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Vapor−Liquid Equilibrium for Dimethyl Ether + Propyl Acetate

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The vapor−liquid equilibria (*P*−*T*−*x*−*y*) data of the binary mixture of dimethyl ether and propyl acetate (*n*-propyl acetate) were obtained by two procedures. First, binary mixtures of dimethyl ether + propyl acetate in various proportions were loaded into vapor−liquid equilibrium cells with an inside volume of 1.56×10^2 cm^3, and the pressure and temperature were measured using the static method after it reached thermodynamic equilibrium. The operating temperature and pressure range from 253.2 K (−20 °C) to 443.2 K (170 °C) and from 100 kPa to 4000 kPa, respectively. Second, the pressure, the mole fractions and volumes of the vapor phase and the liquid phase, were calculated with two equations of state, the Peng−Robinson equation of state and Soave−Redlich−Kwong equation of state, assuming that the binary interaction parameter, k_{ij}, was zero. Finally, the optimum binary interaction parameters for these two equations of state were determined as a function of temperature by minimizing the difference between calculated pressure and experimental data.

1. Introduction

The strain on the electric power supply because of an increasing use of air conditioning in summer has become a serious problem in Japan. One of the solutions to this problem could be the use of low-electric-energy-consumption absorption heat pumps in air conditioning systems. In current absorption-type air conditioning systems, water and LiBr aqueous solution are commonly used as refrigerant and absorbent, respectively. Current systems can be used only as boilers in winter. They cannot be used as heat pumps because the working fluid is frozen. In addition, current absorption-type air conditioning systems require periodic maintenance, and it is difficult to convert to the air-cooled type. It is important to develop a new pair of working fluids. A working fluid must be nontoxic and have a small global warming potential. There are many candidates for a working fluid pair. The thermophysical properties of some have been studied by Herraiz et al.[1] and Bobbo et al.[2,3] We have selected dimethyl ether and propyl acetate as refrigerant and absorbent, respectively (Hisajima et al.[4]). Though several models[5−7] for estimating vapor−liquid equilibrium have been suggested, high-accuracy vapor−liquid equilibria data are still important for the development of absorption heat pumps, because the main driving force of absorption heat pumps is the concentration difference between refrigerant and absorbent.

In the present work, the vapor−liquid equilibria (*P*−*T*−*x*−*y*) data of the binary mixture of dimethyl ether and propyl acetate were with two procedures. First binary mixtures of dimethyl ether and propyl acetate in various proportions were loaded in the VLE cell, and pressure and temperature were measured using the static method after thermodynamic equilibrium was reached. The operating temperature and pressure in the VLE cell ranged from 253.2 K (−20 °C) to 443.2 K (170 °C) and from 100 kPa to 4000 kPa, respectively. The pressure, temperature, and the total feed composition were obtained from this experiment, but the compositions of the liquid phase and the vapor phase, *x* and *y*, were not measured. Second, the pressure, the mole fractions and volumes of the vapor phase and the liquid phase, were calculated with two equations of state, the Peng−Robinson equation of state (PR-EOS)[8] and Soave−Redlich−Kwong equation of state (SRK-EOS),[9,10] assuming that the binary interaction parameter, k_{ij}, was zero. Finally the optimum binary interaction parameters were determined as a function of temperature for these two equations of state by minimizing the difference between calculated pressure and experimental pressure, and the effect of these binary interaction parameters on the error in the calculated pressures was estimated.

2. Experimental Section

Chemicals. The dimethyl ether was purchased from Sumitomo Seika Co., Ltd. with a purity of 99.9%. The propyl acetate was from Junsei Chemical Co., Ltd. with a purity of 99.5%.

