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Two component phase equilibria for the 3-methoxy-3-methyl-1-butanol and 1-methoxy-2-methyl-2-propanol in supercritical carbon dioxide

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Abstract−Two component mixtures, 3-methoxy-3-methyl-1-butanol (MMB)+carbon dioxide and 1-methoxy-2-methyl-2-propanol (MMP)+carbon dioxide, were investigated at 313.2, 333.2, 353.2, 373.2 and 393.2 K and at 4.29 to 20.95 MPa to get phase equilibrium data. The phase separation of vapor+liquid behavior for the MMB and MMP plays a momentous function as the organic solvent in a diversity of industrial processes. The two MMB+carbon dioxide and MMP+carbon dioxide components have mixture critical curves that have maxima in the p-T plot between the T_c (critical temperatures) of MMB and carbon dioxide or MMP and carbon dioxide. The two component systems of MMB+carbon dioxide and MMP+carbon dioxide mixture display type-I in simplest behavior. The measured results for the two component mixtures, MMB+carbon dioxide and MMP+carbon dioxide, are modelled with a general cubic equation of state, the Peng-Robinson, containing the k_{ij}, η_{ij} adjustable factor.

Keywords: 3-Methoxy-3-methyl-1-butanol, High Pressure Phase Equilibria, 1-Methoxy-2-methyl-1-propanol, Carbon Dioxide

INTRODUCTION

In many fine chemical industrial fields, 3-methoxy-3-methyl-1-butanol (MMB) is a biodegradable solvent, comparable to isomer ethylene glycol monobutyl ether. This solvent is employed as raw material for the production of industrial detergents and has been broadly used as a solvent for inks, fragrances and paints [1-3]. MMB is also intended as an alternative solvent to improve the risk of fire and explosion from manufacturing processes of lithium secondary batteries.

The knowledge of thermodynamic information of equilibrium data in two-component mixtures under compressed liquid fluids is understood for positive application of chemical processes, polymer processes, extraction and several industries [4-8]. In particular, MMB monomers have been used in the manufacture of inks and coatings, dry soaps, insecticides and pesticides, and industrial cleaners [9]. The 1-methoxy-2-methyl-2-propanol (MMP) monomers have also been used in the pharmaceutical and chemical industries as intermediate. They are generally a versatile solvent for leather dyeing, printing ink, anti-icer and coating material [10].

Equilibrium data in two-component systems under solvent fluids are available for an extensive range of applications. Among solvent fluids carbon dioxide been proposed as a solvent for several industrial reactions, because not only is it a non-poisonous, affordable, non-hazardous, eco-friendly solvent in a non-polar molecule, it is a solvent with no dipole or quadrupole moment [11].

Equilibrium data of two-component solutions in carbon dioxide have been reported of dew-point data (DP), bubble-point data (BP), and critical-point data (CP) curves [12,13]. The thermodynamic application of the two-component mixtures of alcohol monomer+carbon dioxide solution was demanded for actual use.

Measured data for the two-component mixture of MMB and MMP monomers at high pressure carbon dioxide is meaningful for the polymerization condition and polymer processes. Hsieh et al. [14], Secuianu et al. [15] and Byun and Kwak [16] reported the experimental phase behavior data for the alcohols+carbon dioxide solutions. Hsieh et al. [14] measured the solutions at 333.2 K and 353.2 K in the pressure range 5.33-12.8 MPa with a supercritical technique based on the static method in the phase behavior for the C_1-C_5 alcohols+carbon dioxide systems. Also, these alcohols are used as co-solvents to increase the solubility of polar solutes in carbon dioxide. Secuianu et al. [15] reported global phase behavior data for the two-component 1-propanol+carbon dioxide system at 293.15 to 353.15 K and at pressure between 0.61 and 12.64 MPa. Byun and Kwak [16] measured two-component mixtures of 1-butanol+carbon dioxide and 1-octanol+carbon dioxide mixture at 313-393 K and pressures up to 22.0 MPa by a synthetic type at a high-pressure.

This research was aimed at gaining the measured data for the MMB+carbon dioxide and MMP+carbon dioxide mixtures at high pressure. The data of MMB+carbon dioxide and MMP+carbon dioxide solution gained from these experiments are modelled with the general cubic equation, the Peng and Robinson equation [17], using a two k_{ij}, η_{ij} adjusted factors. The method of Lee/Kesler [18] and group contributions method of Joback/Lydersen [18] was used to calculate the ω, P_c, and T_c acentric factor, critical pressure, and critical temperature for the MMB and MMP, respectively.

