

Phase behavior of binary and ternary mixture for the poly(TBAEMA) and TBAEMA in supercritical solvents

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Abstract—The cloud-point pressure of poly(*t*-butylaminoethyl methacrylate) [Poly(TBAEMA)] in various solvents such as supercritical carbon dioxide (CO₂), dimethyl ether (DME) and *t*-butylaminoethyl methacrylate (TBAEMA) was measured to maximum pressure and temperature of 218.79 MPa and 452.9 K, respectively. The phase behavior for the Poly(TBAEMA)+CO₂+TBAEMA mixture was investigated according to the various contribution factors, such as pressure, temperature and concentration with TBAEMA mass fraction of 9.9 wt%, 10.4 wt%, 14.9 wt%, 24.4 wt% and 35.2 wt%. The cloud point curves for the Poly(TBAEMA)+CO₂+DME (15.6–78.7 wt%) systems show the variation of the (*p*, *T*) curve from upper critical solution temperature (UCST) region to lower critical solution temperature (LCST) region as DME concentration increases. The experimental data for the CO₂+TBAEMA system were reported at the broad temperature range of 313.2 K to 393.2 K and the pressure range of 3.70 MPa to 20.62 MPa. The CO₂+TBAEMA binary system shows the type-I phase behavior with a continuous critical mixture curve, and is correlated by Peng-Robinson equation of state with the critical properties for TBAEMA obtained by Joback and Lydersen group contribution method.

Keywords: Poly(*t*-Butylaminoethyl Methacrylate), *T*-butylaminoethyl Methacrylate, High Pressure Phase Behavior, Cloud Point Behavior, Carbon Dioxide, Dimethyl Ether

INTRODUCTION

Supercritical process technology has been widely used in various chemical engineering processes for chemical separation, pharmaceuticals, biological materials, inorganic material, particle/film technology and related industry [1–5]. The researches on phase behavior of polymers in multi-component mixtures containing supercritical fluid (SCF) solvents form the basis of the design and operation for various polymer industrial processes [6–8]. In addition, the mutual solubilities for the carbon dioxide+hydrocarbon binary systems at high pressure give useful information for numerous chemical processes such as process design [9,10], SCF extraction [11,12], polymerization condition [13,14] and fine chemical industry.

Methacrylate-based polymers have been extensively applied to the plastic engineering technology, and along with methacrylate-based monomers have been mainly used in contact lenses, coatings, prostheses and adhesives [15,16]. For the chemical plant design to treat these systems, therefore, experimental data for methacrylate-based monomers in SCF solvents are required because those provide valuable thermodynamics information on polymerization conditions at relevant conditions of pressure, temperature and composition. Especially, Poly(*t*-butylaminoethyl methacrylate) [Poly(TBAEMA)] has a large number of potential uses, including as anti-

fungal agent or antiseptic into tissue conditioners [17] and denture acrylic resins [18], as well as an antifouling paints and coating of surfaces [19] and for wettability of interface [20]. *t*-Butylaminoethyl methacrylate (TBAEMA) as a component of copolymers in the polymer industry [21] is used as various industrial materials for coatings, paints, and dental composites [22]. Furthermore, TBAEMA is a very useful feedstock for chemical syntheses because of easy addition reactions with a wide variety of organic and inorganic compounds, excellent adhesion to metallic and plastic substrates, and low shrinkage properties [22].

Previous work has demonstrated that the cloud point pressures in the solutions consisting of polymer and cosolvent in SCF solvent shifted to lower pressures according to adding cosolvent [23–26]. Gornert and Sadowski [23] reported the experimental and correlated results for poly(methyl methacrylate) (*M_w*=17.9 kg/mol and 101 kg/mol)/methyl methacrylate/carbon dioxide ternary system to maximum pressure of 15 MPa and at temperature range from 338.15 K to 353.15 K. Domingo et al. [24] carried out the solubility measurement for poly(methyl methacrylate)-based systems in supercritical CO₂ and CO₂ plus cosolvent. Bae et al. [25] reported experimental data for poly(vinyl pyrrolidone)/*N*-vinyl-2-pyrrolidone/carbon dioxide system at the various conditions of temperature (from 320 K to 458 K), pressures (up to 212 MPa), and cosolvent concentrations (24.8 wt%–44.4 wt%), and for CO₂/*N*-vinyl-2-pyrrolidone binary mixture to maximum pressure of 19.0 MPa and temperatures ranging from 324 K to 355 K. Liu et al. [26] revealed the experimental data for Poly(2-ethylhexyl methacrylate)+CO₂+2-ethylhexyl methacrylate ternary system to maximum pressure and temperature of 248 MPa and 478 K, respectively. In addi-

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*This article is dedicated to Prof. Ki-Pung Yoo on the occasion of his retirement from Sogang University.