Apparatus and Procedure. The experimental apparatus consists of (a) a stainless steel VLE cell with a pressure transducer and a thermocouple and (b) a thermostatic bath. Figure 1 shows the schematic diagram of the experimental apparatus. The VLE cell with an inside volume of 1.56×10^2 cm^3 containing the required amount of dimethyl ether and propyl acetate was immersed in a thermostat of about 0.3 m^3 capacity. The overall volume of the VLE cell was calibrated with pure water. We prepared two thermostats covering different temperature ranges. The thermostat for low temperature [253.2 K (−20 °C) − 323.2 K (50 °C)] contained an antifreeze coolant, and the thermostat for high temperature [323.2 K (50 °C) − 443.2 K (170 °C)] contained silicon oil. Both thermostats are stirred to make the liquid temperature distribution homogeneous and the liquid temperature was controlled within ±0.5 K by a PID controller. After thermodynamic equilibrium was reached, the pressure and temperature were measured. The pressure was measured by two types of pressure transducers (Kyowa Electronic Instruments, model PA-10KB and PHS-50KA) covering different pres-

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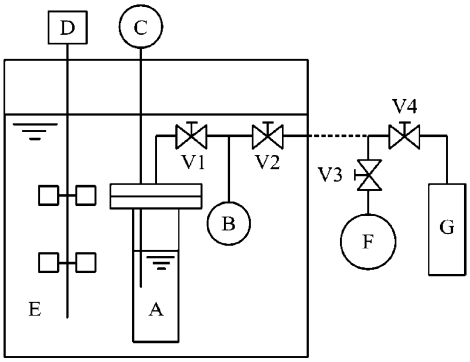

Figure 1. Schematic diagram of experimental apparatus: (A) VLE cell; (B) pressure transducer; (C) thermocouple; (D) stirrer; (E) thermostat; (F) vacuum pump; (G) gas cylinder; (V1−V4) valves.

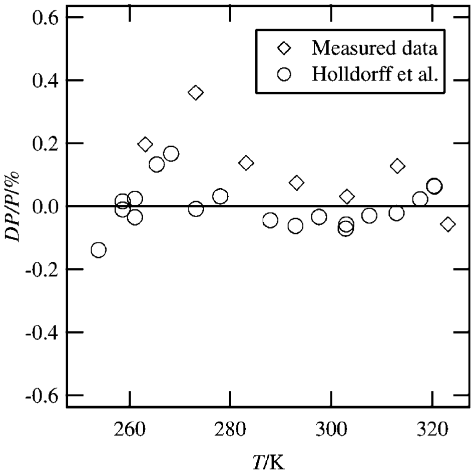

Figure 2. Relative pressure derivation of measured data and the values calculated using the Antoine equation and the coefficients proposed by Holldorff et al.[11] The measured data of Holldorff et al. were also plotted.

Table 1. Mass of Each Component for the Experiment to Investigate the Effect of Overall Mass on Pressure[a]

	dimethyl ether	propyl acetate	mass fraction of dimethyl ether
set	g	g	
L1	25.06	25.10	0.50
L2	29.86	29.95	0.50
L3	35.95	36.01	0.50
L4	39.98	40.03	0.50
L5	45.09	44.91	0.50
H1	19.84	19.81	0.50
H2	24.95	24.94	0.50
H3	29.65	29.82	0.50
H4	35.06	35.04	0.50
H5	39.08	39.03	0.50

[a] The measurements of sets L1−L5 and sets H1−H5 were carried out in the low temperature thermostat and the high temperature thermostat, respectively.

sure ranges, of which the full scales are 1000 kPa and 5000 kPa, respectively. They were calibrated by a pressure gauge with a quartz spiral (Tsukasa Sokken, model 660) with a precision of ±0.3 kPa, and the estimated accuracies of the pressure transducers were ± 0.5%. The temperature was measured by a thermocouple within an estimated uncertainty of ±0.1 K.

When dimethyl etherand propyl acetate were fed into the VLE cell, the VLE cell was out of the thermostat. A sample was fed by the following procedures. (a) The liquid propyl acetate was poured in the VLE cell directly, and air in the VLE cell was evacuated by a vacuum pump. (b) After the vacuum pump was detached from the VLE cell, the weight of the VLE cell containing propyl acetate was measured by a digital balance (Sartorius, model LP4200S) with a precision of ±0.01 g. (c) The VLE cell was connected to both the vacuum pump and the gas cylinder containing a required amount of gas dimethyl ether, and then air in the connecting tubes was evacuated. (d) The gas dimethyl ether was fed from the gas cylinder to the VLE cell. In this process, the VLE cell was cooled by dry ice so that gas dimethyl ether condensed into the VLE cell. (e) After the vacuum pump and the gas cylinder were detached from the VLE cell, the weight of the VLE cell containing the mixture of dimethyl ether and propyl acetate was measured by the digital balance.