EXPERIMENTAL SECTION

1. Materials

Carbon dioxide, purity of more than 0.999, CAS RN 124-38-9, in eco-friendly solvent was obtained from Deokyang Co. 3-Methoxy-

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Table 1. The Name, purity, purification and analysis method of the chemical used

Chemical name	Source	Mass fraction purity[a]	Purification method	Analysis method[a]
Carbon dioxide	Deok Yang Gas Co.	>0.999	None	-
MMB[c]	Sigma-Aldrich	>0.980	None	GC[b]
MMP[d]	Sigma-Aldrich	>0.990	None	GC[b]

[a]Both the analysis method and the mass fraction purity were provided by the suppliers.
[b]Gas chromatography.
[c]MMB: 3-methoxy-3-methyl-1-butanol.
[d]MMP: 1-methoxy-2-methyl-2-propanol.

3-methyl-1-butanol (MMB, purity of more than 0.980, $(CH_3)_2C(OCH_3)CH_2CH_2OH$, CAS RN 56539-66-3) and 1-methoxy-2-methyl-2-propanol (MMP, purity of more than 0.980, $CH_3C(CH_3)(OH)CH_2OCH_3$, CAS RN 3587-64-2) were obtained from Alfa Aesar Co., Ltd. Two organic monomers were used without more purification. Table 1 shows the chemicals used in the research.

2. Research Apparatus and Experimental Procedure

Fig. 1 presents the chart of the high-pressure (HP) system used in this research. To measure the phase equilibria of MMB and MMP under carbon dioxide, the HP apparatus was used; specific explanation can be found elsewhere [19,20]. A view cell apparatus of static-type used driving pressures to 100.0 MPa for obtaining the measurement data. The small cylinder was used to inject gases with precision of ±0.002 g to add carbon dioxide in the equilibrium cell. To eliminate organic solvent from the empty cell, it was purged 3three times under carbon dioxide and N_2. The monomer injection was charged with a syringe by standard uncertainty of 0.0008.

To reach the desired pressure, the mixed solution was compressed by water pressurized using a HP generator (model: 37-5.75-60). The mixed solution pressure was obtained by a Heise gauge (accuracy: ±0.02 MPa, model CM-53920). The phenomena in the cell can be seen on a monitor by an FLIR (model BFLY-U3-13S2C) connected to a borescope with Olympus Corp (model F100-038-000-50).

For attaining the single phase, the mixed solution was compressed to a constant temperature. The mixed solution was maintained in the single-phase domain for about 30-40 min at the desired temperature to reach phase equilibrium. From that, to obtain the measurement data, the equilibrium data was decreased at slow speed until 2-phases were revealed. When reducing pressure from 1-phase to 2-phases, we dropped pressure little by little, close to the two phases. To determine BP, DP and CP, a DP was adopted, and thereafter fine a mist was revealed, while a BP was adopted when tiny bubbles appeared in the cell.

Fig. 1. Schematic diagram of 3-methoxy-3-methyl-1-butanol (MMB) and 1-methoxy-2-methyl-2-propanol (MMP).

RESULTS AND DISCUSSION

Measured experimental data on the MMB and MMP in carbon dioxide were reported. The standard (SD) uncertainty of p and T at experiment was estimated at 0.2 K and at 0.2 MPa [21,22]. The MMB and MMP mole fractions of SD uncertainties were calculated using 0.0008 [21]. So far, the measured data for the MMB+carbon dioxide and MMP+carbon dioxide solutions have not been presented in the reference.

Fig. 2(a) and Table 2 depict the measured p, x diagram at T=313.2 K to 393.2 K, and at 5.90 MPa to 20.95 MPa for the MMB+carbon dioxide solution. Fig. 2(a) shows that at various tempera-

