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Vapor-Liquid Equilibria for CO₂ - Nonionic Surfactant System at Elevated Pressures

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Introduction

- Surfactants systems, especially micelle and microemulsion systems, was *highly non-ideal behavior* due to the *hydrogen bonding* and *hydrophobic interaction*.
- Surfactants + water and surfactants + alkane phase equilibrium data has been extensively investigated at low pressures, but only a few data of *surfactant + CO₂ vapor-liquid Equilibria* are available at elevated pressures.
- Furthermore, VLE measurements for CO₂ and surfactant mixtures are especially important because the properties of such mixtures are difficult to be predicted from the pure component values.
- In this work, *Vapor-Liquid Equilibria for the binary CO₂ + alkyl polyoxyethylene alcohol surfactant systems* were investigated at elevated pressures.



Apparatus and Materials

■ *Materials*

CO₂ : Korea Gas industry with 99.99% purity

C3E1 : Ethylene glycol monopropyl ether, Aldrich with 99.5% purity

■ *Thermometer*

probe : 5614, Indicator : 1560 supplied by Hart Scientific Co.
(accuracy ± 0.03 K in 373~673 K)

■ *Pressure transducer*

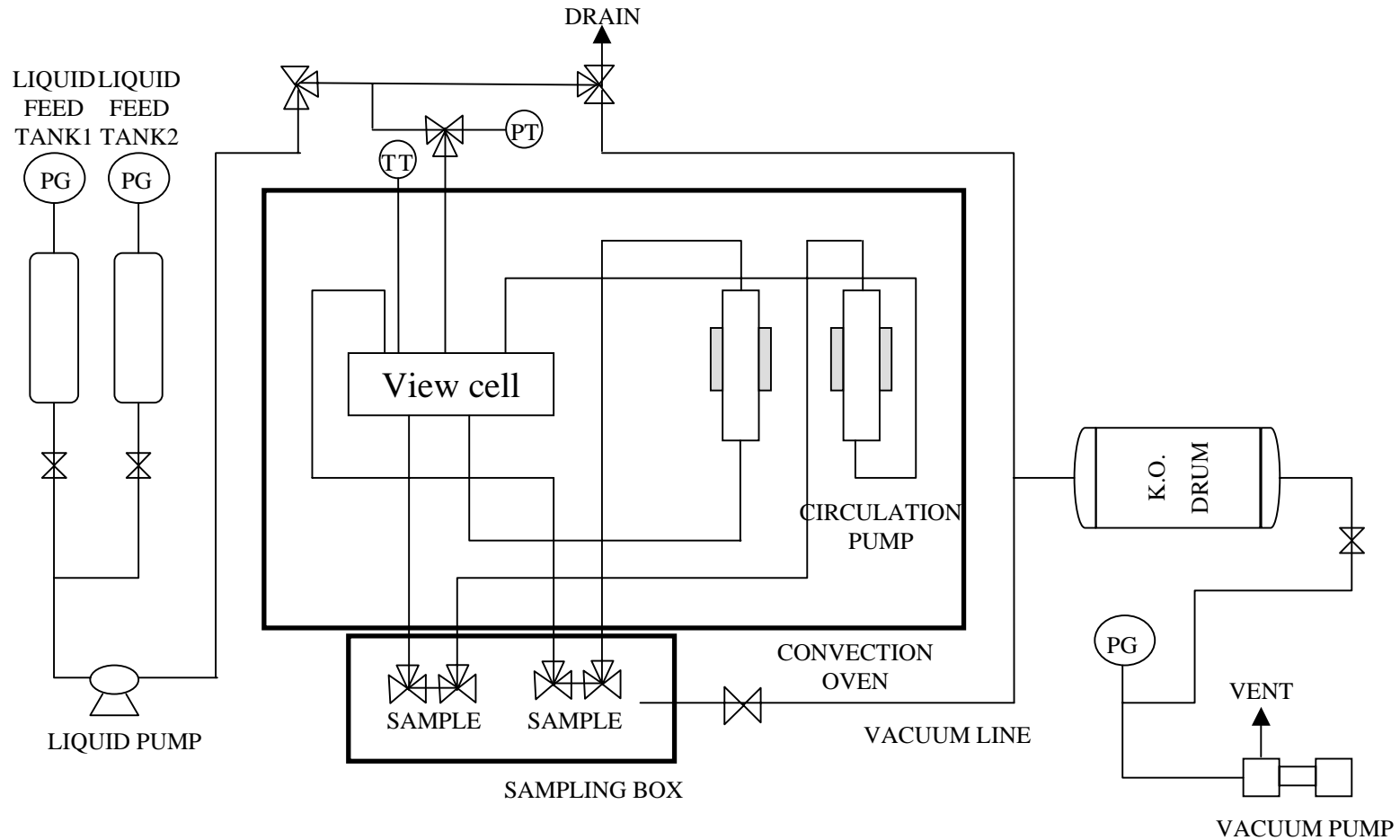
STJE/1833-2 supplied by Sensotec Co.
(range <1000 psia, accuracy $\pm 0.1\%$)