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tion, the phase behaviors for CO₂+alkyl methacrylate systems have been reported by several researchers [8,27-29]. These systems show the phase behavior of type-I of the six types of simple pressure-temperature diagrams, which is described in detail by Scott and Konynenburg [27], and McHugh and Krukoni [8]. To obtain thermodynamics information of phase behavior for polymer mixtures in SCF solvent, theoretical studies about them are necessary, but their pure thermodynamic properties (i.e., liquid density and saturated vapor pressure) to estimate pure component parameters do not exist or found in the literature. Therefore, the Peng-Robinson equation of state (P-R EOS) [28,29] has been generally applied by using critical property information obtained from group contribution methods. These results can give valuable information for the rational design and operation of the supercritical fluid region.

In this work, the effect of TBAEMA and dimethyl ether (DME) cosolvent on the phase behavior of Poly(TBAEMA)+supercritical CO₂ mixture is investigated. The experimental data for the CO₂+DME binary system reported by Tsang and Streett [33] have a critical-mixture curve and a highest pressure of 7.9 MPa at about 335 K. The experimental data for the CO₂+TBAEMA system have not so far been found in the literature. To complement the Poly(TBAEMA)+CO₂+TBAEMA data, the vapor-liquid equilibria (VLE) for the CO₂+TBAEMA mixture are also measured. The measured experimental data for CO₂/TBAEMA binary system is correlated by the P-R EOS [34] to predict phase separation curves at elevated temperatures and pressures. The critical properties (T_c , p_c), acentric factor (ω), polarizability (α), dipole moment (μ), and quadrupole moment (Q) of solvents used in this study are listed in Table 1 [30-32].

EXPERIMENTAL SECTION

1. Materials

CO₂ (>99.9% purity, CAS RN 124-38-9) was obtained from Deok Yang Co., and dimethyl ether (DME) (>99.5% purity, CAS RN

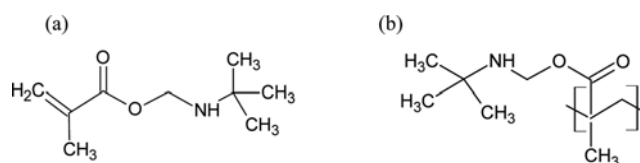


Fig. 1. Chemical structure of (a) t-butylaminoethyl methacrylate and (b) poly(t-butylaminoethyl methacrylate).

115-10-6) from E1 Co. These materials were used with no further purification. Poly(TBAEMA) ($M_w=44,000$; M_w/M_n : 1.6; $T_g=306$ K, CAS RN 26716-20-1, USA) and TBAEMA (>97.5% purity, CAS RN 3775-90-4, USA) were obtained from Scientific Polymer Products, Inc. The chemical structure of Poly(TBAEMA) and TBAEMA is represented in Fig. 1. The specifications of all chemicals used in this work are summarized in Table 2.

2. Apparatus and Procedure

The various thermodynamic properties such as bubble-point, critical-point, dew-point and cloud-point were obtained using an experimental apparatus shown in Fig. 2, variable-volume view cell, which is described in detail elsewhere [35-38]. This experimental apparatus showed good performance for constructing the (p , x) isotherms for the TBAEMA+CO₂ binary mixtures [35-37] and measuring the cloud point pressure for the polymer+SCF solvent+cosolvent mixtures [38]. The stainless-steel view cell was fitted on one side with a sapphire window (1.90 cm OD×1.90 cm ID, GT Advanced Technologies, USA) for visual observation, and its volume could be varied by a piston (2.54 cm length) connected to a manual pressure generator (Model: HIP 37-5.75-60, USA) using water as hydrostatic fluid. The mixture pressure in the view cell was measured with a Heise gauge (Model: Dresser CM-108952, USA, 0-345.0 MPa, the standard uncertainties of $u(p)=0.35$ MPa; Model: Dresser CM-53920, USA, 0-34.0 MPa, the standard uncertainties of $u(p)=0.04$ MPa).