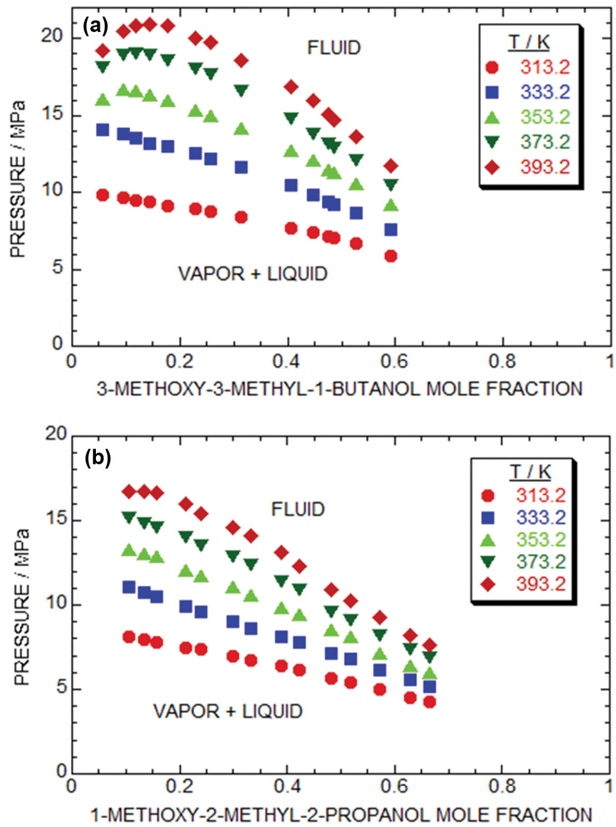

Fig. 2. Diagram of pressure vs mole fraction plot for the experimental result of (a) 3-methoxy-3-methyl-1-butanol+carbon dioxide) {x $((CH_3)_2C(OCH_3)CH_2CH_2OH)+(1-x)\ CO_2$} and (b) 1-methoxy-2-methyl-2-propanol+carbon dioxide) {x $(CH_3C(CH_3)(OH)\ CH_2OCH_3)+(1-x)\ CO_2$} systems.

Table 2. Data for the 3-methoxy-3-methyl-1-butanol (1)+carbon dioxide (2) system

x_1	p^a/MPa	Transition[b]	x_1	p/MPa	Transition
T/K=313.2			T/K=333.2		
0.056	9.63	BP	0.056	13.83	BP
0.095	9.61	BP	0.095	13.76	BP
0.117	9.46	BP	0.117	13.56	BP
0.145	9.36	BP	0.145	13.20	BP
0.178	9.15	BP	0.178	12.96	BP
0.229	8.97	BP	0.229	12.52	BP
0.256	8.75	BP	0.256	12.20	BP
0.314	8.37	BP	0.314	11.62	BP
0.406	7.66	BP	0.406	10.43	BP
0.446	7.41	BP	0.446	9.85	BP
0.477	7.12	BP	0.477	9.37	BP
0.487	7.02	BP	0.487	9.21	BP
0.526	6.66	BP	0.526	8.62	BP
0.592	5.90	BP	0.592	7.62	BP
T/K=353.2			T/K=373.2		
0.056	16.03	DP	0.056	18.18	DP
0.095	16.66	CP	0.095	18.98	DP
0.117	16.59	BP	0.117	19.04	CP
0.145	16.35	BP	0.145	18.90	BP
0.178	16.01	BP	0.178	18.60	BP
0.229	15.35	BP	0.229	18.01	BP
0.256	15.00	BP	0.256	17.64	BP
0.314	14.17	BP	0.314	16.60	BP
0.406	12.77	BP	0.406	14.80	BP
0.446	12.07	BP	0.446	13.83	BP
0.477	11.50	BP	0.477	13.19	BP
0.487	11.31	BP	0.487	12.95	BP
0.526	10.52	BP	0.526	12.05	BP
0.592	9.16	BP	0.592	10.48	BP
T/K=393.2					
0.056	19.21	DP			
0.095	20.49	DP			
0.117	20.79	DP			
0.145	20.95	CP			
0.178	20.79	BP			
0.229	20.00	BP			
0.256	19.73	BP			
0.314	18.62	BP			
0.406	16.90	BP			
0.446	15.96	BP			
0.477	15.05	BP			
0.487	14.73	BP			
0.526	13.64	BP			
0.592	11.73	BP			

[a]Standard uncertainties are p=0.05 MPa and T=0.2 K.
[b] BP, CP and DP is Bubble-Point, Critical-Point and Dew-Point.