■ *Gas Chromatography*

detector : TCD

column : Porapak S in 0.95 cm O.D. and 160 cm long

Experimental apparatus



Experiment : CO₂ + C3E1 System

T(K)	P(bar)	x₁	y₁	T(K)	P(bar)	x₁	y₁
313.15	3.35	0.046	0.985	323.15	4.22	0.061	0.987
	7.31	0.102	0.988		7.22	0.090	0.989
	12.12	0.145	0.991		12.67	0.141	0.992
	19.73	0.210	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		



Cubic Equation of State

■ Peng – Robinson Equation of State

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

$$a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \times \alpha(T_r, \omega) \quad \alpha^{1/2} = 1 + \kappa(1 - T_r^{1/2}) \quad \kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

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

■ van der Waals 1-fluid mixing rule

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad a_{ij} = \sqrt{a_{ii} a_{jj}} (1 - k_{ij})$$

$$b_m = \sum_i \sum_j x_i x_j b_{ij} \quad b_{ij} = \frac{(b_{ii} + b_{jj})}{2}$$

Ind. Eng. Chem. Fundam., Vol. 15, No. 1, 59 (1976)



Statistical Associated Fluid Theory (SAFT)

$$Z_{res} = Z_{hs} + Z_{disp} + Z_{chain} + Z_{assoc}$$

$$Z_{hs} = \frac{6}{\pi N_A \rho} \left[\frac{\xi_0 \xi_3}{1 - \xi_3} + \frac{3 \xi_1 \xi_2}{(1 - \xi_3)^2} + \frac{(3 - \xi_3) \xi_2^3}{(1 - \xi_3)^3} \right] \quad \xi_k = \frac{\pi N_A \rho}{6} \sum_{i=1}^m x_i r_i (d_i)^k$$

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

$$Z_{chain} = \sum_{i=1}^m x_i (1 - r_i) L(d_i) \quad L(d_i) = \frac{2\xi_3 + 3d_i \xi_2 - 4\xi_3^2 + 2d_i^2 \xi_2^2 + 2\xi_3^3 + d_i^2 \xi_2^2 \xi_3 - 3d_i \xi_2 \xi_3^2}{(1 - \xi_3)(2 - 4\xi_3 + 3d_i \xi_2 + 2\xi_3^2 + d_i^2 \xi_2^2 - 3d_i \xi_2 \xi_3)}$$

$$Z_{assoc} = \rho \sum_{i=1}^m x_i \left[\sum_{S_i} \left(\frac{1}{X^{S_i}} - \frac{1}{2} \right) \frac{\partial X^{S_i}}{\partial \rho} \right] \quad X^{S_i} = \left(1 + N_{Av} \sum_{j=1}^m \sum_{Y_j} x_j \rho X^{Y_j} W_{ij} \right)^{-1}$$

Ind. Eng. Chem. Res., 30, 1994 (1991)



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Sanchez-Lacombe EOS

$$Z = r \left[-\frac{1}{\tilde{\rho}} \ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right) - \frac{\tilde{\rho}}{\tilde{T}} \right]$$

$$\frac{\mu_i}{kT} = \ln \phi_i + 1 - \frac{r_i}{r} + r_i \left[-\frac{\tilde{\rho}}{\tilde{T}} + \frac{\tilde{P}\tilde{v}}{\tilde{T}} + (\tilde{v} - 1) \ln(1 - \tilde{\rho}) + \frac{1}{r_i} \ln \tilde{\rho} \right] + r_i \tilde{\rho} \left(\sum_{j=1} \phi_j \chi_{ij} - \sum_{j=1} \sum_{k=j+1} \phi_j \phi_k \chi_{jk} \right)$$