Table 2. $P-T$ Data from Isochoric Measurement for the Experiment to Investigate the Effect of Overall Mass on Pressure

set	L1	L2	L3	L4	L5
T	P	P	P	P	P
K	kPa	kPa	kPa	kPa	kPa
263.2	128.1	128.1	129.1	131.4	133.5
273.2	180.9	181.2	183.4	185.4	187.3
283.2	251.5	251.9	253.6	255.9	258.0
293.2	338.2	339.8	341.3	344.2	345.1
303.2	446.5	448.5	450.4	454.0	454.6
313.2	578.0	582.3	583.3	587.8	590.0
323.2	732.7	739.8	740.6	745.7	748.7

set	H1	H2	H3	H4	H5
T	P	P	P	P	P
K	kPa	kPa	kPa	kPa	kPa
323.2	723.2	730.2	731.1	740.1	742.5
343.2	1099.3	1119.2	1121.3	1138.2	1143.5
363.2	1580.9	1619.9	1628.9	1655.8	1667.2
383.2	2157.8	2225.4	2253.6	2300.6	2322.1
403.2	2831.2	2946.3	3005.8	3082.4	3121.1
423.2	3579.3	3763.5	3877.1	4020.5	4103.5

Table 3. Mass of Each Component[a]

	dimethyl ether	propyl acetate	mass fraction of dimethyl ether
set	g	g	
L1	50.00	0.00	1.00
L2	45.61	5.08	0.90
L3	48.12	12.08	0.80
L4	44.00	18.89	0.70
L5	39.40	26.32	0.60
L6	39.98	40.03	0.50
L7	28.05	42.08	0.40
L8	17.92	41.95	0.30
L9	11.92	47.83	0.20
L10	7.00	63.01	0.10
H1	50.00	0.00	1.00
H2	45.00	5.01	0.90
H3	48.05	12.03	0.80
H4	44.01	18.85	0.70
H5	39.63	26.43	0.60
H6	39.08	39.03	0.50
H7	27.97	42.03	0.40
H8	21.02	49.01	0.30
H9	11.98	47.99	0.20
H10	6.98	62.96	0.10
H11	0.00	70.00	0.00

[a] The measurements of sets L1−L10 and sets H1−H11 were carried out in the low temperature thermostat and the high temperature thermostat, respectively.

Before obtaining the vapor−liquid equilibria data of the mixtures in various proportions, the vapor pressure vs temperature curve of dimethyl ether was measured to

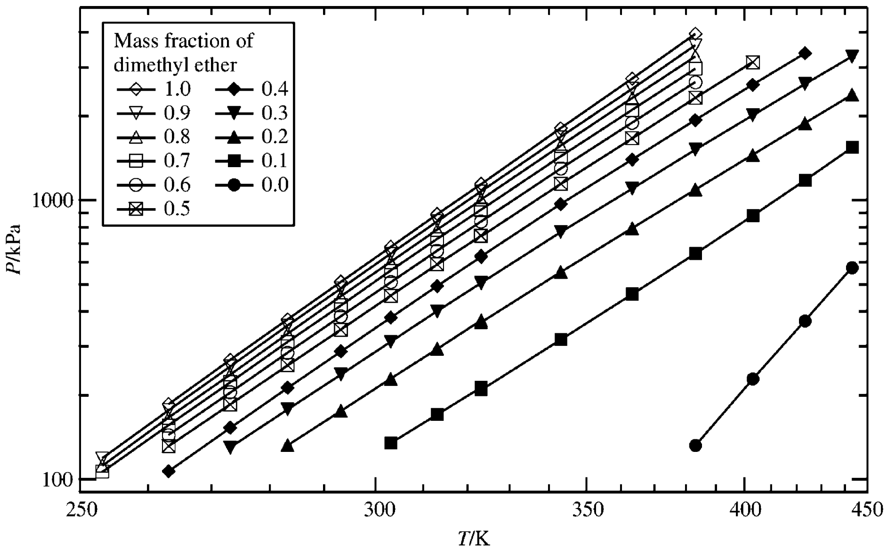

Figure 3. Measured pressure and temperature for each sample.

