

Vapor-liquid equilibria of carbon dioxide and nonionic surfactant system at elevated pressures

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Abstract—Aqueous solutions of the polyoxyethylene nonionic amphiphiles have been extensively investigated at atmospheric pressure, but only a few data of nonionic amphiphile - carbon dioxide system are available at elevated pressures. Isothermal vapor-liquid equilibrium data for the binary ethylene glycol propyl ether (C3E1) - carbon dioxide system at 313.15 K, 323.15 K were measured at elevated pressures. We used two-phase circulating type equipment with a view cell. Modeling of the experimental data has been performed using the Peng-Robinson equation of state, statistical associating fluid theory (SAFT) and Sanchez-Lacombe equation of state.

Key words: Nonionic Surfactant, Carbon Dioxide, Elevated Pressure

INTRODUCTION

Surfactant molecules constitute an important class of chemicals with numerous applications in chemical industries and in pharmaceutical and food industries. Phase equilibria, such as vapor-liquid equilibria, liquid-liquid equilibria are essential in the design and operation of separation processes. Many experimental and theoretical investigations have been performed in chemical engineering problems concerning phase equilibria.

Amphiphile systems, especially micelle and microemulsion systems, showed highly non-ideal behavior due to the hydrogen bonding and hydrophobic interaction. Aqueous solutions of the polyoxyethylene nonionic amphiphiles have been extensively investigated at atmospheric pressure [Oh et al., 1987; Lai and Chen, 1999], but only a few data of the nonionic amphiphile - carbon dioxide system are available at elevated pressures.

Isothermal vapor-liquid equilibrium data for the binary ethylene glycol propyl ether (C3E1) - carbon dioxide system at 313.15 K, 323.15 K were measured at elevated pressures. We used two-phase circulating type equipment with a view cell. Modeling of the experimental data has been performed by using the Peng-Robinson equation of state, statistical associating fluid theory (SAFT), and Sanchez-Lacombe equation of state.

EXPERIMENTS

1. Materials

CO₂ of 99.99% purity was supplied by Korean industries gases. Ethylene glycol propyl ether (C3E1) of minimum purity 99.5% purity was supplied by Aldrich. Both components were used without further purification.

2. Apparatus and Procedure

Fig. 1 shows a schematic diagram of the experimental apparatus. A convection oven and a sampling box attached to it were main-

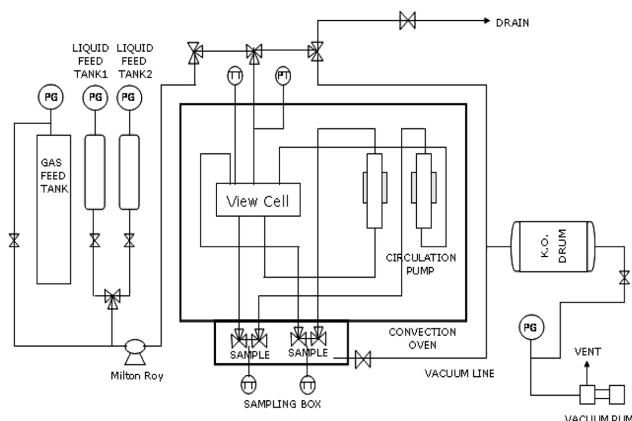


Fig. 1. Schematic diagram of experimental apparatus. TT, thermometer; PT, pressure transducer; PG, pressure gauge.

tained at the same temperature. The equilibrium cell was installed with quartz sight glasses and its internal volume was approximately 150 ml. Two magnetic pumps circulated the chemicals of both phases to promote equilibrium. The accuracy of the temperature measuring system is ± 0.03 K in the range 373 to 673 K, as specified by the manufacturer, and the accuracy of the pressure transducer is $\pm 0.1\%$ on the specification and $\pm 0.05\%$ after the calibration of the Korea Testing Laboratory. The samples are transported to the gas chromatograph (GC) on-line, so no samples were discarded. The transfer circuit between the sampling box and GC was heated to prevent condensation. In order to analyze the samples, we used an online gas chromatograph (GC). TCD and Porapak Q packing column were used.

When the cell reached the desired temperature, we evacuated the cell and sampling loop. Then we introduced the chemicals to the cell and started two magnetic pumps to circulate chemicals of both phases. When equilibrium was reached, samples were taken to the gas chromatograph and the composition of each phase was analysed.