Table 3. Data for the 1-methoxy-2-methyl-2-propanol (1)+carbon dioxide (2) system

x_1	p^a/MPa	Transition[b]	x_1	p/MPa	Transition[b]
T/K=313.2			T/K=333.2		
0.106	8.11	BP	0.106	11.04	BP
0.134	7.97	BP	0.134	10.72	BP
0.156	7.79	BP	0.156	10.48	BP
0.211	7.49	BP	0.211	9.94	BP
0.239	7.35	BP	0.239	9.62	BP
0.298	6.97	BP	0.298	9.00	BP
0.332	6.73	BP	0.332	8.62	BP
0.390	6.42	BP	0.390	8.10	BP
0.423	6.14	BP	0.423	7.76	BP
0.482	5.70	BP	0.482	7.17	BP
0.518	5.43	BP	0.518	6.80	BP
0.572	5.02	BP	0.572	6.15	BP
0.629	4.55	BP	0.629	5.58	BP
0.665	4.29	BP	0.665	5.15	BP
T/K=353.2			T/K=373.2		
0.106	13.28	BP	0.106	15.14	BP
0.134	13.07	BP	0.134	14.86	BP
0.156	12.87	BP	0.156	14.58	BP
0.211	12.06	BP	0.211	14.02	BP
0.239	11.69	BP	0.239	13.56	BP
0.298	11.04	BP	0.298	12.91	BP
0.332	10.62	BP	0.332	12.42	BP
0.390	9.82	BP	0.390	11.44	BP
0.423	9.41	BP	0.423	10.90	BP
0.482	8.51	BP	0.482	9.61	BP
0.518	8.10	BP	0.518	9.10	BP
0.572	7.15	BP	0.572	8.18	BP
0.629	6.40	BP	0.629	7.39	BP
0.665	5.98	BP	0.665	6.91	BP
T/K=393.2					
0.106	16.69	DP			
0.134	16.77	CP			
0.156	16.67	BP			
0.211	15.97	BP			
0.239	15.41	BP			
0.298	14.56	BP			
0.332	14.08	BP			
0.390	13.09	BP			
0.423	12.28	BP			
0.482	10.89	BP			
0.518	10.23	BP			
0.572	9.24	BP			
0.629	8.21	BP			
0.665	7.60	BP			

[a]Standard uncertainties are p=0.05 MPa and T=0.2 K.
[b]BP, CP and DP is Bubble Point, Critical Point and Dew Point.

tures, the three phases were not monitored. The critical-point pressures of the mixture for the temperatures were 16.66, 19.04 and 20.95 MPa at 353.2, 373.2 and 393.2 K, respectively. The (p, x) diagrams shown in Fig. 2(a) are in consensus with a type-I region

Table 4. Pure component properties for the equation of state

Compounds	M_w	Chemical structure	T_b/K	T_c/K	p_c/MPa	ω
Carbon dioxide	44.01	O=C=O		304.2	7.38	0.225
3-Methoxy-3-methyl-1-butanol	118.17	$(CH_3)_2C(OCH_3)CH_2CH_2OH$	446.2-448.2[a]	595.5	3.48	0.918
1-Methoxy-2-methyl-2-propanol	104.15	$CH_3C(CH_3)(OH)CH_2OCH_3$	388.2-389.2[a]	545.8	3.89	0.678

[a]Sigma-Aldrich, Fisher Scientific, Alfa Aesar.

[23,24], where a maximum takes place in the critical slope for the mixture p, T space. The type-I behavior for a two-component solution was a simple curve. The properties of type-I shape indicate that only one phase exists throughout the phase chart and that the critical trace of mixture runs sequentially from the CP of carbon dioxide solvent to that of the MMB component. The phase equilibria curve of carbon dioxide diminished as the temperature moved higher at constant pressure.

Table 3 and Fig. 2(b) depict the equilibrum data at 313.2-393.2 K, and at 4.29 to 19.96 MPa for the MMP+carbon dioxide solution. In Fig. 2(b), the critical-point of mixture pressures for temperature is 16.77 MPa at T=393.2 K. At various temperatures which we investigated, the MMP+carbon dioxide system did not display three phases. The critical-curve of mixture for the MMP+carbon dioxide solution exhibits at the maximum pressure in p, T curves.

The equilibrium data on the measured result is correlated using the Peng-Robinson equation. Here, the Peng-Robinson equation is simply represented and is described as follows [17]:

$$P=\frac{RT}{V-b}-\frac{a(T)}{V^2+2bV-b^2} \tag{1}$$

$$a(T)=0.457235\frac{\alpha(T)R^2T_c^2}{p_c} \tag{2}$$

$$b=0.077796\frac{RT_c}{p_c} \tag{3}$$

$$\alpha(T)=[1+\kappa(1-T_r^{0.5})]^2 \tag{4}$$

$$\kappa=0.37464+1.54226\omega-0.26992\omega^2 \tag{5}$$

where, ω, p_c, and T_c are critical properties of the monomer samples. The Peng-Robinson equation was used with the following:

$$a_{mix}=\sum_i\sum_j x_i x_j a_{ij} \tag{6}$$

$$a_{ij}=(1-k_{ij})(a_{ii}a_{jj})^{1/2} \tag{7}$$

$$b_{mix}=\sum_i\sum_j x_i x_j b_{ij} \tag{8}$$

$$b_{ij}=(1-\eta_{ij})\left[\frac{1}{2}(b_{ii}+b_{jj})\right] \tag{9}$$

where, a_{ii}, b_{ii}, a_{jj} and b_{jj} are pure monomer variables by the Peng-Robinson equation [17], and η_{ij} and k_{ij} are two monomer interaction (i, j) factors decided by the fitting (p, x) spaces. The objectve function (OF) and root mean squared relative deviation (RMSD) of these equations are described by

$$OF=\sum_i^N\left(\frac{P_{exp}-P_{cal}}{P_{exp}}\right)^2 \tag{10}$$

$$RMSD(\%)=\sqrt{\frac{OF}{ND}}\times 100 \tag{11}$$

The monomer molecular weight (M_w), ω, p_c and T_c for pure MMB [18], MMP [18] and carbon dioxide [18] appear in Table 4. The boiling point of two monomers is found in the literature [25,26].

To predict the critical characteristics and vapor pressure, MMB and MMP monomers the Joback/Lyderson group contribution method [18] and the Lee/Kesler method [18] are used, respectively.

Fig. 3 expresses the comparison of measured data for the (a) MMB+carbon dioxide and (b) MMP+carbon dioxide systems, and

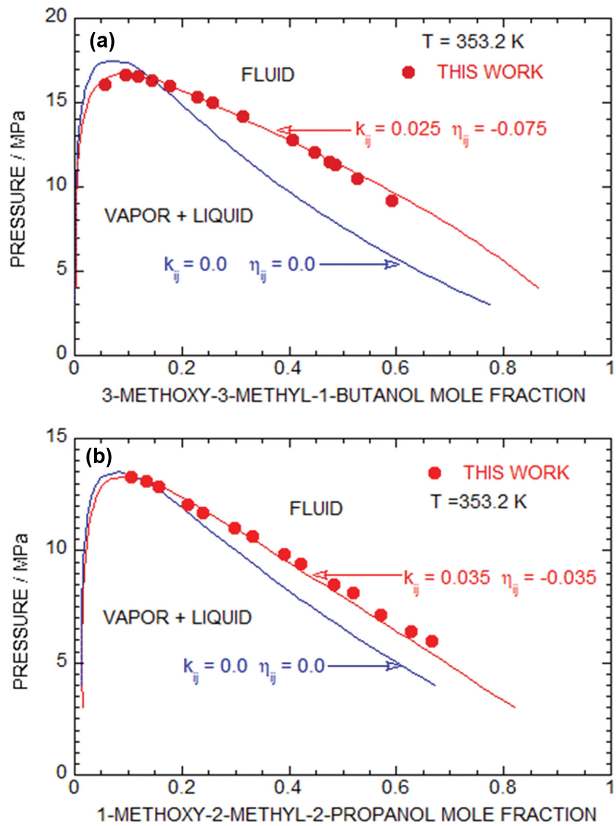

Fig. 3. Diagram of pressure vs mole fraction plot that compares the experimental results (symbols) of the (a) 3-methoxy-3-methyl-1-butanol+carbon dioxide) {x $((CH_3)_2C(OCH_3)CH_2CH_2OH)$+(1−x) CO_2} and (b) (1-methoxy-2-methyl-2-propanol+carbon dioxide) {x $(CH_3C(CH_3)(OH)\ CH_2OCH_3)$+(1−x) CO_2 } systems, calculated from the Peng-Robinson equation of state with k_{ij} and η_{ij} set equal to zero (blue curves), k_{ij}=0.025 and 0.035, η_{ij}=−0.075 and −0.035 for the 3-methoxy-3-methyl-1-butanol+carbon dioxide and 1-methoxy-2-methyl-2-propanol+carbon dioxide, respectively (red curves), at 353.2 K.