Table 4. *P-T* Data from Isochoric Measurement

set	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10
T	*P*	*P*	*P*	*P*	*P*	*P*	*P*	*P*	*P*	*P*
K	kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa
253.2		119.1	111.9	106.4						
263.2	185.6	176.5	165.8	156.0	144.0	131.4	106.8			
273.2	267.7	253.7	237.8	223.0	204.6	185.4	152.8	130.1		
283.2	373.9	355.1	332.9	310.5	284.1	255.9	212.6	178.1	132.5	
293.2	510.1	483.0	451.8	420.4	383.6	344.2	287.1	237.8	175.6	
303.2	680.6	643.1	600.7	557.7	507.6	454.0	379.4	310.9	228.7	134.8
313.2	891.2	840.0	783.4	725.5	658.8	587.8	492.7	400.6	293.6	170.8
323.2			1002.8	926.3	838.8	745.7	625.5	504.7	370.5	213.6

set	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10	H11
T	*P*	*P*	*P*	*P*	*P*	*P*	*P*	*P*	*P*	*P*	*P*
K	kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa	kPa
323.2	1142.9	1074.9	1004.3	924.0	839.5	742.5	629.5	505.4	365.2	209.1	
343.2	1808.6	1683.4	1566.9	1433.8	1296.6	1143.5	968.1	767.2	553.6	316.5	
363.2	2721.2	2509.0	2318.0	2104.7	1893.5	1667.2	1398.5	1102.6	794.4	460.7	
383.2	3940.5	3581.4	3276.2	2961.9	2645.2	2322.1	1935.4	1517.0	1091.2	644.4	132.1
403.2						3121.1	2585.5	2015.2	1451.0	880.0	228.3
423.2							3352.3	2603.1	1883.4	1176.3	369.1
443.2								3269.2	2385.1	1543.6	573.1

check the functioning of the complete system and the accuracy of the instrumentation. Figure 2 shows the relative pressure derivation of measured data and the values calculated using Antoine equation and the coefficients proposed by Holldorff et al.[11] The measured data by Holldorff et al. are also plotted in Figure 2. The scattering of the present measured data is larger than that of Holldorff et al., but all relative pressure derivations are within ±0.36%. Then the effect of the overall mass of a sample on the pressure was checked. The binary mixtures of dimethyl ether and propyl acetate of various masses, of which overall mass fraction of dimethyl ether was 0.5, were prepared. The masses of each component are listed in Table 1. The overall mass ranged from 40 to 90 g. After thermodynamic equilibrium was reached, the pressure and temperature in the VLE cell were measured. The measured pressure and temperature in the two different temperature regions are listed in Table 2. The difference between the highest measured pressure and the lowest one was about 5 kPa at 263.2 K, and the difference was about 500 kPa at 423.2 K. The effect of the overall mass of a sample on the pressure becomes large as temperature increases. Because the mass of dimethyl ether in the gas phase is comparable to that in the liquid phase at high temperature particularly when the overall mass is small, the compositions of the liquid-phase cannot be assumed to be the same as the total feed compositions.

To obtain the vapor−liquid equilibria data in various proportions, the mass of each component was determined as listed in Table 3. The mass fraction of dimethyl ether ranges from 0 to 1 with an interval of 0.1. Figure 3 shows the measured pressure and temperature for each sample and the corresponding data are listed in Table 4.

3. Calculations

The vapor−liquid-phase equilibrium calculations can be defined using the *K* factors of the components in the mixture.[5] For the component *i*, it is defined as

$$K_i = \frac{y_i}{x_i} \tag{1}$$

where x_i and y_i are the mole fractions of the component *i* in the liquid phase and the vapor phase, respectively. Assuming an equation of state, the *K* factor can be

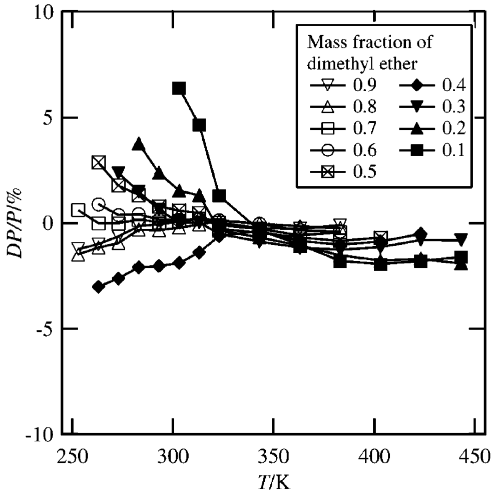

Figure 4. Deviation of calculated pressure, *DP*/*P*, for the PR-EOS at $k_{ij} = 0$.