Table 1. Critical temperatures, critical pressures, polarizabilities, dipole moments, and quadrupole moments of solvents used in this study [28-32]

Solvents	T_c/K	p_c/MPa	ω^{**}	$\alpha \cdot 10^{30}/m^3$	$\mu \cdot 10^{30}/C \cdot m$	$Q \cdot 10^{40}/C \cdot m^2$
Carbon dioxide*	304.3	7.38	0.225	2.65	0.00	-14.34
Dimethyl ether	400.0	5.30	0.203	5.22	4.34	3.94
t-Butylaminoethyl methacrylate	623.6	2.28	0.631			

*Carbon dioxide has no dipole moment

**Acentric factor

Table 2. Specifications of the chemical used in this work

Chemical name	Source	Mass fraction purity ^a	Purification method	Analysis method ^a
Carbon dioxide	Deok Yang Co.	>0.999	None	-
Dimethyl ether	E1 Co.	>0.995	None	-
t-Butylaminoethyl methacrylate	Scientific Polymer Products, Inc.	>0.975	None	GC ^b
Poly(t-butylaminoethyl methacrylate)	Scientific Polymer Products, Inc.	$M_w=40,000$, $T_g=33$ °C	None	GPC ^c

^aBoth the analysis method and the mass fraction purity were provided by the suppliers

^bGas-liquid chromatography

^cGel permeation chromatography

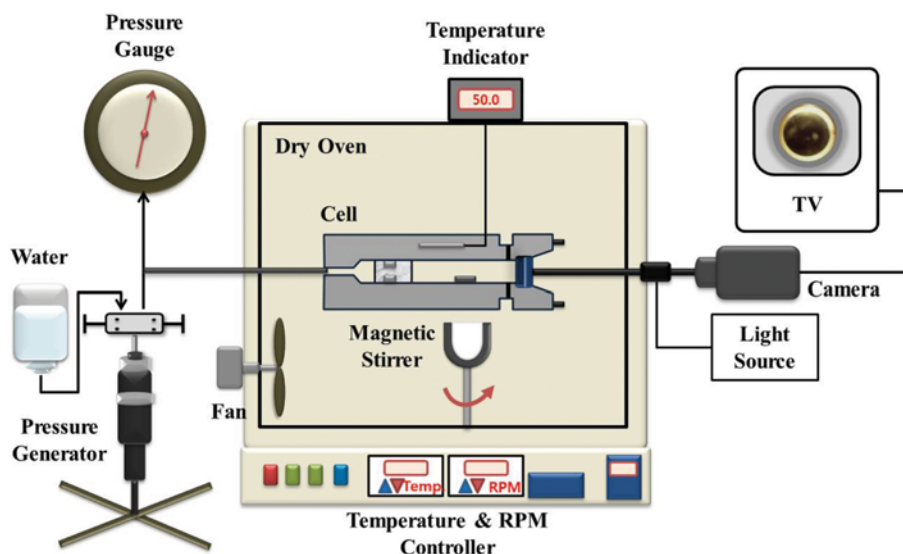


Fig. 2. Schematic diagram of high-pressure apparatus for phase behavior experiment.

The synthetic method was used to measure the bubble-point, dew-point and critical-point phase behavior for the CO_2 +TBAEMA system. First, the view cell was purged several times with CO_2 and N_2 at low pressure and temperature. To make the contents in the cell homogeneous phase at a fixed temperature, the magnetic stirrer was continuously rotated, and to reach phase equilibrium, the solution was maintained in the one phase for at least 30–40 minutes. The pressure was then slowly decreased until bubble, dew and critical-point appeared. A bubble point pressure is obtained when small vapor bubbles appear first in the cell, while a dew point pressure is obtained if a fine mist appears. On the other hand, critical points are obtained by adjusting the temperature and pressure of the mixture until critical opalescence is observed along with equal liquid and vapor volume upon the formation of the two phases. Each experimental point for the CO_2 +TBAEMA mixtures was reproduced at least twice with the standard uncertainties of pressure, temperature and TBAEMA mole fractions of 0.03 MPa, 0.12 K and 0.0008 [39,40], respectively.

Cloud-point pressure was measured for each polymer solution at fixed Poly(TBAEMA) concentration of about 5.0 wt%, which is typically studied in polymer+SCF solvent systems. Then polymer component was loaded into the cell with the standard uncertainty of 0.001 g, which was then purged with nitrogen followed by CO_2 to ensure all of the air removed. TBAEMA was injected into the cell with the standard uncertainty of 0.002 g using a syringe, followed by gravimetric transfer of supercritical solvents into the cell with the standard uncertainty of 0.004 g using a high-pressure bomb cylinder. The measured cloud points were reproduced at least twice with the standard uncertainty of pressure and temperature of 0.28 MPa and 0.2 K, respectively [39,40].

