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Measurement and Correlation of Vapor−Liquid Equilibria for Water + 2-Propanol, Water + 2-Butanol, and Water + 2-Pentanol Systems at High Temperatures and Pressures

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The vapor−liquid equilibria for water + 2-propanol, water + 2-butanol, and water + 2-pentanol systems were measured at (523 to 573) K and (3.30 to 11.48) MPa by a flow method. The vapor−liquid equilibrium data for the water + 2-propanol system at (548 and 573) K were compared with the literature data to confirm the validity of the experimental apparatus and procedure. The phase behavior was elucidated by changing the temperatures and the carbon number of the secondary alcohols. The experimental data obtained in this work were correlated by a modified Soave−Redlich−Kwong (MSRK) equation of state. An exponent-type mixing rule was applied to the energy parameters in the equation of sate. The correlated results are in good agreement with the experimental data.

Introduction

Sub- and supercritical water have been applied to various fields as a reaction medium because the physical and chemical properties can be changed continuously by changing temperature and pressure, and water can behave as a nonpolar solvent in the supercritical region.[1−7] Hydrolysis and cracking processes of heavy hydrocarbons and waste plastics utilizing sub- and supercritical water have received much attention from the point of view of recycling of resources and conservation of the environment.[1,2,4] Hydration processes of olefin in sub- and supercritical water have been also proposed recently.[7] In these processes, low molecular weight hydrocarbons such as alkanes, alkenes, and secondary alcohols are produced as products. Therefore, it is required for process design to elucidate the phase behavior of the mixtures consisting of water and these compounds at high temperatures and pressures near the critical point of water. In previous works, the liquid−liquid equilibria for water + hydrocarbon binary systems and water + hydrocarbon + hydrocarbon and water + hydrocarbon + secondary alcohol ternary systems at high temperatures and pressures have been measured and correlated.[8−11] The vapor−liquid equilibria (VLE) for water + alcohol systems are also needed in process design. Griswold and Wong[12] reported the VLE for water + methanol system at high temperatures and pressure. The VLE for water + ethanol and water + 2-propanol systems were reported by David and Dodge[13] at high temperatures and pressures by a circulation method. In this work, a flow method was applied to measure the VLE for water + secondary alcohol systems at high temperatures and pressures to prevent the pressure fluctuation during samplings. 2-Propanol, 2-butanol, and 2-pentanol were selected as secondary alcohols. The VLE data for water + 2-propanol system at (548 and 573) K were compared with the literature data to ascertain the soundness of the experimental apparatus and procedure in this work. The VLE for water + 2-butanol and water + 2-pentanol systems were also measured to elucidate the phase behavior by changing the carbon number of secondary alcohol and by changing temperature. The VLE data obtained in this work were correlated by a modified SRK (Soave−Redlich−Kwong) equation of state proposed by Sandarusi et al.[14] An exponent-type mixing rule proposed by Higashi et al.[15] was applied to the energy parameters of the equation of state.

Experimental Section

Materials. Ultrapure water was used. It was purified by deionization using Milliq Labo (Millipore Corporation). The resistivity was (18.0 to 18.2) MΩ·cm. 2-Propanol, 2-butanol, 2-pentanol, and ethanol used in this work were analytical grade reagent and were supplied by Wako Pure Chemical Industries, Ltd. Their purities were checked with gas chromatograph by the authors. The peak percentages of the main compounds for 2-propanol, 2-butanol, and 2-pentanol were 99.9 %, 99.9 %, and 99.8 %, respectively. These materials were used without further purification.

Apparatus and Procedure. A flow-type apparatus was adopted to avoid oxidative decomposition of secondary alcohols and pressure fluctuation caused by sampling. The apparatus was quite similar to that used in previous works,[10,11] and a detailed description of the apparatus and operating procedures were given in the previous work. The apparatus and procedures are only briefly described here. This apparatus consists of a feed system, an equilibrium cell, pressure and temperature measurement and control systems, and a sampling effluent system. Figure 1 shows the details of the equilibrium cell, which was modified from the previous work. It was made of Hastelloy and equipped with sapphire windows to observe the phase behavior inside the cell. The inner diameter was 20 mm, and the volume of the cell was 31 mL, respectively. The diameter of sapphire windows was