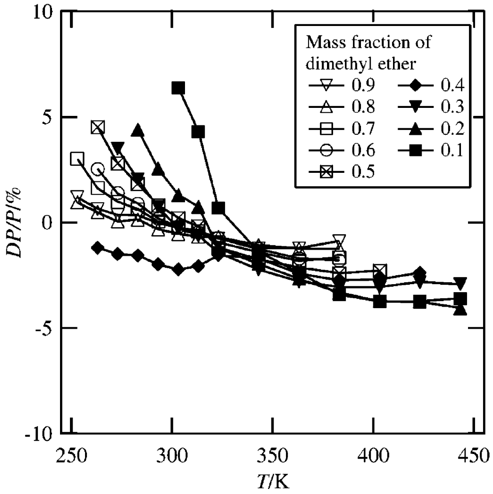

Figure 5. Deviation of calculated pressure, *DP*/*P*, for the SRK-EOS at $k_{ij} = 0$.

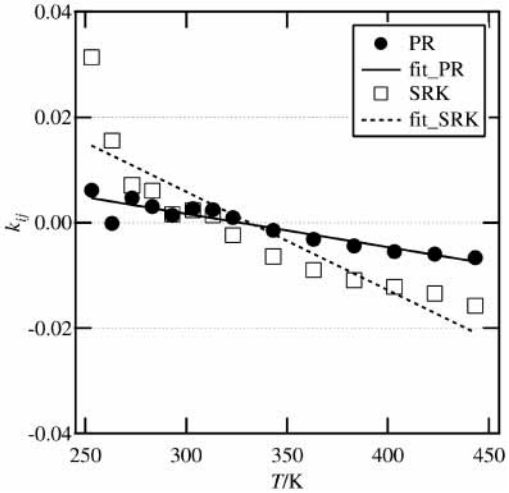

Figure 6. Optimum binary interaction parameters and the fitted lines.

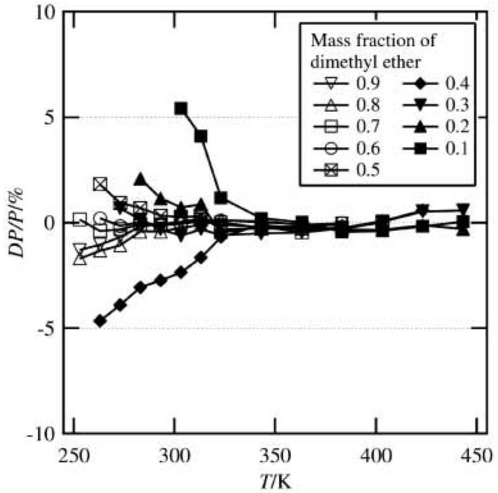

Figure 7. Deviation of calculated pressure, *DP*/*P*, for the PR-EOS at $k_{ij} = 0.0207 - 0.63 \times 10^{-4} \times T/\mathrm{K}$ [eq 11].

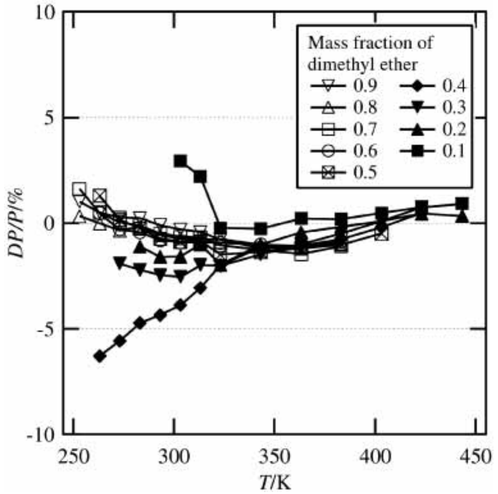

Figure 8. Deviation of calculated pressure, *DP*/*P*, for the SRK-EOS at $k_{ij} = 0.0618 - 1.87 \times 10^{-4} \times T/\mathrm{K}$ [eq 12].