RESULTS AND DISCUSSION

1. Phase Behavior for Poly(TBAEMA)+ CO_2 +TBAEMA Mixture

The cloud-point pressure for Poly(TBAEMA)+ CO_2 +TBAEMA systems has a significant effect on TBAEMA concentration, and

the experimental data are reported in Table 3. Poly(TBAEMA) does dissolve in pure CO_2 at temperatures higher than 463 K and pressures higher than about 250 MPa. The cloud-point behavior for Poly(TBAEMA)+TBAEMA mixture in supercritical CO_2 shows an upper critical solution temperature (UCST) curve [41,42]. When TBAEMA monomer of 9.9 wt% and 10.4 wt% is added to the solution, the cloud-point curve exhibits UCST-type phase behavior with negative slopes. The phase behavior for Poly(TBAEMA)+ CO_2 +TBAEMA (with 9.9 wt% and 10.4 wt%) system is distributed in the range of temperature from 433.3 K to 452.9 K and of pressure from 136 MPa to 207 MPa. As shown in Fig. 3, the cloud-point pressure curve shows rapid increase below 442 K (9.9 wt%) and 433 K (10.4 wt%), respectively. Such steep increase of the cloud-point pressure with the decrease of temperature is caused by the polar interaction between polymer and polymer, and/or cosolvent and cosolvent molecules, which leads to the phase separation. Hence, the Poly(TBAEMA) polymer precipitates out of the binary and ternary mixtures, which may be due to strong interactions between polymer and polymer. When TBAEMA monomer is 14.9 wt%, though the negative slope of UCST phase behavior is not strong like the value of 9.9 wt% and 10.4 wt%, a similar phenomenon is found. For the pressure difference of the P(TBAEMA)+ CO_2 +10.4 wt% TBAEMA and P(TBAEMA)+ CO_2 +14.9 wt% TBAEMA systems, it is shifted to lower pressure, more than likely due to the decrease in the free volume difference between polymer and mixed solvent. The cloud-point pressure for polymer solution with 24.4 wt% TBAEMA smoothly increases at about 81.5 ± 7.8 MPa according to the temperature decrease in the range of 393 K to 443 K, and that system exhibits the UCST region phase behavior with slightly negative slope. However, the phase behavior for polymer solution with 35.2 wt% TBAEMA shows an almost flat LCST curve at temperature range of 374 K to 433 K and at pressure below about 49 MPa.

2. Phase Behavior for Poly(TBAEMA)+ CO_2 +DME Mixture

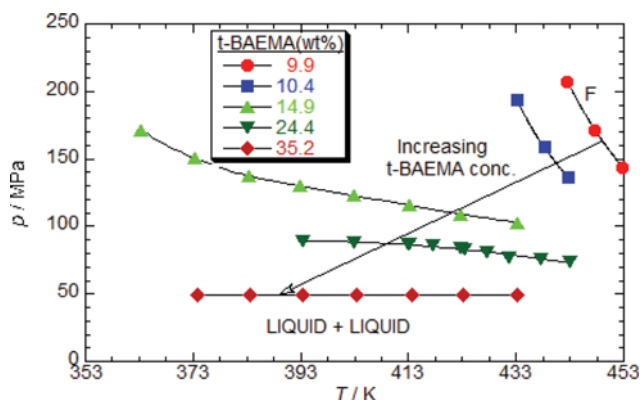
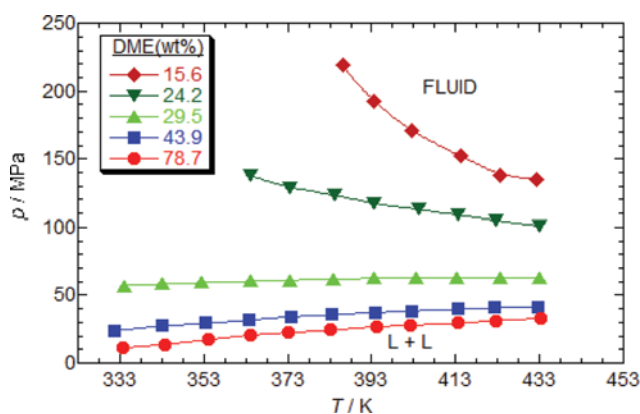
The effect of DME concentration on the phase behavior in the Poly(TBAEMA)+ CO_2 +DME mixture is represented in Fig. 4, and the experimental values are reported in Table 4. The cloud-point

Table 3. Experimental cloud-point data for the poly(*t*-butylaminoethyl methacrylate) [Poly(TBAEMA)]+CO₂+*t*-butylaminoethyl methacrylate (TBAEMA) system measured in this study