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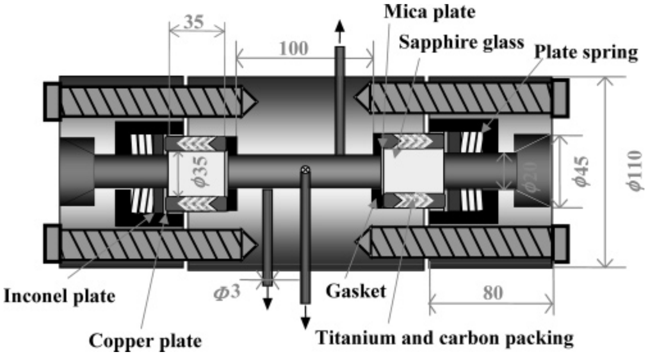

Figure 1. Equilibrium cell.

changed to 35 mm from 45 mm, and the packing type for these windows was changed to V-shaped packing to accommodate the thermal expansion of the sapphire. The equilibrium cell was connected with four lines, a feed line, two sampling lines for the vapor and liquid phases, and a subsidiary line. The subsidiary line was used to maintain the position of the phase interface at the center of the cell.

The system was heated to the desired temperature by electric heaters. Pure water and secondary alcohol were individually supplied by pumps. For the water + 2-propanol system, however, only one feed line with preheating coil was used because water and 2-propanol are fully miscible at room temperature and atmospheric pressure. The solutions were fed with nonpulsating HPLC pumps (PUS/PUD, GL Sciences). The feed rates were measured by electronic balances and confirmed to be constant during measurement. The feed rates were from (5.7 to 7.7) g·min^{-1}. Pressurized water and the secondary alcohol were sufficiently mixed through a line mixer before entering the equilibrium cell. The phase behavior inside the cell was observed with a video camera attached to a 42-power telescope (CCD-TR3300, Sony). The residence time in the equilibrium cell was about (4.4 to 6.2) min by judging from the flow rate. It was found that the experimental results were independent of the flow rate when the experiments were carried out in this range. The temperatures of entrance, top, and bottom of the cell were controlled within ± 0.5 K. The pressure fluctuation was held to ± 0.02 MPa. Samplings of each phase were carried out after the phase interface was well stabilized. The samples of the water + 2-propanol mixture were trapped into the sampling bottles without solvents. On the other hand, for water + 2-butanol and water + 2-pentanol mixtures, the bottles containing ethanol were used to obtain homogeneous solutions because water is partially miscible with 2-butanol and 2-pentanol at room temperature and atmospheric pressure. The concentration of water in ethanol was checked by a Karl Fischer moisture titrator (Kyoto Electronics Manufacturing Co., Ltd.) prior to use. Large volumes (about 15 mL) of samples were trapped to reduce experimental errors in determination of compositions. The samples in vapor and liquid phases were analyzed by gas chromatograph with a thermal conductivity detector (GC309, GL Sciences). Decomposition of 2-propanol, 2-butanol, and 2-pentanol was not observed during measurement because other peaks were not detected.

Results and Discussion. The experimental results of VLE for water + secondary alcohol binary systems are shown in Tables 1 to 3 and Figures 2 to 4. The data in this work were determined from the arithmetic average of four to seven data points. The experimental results for the water + 2-propanol system were compared with the literature data at 548 K and 573 K in Figure 2. As shown in Figure 2, the experimental results for the water + 2-propanol system measured in this work at (548 and 573) K are in good agreement with the literature data reported by David and Dodge.[13] The validity of the experimental apparatus and procedure in this work was ascertained.

Table 1. Vapor−Liquid Equilibria for Water (1) + 2-Propanol (2) System

T/K	σ_T[a]	p/MPa	σ_p[b]	x_1[c]	N_x[e]	$S_x \times 10^3$[g]	y_1[d]	N_y[f]	$S_y \times 10^3$[h]
548	0.2	6.49	0.01	0.986	7	1.66	0.927	7	4.06
		7.43	0.03	0.956	7	1.92	0.813	7	5.46
		7.99	0.01	0.917	4	1.14	0.764	4	1.76
573	0.4	9.56	0.01	0.976	6	0.82	0.912	6	2.74
		10.13	0.01	0.953	6	0.91	0.862	6	1.46
		10.54	0.01	0.932	5	1.65	0.812	5	1.67
		10.87	0.02	0.915	6	3.10	0.803	6	4.54
		11.28	0.01	0.870	6	2.16	0.759	4	4.45
		11.48	0.01	0.854	6	1.64	0.758	6	1.94

[a] σ_T, standard deviation of temperature. [b] σ_p, standard deviation of pressure. [c] x_j, mole fraction of component j in liquid phase. [d] y_j, mole fraction of component j in vapor phase. [e] N_x, number of data points in liquid phase for arithmetic average. [f] N_y, number of data points in vapor phase for arithmetic average.

