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Measurement and Correlation of Phase Equilibria for Water + Decane + 2-Propanol, Water + Hexane + 2-Propanol, and Water + Decane + 2-Butanol Ternary Systems at 573 and 593 K and 15.0 and 20.0 MPa

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The phase equilibria for the water + decane + 2-propanol system at (573 and 593) K and (15.0 and 20.0) MPa, the water + hexane + 2-propanol system at 573 K and 20.0 MPa, and the water + decane + 2-butanol system at 573 K and 20.0 MPa were measured with a flow type apparatus. The experimental results were correlated by a modified SRK equation of state. An exponent type mixing rule and a conventional mixing rule were applied for the energy and size parameters of the equation of state, respectively. The average deviation between the mole fractions of experiment and correlation is 0.006.

Introduction

New chemical processes using sub- and supercritical water as a reaction solvent are proposed for applications in various fields.[1−6] 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. In these processes, low molecular weight hydrocarbons such as alkanes, alkenes, and aromatic hydrocarbons are produced as decomposed products.[1,2,4] Therefore, it is very useful for process design to elucidate the phase behavior for the mixtures including water and these compounds at high temperatures and pressures (near the critical point of water). In previous works,[7−9] phase equilibria for water + hydrocarbon binary systems and water + hydrocarbon + hydrocarbon ternary systems at high temperatures and pressures were measured and correlated.

In addition to these compounds, secondary alcohols such as 2-propanol and 2-butanol are also produced from hydration of alkenes.[1] However, no phase equilibrium data for water + hydrocarbon + secondary alcohol systems at high temperatures and pressures are available. In this work, therefore, the phase equilibria for water + hydrocarbon + secondary alcohol systems at high temperatures and pressures were measured with a flow type apparatus. The phase behavior of these systems has been studied by changing the temperature, the pressure, the number of carbon atoms in the hydrocarbon, and the type of secondary alcohol. The measured phase equilibrium data were correlated by a modified SRK (Soave−Redlich−Kwong) equation of state proposed by Sandarushi et al.[10] An exponent type mixing rule proposed by Higashi et al.[11] was applied to the attractive term of the equation of state.

Experiment

Materials. Ultrapure water was used. It was purified by deionization using MILLIQ LABO (Millipore Corporation). The resistivity was 18.0−18.2 MΩ cm. Hexane, decane, 2-propanol, 2-butanol, ethylbenzene, and ethanol used in this work were analytical grade reagents and were supplied by Wako Pure Chem. Ind. Their purities were checked with gas chromatography by the authors. The peak percentages of the main compounds were more than 99.9%, 99.8%, 99.8%, 99.8%, 99.9%, and 99.8%, respectively. These materials were used without further purification.

Apparatus and Procedure. An apparatus based on a flow method was used to measure the phase equilibria for the water + hydrocarbon + secondary alcohol systems at high temperatures and pressures. A detailed description of the apparatus and operating procedures were given in the previous work.[9] Therefore, the apparatus and procedures are only briefly described here. The apparatus consists of a feed system, an equilibrium cell, and a sampling effluent system. The equilibrium cell was made of Hastelloy and equipped with sapphire windows. The inside diameter and volume were 20 mm and 31 mL, respectively. The cell was connected with four lines, a feed line, sampling lines for the top and bottom phases, and a subsidiary line. The subsidiary line was equipped with a back-pressure-regulator which controlled pressure in the system. This 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 with electric heaters. Pure water and a mixture of hydrocarbon and secondary alcohol were supplied by a double plunger pump. The feed rates were measured by electronic balances and confirmed to be constant during measurements. The feed rates of water and the mixture were (5.10 ± 0.02 and 3.20 ± 0.04) g min^{-1}, respectively. Pressurized water and the mixture were sufficiently mixed through a line mixer and supplied to the equilibrium cell. The phase behavior in the cell was observed with a telescope of 42 magnification (CCD-TR3300, SONY). The residential time in the equilibrium cell was (4.0 ± 1.0) min. The temperature of the entrance, top, and bottom of the cell was controlled within ±0.5 K. The pressure fluctuation during the experiments was within ±0.1 MPa. Samplings of each phase were

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Table 1. Phase Equilibria for the Water (1) + Decane (2) System[a]

T/K	p/MPa	x_1^{I}	N^{I}	10^3S^{I}	x_1^{II}	N^{II}	10^3S^{II}
573	15.0	1.000	5	0.00	0.511	4	6.21
573	20.0	0.999	7	0.29	0.466	5	4.91
593	20.0	0.999	5	0.31	0.622	3	2.52

[a] N = number of data points used for the arithmetic average. x_i = mean value of the mole fraction of component i. $x_{i,n}$ = mole fraction of component i for point n. $S = [(1/2N)\sum_{i=1}^{2}(\sum_{n=1}^{N}|x_{i,n} - x_i|)^2]^{1/2}$. Superscripts: I, water rich phase; II, hydrocarbon rich phase.