T ^a /K	p ^a /MPa
4.8 wt% Poly(TBAEMA)+9.9 wt% TBAEMA	
442.7	207.07
447.8	171.55
452.9	143.97
5.0 wt% Poly(TBAEMA)+10.4 wt% TBAEMA	
433.3	193.62
438.4	158.45
442.8	136.38
4.8 wt% Poly(TBAEMA)+14.9 wt% TBAEMA	
363.5	171.55
373.5	150.27
383.4	137.24
393.0	130.00
402.9	122.93
413.3	115.86
422.9	109.14
433.3	102.93
5.1 wt% Poly(TBAEMA)+24.4 wt% TBAEMA	
393.4	89.31
403.1	88.10
413.3	86.72
417.7	85.69
422.8	84.14
423.6	82.59
427.7	80.52
431.9	77.41
437.8	75.69
443.0	73.97
5.0 wt% Poly(TBAEMA)+35.2 wt% TBAEMA	
374.0	49.14
383.9	49.14
393.6	49.14
403.5	49.14
413.8	49.48
423.4	49.48
433.4	49.48

^aStandard uncertainties *u* are *u*(T)=0.2 K and *u*(p)=0.40 MPa

pressure for the Poly(TBAEMA)+CO₂+15.6 wt% DME system is measured at temperature from 386 K to 432 K. Above 413 K, the cloud-point curve is shifted to moderately lower pressures, more than likely due to the decrease in the free volume difference between polymer and mixed solvent. At lower temperature than 413 K, the cloud-point curve does exhibit a rapid increase in pressure indicated in UCST curves because of a large increase of interactions between polymer and polymer than between polymer and solvent. The cloud-point curve of polymer solution with 24.2 wt% DME shows the UCST phase behavior below a temperature of

**Fig. 3.** The effect of TBAEMA concentration on the Poly(TBAEMA)+CO₂+TBAEMA mixture in this work.**Fig. 4.** The effect of DME concentration on the phase behavior for the Poly(TBAEMA)+CO₂+DME system. The concentration of polymer is about 5.0 wt% for each solution.**Table 4.** Experimental cloud point data for the poly(*t*-butylaminoethyl methacrylate) [Poly(TBAEMA)]+CO₂+dimethyl ether (DME) system measured in this work

T ^a /K	p ^a /MPa
4.9 wt% Poly(TBAEMA)+15.6 wt% DME	
386.3	218.79
393.8	192.41
402.7	171.21
414.4	151.90
423.9	138.45
432.6	134.66
5.0 wt% Poly(TBAEMA)+24.2 wt% DME	
364.3	137.93
373.8	128.97
384.3	123.28
393.5	117.24
404.4	112.76
413.6	108.97
422.8	104.83
433.3	100.86

Table 4. Continued

T ^a /K	p ^a /MPa
5.0 wt% Poly(TBAEMA)+29.5 wt% DME	
334.2	57.07
343.3	58.28
352.6	59.31
364.2	60.33
373.5	61.21
383.9	61.90
393.8	62.59
403.6	62.76
413.5	62.93
423.7	62.93
433.1	63.28
4.9 wt% Poly(TBAEMA)+43.9 wt% DME	
331.7	23.62
343.3	27.41
353.6	29.48
363.8	31.55
374.1	34.31
383.5	35.69
394.1	37.41
402.6	38.45
413.8	39.83
422.6	41.03
432.6	41.72
5.0 wt% Poly(TBAEMA)+78.7 wt% DME	
333.8	11.21
343.8	13.97
354.3	17.41
364.2	20.69
373.4	22.59
383.3	24.31
394.3	26.90
402.4	27.93
413.6	29.48
422.9	31.21
433.3	33.28

^aStandard uncertainties u are u(T)=0.2 K and u(p)=0.40 MPa

433 K. However, the cloud-point curve for Poly(TBAEMA) solution with over 29.5 wt% DME shows the LCST-type curve with positive slope, which is mainly controlled by entropic contributions. The LCST-type phase behavior may be due to the difference in free volume among Poly(TBAEMA) with weak polar functional group (see in Fig. 1), nonpolar CO₂ (i.e., dipole moment=0.0 C·m), and strong polar DME (i.e., dipole moment=4.34 • 10⁻³⁰ C·m) molecules.

3. Phase Behavior for Poly(TBAEMA)+DME Solvents Mixture

The phase behavior of Poly(TBAEMA) in supercritical DME was investigated in varied weight fraction conditions of 13.5 wt%, 23.3 wt% and 49.1 wt% polymer and the measured cloud-point pressure is listed in Table 5. DME has a dipole moment and polar-

Table 5. Experimental phase behavior data for the poly(2-dimethyl-aminoethyl methacrylate) [Poly(TBAEMA)]+dimethyl ether (DME) system measured in this work