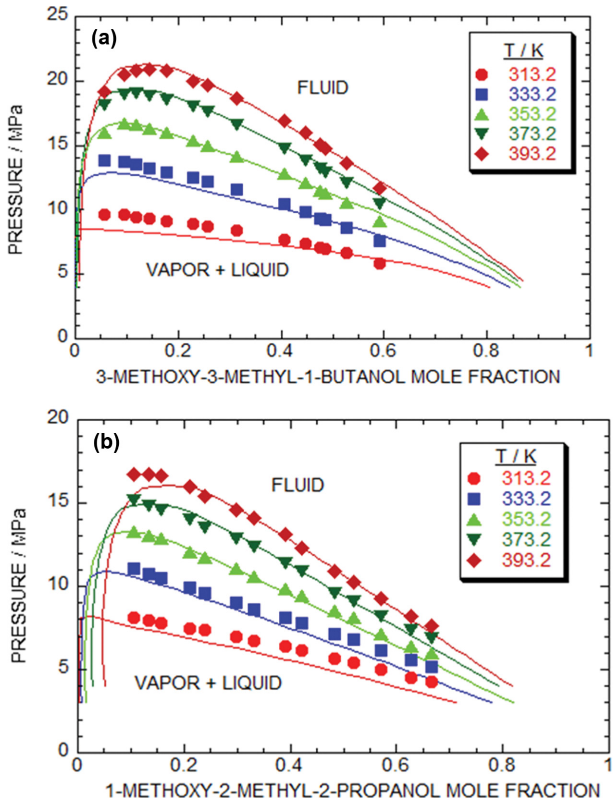

Fig. 4. Diagram of the pressure vs mole fraction plot that compares the experimental results (symbols) of the (a) 3-methoxy-3-methyl-1-butanol+carbon dioxide) {x ($(CH_3)_2C(OCH_3)CH_2CH_2OH$)+(1−x) CO_2} and (b) (1-methoxy-2-methyl-2-propanol+carbon dioxide) {x ($CH_3C(CH_3)(OH)\ CH_2OCH_3$)+(1−x) CO_2 } systems with calculations (solid curves) obtained from the Peng-Robinson equation; k_{ij}=(0.025 and 0.035), η_{ij}= −0.075 and −0.035) for the 3-methoxy-3-methyl-1-butanol+carbon dioxide and 1-methoxy-2-methyl-2-propanol+carbon dioxide, respectively. ●, 313.2 K; ■, 333.2 K; ▲, 353.2 K; ▼, 373.2 K; ◆, 393.2 K.

the estimated data gained by the Peng-Robinson equation at T= 353.2 K. The interaction factors k_{ij}, η_{ij} for the 2-component mixture for the Peng-Robinson equation are fitted with the measured results at 353.2 K. Optimized factors of the Peng-Robinson equation of the (a) MMB+carbon dioxide and (b) MMP+carbon dioxide mixtures are k_{ij}=0.025 and 0.035, and η_{ij}=−0.075 and −0.035 (measured data=(14 and 14) points, RMSD=1.83 and 3.96%), respectively.

Fig. 4(a) compares the measured data with the estimated p, x isotherms at 313.2 to 393.2 K for the MMB+carbon dioxide mixture by the adjusted k_{ij} and η_{ij} (measured data=14, RMSD=1.83%) determined at 353.2 K. In Fig. 4(a), measured data were well-fitted with the Peng-Robinson equation using adjusted factors for the MMB+carbon dioxide (measured data=70, RMSD=5.00%).

Fig. 4(b) compares the measured data with predicted p, x isotherms at T=313.2, 333.2, 353.2, 373.2 and 393.2 K for the MMP+carbon dioxide system. In a similar way as above, these isotherms were estimated using the adjusted factor of k_{ij}=0.035 and η_{ij}=–0.035 (measured data=14, RMSD=3.96%) decided at 353.2 K. RMSD