THERMODYNAMIC MODELS

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1. Sanchez-Lacombe Model with Consistent Phase Calculation Method

The Sanchez and Lacombe equation of state [Sanchez and Lacombe, 1976] is

$$\frac{P}{T\bar{\rho}} = -\frac{1}{\bar{\rho}} \ln(1-\bar{\rho}) - \left(1 - \frac{1}{r}\right) - \frac{\bar{\rho}}{T} \quad (1)$$

in which

$$\bar{T} = \frac{T}{T^*} = \frac{RT}{\varepsilon^*} \quad \bar{P} = \frac{P}{P^*} = \frac{P v^*}{\varepsilon^*} \quad \bar{\rho} = \frac{\rho}{\rho^*} \quad (2)$$

and the configurational chemical potentials are

$$\begin{aligned} \frac{\mu_i^{conf}}{RT} = & \ln \phi_i + 1 - \frac{r_i}{r} + \ln \bar{\rho} + r_i \left[\left(\frac{1}{\bar{\rho}} - 1 \right) \ln(1-\bar{\rho}) - \frac{\bar{\rho}}{T} + \frac{\bar{P}}{T\bar{\rho}} \right] \\ & + \frac{Z}{r} \left[\frac{nr}{v^*} \left(\frac{\partial v^*}{\partial n_i} \right)_{n_j} \right] - \frac{\bar{\rho}}{T} \left[\frac{nr}{\varepsilon^*} \left(\frac{\partial \varepsilon^*}{\partial n_i} \right)_{n_j} \right] \end{aligned} \quad (3)$$

where the compressibility factor Z is calculated from equation of state, r_i is the segment number of component i and the segment fraction ϕ_i is:

$$\phi_i = \frac{X_i r_i}{r}, \quad r = \sum X_i r_i \quad (4)$$

A consistent method for phase equilibrium calculation using the Sanchez and Lacombe equation of state was represented by Neau [2002]. It was shown that, whatever the mixing rules considered, the configurational chemical potentials derived from configurational partition function are thermodynamically inconsistent and the fugacity coefficients derived from the equation of state are thermodynamically consistent for calculating consistent phase equilibrium conditions.

The fugacity coefficients derived from the Sanchez and Lacombe equation of state are expressed as follows,

$$\begin{aligned} \ln \phi_i = & -\ln Z + r_i \left[-\ln(1-\bar{\rho}) - 2\frac{\bar{\rho}}{T} \right] + \frac{Z-1}{r} \left[\frac{nr}{v^*} \left(\frac{\partial v^*}{\partial n_i} \right)_{n_j} \right] \\ & - \frac{\bar{\rho}}{T} \left[\frac{nr}{\varepsilon^*} \left(\frac{\partial \varepsilon^*}{\partial n_i} \right)_{n_j} \right] \end{aligned} \quad (5)$$

In this study, the van der Waals one fluid mixing rules with one binary interaction parameter were used as follows.

$$\varepsilon^* = \sum_i \sum_j \phi_i \phi_j \varepsilon_{ij}^*, \quad \varepsilon_{ij}^* = \sqrt{\varepsilon_{ii}^* \varepsilon_{jj}^*} (1 - k_{ij}) \quad (6)$$

$$v^* = \sum_i \phi_i v_i^* \quad (7)$$

2. Peng-Robinson Equation of State

The Peng-Robinson equation of state [Peng and Robinson, 1976] is as follows.

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \quad (8)$$

$$a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T) \quad (9)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (10)$$

$$\alpha(T) = \left[1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (11)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (12)$$

Where T_c and P_c are the critical temperature and the critical pressure of the pure substance, respectively, and ω is the acentric factor. The van der Waals one fluid mixing rules used in this study are given by

$$a = \sum_i \sum_j X_i X_j a_{ij} \quad (13)$$

$$b = \sum_i X_i b_i \quad (14)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (15)$$

where k_{ij} is the binary interaction parameter.