T ^a /K	p ^a /MPa	Transition ^b
49.1 wt% Poly(TBAEMA)+50.9 wt% DME		
404.5	14.66	CP
414.4	17.41	CP
423.3	18.97	CP
433.7	21.21	CP
23.3 wt% Poly(TBAEMA)+76.7 wt% DME		
332.1	2.16	BP
342.9	2.45	BP
352.8	4.48	CP
363.4	7.24	CP
374.5	9.83	CP
383.2	11.90	CP
393.8	14.14	CP
403.6	16.55	CP
413.3	18.62	CP
422.9	20.17	CP
434.1	22.24	CP
13.5 wt% Poly(TBAEMA)+86.5 wt% DME		
334.7	2.24	BP
344.5	2.58	BP
352.5	6.53	CP
364.4	9.48	CP
372.1	10.86	CP
383.8	13.62	CP
393.7	16.21	CP
405.1	18.28	CP
413.5	20.14	CP
422.2	21.86	CP
433.7	23.50	CP

^aStandard uncertainties u are u(T)=0.2 K and u(p)=0.40 MPa

^bCP is cloud-point and BP is bubble-point

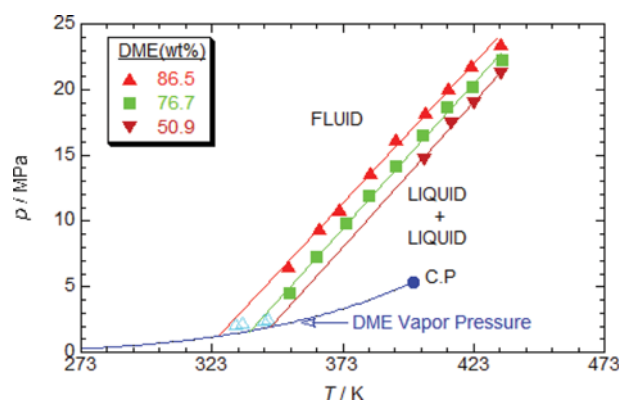


Fig. 5. Phase behavior of Poly(TBAEMA) dissolved in supercritical DME.

izability (see Table 1). Such properties of DME induce the higher solubility of Poly(TBAEMA) than in CO₂. As shown in Fig. 5, the

Table 6. Experimental data for the CO₂+t-butylaminoethyl methacrylate (TBAEMA) system measured in this work

TBAEMA mole fraction	p^a/MPa	Transition ^b
$T^a/\text{K}=313.2$		
0.052	8.86	BP
0.087	8.72	BP
0.121	8.36	BP
0.160	8.09	BP
0.187	7.84	BP
0.208	7.69	BP
0.255	7.28	BP
0.302	6.72	BP
0.335	6.30	BP
0.391	5.79	BP
0.460	5.12	BP
0.520	4.31	BP
0.610	3.70	BP
$T/\text{K}=333.2$		
0.052	13.10	BP
0.087	12.85	BP
0.121	12.17	BP
0.160	11.62	BP
0.187	11.11	BP
0.208	10.65	BP
0.255	9.83	BP
0.302	9.39	BP
0.335	8.86	BP
0.391	8.38	BP
0.460	7.46	BP
0.520	6.68	BP
0.610	5.67	BP
$T/\text{K}=353.2$		
0.052	15.90	CP
0.087	15.66	BP
0.121	15.23	BP
0.160	14.59	BP
0.187	14.14	BP
0.208	13.37	BP
0.255	12.47	BP
0.302	11.76	BP
0.335	10.79	BP
0.391	10.10	BP
0.460	9.00	BP
0.520	8.17	BP
0.610	6.89	BP

cloud-point behavior shows the LCST-type behavior with positive slope over the temperature range of 332 K to 434 K. At fixed pressures and temperatures, a fluid phase (i.e., single phase) region exists to the left of the LCST line, while a liquid-liquid phase separation region exists to the right side.

4. Vapor-liquid Equilibria for CO₂+TBAEMA Mixture

The vapor pressure for CO₂+TBAEMA system was measured

Table 6. Continued

TBAEMA mole fraction	p^a/MPa	Transition ^b
$T/\text{K}=373.2$		
0.052	18.66	DP
0.087	18.79	CP
0.121	18.52	BP
0.160	17.34	BP
0.187	16.73	BP
0.208	15.76	BP
0.255	14.38	BP
0.302	13.62	BP
0.335	12.52	BP
0.391	11.62	BP
0.460	10.24	BP
0.520	9.21	BP
0.610	7.94	BP
$T/\text{K}=393.2$		
0.052	19.91	DP
0.087	20.52	DP
0.121	20.62	CP
0.160	19.88	BP
0.187	19.14	BP
0.208	18.38	BP
0.255	17.00	BP
0.302	15.52	BP
0.335	14.38	BP
0.391	13.00	BP
0.460	11.41	BP
0.520	10.59	BP
0.610	8.80	BP

