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Phase behavior for the poly(2-methoxyethyl acrylate)+supercritical solvent+cosolvent mixture and CO_2+2-methoxyethyl acrylate system at high pressure

Yoon-Seok Jang, Yong Seok Choi, and Hun-Soo Byun†

Department of and Chemical and Biomolecular Engineering, Chonnam National University, Yeosu, Jeonnam 550-749, Korea

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Abstract–High pressures phase equilibrium data were presented for the CO_2+2-MEA system at temperatures ranging from (313.2 to 393.2) K and pressures up to ca. 17.97 MPa. The CO_2+2-MEA system exhibited type-I phase behavior and was modeled using the Peng-Robinson equation of state. The phase behavior data were reported for poly(2-methoxyethyl acrylate) [P(2-MEA)] in supercritical CO_2 and dimethyl ether (DME), as well as for the P(2-MEA)+2-methoxyethyl acrylate (2-MEA) (or DME) in CO_2. The cloud-point data were measured for the P(2-MEA)+DME in supercritical CO_2 at temperature range of (333-453) K and a pressure range of (8.79-199.14) MPa. The P(2-MEA) in supercritical CO_2 was soluble to 453 K and pressure of 199 MPa. The phase behavior for the P(2-MEA)+CO_2+2-MEA mixture was measured in changes of the pressure-temperature (p, T) slope and with 2-MEA mass fraction of 0.0 wt%, 8.4 wt%, 17.1 wt%, 45.4 wt% and 65.0 wt%. With 74.5 wt% 2-MEA to the P(2-MEA)+CO_2 solution, the cloud-point curves took on the appearance of a typical lower critical solution temperature boundary, liquid+liquid transition and liquid+vapor transition. The location of the P(2-MEA)+CO_2 cloud-point curve shifted to lower temperatures and pressures upon the addition of 2-MEA or DME.

Keywords: Poly(2-Methoxyethyl Acrylate), 2-Methoxyethyl Acrylate, High Pressure Phase Behavior, Cloud-point Pressures, Supercritical CO_2, Dimethyl Ether

INTRODUCTION

Information on phase behavior for the binary and ternary mixtures of acrylate monomers and polymers in supercritical fluid solvents is of importance in chemical separation processes, polymerization processes and related industrial processes. Supercritical fluid technology has been widely applied to the processing of various chemicals, pharmaceuticals, biological materials, and polymers [1-7].

The 2-methoxyethyl acrylate polymer and monomer has a potential of being used in biomedical applications and human patients as a coating for artificial organs [8] due to its outstanding biocompatibility [9-12]. A major effort in this field of biomaterials technology has been directed towards developing biomaterials having improved blood compatibility. Tanaka and Mochizuki [12,13] reported excellent blood compatibility with respect to coagulation, complement, leukocyte, and platelet systems. Generally, blood compatibility depends on various properties of the material surface such as the surface charge wettability, topography, and the presence of chemical groups on the surface [14].

Therefore, high-pressure phase equilibria data for mixtures containing carbon dioxide and hydrocarbons plays a major role in many industrial and scientific fields. In fact, large amounts of information relevant to the data exist in the literature. Most of the reported studies related to binary systems of CO_2+ alkane [15], +alkene [16], +nitrile [17], +acetate [18], +acrylate [19] and +methacrylate [20] mixtures have been at high pressures and temperatures. Several articles and reviews (1978-2008) have been published for the phase behavior data [21-25]. The previous work for the CO_2+acrylate monomers and polymer+supercritical solvent+cosolvent mixture have revealed that phase behavior for binary and ternary systems consist of polymers, supercritical solvents and cosolvent at high-pressure and high-temperature [26-28]. McHugh et al. [26] reported the cloud-point data for ternary mixture of poly(butyl acrylate)+CO_2+butyl acrylate and poly(ethylhexyl acrylate)+CO_2+ethylhexyl acrylate system at temperature up to 493 K and pressure up to 200 MPa. Also, the bubble-point curves for the CO_2+butyl acrylate system are presented by static method with variable-volume view cell at temperature of 308.2 K and 348.2 K. Rindfleisch [27] studied the solubility of poly(methyl acrylate), poly(ethyl acrylate) and poly(octadecyl acrylate) in supercritical CO_2 at pressures and temperatures up to 300 MPa and 543 K, respectively. Experimental cloud-point data up to 478 K and 248.0 MPa for the binary and ternary mixtures of poly(2-butoxyethyl acrylate)+supercritical solvents+2-butoxyethyl acrylate or dimethyl ether and CO_2+2-butoxyethyl acrylate systems were reported by Jang and Byun [28].

The goal of this work was to determine the impact of 2-methoxyethyl acrylate (2-MEA) cosolvent on the phase behavior of poly (2-methoxyethyl acrylate)[P(2-MEA)]+supercritical CO_2. Cloud-point data are obtained regarding the effect of DME cosolvent on the P(2-MEA)+supercritical CO_2 binary system. Also, the experimental data for the CO_2+2-MEA mixture was reported at elevated pressures and temperatures. The phase behavior curves for the CO_2+

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†To whom correspondence should be addressed.
E-mail: hsbyun@jnu.ac.kr

‡This article is dedicated to Prof. Hwayong Kim on the occasion of his retirement from Seoul National Univerisity.