$$\phi_i = \frac{x_i r_i}{r}, \quad r = \sum x_i r_i \quad \text{or} \quad \frac{1}{r} = \sum \frac{\phi_i}{r_i} \quad \chi_{ij} = \frac{(\varepsilon_{ii}^* + \varepsilon_{jj}^* - 2\varepsilon_{ij}^*)}{kT}$$

$$\varepsilon^* = \sum_i \sum_j \phi_i \phi_j \varepsilon_{ij}^*, \quad v^* = \sum_i \phi_i v_i^*$$

$$\varepsilon_{ij}^* = \sqrt{\varepsilon_{ii}^* \varepsilon_{jj}^*} (1 - k_{ij}), \quad v_{ij}^* = \frac{(v_{ii}^* + v_{jj}^*)}{2}$$

Macromolecule, Vol. 11, No. 6, 1145 (1978)



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Pure parameters for EOS

■ Pure parameters for PR EOS

	$T_c(K)$	$P_c(bar)$	ω	Reference
CO ₂	304.21	73.83	0.224	Exp. Data
C1E1	564.00	50.10	0.733	Lydensen Method
C2E1	569.00	42.40	0.758	Lydensen Method
C3E1	615.20	36.51	0.487	Exp. Data

■ Segment and site-site parameters for SAFT EOS

	v^∞	m	u^0/k	ϵ^{AA}/k	$10^2 k^{AA}$
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

■ Pure parameters for Sanchez-Lacombe, Consistent Sanchez-Lacombe EOS

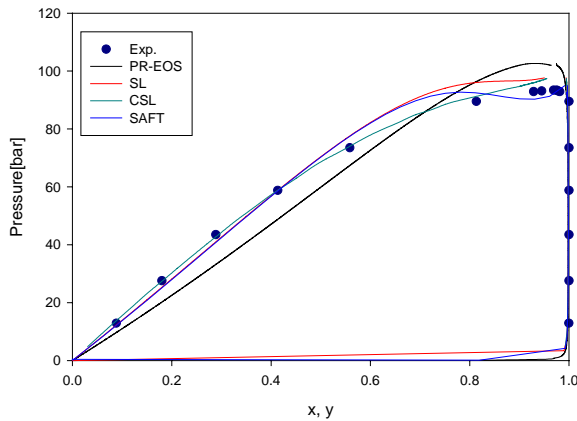
	$T^*(K)$	$P^*(bar)$	$\rho^*(g/cm^3)$
CO ₂	290.84	6619.50	1.573
C1E1	506.75	7272.25	1.122
C2E1	506.78	6122.24	1.088
C3E1	569.92	4461.00	1.016

Fluid Phase Equilibria, Vol. 185, 219(2001)

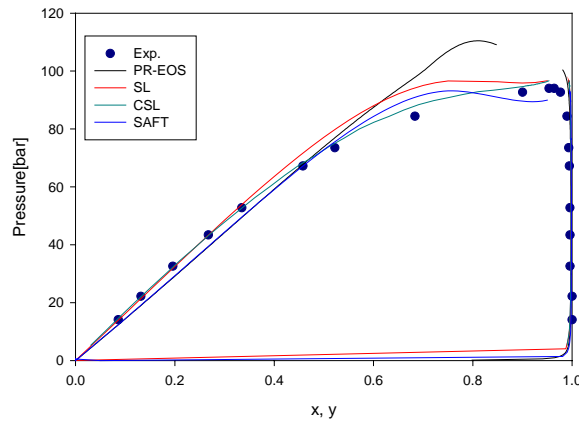


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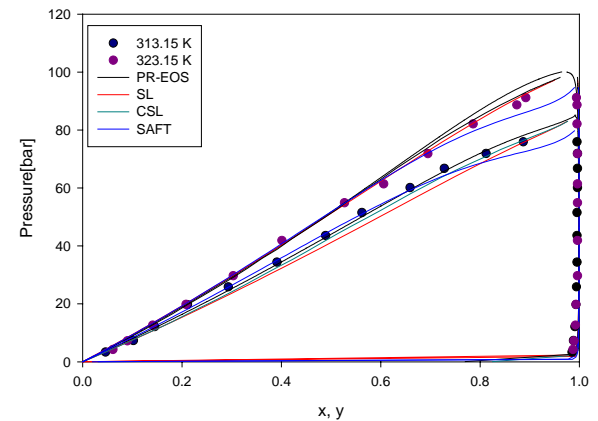
Correlation Result : compared with PR, SAFT EOS