3. Statistical Associating Fluid Theory (SAFT) Equation of State

The SAFT equation of state [Huang and Radosz, 1990, 1991] consists of hard sphere, dispersion, chain and association contributions to the compressibility factor of the fluid mixtures.

$$Z = 1 + A_{hs} + Z_{disp} + Z_{chain} + Z_{assoc} \quad (16)$$

$$Z_{hs} = \frac{6}{\pi N_A \rho} \left[\frac{\xi_0 \xi_3}{1 - \xi_3} + \frac{3 \xi_1 \xi_2}{(1 - \xi_3)^2} + \frac{(3 - \xi_3) \xi_2^2}{(1 - \xi_3)^3} \right] \quad (17)$$

$$\text{with } \xi_k = \frac{\pi N_A \rho}{6} \sum_i X_i r_i (d_i)^k, \quad k = 0, 1, 2, 3 \quad (18)$$

$$Z_{chain} = \sum_{i=1}^m X_i (1 - r_i) L(d_i), \quad (19)$$

$$\text{with } L(d_i) = \frac{2 \xi_3 + 3 d_i \xi_2 - 4 \xi_3^2 + 2 d_i^2 \xi_2^2 + 2 \xi_3^3 + d_i^2 \xi_2 \xi_3 - 3 d_i \xi_2 \xi_3^2}{(1 - \xi_3)(2 - 4 \xi_3 + 3 d_i \xi_2 + 2 \xi_3^2 + d_i^2 \xi_2^2 - 3 d_i \xi_2 \xi_3)} \quad (20)$$

$$Z_{disp} = r \sum_n \sum_m m D_{nm} (u/kT)^n (\xi_3 / \xi_{3cp})^m \quad (21)$$

$$Z_{assoc} = \rho \sum_{i=1}^m X_i \left[\sum_{A_i} \left(\frac{1}{X^{A_i}} - \frac{1}{2} \right) \frac{\partial X^{A_i}}{\partial \rho} \right] \quad (22)$$

Table 1. Pure parameters of the Peng-Robinson, the Sanchez-Lacombe, and the SAFT model

PR	T _c (K)	P _c (bar)	w	Reference	
CO ₂	304.2	73.83	0.224	Exp. data	
C1E1	564.0	50.10	0.733	Joback	
C2E1	569.0	42.40	0.758	Joback	
C3E1	615.2	36.51	0.487	Exp. data	
SL	T* (K)	P* (bar)	ρ* (g/cm ³)	Remark	
CO ₂	290.84	6619.50	1.573		
C1E1	506.75	7272.25	1.122		
C2E1	506.78	6122.24	1.088		
C3E1	569.92	4461.00	1.016		
SAFT	v ^{oo} (ml/mol)	m	u ⁰ /k (K)	ε ^{AA} /k (K)	10 ² κ ^{AA}
CO ₂	13.60	1.414	215.63		
C1E1	12.00	4.178	260.19	2290.45	0.462
C2E1	12.00	4.183	256.23	2051.24	1.227
C3E1	12.00	4.756	254.32	1571.79	1.228

where ρ is the total molar density, r_i is the number of segments per molecule i , d_i is the temperature-dependent segment diameter, D_{nm} are universal constants, $\zeta_{sep}=0.74048$, A_i is the total number of association sites in compound i , and X^{A_i} is the mole fraction of sites A_i which are not bonded. In this study, the van der Waals one fluid mixing rules with one binary interaction parameter were used.

Pure parameters of the Sanchez-Lacombe, Peng-Robinson and SAFT EOS (equation of state) for CO₂, C1E1, C2E1 and C3E1 are listed in Table 1. For C1E1 and C2E1, pure parameters of the Peng-Robinson EOS are obtained by using the group contribution method [Joback, 1984] and pure parameters of the Sanchez-Lacombe and SAFT EOS are obtained by using vapor pressure and saturated liquid density. Vapor pressure can be obtained from boiling point and critical properties, and liquid density also can be obtained by using the group contribution method [Yamada and Gunn, 1973] with one experimental density at 25 °C and critical properties.

RESULTS AND DISCUSSION

The experimental vapor-liquid equilibrium data of carbon dioxide and ethylene glycol propyl ether (C3E1) system at 313.15 K and 323.15 K are given in Table 2. The experimental data were correlated with the Sanchez-Lacombe EOS with original expression and consistent expression, the PR EOS and the SAFT EOS. The simplex algorithm was used to determine the binary interaction parameter. Only one binary interaction parameter was used for all models in this study. The objective function (OF) used in the regression is as follows.

$$OF = \sum_i^N \left| \frac{P^{exp} - P^{cal}}{P^{exp}} \right| \quad (23)$$

Where N is the number of experimental data points and P^{exp} and P^{cal} are the experimental and the calculated pressures, respectively.