Table 2. Phase Equilibria for the Water (1) + Decane (2) + 2-Propanol (3) System[a]

x_1^{I}	x_2^{I}	x_3^{I}	N^{I}	10^3S	x_1^{II}	x_2^{II}	x_3^{II}	N^{II}	10^3S^{II}
T = 573 K, p = 20.0 MPa									
0.989	0.001	0.010	4	0.43	0.505	0.448	0.047	3	5.07
0.974	0.002	0.024	4	0.52	0.553	0.348	0.099	3	4.27
0.929	0.006	0.065	4	0.19	0.678	0.165	0.157	4	4.89
0.915	0.008	0.077	5	0.25	0.712	0.129	0.159	4	4.56
0.896	0.013	0.091	3	1.19	0.751	0.093	0.156	3	3.08
0.949	0.003	0.048	5	0.96	0.620	0.234	0.146	4	4.64
0.964	0.002	0.034	4	0.59	0.579	0.300	0.121	3	4.12
T = 573 K, p = 15.0 MPa									
0.977	ND	0.023	5	0.67	0.612	0.293	0.095	3	3.63
0.957	ND	0.043	5	1.06	0.673	0.187	0.140	4	3.25
0.905	0.010	0.085	5	1.19	0.782	0.073	0.145	5	2.29
0.989	ND	0.011	5	0.73	0.552	0.397	0.051	3	2.53
0.940	0.001	0.059	5	3.10	0.733	0.119	0.148	5	3.95
T = 593 K, p = 20.0 MPa									
0.986	0.002	0.012	5	0.80	0.671	0.290	0.039	4	4.09
0.983	0.002	0.015	5	0.58	0.689	0.259	0.052	4	7.46
0.974	0.003	0.023	5	0.66	0.723	0.206	0.071	4	3.77
0.963	0.004	0.033	5	0.58	0.758	0.156	0.086	4	2.94
0.955	0.006	0.039	5	0.71	0.806	0.102	0.092	5	5.27

[a] ND = not detected. $S = [(1/3N)\sum_{i=1}^{3}(\sum_{n=1}^{N}|x_{i,n} - x_i|)^2]^{1/2}$. See Table 1 for nomenclature.

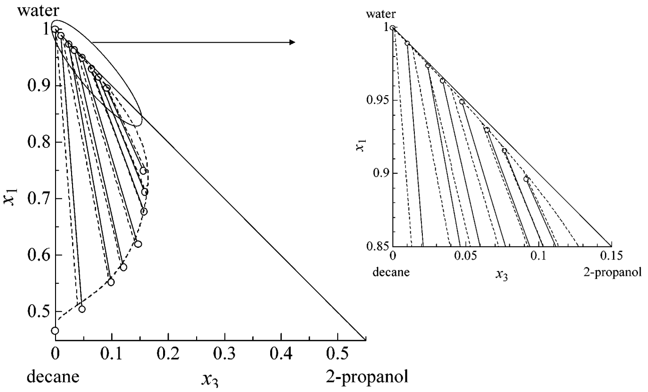

Figure 1. Phase equilibria for the water (1) + decane (2) + 2-propanol (3) system at 573 K and 20.0 MPa: (○—○) experimental results; (- - -) correlated results.