^aStandard uncertainties u are $u(T)=0.2$ K, $u(p)=0.2$ MPa and $u(x)=0.0008$

^bBP is a bubble-point, CP is a critical point, and DP is a dew point

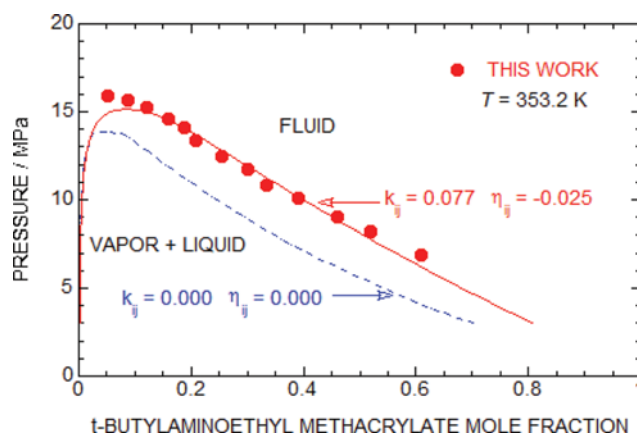


Fig. 6. Plot of pressure against mole fraction to illustrate the comparison of experimental data (symbols) for the CO₂+TBAEMA system with calculation obtained from the Peng-Robinson equation of state by k_{ij} and η_{ij} equal to zero (solid line), and k_{ij} equal to 0.077 and η_{ij} equal to -0.025 (dashed line) at 353.2 K.

Table 7. Pure component properties for the Peng-Robinson equation of state

Compound	M_w	Structure	T_b/K	T_c/K	p_c/MPa	ω
Carbon dioxide	44.01	O=C=O	-	304.2	7.38	0.225
TBAEMA ^a	185.27	C ₁₀ H ₁₉ NO ₂	460.2 ^b	623.6	2.28	0.631

^at-Butylaminoethyl methacrylate^bScientific Polymer Products Co., Ltd.

at broad temperature range of 313.2 K to 393.2 K, and the results are reported in Table 6. The obtained experimental data were correlated using the P-R EOS [34] and the calculated result is represented in Fig. 6. The properties for CO₂ [30] and TBAEMA [30] used in calculation are given in Table 7. The normal boiling point ($T_b=460.2$ K) of TBAEMA was obtained from Scientific Polymer Products Co. Inc. [43]. The property of TBAEMA was calculated by the group-contribution methods [30], and the vapor pressures were calculated by the Lee-Kesler method [30]. Two binary interaction parameters in P-R EOS were determined by regressing experimental data at 353.2 K, and by minimizing the objection function (OBF),

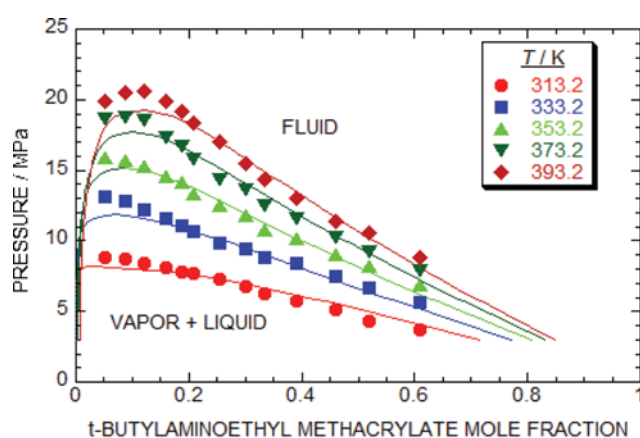
$$\text{OBF} = \sum_i^N \left(\frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}} \right)^2 \quad (1)$$

$$\text{RMSD}(\%) = \sqrt{\left(\frac{\text{OBF}}{\text{ND}} \right)} \times 100 \quad (2)$$

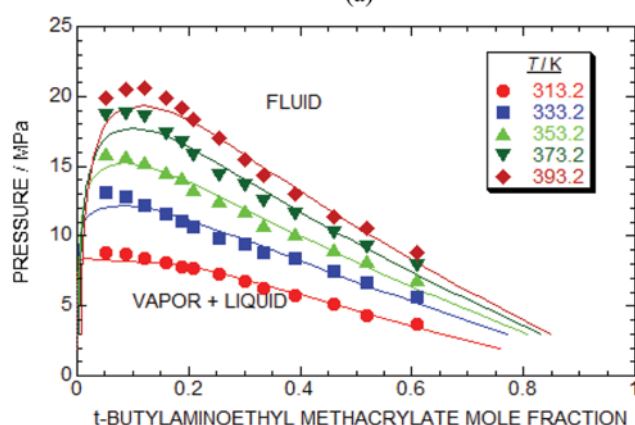
where P_{exp} and P_{cal} mean the pressure value of experiment and calculation, respectively. ND in Eq. (2) means the number of data points. The calculation result for the CO₂+TBAEMA system shows the root mean squared relative deviation (RMSD) error of 3.42%, and then the values of the adjusted parameters are 0.077 and -0.025 for k_{ij} and η_{ij} , respectively. These adjusted values determined at 353.2 K were extended to correlate the experimental data (ND=65) at different temperature (313.2 K, 333.2 K, 353.2 K, 373.2 K and 393.2