2-MEA system obtained in this work are correlated with Peng-Robinson equation of state using two adjustable parameters (k_{ij}, η_{ij}). The critical pressure, critical temperature and acentric factor of 2-MEA are estimated by the Joback-Lydersen method with group contributions [29].

EXPERIMENTAL SECTION

1. Materials

Poly(2-methoxyethyl acrylate) [P(2-MEA)] [T_g=223 K, M_w=100,000 (GPC)] and 2-methoxyethyl acrylate (2-MEA) (>0.980 mass fraction purity) used in this work were obtained from Scientific Polymer Products, Inc. and used as received. The chemical structure of 2-methoxyethyl acrylate and poly(2-methoxyethyl acrylate) is shown in Fig. 1. The P(2-MEA) was in a toluene solution, the polymer solution was placed under vacuum pump (ULVAC KIKO Inc., model GVD-050A, Japan) for at least 10 hrs in the Rotavapor R-205 (Büchi, including bath B-490) for toluene removal. CO_2 (>0.999 mass fraction purity) was obtained from Daesung Industrial Co., and dimethyl ether (>0.995 mass fraction purity) was obtained from LG Gas (E1). The specifications of all chemicals used in this work are listed in Table 1.

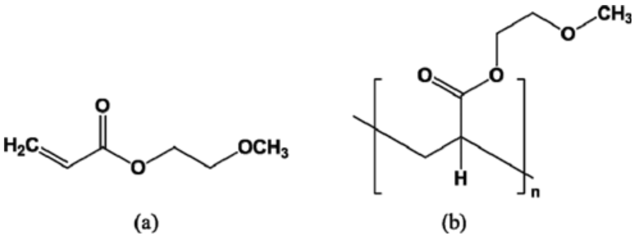

Fig. 1. Chemical structure of (a) 2-methoxyethyl acrylate and (b) poly(2-methoxyethyl acrylate).

2. Apparatus and Procedure

Fig. 2 shows the schematic diagram of a typical variable-volume view cell apparatus used for phase behavior measurement of ternary and binary mixture for the polymer+SCF solvents+cosolvents and SCF solvent+cosolvent systems, which has already been described [30,31]. Cloud-points are measured for the polymer solutions at a fixed P(2-MEA) concentration of 5.0±0.5 wt%, which is typical concentrations used for the polymer+SCF slovents or polymer+SCF solvent+cosolvent mixture. Polymer was loaded into the cell to within ±0.002 g, and then the cell was purged with nitrogen several times, and then with SCF solvent to ensure that all of the air and organic matter had been removed. Liquid 2-MEA was injected into the cell to within ±0.0008 g using a syringe, and SCF solvent and cosolvent were transferred into the cell gravimetrically to within ±0.004 g using a high-pressure bomb. The mixture was compressed to the desired pressure using an internal piston with water by operating a high pressure generator (HIP Inc., model 37-5.75.60), and the pressure of the mixture was measured with a Heise gauge [Dresser Ind., model CM-108952, (0-345.0) MPa, accurate to within ±0.35 MPa; CO_2+monomer: model CM-53920, (0 to 34.0) MPa, accurate to within ±0.034 MPa]. The system temperature

Table 1. Specifications of the chemical used

Chemical name	Mass fraction purity	Source	CAS RN
CO_2	>0.999	Daesung Industrial Gases Co.	124-38-9
Dimethyl ether	>0.995	LG Gas (E1)	115-10-6
2-Methoxyethyl acrylate	>0.980	Scientific Polymer Products, Inc.	3121-61-7
Poly(2-methoxyethyl acrylate)		Scientific Polymer Products, Inc. M_w=100,000	28628-64-0

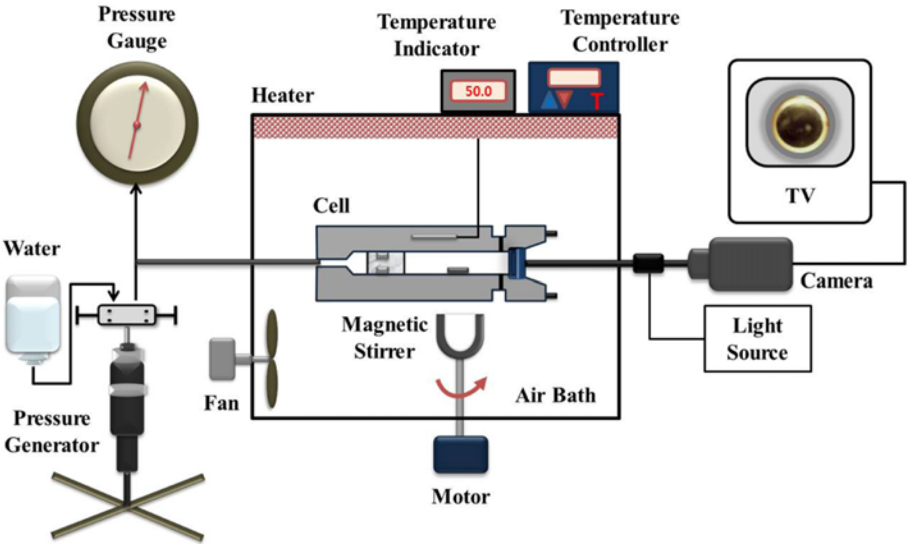

Fig. 2. Schematic diagram of phase behavior measurement apparatus at high-pressure.

was typically maintained to within ±0.2 K below 473.0 K. The inside of the cell was viewed on a video monitor with a camera coupled to a borescope (Olympus Corp., model F100-038-000-50) placed against the outside of the sapphire window.