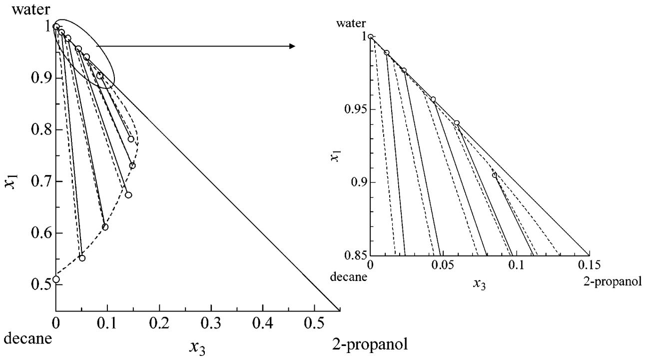

Figure 2. Phase equilibria for the water (1) + decane (2) + 2-propanol (3) system at 573 K and 15.0 MPa: (○—○) experimental results; (- - -) correlated results.

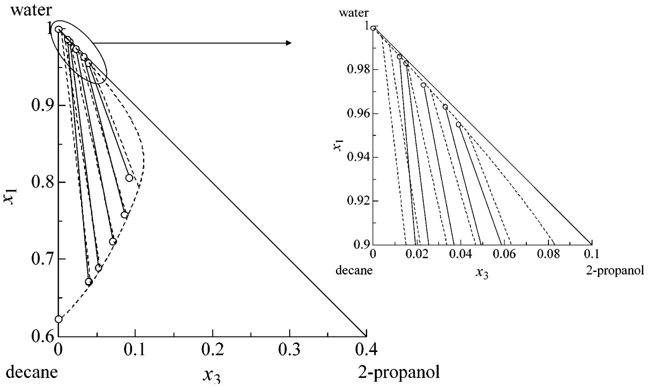

Figure 3. Phase equilibria for the water (1) + decane (2) + 2-propanol (3) system at 593 K and 20.0 MPa: (○—○) experimental results; (- - -) correlated results.

carried out after the phase interface was well stabilized. The effluents from the top and bottom phases were depressurized through expansion valves and cooled with a water bath. Samples were trapped in sampling bottles containing ethanol to obtain homogeneous solutions, because these mixtures show phase separation at room temperature and atmospheric pressure. The tube exits were soaked in ethanol to prevent volatilization of water, hydrocarbon, and secondary alcohol during sampling. The concentration of water in ethanol was analyzed with a Karl Fischer moisture titrator (Kyoto Elec. Manu. Co., Ltd) prior to use. The samples of each phase were analyzed by gas chromatography with a thermal conductivity detector. The compositions of samples were determined by an internal standard method. Ethylbenzene was used as the internal standard.

Results and Discussion

Table 1 lists the results of the phase equilibria for the water + decane binary system measured in this work.

The experimental results of the water + decane + 2-propanol system are listed in Table 2 and shown in Figures 1−3. The values of mole fractions listed in Table 2 were obtained from the arithmetic average of several measurements. According to the classification of Treybal,[12] the phase equilibria measured in this work belong to type I. In type I, one liquid pair, such as water + hydrocarbon, is partially miscible. On the other hand, both liquid pairs, such as water + secondary alcohol and hydrocarbon + secondary alcohol, are fully miscible. The mole fractions of water increase in the hydrocarbon rich phase, and they decrease in the water rich phase with increasing mole fraction of 2-propanol. A comparison of the results at 20.0 MPa with those at 15.0 MPa is shown in Figures 1 and 2. The mole fractions of water in both hydrocarbon and water rich phases decrease with increasing pressure. A reason for this may be that water is more condensable than decane at the measured conditions, which is different from the case of the vapor−liquid equilibrium region for the water + decane binary system reported by Wang and Chao.[13] The phenomena can be explained from the phase diagram of the liquid−liquid equilibria for the water + decane binary system.[7] A comparison of the results at 573 K with those at 593 K is shown in Figures 1 and 3. The mole fractions of water in hydrocarbon and water rich phases increase and decrease with increasing temperature, respectively.

Table 3. Phase Equilibria for the Water (1) + Hexane (2) + 2-Propanol (3) System[a]

x_1^{I}	x_2^{I}	x_3^{I}	N^{I}	10^3S^{I}	x_1^{II}	x_2^{II}	x_3^{II}	N^{II}	10^3S^{II}
T = 573 K, p = 20.0 MPa									
0.991	0.003	0.006	3	0.64	0.548	0.425	0.027	3	5.64
0.984	0.004	0.012	4	1.22	0.564	0.383	0.053	3	5.45
0.965	0.006	0.029	4	2.14	0.626	0.275	0.099	3	2.61
0.953	0.008	0.039	4	7.61	0.648	0.239	0.113	3	14.3
0.976	0.006	0.018	4	2.53	0.592	0.335	0.073	4	5.84
0.928	0.016	0.056	4	1.89	0.703	0.166	0.131	4	3.13
0.911	0.021	0.068	4	1.71	0.745	0.126	0.129	4	1.24
0.896	0.028	0.076	4	0.89	0.762	0.111	0.127	4	2.85

[a] See Table 2 for nomenclature.