obtained. In this work, we consider two equations of state, the PR-EOS and the SRK-EOS. Many of the common two-parameter cubic equations of state can be expressed by

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + ubV + wb^2} \tag{2}$$

where V is the molar volume of the liquid phase or the vapor phase, V^L or V^V, u and w are the integer values, and a and b are two parameter. The integer values of $u = 1$, $w = 0$ and $u = 2$, $w = -1$ are used for the PR-EOS and SRK-EOS, respectively. For the two parameters of mixtures, the following mixing rule was used:[5]

$$a = \sum_i \sum_j z_i z_j \sqrt{a_i a_j}(1 - k_{ij}) \tag{3}$$

$$b = \sum_i z_i b_i \tag{4}$$

where z_i is the mole fraction of the component i in the liquid phase or the vapor phase, x_i or y_i. The two parameters of each component were obtained from the property data bank.[5] For binary mixtures, we have four independent equations, eq 1 for two components and eq 2 for two phases. If T and x_1 are given, four unknowns, P, y_1, V^L, and V^V, are to be found. In this work, because x_1 was unknown, the temperature, T, the overall mole number of component 1, n_1, the total overall mole number, n_{12}, and the volume of the VLE cell, V_T, were given, and then four unknowns, the pressure, P, the mole number of component 1 in the vapor phase, n_1^V, and the total mole number in the vapor

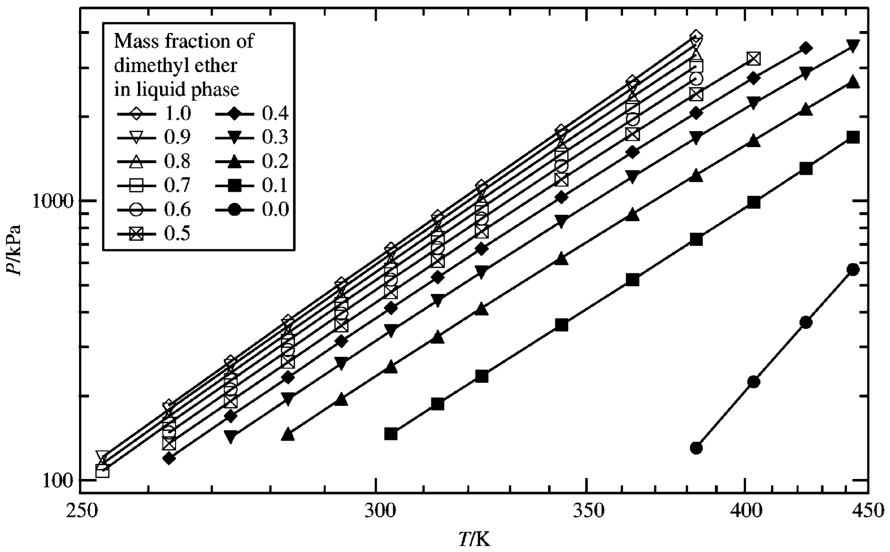

Figure 9. Vapor−liquid equilibrium for dimethyl ether−propyl acetate calculated with the PR-EOS at $k_{ij} = 0.0207 - 0.63 \times 10^{-4} \times T/\mathrm{K}$ [eq 11].

phase, n_{12}^{V}, and the volume of the vapor phase, V_{T}^{V}, were to be found. The relationships between x_1, y_1, V^V, V^L and n_1, n_{12}, n_1^V, n_{12}^V, V_T^V, V_T are as follows:

$$x_1 = \frac{n_1 - n_1^V}{n_{12} - n_{12}^V} \tag{5}$$

$$y_1 = \frac{n_1^V}{n_{12}^V} \tag{6}$$

$$V^L = \frac{V_T - V_T^V}{n_{12} - n_{12}^V} \tag{7}$$

$$V^V = \frac{V_T^V}{n_{12}^V} \tag{8}$$

First, we calculated these equations assuming that the binary interaction parameter, k_{ij}, was zero. Figures 4 and 5 show the deviations of calculated pressure, DP/P, for the PR-EOS and the SRK-EOS, respectively. The deviation of calculated pressure, DP/P, is defined by