Fig. 2 shows the experimental data and correlated results of the original expression of the Sanchez-Lacombe EOS denoted by “SL,” the consistent method of the Sanchez-Lacombe EOS denoted by “CSL,” the Peng-Robinson EOS, and the SAFT EOS for CO₂-C3E1 system. The consistency-considered Sanchez-Lacombe EOS is bet-

Table 2. Measured vapor-liquid equilibrium data for CO₂-C3E1 system

P/bar	x ₁	y ₁	P/bar	x ₁	y ₁
T=313.15 K			T=323.15 K		
3.35	0.046	0.985	4.22	0.061	0.987
7.31	0.102	0.988	7.22	0.09	0.989
12.12	0.145	0.991	12.67	0.141	0.992
19.73	0.211	0.993	19.79	0.208	0.993
25.86	0.293	0.994	29.71	0.303	0.996
34.42	0.391	0.995	41.89	0.401	0.996
43.58	0.489	0.995	54.89	0.527	0.996
51.51	0.562	0.995	61.40	0.606	0.996
60.13	0.659	0.996	71.83	0.695	0.996
66.73	0.728	0.996	82.10	0.786	0.995
71.87	0.812	0.996	88.66	0.874	0.995
75.93	0.887	0.995	91.17	0.892	0.994

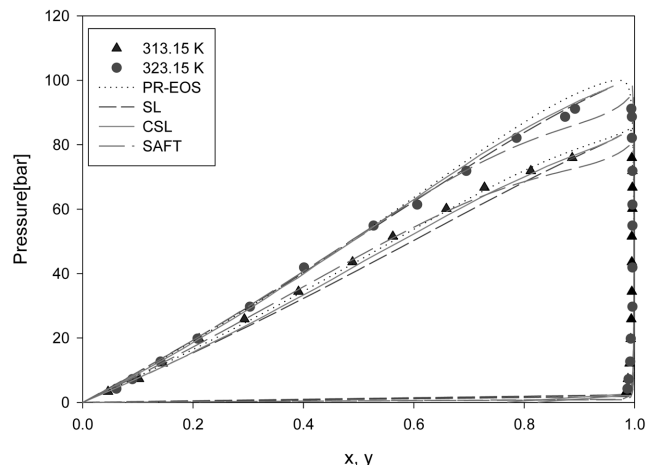


Fig. 2. Experimental data and correlated results of the 4 models for CO₂-C3E1 system at 313.15, 323.15 K.

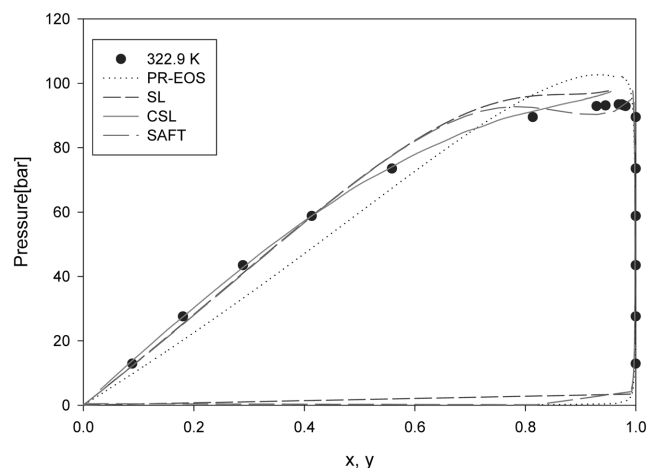


Fig. 3. Correlated results of the 4 models for CO₂-C1E1 system at 323.3 K.