[g]
$$S_x = \left[\frac{1}{N}\sum_{i=1}^{N}\left|x_1^{(i)} - x_1\right|^2\right]^{1/2}$$

[h]
$$S_y = \left[\frac{1}{N}\sum_{i=1}^{N}\left|y_1^{(i)} - y_1\right|^2\right]^{1/2}$$

Table 2. Vapor−Liquid Equilibria for Water (1) + 2-Butanol (2) System

T/K	σ_T	p/MPa	σ_p	x_1	N_x	$S_x \times 10^3$	y_1	N_y	$S_y \times 10^3$
523	0.2	4.80	0.01	0.969	6	11.46	0.809	6	15.25
		4.46	0.01	0.987	5	5.64	0.882	5	6.51
		5.23	0.01	0.868	6	8.92	0.684	6	5.22
		5.33	0.01	0.543	6	3.62	0.591	6	5.05
		5.08	0.01	0.398	6	3.89	0.546	6	0.96
		4.72	0.01	0.273	6	5.97	0.468	6	2.39
548	0.3	6.38	0.01	0.985	6	3.54	0.904	6	1.58
		6.74	0.04	0.969	6	10.00	0.861	6	22.98
		7.22	0.01	0.940	6	4.51	0.804	6	4.27
		7.39	0.01	0.910	5	1.24	0.783	3	0.87
		7.70	0.01	0.826	5	6.53	0.729	5	11.82
		7.89	0.01	0.702	6	3.68	0.684	6	4.66
573	0.3	8.99	0.01	0.988	6	0.00	0.942	6	2.34
		9.78	0.01	0.965	6	2.76	0.872	5	2.28
		10.26	0.01	0.934	6	3.80	0.839	6	6.22
		10.72	0.01	0.877	6	7.33	0.786	6	2.33
		10.90	0.01	0.840	6	6.58	0.770	6	5.98
		11.13	0.01	0.813	6	5.99	0.757	5	4.38

Table 3. Vapor−Liquid Equilibria for Water (1) + 2-Pentanol (2) System

T/K	σ_T	p/MPa	σ_p	x_1	N_x	$S_x \times 10^3$	y_1	N_y	$S_y \times 10^3$
523	0.2	3.30	0.01	0.241	4	7.24	0.431	6	4.13
		4.00	0.01	0.334	5	2.71	0.581	4	2.01
		4.34	0.01	0.416	5	9.77	0.639	4	3.48
		4.34	0.01	0.993	6	0.78	0.901	6	3.01
		4.71	0.01	0.971	6	2.87	0.823	6	0.77
		4.94	0.01	0.864	6	9.36	0.764	6	6.76

Azeotropic points are found in VLE for water + 2-butanol and water + 2-pentanol systems at 523 K. For water + ethanol and water + 2-propanol systems, it is also reported that the azeotropic points exist when the temperature is below the critical points of ethanol and 2-propanol.[13]

The pressures of VLE region for water + secondary alcohol systems depend on the carbon number of the secondary alcohols as shown in Figures 2 to 4. The pressure becomes larger as the carbon number of the secondary alcohols becomes smaller, that is the pressures for water + 2-propnaol system are higher than those for the water + 2-butanol system at (548 and 573) K

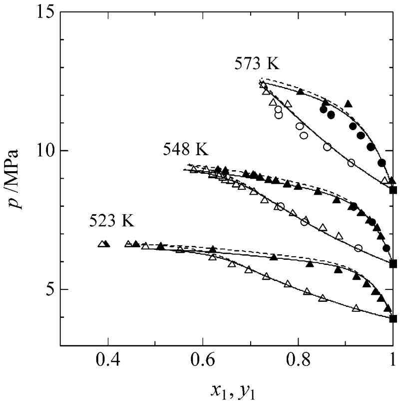

Figure 2. Vapor−liquid equilibria for water (1) + 2-propanol (2) system, experimental results: ○, ●, this work; △, ▲, ref 13; ■, vapor pressure of water;[16] literature data; correlated results: —, exponent-type mixing rule; - -, conventional mixing rule.