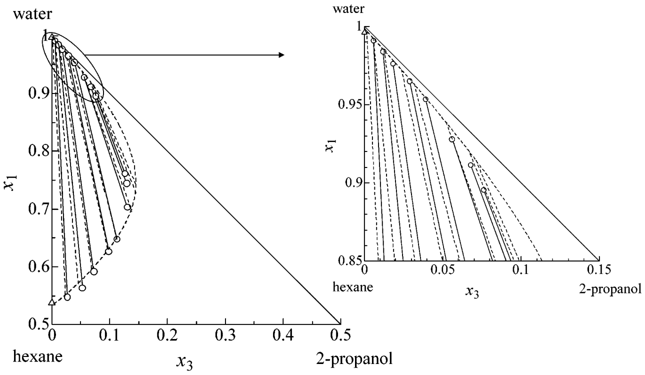

Figure 4. Phase equilibria for the water (1) + hexane (2) + 2-propanol (3) system at 573 K and 20.0 MPa: (○—○ and △) experimental results (this work and literature data[18]); (- - -) correlated results.

Table 4. Phase Equilibria for the Water (1) + Decane (2) + 2-Butanol (3) System[a]

x_1^{I}	x_2^{I}	x_3^{I}	N^{I}	10^3S^{I}	x_1^{II}	x_2^{II}	x_3^{II}	N^{II}	10^3S^{II}
T = 573 K, p = 20.0 MPa									
0.990	0.001	0.009	5	0.82	0.510	0.434	0.056	4	5.81
0.972	0.002	0.026	5	1.71	0.596	0.267	0.137	3	5.98
0.966	0.003	0.031	5	4.80	0.641	0.199	0.160	4	4.93
0.981	0.001	0.018	5	1.56	0.561	0.326	0.113	3	3.45
0.945	0.005	0.050	4	0.90	0.710	0.134	0.156	5	4.53

[a] See Table 2 for nomenclature.

The kinetic energy of the molecules increases with increasing temperature, and the two phase region becomes narrow.

The experimental results of the water + hexane + 2-propanol system are listed in Table 3 and shown in Figure 4. The two phase region becomes large with an increase in the carbon number in hydrocarbon molecules, as shown in Figures 1 and 4. If the carbon number of the alkanes increases, the entropy of the system decreases. The free energy in the system increases, and the system becomes unstable. Therefore, phase separation tends to occur in the system, and the two phase region increases with increasing carbon number. The phenomena can be explained by the entropy effect, which is cleary observed in polymer + solvent systems.[14,15]

The experimental results of the water + decane + 2-butanol system are listed in Table 4 and shown in Figure 5. A comparison of the results in the case of 2-propanol with those of 2-butanol is shown in Figures 1 and 5. The solubility lines are almost the same, though the slopes of tie lines are slightly different. The solubilities of 2-butanol in the water rich and decane rich phases decrease and increase, respectively, in comparing with the results of 2-propanol. This may be due to the fact that the hydrophobicity of 2-butanol is stronger than that of 2-propanol.

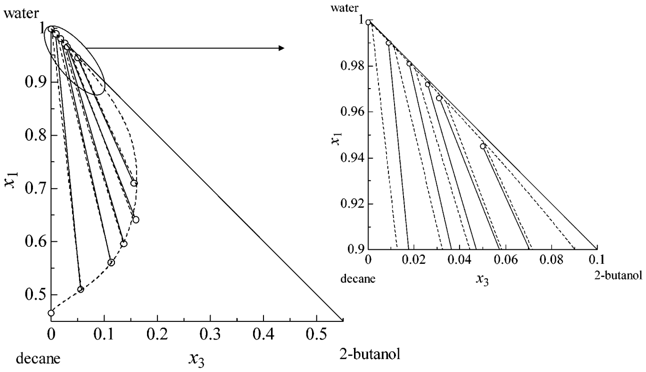

Figure 5. Phase equilibria for the water (1) + decane (2) + 2-butanol (3) system at 573 K and 20.0 MPa: (○—○) experimental results; (- - -) correlated results.