Correlation Result for $CO_2 + C1E1$ System



Correlation Result for $CO_2 + C2E1$ System



Correlation Result for $CO_2 + C3E1$ System

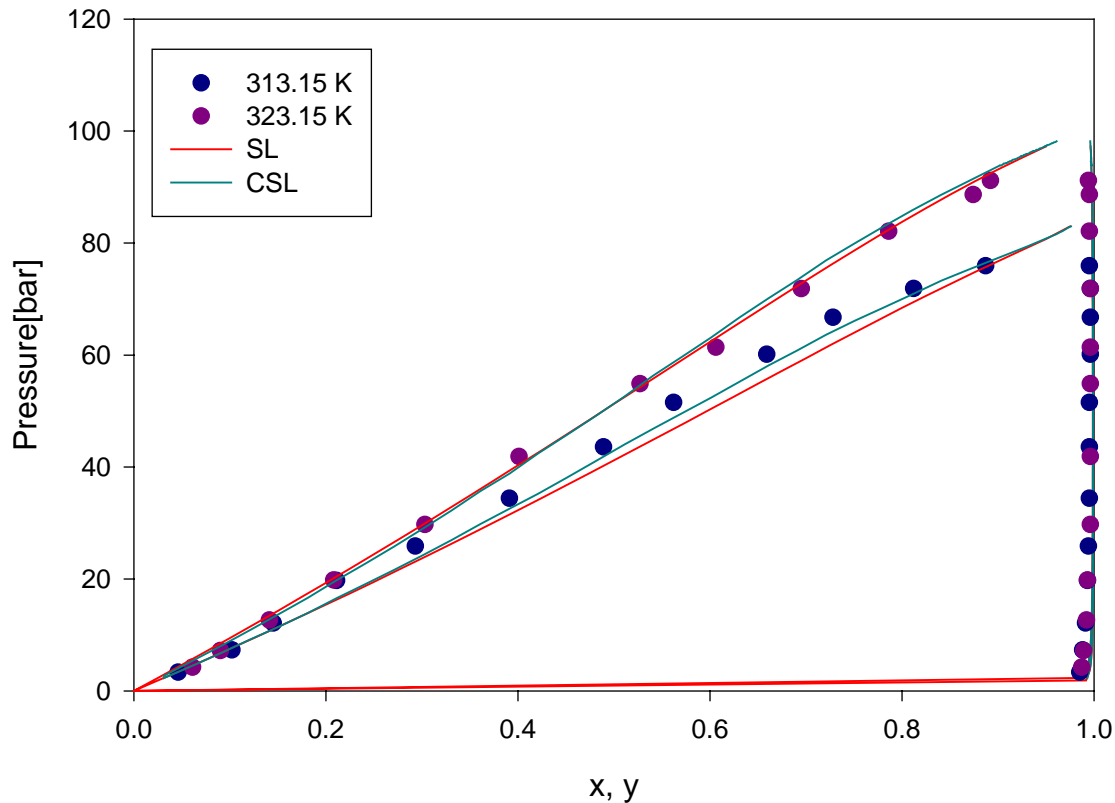
	k_{ij}	AADP
PR	0.0646	0.0932
SL	0.0581	0.0416
CSL	-0.0078	0.0130
SAFT	0.0635	0.0110

	k_{ij}	AADP
PR	0.0659	0.1144
SL	0.0784	0.0506
CSL	-0.0057	0.0213
SAFT	0.0600	0.0243

	k_{ij}	AADP
PR	0.0381	0.0552
SL	0.0988	0.0637
CSL	-0.0659	0.0504
SAFT	0.0407	0.0941



Correlation Result : Consistent Consideration



Comparison of measured data with correlation values for $\text{CO}_2 + \text{C3E1}$ System

at 313.15 K, 323.15 K

— calculated by Sanchez-Lacombe EOS (SL)