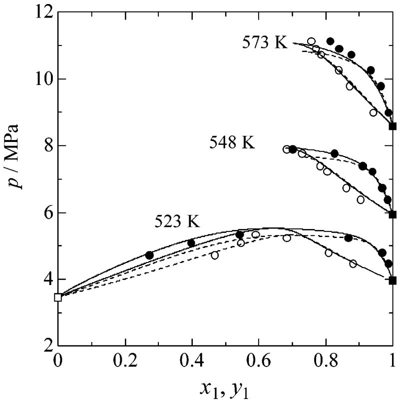

Figure 3. Vapor−liquid equilibria for water (1) + 2-butanol (2) system, experimental results: ○, ●, this work; ■, □, vapor pressures of water and 2-butanol;[16] literature data; correlated results: —, exponent-type mixing rule; - -, conventional mixing rule.

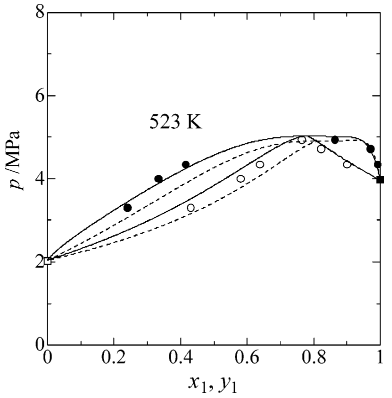

Figure 4. Vapor−liquid equilibria for water (1) + 2-pentanol (2) system, experimental results: ○, ●; □, vapor pressure of 2-pentanol; this work; ■, vapor pressure of water;[16] literature data; correlated results: —, exponent-type mixing rule; - -, conventional mixing rule.

because larger molecular weight alcohols become more condensable (lower vapor pressure).

Correlation

Table 4. Critical Properties and MSRK Parameters *m* and *n* of Pure Compounds[14]

compound	T_c/K	p_c/MPa	m	n
water	647.1	22.1	0.9499	0.1633
2-propanol	508.3	4.76	0.6434	0.7854
2-butanol	536.0	4.20	0.3404[a]	0.8829[a]
2-pentanol	560.3	3.68	0.7940[a]	0.6071[a]

[a] Determined in this work.

Equation of State. The VLE data measured in this work were correlated by a modified SRK equation of state (MSRK). The energy parameter of the original SRK equation of state[17] was modified by Sandarusi et al.[14] to represent well the vapor pressures, especially for polar substances, such as water and alcohols. MSRK is given as follows:

$$p = \frac{RT}{v - b} - \frac{a}{v(v + b)} \tag{1}$$

where p/Pa is the pressure, R/J·mol^{-1}·K^{-1} is the gas constant, T/K is the temperature, and v/m^3·mol^{-1} is the molar volume. The energy parameter (a) and the size parameter (b) are given as follows:

$$a = \frac{0.42747R^2T_c^2}{p_c}\alpha \tag{2}$$

where

$$\alpha = 1 + (1 - T_r)\left(m + \frac{n}{T_r}\right) \tag{3}$$

and

$$b = \frac{0.08664RT_c}{p_c} \tag{4}$$

where the subscripts c and r mean the critical and reduced properties, respectively, and parameters m and n are obtained from a fit to the vapor pressures of pure substances. The critical properties and the parameters m and n for water, 2-propanol, 2-butanol, and 2-pentanol cited from the literature[14] are listed in Table 4.

Conventional Mixing Rules. The conventional mixing rules applied for the energy and size parameters are given by

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{5}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{6}$$

Exponent-Type Mixing Rule. An exponent-type mixing rule proposed by Higashi et al.[15] was also applied for the energy parameter a. The mixing rule for the energy parameter is given by

$$a = \sum_i \sum_j x_i^{\beta_{ij}} x_j^{\beta_{ji}} a_{ij} \tag{7}$$

Introduction of exponential parameter β_{ij} may express the contact probability of molecule i around molecule j. This means that non-randomness in the mixture can be evaluated empirically. As the mixtures treated in this work show very complex behavior caused by strong interaction, this mixing rule is expected to be effective. The value of β_{ii} should be unity because the parameter is for pure compound i. For the size parameter, the conventional mixing rule given in eq 6 was used.