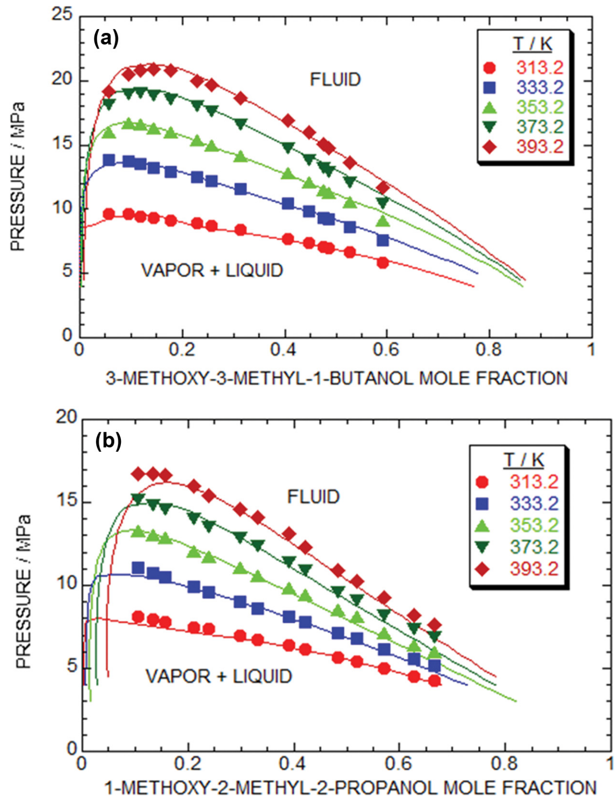

Fig. 5. Diagram of the pressure vs mole fraction plot that compares the experimental data (symbols) of the (a) 3-methoxy-3-methyl-1-butanol+carbon dioxide) {x ($(CH_3)_2C(OCH_3)CH_2CH_2OH$)+(1−x) CO_2} and (b) 1-methoxy-2-methyl-2-propanol+carbon dioxide) {x ($CH_3C(CH_3)(OH)\ CH_2OCH_3$)+(1−x) CO_2} systems with calculations (solid curves) obtained by equation of state from the optimized parameters k_{ij} and η_{ij} at each temperature: ●, 313.2 K; ■, 333.2 K; ▲, 353.2 K; ▼, 373.2 K; ◆, 393.2 K.

for the MMP+carbon dioxide system by the two factors decided at various temperatures was 8.45%. Where, measured data is 70 points. The curves predicted using the Peng-Robinson equation did not show liquid-liquid-vapor region at various temperatures.

Fig. 5 plots the p, x curves to compare the measure data marks for the (a) MMB+carbon dioxide and (b) MMP+carbon dioxide solutions with calculated data (lines) gained from the Peng-Robinson equation by adjusted factors k_{ij}, η_{ij} at every temperatures. In Fig. 5, these curves were calculated using adjusted factors determined at every temperatures. RMSD at every temperatures for the (a) MMB+carbon dioxide system was 1.92, 1.69, 1.83, 2.53 and 1.78% at 313.2, 333.2, 353.2, 373.2 and 393.2 K, measured point= 14, 14, 14, 14 and 14), respectively. The RMSD at various temperatures for the (b) MMP+carbon dioxide mixture was 3.28% (k_{ij}=0.042, η_{ij}=−0.073), 2.97% (k_{ij}=0.035, η_{ij}=−0.062), 3.96% (k_{ij}= 0.025, η_{ij}=−0.075), 2.92% (k_{ij}=0.025, η_{ij}=−0.075) and 3.08% (k_{ij}= 0.025, η_{ij}=−0.075), respectively. Here, a total of 14 measured data were obtained at respective temperatures. The compared result between the measured data and the calculated data shows a good agreement at a variety of temperatures. However, thermodynamic behavior was type-I region [23,24].

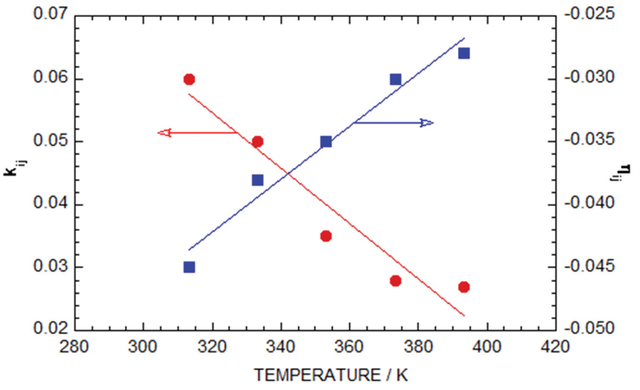

Fig. 6. Diagram of the k_{ij} vs temperature and η_{ij} vs temperature plots for the 1-methoxy-2-methyl-2-propanol+carbon dioxide) {x ($CH_3C(CH_3)(OH)CH_2OCH_3$)+(1−x) CO_2} system from the Peng-Robinson equation of state at all temperature. The equation line for the 1-methoxy-2-methyl-2-propanol+carbon dioxide is k_{ij}=0.1954−0.00044T and η_{ij}=−0.1094+0.00021T (313.2 K≤T≤393.2 K).