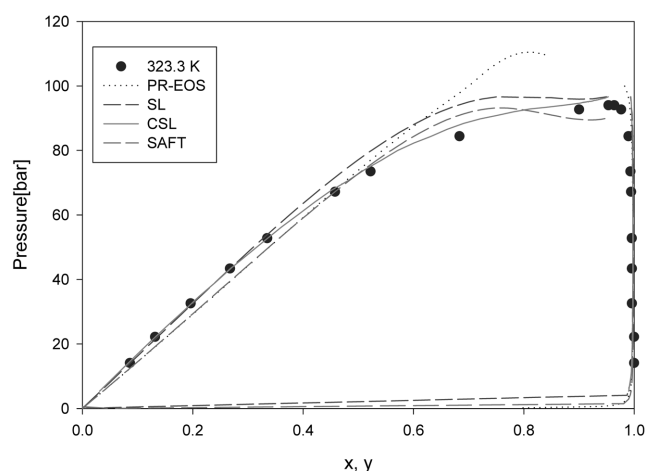


Fig. 4. Correlated results of the 4 models for CO₂-C2E1 system at 322.9 K.

ter than the original Sanchez-Lacombe EOS.

For other group's experimental data [Joung et al., 2001] of CO₂-

Table 3. Correlated results of CO₂-C1E1, C2E2, and C3E1 systems

Models	CO ₂ -C1E1 System		CO ₂ -C2E1 System		CO ₂ -C3E1 System			
	at 323.3 K		at 322.9 K		at 313.15 K		at 323.15 K	
	k_{ij}	AADP*	k_{ij}	AADP	k_{ij}	AADP	k_{ij}	AADP
SL	0.0581	0.0416	0.0784	0.0506	0.1042	0.0559	0.09284	0.0682
CSL	-0.0078	0.0130	-0.0057	0.0213	-0.0582	0.0307	-0.0658	0.0293
PR	0.0646	0.0932	0.0710	0.1042	0.0419	0.0393	0.0259	0.0589
SAFT	0.0635	0.0110	0.0600	0.0243	0.0438	0.0486	0.0432	0.0613

*: $AADP = \frac{1}{n_T} \sum_i \left| \frac{P^{cal} - P^{exp}}{P^{exp}} \right|$, n_T : number of experimental points.

C1E1 and CO₂-C2E1 systems, correlated results of the original expression and the consistency-considered expression of the Sanchez-Lacombe EOS, the Peng-Robinson EOS, and the SAFT EOS are represented in Fig. 3 and Fig. 4, respectively. In both systems, the consistency-considered Sanchez-Lacombe EOS is better than the original expression. The binary interaction parameters and the absolute average deviation of pressure (AADP) for CO₂-C1E1, C2E1 and C3E1 systems are summarized in Table 3.

The consistency-considered Sanchez-Lacombe EOS with even no hydrogen bonding terms shows equivalent results to the SAFT EOS and both of them have more improved results than the Sanchez-Lacombe EOS and the Peng-Robinson EOS.

CONCLUSION

The isothermal vapor-liquid equilibria data for the system CO₂-C3E1 were obtained at 313.15, 323.15 K. The fugacity coefficients derived from the Sanchez-Lacombe EOS are considered for calculating consistent phase equilibrium conditions. The consistency-considered Sanchez-Lacombe EOS shows more improved results than the original expression of the Sanchez-Lacombe EOS. The consistency-considered Sanchez-Lacombe EOS with even no hydrogen bonding terms shows equivalent results to the SAFT EOS and both of them have more improved results than the Sanchez-Lacombe EOS and the Peng-Robinson EOS.

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NOMENCLATURE

a : interaction parameter of the Peng-Robinson model
b : volume parameter of the Peng-Robinson EOS
d : temperature-dependent segment diameter
 D_{nm} : universal constant of the SAFT EOS
 N_A : Avogadro's number
 k_{ij} : binary interaction parameter
P : pressure
 $\tilde{P}$: reduced pressure
 P^* : characteristic parameter of the Sanchez-Lacombe EOS

P_c : critical pressure
r : number of segments
T : temperature
 $\tilde{T}$: reduced temperature
 T_c : critical temperature
 T^* : characteristic parameter of the Sanchez-Lacombe EOS
u/k : interaction parameter of the SAFT EOS
x : mole fraction
 X^{A_i} : mole fraction of sites A_i which are not bonded
w : acentric factor
 ρ : molar density
 $\tilde{\rho}$: reduced density
 ρ^* : characteristic parameter of the Sanchez-Lacombe EOS
 v^* : characteristic parameter of the Sanchez-Lacombe EOS
 ε^* : energy parameter of the Sanchez-Lacombe EOS
 μ : chemical potential
 φ : fugacity coefficient
 ϕ : segment fraction
 ξ : defined by Eq. (18)

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