Phase behavior of binary and ternary system for polymer+solvent +cosolvent mixtures was measured at a fixed polymer concentration. The binary and ternary mixtures in the cell were heated to the desired temperature and pressurized until a single phase was achieved, and they were maintained in the one-phase region at fixed temperature for 30-40 min at least to reach thermal equilibrium conditions. At the one-phase condition, pressure was slowly decreased until the solution became cloudy. The cloud-point pressure and temperature are defined as a point at which the mixture becomes so opaque that it is no longer possible to see the stir bar inside the cell. After a cloud-point was obtained, the solution was recompressed to a single phase, and the process was repeated. Cloud-points were measured and reproduced at least twice. Phase behavior for the P(2-MEA)+SCF solvents+cosolvent mixtures was obtained, and the combined standard uncertainties of pressure and temperature were estimated to be ±0.38 MPa and ±0.16 K for a given loading of the cell [32,33]. The pressure-composition (p, x) isotherms data for the 2-MEA in supercritical CO_2 was measured, and the experimental data was reproduced at least twice to within ±0.02 MPa and ±0.2 K for a given loading of the cell. The combined standard uncertainties of pressure and temperature were estimated ±0.02 MPa and ±0.12 K [32,33]. The combined standard uncertainty of 2-MEA mole fractions is estimated to be ±0.0008 [32]. The P(2-MEA)+supercritical solvents+cosolvent and CO_2+2-MEA systems have not been previously published in the literature.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Phase behavior for the CO_2+2-MEA System

Fig. 3 and Table 2 show the experimental pressure-composition (p, x) isotherms at temperatures of (313.2, 333.2, 353.2, 373.2 and 393.2) K, and pressures from (5.48 to 17.97) MPa for the (CO_2+2-MEA) system. Three phases were not observed at five temperatures. As shown in Fig. 3, the mixture critical pressures are 14.31 MPa at temperature of 353.2 K and 17.97 MPa at temperature of 393.2 K. The (p, x) isotherms and pressure-temperature (p, T) shown in Fig. 3 and Fig. 7 are consistent with those expected from a type-I system [34,35], where a maximum occurs in the mixture-critical curve. The apparent traits of type-I behavior are that only a single phase exists throughout the phase diagram and that the mixture critical curve runs continuously from the critical point of the CO_2 component to the critical point of the 2-MEA component [35]. The

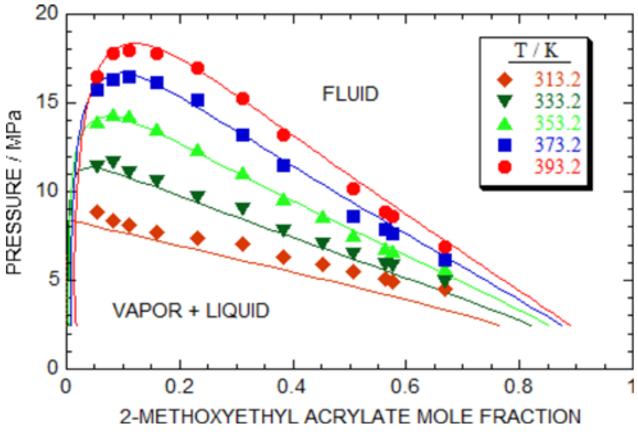

Fig. 3. A comparison of the experimental data (symbols) for the carbon dioxide+2-methoxyethyl acrylate system with calculations (solid lines) obtained using the Peng-Robinson equation of state with k_{ij} equal to 0.029 and η_{ij} equal to −0.044.

Table 2. Experimental data for the CO_2+2-methoxyethyl acrylate system. BP is a bubble point, CP is a critical point and DP is a dew point

2-Methoxyethyl acrylate mole fraction	p^a/MPa	Transition^b
	T^a/K=313.2	
0.054	8.83	BP
0.081	8.38	BP
0.109	8.14	BP
0.159	7.69	BP
0.232	7.38	BP
0.312	7.03	BP
0.384	6.31	BP
0.453	5.90	BP
0.505	5.52	BP
0.564	5.12	BP
0.576	4.97	BP
0.670	4.48	BP
	T/K=333.2	
0.054	11.41	BP
0.081	11.62	BP
0.109	11.07	BP
0.159	10.62	BP
0.232	9.69	BP
0.312	9.03	BP
0.384	7.79	BP
0.453	7.03	BP
0.505	6.44	BP
0.564	5.90	BP
0.576	5.79	BP
0.670	4.97	BP
	T/K=353.2	
0.054	13.97	DP
0.081	14.31	CP
0.109	14.24	BP
0.159	13.55	BP
0.232	12.38	BP
0.312	11.07	BP
0.384	9.59	BP
0.453	8.59	BP
0.505	7.52	BP
0.564	6.83	BP
0.576	6.66	BP
0.670	5.66	BP