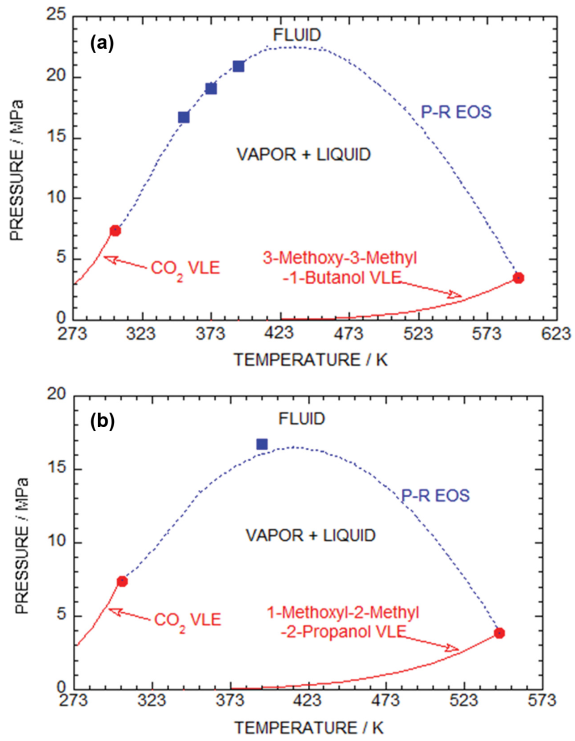

Fig. 7. Diagram of (pressure vs temperature) space for the (a) (3-methoxy-3-methyl-1-butanol+carbon dioxide) {x ($(CH_3)_2C(OCH_3)CH_2CH_2OH$)+(1−x) CO_2} and (b) (1-methoxy-2-methyl-2-propanol+carbon dioxide) {x ($CH_3C(CH_3)(OH)CH_2OCH_3$)+(1−x) CO_2} systems. Closed circles show the critical-point with pure components {(carbon dioxide vs 3-methoxy-3-methyl-1-butanol) or (carbon dioxide vs 1-methoxy-2-methyl-2-propanol)}. Solid curve shows the vapor+liquid curve [18]. Squares are critical points obtained from the isotherm measured data. Dot curve shows calculations decided from the Peng-Robinson equation with k_{ij}=0.025 and 0.035, η_{ij}=−0.075 and −0.035 for the carbon dioxide+3-methoxy-3-methyl-1-butanol and carbon dioxide+1-methoxy-2-methyl-2-propanol, respectively, at 353.2 K.

Fig. 6 plots the k_{ij} and η_{ij} factors against temperature for the MMP+carbon dioxide system with the Peng-Robinson equation at each temperature. The factor equation of the fitting line is k_{ij}= 0.1954–0.00044T (R^2=0.961) and η_{ij}=–0.1094+0.00021T (R^2=0.982) (313.2 K≤T≤393.2 K) decided by the Peng-Robinson equation.

Fig. 7 compares the critical curves of the binary mixture in the measured data with the predicted data by the Peng-Robinson equation for the (a) MMB+carbon dioxide and (b) MMP+carbon dioxide solutions using adjustable interaction factors k_{ij}, η_{ij} at 353.2 K. The calculated critical curve of binary mixture is type-I region. The solid circles signify the critical point of MMB, MMP, and carbon dioxide. The upper part of the curve line is 1-phase, the lower part of it 2-phases. The dashed curve shows the calculated data gained by the Peng-Robinson equation, with k_{ij}=0.025 and η_{ij}=−0.075 (MMB+carbon dioxide) (a) and k_{ij}=0.035 and η_{ij}=−0.035 (MMP+carbon dioxide) (b). The blue squares are the critical points of binary mixture decided with isotherms in measured data.

CONCLUSIONS

The high-pressure measurement data of pressure (p), composition (x) diagram for the MMB+carbon dioxide and MMP+carbon dioxide mixtures were investigated by synthetic apparatus at 313.2 to 393.2 K and until 20.95 MPa. Both MMB+carbon dioxide and MMP+carbon dioxide systems did not exhibit liquid+liquid+vapor phase at the various temperatures. The Peng-Robinson formula is suitable for predicting the equilibria curves for the MMB+carbon dioxide and MMP+carbon dioxide solutions by the two interaction factors. When considering the two adjusted factors of the Peng-Robinson formula used, the critical slopes between the calculated and measured data matched fairly well.

RMSDs of both systems predicted by adjusted factors at each temperature were 1.83% MMB+carbon dioxide and 3.96% MMP+carbon dioxide.

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