Table 8. The RMSD values compared the experimental data with calculation obtained from P-R EOS using optimum parameters (k_{ij} and η_{ij}) at each temperature of the CO₂+TBAEMA system

T/K	k_{ij}	η_{ij}	RMSD
313.2	0.087	0.010	3.58
333.2	0.084	-0.020	3.81
353.2	0.077	-0.025	3.42
373.2	0.077	-0.025	5.61
393.2	0.077	-0.025	4.46



(a)



(b)

Fig. 7. Plot of pressure against mole fraction that compares the experimental data (symbols) for the CO₂+TBAEMA system with calculated data (solid lines) by P-R EOS obtained (a) using $k_{ij}=0.077$ and $\eta_{ij}=-0.025$, and (b) using optimum parameters (k_{ij} and η_{ij}) at each temperature.

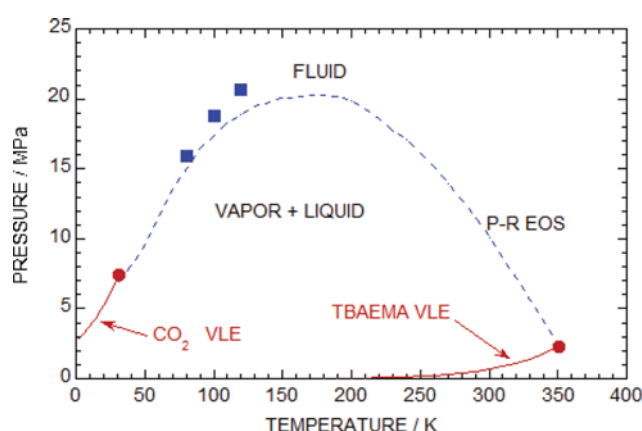


Fig. 8. Plot of pressure against temperature for the CO₂+TBAEMA system. Solid lines (red) and full circles (red) represent the vapor-liquid lines and critical points. Full squares (blue) are measured critical pressure for mixture points. Dashed lines (blue) represent calculations obtained using the Peng-Robinson equation of state with k_{ij} equal to 0.077 and η_{ij} equal to -0.025.

K), and the results are described in Fig. 7(a). The calculated results at five different temperatures show a little high deviation with 5.12% RMSD. Whereas, the correlated results with adjusted two parameters at each temperature are represented in Fig. 7(b). The optimized parameters and RMSD errors are reported in Table 8.

Fig. 8 represents the critical pressure values of experimental data and that of calculation results by the P-R EOS for the CO₂+TBAEMA system. The calculated critical pressure behavior curve shows type-I, which is in a good agreement with experimental observations at the two temperatures. Then, the dashed lines obtained using two adjustable parameters of $k_{ij}=0.077$ and $\eta_{ij}=-0.025$. Solid lines represent the saturated vapor pressure for pure CO₂ [30] and TBAEMA [30]. The vapor pressure line for pure TBAEMA was obtained by the Lee-Kesler method [30]. The full circles represent the critical point for pure CO₂ and TBAEMA. The upper range of the dashed line is in single phase (fluid), while the lower range exist vapor and liquid phase.

CONCLUSIONS

The cloud-point phase behavior for the several systems of Poly(TBAEMA)+cosolvent mixture in supercritical CO₂ and DME is presented at temperatures from 331 K to 453 K and at pressures from 2.16 MPa to 218.79 MPa. Experimental cloud-point curves for the Poly(TBAEMA)+CO₂+TBAEMA mixture were obtained at temperatures below 452.9 K and pressures up to 207.07 MPa. The effect of DME on the Poly(TBAEMA)+DME (15.6 wt% to 78.7 wt%) system in supercritical CO₂ is presented at temperatures below 433 K and at pressures ranging from 11.21 MPa to about 218.88 MPa. The vapor-liquid equilibrium data for CO₂+TBAEMA binary system is distributed at temperatures ranging from 313.2 K to 393.2 K and at pressures up to 20.62 MPa. The CO₂+TBAEMA system shows the type-I phase behavior. Experimental data for the CO₂/TBAEMA system is correlated by the P-R EOS. The calculated RMSD error with optimum parameter at each temperature was about 4.18%.

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