Table 2. Continued

2-Methoxyethyl acrylate mole fraction	p^a/MPa	Transition^b
	T/K=373.2	
0.054	15.76	DP
0.081	16.35	DP
0.109	16.45	BP
0.159	16.17	BP
0.232	15.21	BP
0.312	13.24	BP
0.384	11.48	BP
0.505	8.62	BP
0.564	7.86	BP
0.576	7.62	BP
0.670	6.17	BP
	T/K=393.2	
0.054	16.48	DP
0.081	17.83	DP
0.109	17.97	CP
0.159	17.79	BP
0.232	17.00	BP
0.312	15.24	BP
0.384	13.21	BP
0.505	10.14	BP
0.564	8.83	BP
0.576	8.59	BP
0.670	6.86	BP

[a] Standard uncertainties are u(T)=T±0.12 K and u(p)=p±0.02 MPa
[b] BP: bubble-point, CP: critical-point, DP: dew-point

solubility of CO_2 decreases as temperatures shift higher under a constant pressure.

In this work, the experimental data is modeled with the Peng-Robinson equation of state. The Peng-Robinson equations are briefly described here. The Peng-Robinson equation of state [36] was used with the following mixing rules:

$$a_{mix}=\sum_i\sum_j x_i x_j a_{ij} \tag{1}$$

$$a_{ij}=(a_{ii}a_{jj})^{1/2}(1-k_{ij}) \tag{2}$$

$$b_{mix}=\sum_i\sum_j x_i x_j b_{ij} \tag{3}$$

$$b_{ij}=0.5(b_{ii}+b_{jj})(1-\eta_{ij}) \tag{4}$$

where k_{ij} and η_{ij} were binary interaction parameters determined by fitting P−x isotherms curves, and a_{ii} and b_{ii} were pure component parameters as defined by Peng and Robinson [36]. The objection function (OBF) and root mean squared relative deviation (RMSD) percent of this calculation were defined by

$$OBF=\sum_i^N\left(\frac{P_{exp}-P_{cal}}{P_{exp}}\right)^2 \tag{5}$$

$$RMSD(\%)=\sqrt{\frac{OBF}{ND}}\times 100 \tag{6}$$

Table 3. Pure component critical properties with the Peng-Robinson equation state

Components	M_w	T_b/K	T_c/K	p_c/MPa	ω
Carbon dioxide	44.01		304.2	7.37	0.225
2-Methoxyethyl acrylate	130.15	435.2^a	621.7	3.21	0.508

[a] ChemSpider Co. (or Alfa Aesar)

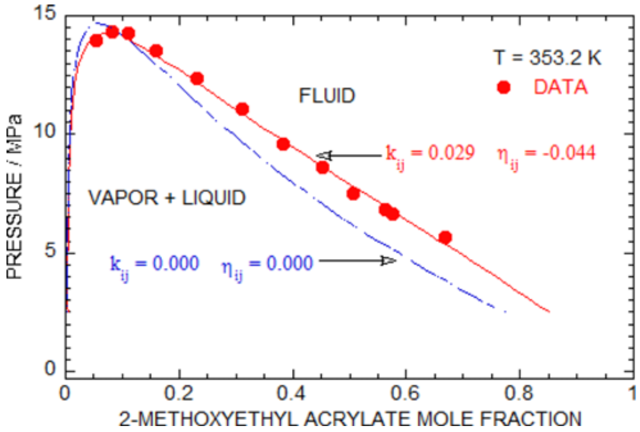

Fig. 4. Comparison of the best fit of Peng-Robinson equation of state to CO_2+2-methoxyethyl acrylate system obtained in this work (●) at 353.2 K.

Table 3 lists the pure component critical temperatures (T_c), critical pressures (p_c) as well as the acentric factors (ω) for CO_2, [29] and 2-MEA [29], all of which were used with the Peng-Robinson equation of state. The boiling point for the property calculation was obtained from the literature [37]. The properties of 2-MEA were calculated by the Joback-Lyderson group-contribution method [29]. Furthermore, the vapor pressure was calculated by the Lee-Kesler method [29].

Fig. 4 shows the comparison between the experimental results of the CO_2+2-MEA system and calculates values obtained using the Peng-Robinson equation at 353.2 K. The binary interaction parameters of the Peng-Robinson equation of state were fitted with the experimental data at 353.2 K. The optimized parameter value of the Peng-Robinson equation of state for the (CO_2+2-MEA) system was k_{ij}=0.029 and η_{ij}=–0.044 (experimental data no.: 12; RMSD: 2.3%).

Fig. 3 compares the experimental results with the calculated (P−x) isotherms at temperatures of (313.2, 333.2, 353.2, 373.2 and 393.2) K for the (CO_2+2-MEA) system using the optimized k_{ij} and η_{ij} values determined at 353.2 K. As shown in Fig. 3, obtained were well-fitted data with the Peng-Robinson equation using adjustable mixture parameters for the (CO_2+2-MEA) system. RMSD for the CO_2+2-MEA system at a five temperatures using two parameters determined at 353.2 K were 7.1% (experimental data no.: 58). The curves calculated by the Peng-Robinson equation of state did not demonstrate three phases at a five temperatures. Since RMSD for the CO_2+2-MEA system was high when the parameters were applied to this system, we needed to obtain optimized parameters for each temperature to lose RMSD.