$$\frac{DP}{P} = \frac{P^e - P^c}{P^e} \times 100\ (\%) \tag{9}$$

where P^e is the experimental pressure and P^c is the corresponding calculated pressure. The DP/P data are close to zero when the temperature is around 300 K and the mass fraction of dimethyl ether is close to 1. Most DP/P data are within ±5%. The averaged deviations of calculated pressure, $\overline{DP}/P$, is defined by

$$\frac{\overline{DP}}{P} = \frac{1}{N}\sum_{n=1}^{N}\frac{|P^e - P^c|}{P^e} \times 100\ (\%) \tag{10}$$

where N is the number of data. The $\overline{DP}/P$ for the PR-EOS and the SRK-EOS are 0.9% and 1.7%, respectively.

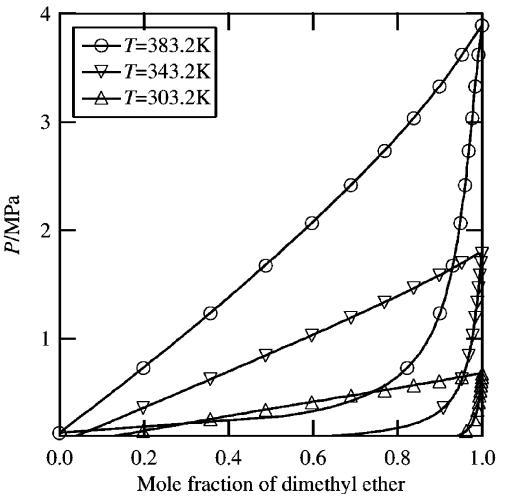

Figure 10. Vapor−liquid equilibrium for dimethyl ether−propyl acetate calculated with the PR-EOS at $k_{ij} = 0.0207 - 0.63 \times 10^{-4} \times T/\mathrm{K}$ [eq 11].

4. Discussion

Because the DP/P data depend on temperature in Figures 4 and 5, the binary interaction parameter was optimized as a function of temperature. Figure 6 shows the optimized binary interaction parameters and the lines fitted to these parameters for the PR-EOS and the SRK-EOS. The optimized parameters are the ones, which minimize DP/P at each temperature. The optimized parameters for both equations decrease with an increase of temperature. The fitted lines for the PR-EOS and the SRK-EOS are expressed as the following equations:

$$k_{ij}(T) = 0.0206 - 0.63 \times 10^{-4} \times T/\mathrm{K}\ (\text{PR-EOS}) \tag{11}$$

$$k_{ij}(T) = 0.0618 - 1.86 \times 10^{-4} \times T/\mathrm{K}\ (\text{SRK-EOS}) \tag{12}$$

Figures 7 and 8 show the DP/P data for the PR-EOS and the SRK-EOS, in which the binary interaction parameters were given by eqs 11 and 12, respectively. The DP/P data in Figures 7 and 8 are smaller than the corresponding data in Figures 4 and 5 except the data for mass fraction of dimethyl ether of 0.4. The averaged deviations of calculated pressure, $\overline{DP}/P$, are 0.6% and 1.1%, respectively. The $\overline{DP}/P$ for the PR-EOS was smaller than that for the SRK-EOS. Finally the vapor−liquid equilibria (P−T−x−y) data of the binary mixture of dimethyl ether + propyl acetate were calculated with the PR-EOS and the binary interaction parameter given by eq 11. Figures 9 and 10 show the $P-T$ curves at constant mass fractions in the liquid phase, x, ranging from 0 to 1 with an interval of 0.1, and examples of $P-x-y$ diagrams at $T = 303.2$ K, 343.2 K, and 383.2 K, respectively. In comparison between Figures 3 and 9, because the overall mass fraction of dimethyl ether is larger than the mass fraction of dimethyl ether in the liquid phase, $P-T$ curves in Figure 9 are slightly higher than the corresponding curves in Figure 3.

5. Conclusions

The optimized binary interaction parameters, k_{ij}, for the binary mixture of dimethyl ether + propyl acetate for the PR-EOS and the SRK-EOS were obtained as a function of temperature. The temperature and pressure range from 253.2 K (−20 °C) to 443.2 K (170 °C) and from 100 kPa to 4000 kPa, respectively. The averaged deviations of calculated pressure are 0.6% and 1.1%, respectively.

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