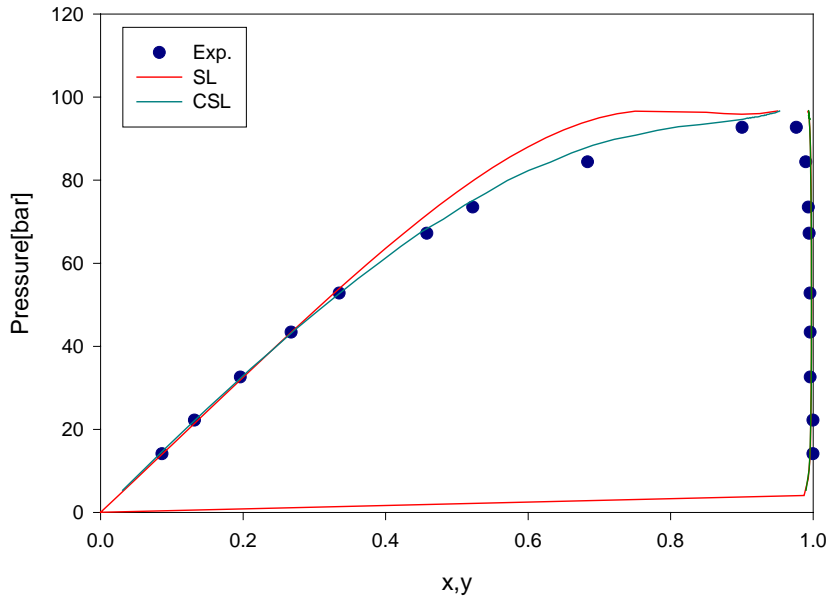
with $k_{ij} = 0.0988$, $AADP = 0.0637$

— calculated by Consistent Sanchez-Lacombe EOS (CSL)

with $k_{ij} = -0.0659$, $AADP = 0.0504$

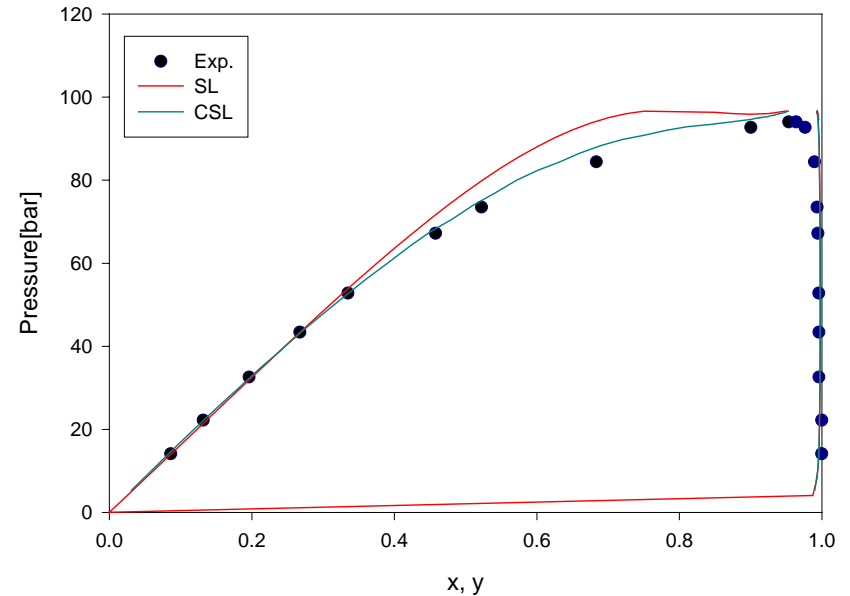


Correlation Result : Consistent Consideration



Correlation Result for CO₂ + C1E1 System at 322.90 K

SL : $k_{ij} = 0.0581$, AADP = 0.0416, CSL : $k_{ij} = -0.0078$, AADP = 0.0130



Correlation Result for CO₂ + C2E1 System at 323.3 K

SL : $k_{ij} = 0.0784$, AADP = 0.0506, CSL : $k_{ij} = -0.0057$, AADP = 0.0213



Conclusion

- *The isothermal VLE data for the system $\text{CO}_2 + \text{C3E1}$ were obtained at 313.15, 323.15 K at elevated pressures.*
- *The consistent Sanchez-Lacombe equation of state showed more improved results in the isothermal $\text{CO}_2 +$ surfactant VLE correlation than the Sanchez-Lacombe equation of state and compared with Peng-Robinson equation of state and SAFT equation of state.*
- *The Fugacity coefficients derived from the Sanchez-Lacombe equation of state are considered for calculating consistent phase equilibrium conditions.*