Fig. 5 plot the pressures against mole fraction in order to compare the experimental data (symbols) of the CO_2+2-MEA system

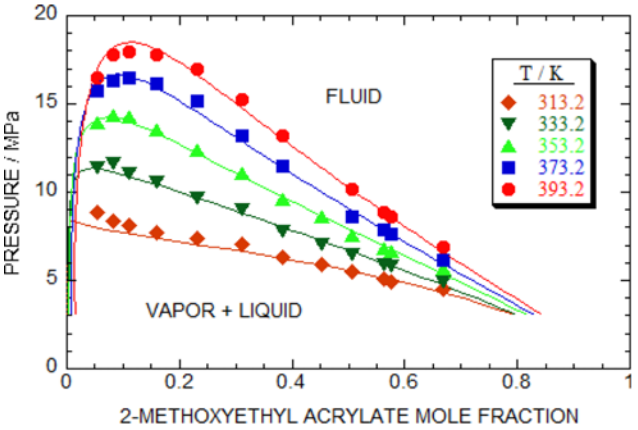

Fig. 5. **Curve of the best fit for the CO_2+2-methoxyethyl acrylate system obtained at each temperature.**

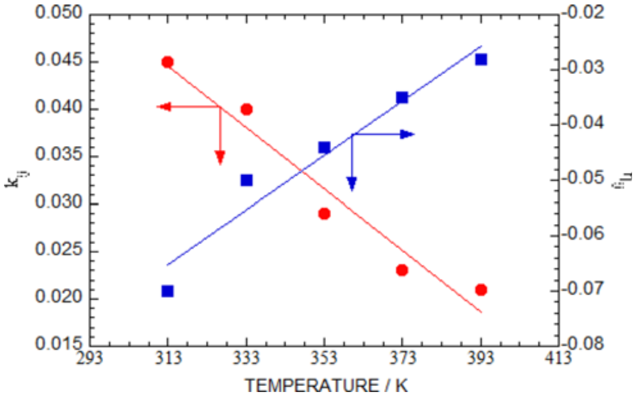

Fig. 6. **Tendency curve of k_{ij} and η_{ij} parameter according to temperature for the CO_2+2-methoxyethyl acrylate system.**

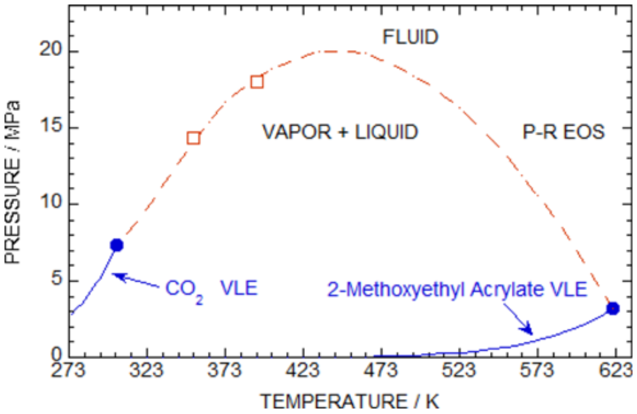

Fig. 7. **Pressure-temperature diagram for the carbon dioxide+2-methoxyethyl acrylate system. The solid line and the solid circles represent the vapor-liquid line and the critical point for pure carbon dioxide and 2-methoxyethyl acrylate. The open squares are critical points determine from isotherms measured in this study. The dashed line represents calculated values obtained using the Peng-Robinson equation of state with k_{ij} equal to 0.029 and η_{ij} equal to −0.044.**

with calculations (solid lines) obtained with the Peng-Robinson equation of state using optimum parameters (k_{ij} and η_{ij}) at each temperature. As shown in Fig. 5, these curves were calculated using optimized values determined at each temperature. RMSD at five temperatures (313.2, 333.2, 353.2, 373.2 and 393.2 K) for the CO_2+2-MEA system was 4.6% (k_{ij}=0.045, η_{ij}=−0.070), 2.7% (k_{ij}=0.040, η_{ij}=−0.050), 2.3% (k_{ij}=0.029, η_{ij}=−0.044), 2.6% (k_{ij}=0.023, η_{ij}=−0.035) and 2.3% (k_{ij}=0.021, η_{ij}=−0.028), respectively. Here, experimental data numbers are 12 and 11 at temperature of 313.2, 333.2 and 353.2 K and at temperatures of 373.2 K and 393.2 K, respectively. The comparison between the experimental data and calculated curve shows a good agreement at a five temperatures. According to calculated results, the critical mixture curve was type-I.

Fig. 6 and Table 4 plot k_{ij} and η_{ij} parameters obtained from the Peng-Robinson equation of state against temperature for the CO_2+2-MEA system at each temperature. The equation of parameter for the fitted line was good for the k_{ij} and η_{ij} at temperature ranges from (313.2 K to 393.2 K) in the case of CO_2+2-MEA system.