Combining Rules. The geometric and arithmetic averages were used to represent the energy and size parameters of

Table 5. Binary Parameters and Correlated Performance of Vapor−Liquid Equilibria for Water (1) + Secondary Alcohol (2) Systems

		conventional mixing rule			exponent-type mixing rule				
alcohol	N^a	k_{12}	l_{12}	δ^b	k_{12}	l_{12}	β_{12}	δ^b	ref
2-propanol	21	0.050	0.160	1.7	0.036	0.149	0.983	1.5	13 and this work
2-butanol	18	0.111	0.222	3.7	0.127	0.245	1.070	3.2	this work
2-pentanol	6	0.137	0.235	4.6	0.142	0.249	1.112	1.9	this work

[a] N = number of data set for vapor−liquid equilibria. [b]

$$\delta = \frac{1}{2N}\left(\sum_{i=1}^{N}\frac{|y_{1,\mathrm{calc}}^{(i)} - y_{1,\mathrm{exp}}^{(i)}|}{y_{1,\mathrm{calc}}^{(i)}} + \sum_{i=1}^{N}\frac{|p_{\mathrm{calc}}^{(i)} - p_{\mathrm{exp}}^{(i)}|}{p_{\mathrm{calc}}^{(i)}}\right) \times 100$$

molecules $i-j$ pair, which are given in eqs 8 and 9:

$$a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \tag{8}$$

$$b_{ij} = (1 - l_{ij})\frac{b_i + b_j}{2} \tag{9}$$

where k_{ij} ($k_{ij} = k_{ji}$ and $k_{ii} = 0$) and l_{ij} ($l_{ij} = l_{ji}$ and $l_{ii} = 0$) are the binary parameters.

Optimization of Interaction Parameters. The binary parameters k_{ij}, l_{ij}, and β_{ij} were determined by fitting to the experimental data of each system by using the Marquardt method.[18] The parameter β_{12} alone was treated as a fitting parameter in exponent-type mixing rule because β_{12} is more effective than β_{21} in the calculated phase equilibria of the water (1) + secondary alcohol (2) systems. The value of β_{21} was set to be unity to reduce the fitting parameters. Therefore, the three fitting parameters k_{12}, l_{12}, and β_{12} were adopted.

The binary parameters between the water (1)−secondary alcohol (2) pair were determined based on the objective function shown below:

$$F = \sum_{i=1}^{N}\frac{|y_{1,\mathrm{calc}}^{(i)} - y_{1,\mathrm{exp}}^{(i)}|}{y_{1,\mathrm{calc}}^{(i)}} + \sum_{i=1}^{N}\frac{|p_{\mathrm{calc}}^{(i)} - p_{\mathrm{exp}}^{(i)}|}{p_{\mathrm{calc}}^{(i)}} \tag{10}$$

where N is the number of experimental data points. The VLE calculations were performed at the given temperature and the mole fraction of water in liquid phase. The values of binary parameters (k_{12}, l_{12}, and β_{12}) determined in this work are listed in Table 5 with the data source used for optimization of the binary parameters.

Results and Discussion. The correlated results with the exponent-type mixing rule applied for the energy parameter are compared with those with the conventional mixing rule. The correlated results are shown in Table 5 and Figures 2 to 4. The results were improved by using the exponent-type mixing rule for the energy parameter in the equation of state, especially for water + 2-butanol and water + 2-pentanol systems. It may be considered that the hydrophobic interaction between water−2-butanol and water−2-pentanol molecules is stronger than that between water−2-propanol; therefore, this mixing rule is more effective for water + 2-butanol and water + 2-pentanol systems. The value of the exponent parameter β_{12} increases as the carbon number of secondary alcohols increases, and this fact coincides with the hydrophobic behavior of secondary alcohols qualitatively. The values of β_{12} for water−2-butanol and water−2-pentanol are larger than unity. That means that the local compositions of water around these secondary alcohols are smaller than its bulk compositions. The azeotropic points are found for water + 2-butanol and water + 2-pentanol systems at 523 K. The azeotropic points calculated by the exponent-type mixing rule are $x_1 = y_1 = 0.643$ and $p = 5.53$ MPa for the water (1) + 2-butanol (2) system and $x_1 = y_1 = 0.777$ and $p = 5.02$ MPa for the water (1) + 2-pentanol (2) system.

Conclusion

The VLE for water + 2-propanol, water + 2-butanol, and water + 2-pentanol systems were measured at high temperatures and pressures by a flow method. The phase behavior for water + secondary alcohol systems was elucidated by changing the temperature and carbon atom number of the secondary alcohols. The azeotropic points are founded for water + 2-butanol and water + 2-petanol systems at 523 K. New VLE data at high temperatures and pressures are presented.

The VLE data were correlated by a modified SRK equation of state. The correlated results are improved by using the exponent-type mixing rule for the energy parameters of the equation of state and are in good agreement with the experimental data.

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