental volume expansion coefficient, $\Delta V/V^\circ$, could be obtained by using the following equation.

$$\frac{\Delta V}{V^\circ} = \frac{V^\circ \rho^\circ + W - V^T \rho^V}{V^\circ (\rho^L - \rho^V)} - 1 \quad (\text{A1})$$

If the liquid-phase volume, V^L , can be calculated from the liquid-phase molar volume, v^L , the theoretical volume expansion coefficient, $\Delta V/V^\circ$, could be calculated by the following equations:

$$V^L = (X)(N)(v^L) \quad (\text{A2})$$

$$\frac{\Delta V}{V^\circ} = \frac{V^L}{V^\circ} - 1 \quad (\text{A3})$$

Gas solubility in the liquid solvent

Determination of the nonidealities in the fluid phase, as described by ϕ_i , is the key challenge in the calculation of the phase equilibrium. With the measured solubility of carbon dioxide in the solvent, the Peng-Robinson equation of state¹⁰⁾ was used to optimize two parameters, r_{ij} and k_{ij} , and to predict the solubility of carbon dioxide by the following mixing rule and equations.

The mixture parameters a , b , are defined by the mixing rules

$$a = \sum \sum x_i x_j a_{ij} \quad (\text{A4})$$

$$b = \sum \sum x_i x_j b_{ij} \quad (\text{A5})$$

$$a_{ij} = (1 - r_{ij})(a_{ii} a_{jj})^{1/2} \quad (\text{A6})$$

$$b_{ij} = \frac{(1 - k_{ij})(b_{ii} + b_{jj})}{2} \quad (\text{A7})$$

At the vapor-liquid equilibrium the fugacities of the components are equal and the gas solubility in the liquid solvent can be defined as:

$$x_i = \left(\frac{\phi_i^V}{\phi_i^L} \right) y_i \quad (\text{A8})$$

Nomenclature

A^*, B^*, C^*	= constants in the Antoine equation	
a	= energy-related parameter in PREOS	[MPa · cc ² /mol ²]
b	= size-related parameter in PREOS	[cm ³ /mol]
f	= fugacity	[MPa]
k	= size-related interaction parameter	
N	= total moles of carbon dioxide and solvent charged into the absorption column, determined from the experimental data	[mol]
P	= pressure	[MPa]
R	= gas constant (= 8.206)	[MPa · cm ³ /mol/K]
r	= energy-related interaction parameter	
T	= temperature	[K]
T_b	= boiling temperature	[K]
V	= volume	[cm ³]
v	= molar volume	[cm ³ /mol]
\bar{v}	= partial molar volume	[cm ³ /mol]
W	= total weight of carbon dioxide charged	

	into the absorption column	[g]
X	= mole fraction of liquid phase in the absorption column, obtained by inverse lever rule ¹⁹⁾	[—]
x	= mole fraction of the component in the liquid phase	[—]
y	= mole fraction of the component in the vapor phase	[—]
Δ	= difference	
ϕ	= fugacity coefficient	[—]
γ	= activity coefficient	[—]
ρ	= density	[g · cm ⁻³]
τ	= period of vibration of the fluid, given by densitometer	[—]
ω	= acentric factor	[—]

<Subscripts>

1	= component 1 (carbon dioxide)
2	= component 2 (liquid solvent)
c	= critical
i, j	= component i, j

<Superscripts>

^o	= unexpanded state (or reference state)
sat	= saturated state
L	= liquid phase
V	= vapor phase
T	= total

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