Fig. 7 compares the mixture-critical curves of the experimental data with the calculated values by the PR-EOS for the CO_2+2-MEA system using two interaction parameters (k_{ij} and η_{ij}) determined at 353.2 K. The calculated mixture-critical curve is the type-I region. The solid line represents the vapor pressure of pure 2-MEA obtained by the Lee-Kesler method [29]. The solid circles signify the critical point for pure CO_2 and 2-MEA. The dash lines represent the calculated values obtained from the PR-EOS, with k_{ij}=0.029 and η_{ij}=−0.044 for the CO_2+2-MEA system. The open squares are the

Table 4. **Data of k_{ij} and η_{ij} parameters and the value of RMSD against temperature for the CO_2+2-methoxyethyl acrylate system with the Peng-Robinson equation of state**

System		313.2 K	333.2 K	353.2 K	373.2 K	393.2 K
CO_2+2-methoxyethyl acrylate	k_{ij}	0.045	0.040	0.029	0.023	0.021
	η_{ij}	−0.070	−0.050	−0.044	−0.035	−0.028
	RMSD	4.6%	2.7%	2.3%	2.6%	2.3%

Table 5. **Critical temperatures, critical pressures, critical densities, polarizabilities, dipole moments, and quadrupole moments of solvents used in this study [29,38]**

Solvents	T_c/K	p_c/MPa	ρ_c/kg m^{-3}	ω	$\alpha\bullet 10^{30}/m^3$	$\mu\bullet 10^{30}$/C·m	Q•10^{40}/C·m^2
CO_2	304.2	7.38	469	0.225	2.65	0.00	−14.34
Dimethyl ether	400.0	5.30	258	0.192	5.22	4.34	4.00

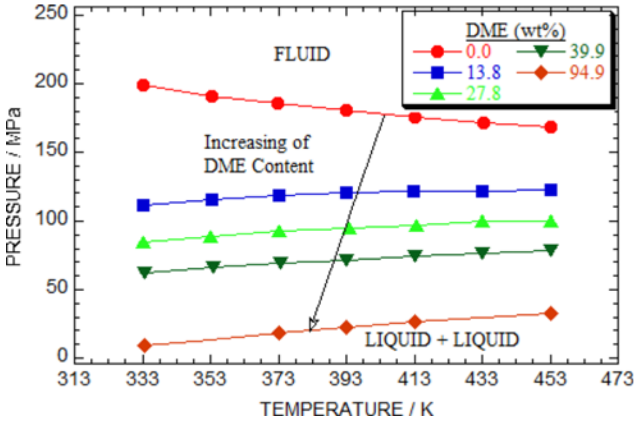

Fig. 8. Effect of DME as a cosolvent for poly(2-methoxyethyl acrylate) in supercritical CO$_2$. The concentration of polymer is ~5.0 wt% for each solution.

mixture-critical points determined from isotherms measured in this experiment.

2. Phase behavior for the P(2-MEA)+CO$_2$+2-MEA (or DME) Mixture

Table 5 lists the critical temperature (T_c), critical pressure (p_c), critical density (ρ_c) acentric factor (ω), polarizability (α), dipole moment (μ), and quadrupole moment (Q) of CO$_2$ and DME used in this study [29,38]. CO$_2$ has a critical temperature near room temperature, a modest critical pressure, and a higher density than most supercritical fluids, which means that at temperatures slightly above room temperature it is possible to obtain liquid-like densities and, by implication, liquid-like solvent characteristics. DME has a significant dipole moment that allows the effect of dipole interactions to be compared with that of quadrupole interactions found with CO$_2$.

Tsang and Streett [39] previously reported a thorough experimental data set for the binary CO$_2$+DME system which has a critical-mixture curve with a highest pressure of about 8 MPa. The DME +CO$_2$ data complement the P(2-MEA)+CO$_2$+DME data obtained in the current study. Fig. 8 and Table 6 show the phase behavior in the P(2-MEA)+CO$_2$+DME mixture. A single-phase region in the P(2-MEA)+CO$_2$ mixture was obtained at temperatures in the range of (333.3 to 453.4) K and at high pressures such as 199.14 MPa (at 333.3 K), while the one in the P(2-MEA)+DME mixture was obtained at temperatures in the range of (333.7 to 453.2) K and at relatively low pressures, but higher than 33 MPa (at 453.2 K). The pressure difference between two systems was due to the presence of a dipole moment in DME [4.34×10^{-30} C·m] and CO$_2$ [0.0×10^{-30} C·m], as shown in Table 5. The P(2-MEA)+CO$_2$+(13.8 to 39.9) wt% DME mixture show LCST behavior of positive slope at below 122 MPa and at temperature range from (333 to 453) K, while their pressures decrease smoothly below about 453 K. As shown in Fig. 8, the location in which the curve demonstrates LCST behavior is mainly controlled by entropic contributions, which are sensitive to the changes in pressure. This type of phase behavior is probably caused by the difference in free volume among P(2-MEA), CO$_2$, and DME [40,41].

Table 6. Experimental cloud-point data for the poly(2-methoxyethyl acrylate) [P(2-MEA)]+CO$_2$+x wt% dimethyl ether (DME) system with different DME content

T^a/K	p^a/MPa
5.0 wt% P(2-MEA)+0.0 wt% 2-MEA	
333.3	199.14
353.5	190.86
372.9	185.34
393.2	180.86
413.5	176.03
433.8	171.90
453.4	168.45
5.0 wt% P(2-MEA)+13.8 wt% DME	
333.3	111.21
353.8	115.34
373.6	118.45
393.3	120.52
412.9	121.55
433.4	121.90
453.5	122.24
5.0 wt% P(2-MEA)+27.8 wt% DME	
333.3	85.00
353.3	89.14
373.5	92.59
394.1	95.35
413.8	97.07
433.3	99.69
453.5	99.83
5.0 wt% P(2-MEA)+39.9 wt% DME	
333.7	62.24
353.9	66.03
373.9	69.14
393.2	71.90
413.3	74.66
433.4	76.72
453.3	78.45
5.0 wt% P(2-MEA)+94.9 wt% DME	
333.7	8.79
353.4	13.62
373.3	18.45
393.4	22.59
413.2	26.38
433.4	30.17
453.2	32.93

[a] Standard uncertainties are u(T)=T±0.16 K and u(p)=p±0.38 MPa

Fig. 9 and Table 7 show the cloud-point behavior of the P(2-MEA) +CO$_2$+2-MEA system obtained in this work. P(2-MEA) does dissolve in pure CO$_2$ at 454 K and about 224 MPa. The cloud-point behavior for P(2-MEA) in supercritical CO$_2$ shows an upper critical solution temperature (UCST) curve [41]. When 8.4 wt% 2-MEA is added to the solution, the cloud-point curve exhibits UCST-type phase behavior with negative slopes. P(2-MEA)+CO$_2$+8.4 wt% 2-MEA system does dissolve at below pressure of 137.2 MPa. The

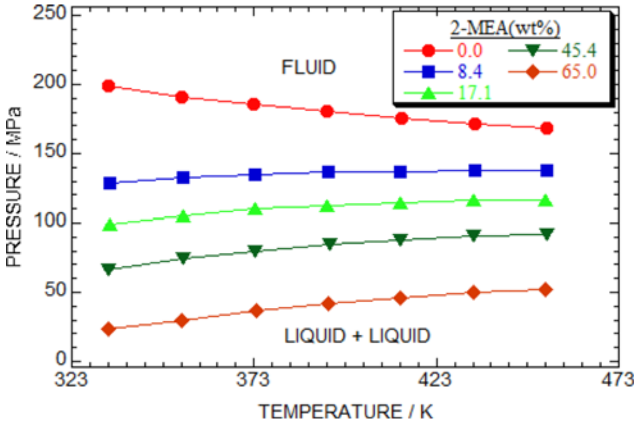

Fig. 9. Impact of 2-MEA on the phase behavior of the P(2-MEA) +CO_2+x wt% 2-MEA system. The concentration of polymer is ca. 5 wt% for each solution.

Table 7. Experimental cloud-point data for the poly(2-methoxyethyl acrylate) [P(2-MEA)]+CO_2+x wt% 2-methoxyethyl acrylate (2-MEA) system with different 2-MEA content

T^a/K	p^a/MPa
5.0 wt% P(2-MEA)+8.4 wt% 2-MEA	
333.7	129.14
353.6	132.59
373.6	135.00
393.6	136.72
413.2	137.07
433.8	137.41
453.6	137.41
4.9 wt% P(2-MEA)+17.1 wt% 2-MEA	
333.6	99.48
353.8	105.69
373.5	109.83
394.1	112.24
413.5	114.66
433.6	116.03
453.2	116.03
4.8 wt% P(2-MEA)+45.4 wt% 2-MEA	
333.2	66.38
353.8	74.31
373.5	80.17
393.9	84.66
413.2	88.10
433.4	90.86
453.3	91.90
5.1 wt% P(2-MEA)+65.0 wt% 2-MEA	
333.3	23.28
353.3	30.17
373.7	36.38
393.4	41.55
413.2	46.03
433.2	49.83
453.2	52.59

[a] Standard uncertainties are u(T)=T±0.16 K and u(p)=p±0.38 MPa

phase behavior for the P(2-MEA)+CO_2+(17.1 to 65.0 wt%) 2-MEA system exhibits LCST behavior in which temperature and pressure decreased smoothly from (453 to 333) K and at pressure below 116 MPa. The cloud-point curves for the P(2-MEA)+CO_2+(17.1, 45.4 and 65.0 wt%) 2-MEA are a positive slope at about 0.14 MPa/K (17.1 wt% 2-MEA), 0.21 MPa/K (45.4 wt% 2-MEA) and 0.25 MPa/K (65.0 wt% 2-MEA), respectively.

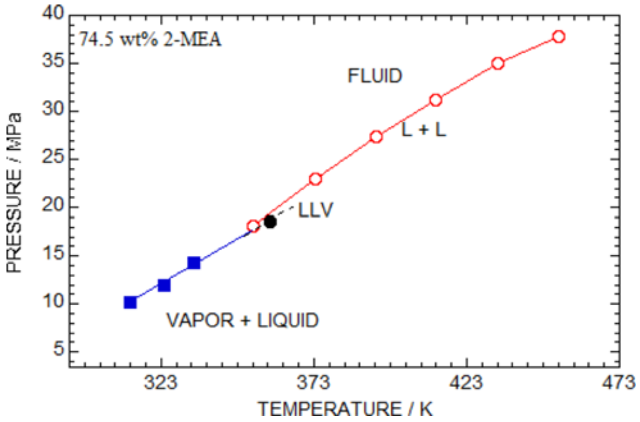

Fig. 10. Impact of 74.5 wt% 2-MEA monomer (on a polymer-free basis) in the phase behavior of the poly(2-methoxyethyl acrylate)+CO_2+2-methoxyethyl acrylate system. ○, fluid→liquid+liquid transition; ■, fluid→liquid+vapor transition; ---------, suggested extension of the LLV line.

Table 8. Phase behavior of cloud-point and bubble-point for the poly (2-methoxyethyl acrylate) [P(2-MEA)]+carbon dioxide+74.5 wt% 2-methoxyethyl acrylate (2-MEA) system

T^a/K	p^a/MPa	Transition
4.8 wt% P(2-MEA)+74.5 wt% 2-MEA		
Cloud-point transition		
353.3	18.10	CP
373.6	22.93	CP
393.4	27.41	CP
413.2	31.21	CP
433.6	35.00	CP
453.4	37.76	CP
Liquid+liquid+vapor transition		
358.9	18.52	LLV
Bubble-point transition		
313.2	10.17	BP
324.0	11.90	BP
333.7	13.61	BP

[a] Standard uncertainties are u(T)=T±0.16 K and u(p)=p±0.38 MPa

Fig. 10 and Table 8 show the impact of 74.5 wt% 2-MEA monomer on the phase behavior of the P(2-MEA)+CO_2 solution. At 410

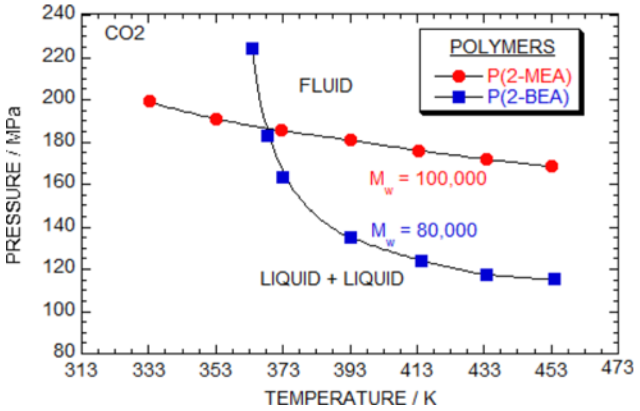

Fig. 11. Phase behavior of binary system for the poly(2-methoxyethyl acrylate) and poly(2-butoxyethyl acrylate) [28] in supercritical carbon dioxide. The concentration of polymer is about 5 wt% for the each solution.

K, the phase boundary has shifted the pressure lower as the concentration of 2-MEA increases. The P(2-MEA)+CO_2+74.5 wt% 2-MEA phase behavior curve intersects the fluid→liquid+vapor (LV) curve at ca. 350 K and ca. 17 MPa. These results clearly demonstrate that it is possible to obtain a single phase extending over a large temperature range at modest pressures if sufficient amount of free acrylate monomer is added to the solution.

Fig. 11 shows the comparison between curves on the phase behavior for the P(2-MEA)+CO_2 and poly(2-butoxyethyl acrylate) [P(2-BEA)]+CO_2 [28] systems. At 413 K, the phase behavior boundary of two curves has a pressure difference of about 45 MPa due to the difference in weight average molecular weight (M_w). This tendency shows the similarity in phase behavior curves for the poly(methyl acrylate) and poly(butyl acrylate) in CO_2 reported by Rindfleisch et al. [27].

CONCLUSIONS

The pressure-composition (p, x) isotherms for the CO_2+2-MEA binary mixture system were measured using a variable-volume view cell apparatus at temperature ranges from (313.2 to 393.2) K and pressure up to 17.97 MPa. This system exhibits type-I phase behavior and does not exhibit three phases at any five temperatures. The Peng-Robinson equation of state is able to predict the phase behavior for the system using two binary mixture interaction parameters (k_{ij} and η_{ij}) obtained at 353.2 K. RMSD for the CO_2+2-MEA system using two parameters determined at 353.2 K is 7.1%. When applying the optimized parameters for each temperature, RMSD for the system ranges from 2.3% to 4.6% for the CO_2+2-MEA system.

Cloud-point curve for the P(2-MEA) in supercritical CO_2 shows the UCST-type behavior at negative slope. The phase behavior of the ternary system for the P(2-MEA)+2-MEA (or DME) mixture in supercritical CO_2 shows the LCST region at positive slope. Also, when 74.5 wt% 2-MEA is added to the solution, LCST-type phase behavior exhibits with a positive slopes of 0.23 MPa/K. The cloud-point curve intersects the bubble point curve at 350 K and 17 MPa. The bubble-point curve switches to a liquid+liquid+vapor curve at temperatures higher than 353 K.

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