Table 5. Critical Properties and MSRK Parameters *m* and *n*[10]

substance	T_c/K	p_c/MPa	m	n
water	647.3	22.1	0.9500	0.1630
hexane	507.4	3.01	0.7446	0.2476
decane	617.6	2.10	0.8905	0.3863
2-propanol	508.3	4.76	0.6434	0.7254
2-butanol	536.0	4.42	0.4337	0.8483

Correlation

Equation of State. The measured phase equilibrium data were correlated with a modified SRK (MSRK) equation of state (EOS). An energy parameter of the original SRK equation of state[16] was modified by Sandarusi et al.[10] to represent better vapor pressures, especially for polar substances, such as water and alcohols. The MSRK EOS is given as follows.

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

where p is the pressure, R is the gas constant, T is the temperature, and v is the molar volume. The energy parameter $a(T)$ and the size parameter b are given as follows.

$$a(T) = \frac{0.42747R^2\,T_c^{\,2}}{p_c}\,\alpha(T) \tag{2}$$

$$b = \frac{0.08664RT_c}{p_c} \tag{3}$$

and

$$\alpha(T) = 1 + (1 - T_r)\left(m + \frac{n}{T_r}\right) \tag{4}$$

where p is in pascal, R is in joules per mole per kelvin, T is in kelvin, and v *is* in cubic meters per mole, the subscripts c and r mean the critical and reduced properties, respectively, and the 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, hexane, decane, 2-propanol, and 2-butanol cited from the literature[10] are listed in Table 5.

Mixing and Combining Rules. An exponent type mixing rule proposed by Higashi et al.[11] was applied for

Table 6. Data Source for Optimization and Values of the Interaction Parameters k_{ij}, l_{ij}, and β_{ij}

i	j	system	T/K	k_{ij}	l_{ij}	β_{ij}	ref
water	hexane	water + hexane	573	0.49	0.28	1.55	18 and 19
water	decane	water + decane	573 and 593	0.52	0.40	1.87	7 and this work
water	2-propanol	water + 2-propanol	573	0.04	0.15	0.98	20
water	2-butanol	water + 2-propanol	573	0.04	0.15	0.98	20
2-propanol	hexane	water + hexane + 2-propanol	573	0.66	0.72	0.45	this work
2-propanol	decane	water + decane + 2-propanol	573 and 593	0.45	0.45	0.55	this work
2-butanol	decane	water + decane + 2-butanol	573	0.32	0.45	0.61	this work

the energy parameter a. The mixing and combining rules for the energy parameter a are given as follows.

$$a = \sum_i \sum_j x_i^{\beta_{ij}} x_j^{\beta_{ji}} a_{ij}, \quad a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \tag{5}$$

where k_{ij} is the binary parameter ($k_{ij} = k_{ji}$ and $k_{ii} = 0$). Introduction of the exponential parameter β_{ij} may express the contact probability of molecule i with molecule j. This means that nonrandomness in the mixture can be evaluated empirically. As the mixtures in this work show very complex behavior caused by strong interaction, the mixing rule is expected to be effective. The value of β_{ii} should be unity, because the parameter is for pure compound i.

The conventional mixing and combining rules for the size parameter b are given as follows.

$$b = \sum_i \sum_j x_i x_j b_{ij}, \quad b_{ij} = (1 - l_{ij})\frac{b_i + b_j}{2} \tag{6}$$

where l_{ij} is the binary parameter ($l_{ij} = l_{ji}$ and $l_{ii} = 0$).

Optimization of Interaction Parameters. The interaction parameters k_{ij}, l_{ij}, and β_{ij} are determined using phase equilibrium data of binary and ternary systems. The Marquardt method[17] was used to optimize the interaction parameters. It was found that β_{12}, β_{13}, and β_{32} strongly affect the calculated phase equilibria of the water (1) + hydrocarbon (2) + secondary alcohol (3) systems, in comparison with the use of the parameters β_{21}, β_{23}, and β_{31}. Therfore, the values of β_{21}, β_{23}, and β_{31} were set to be unity to reduce the fitting parameters.

The binary parameters between water (1) + hydrocarbon (2) and water (1) + secondary alcohol (3) were determined on the basis of the objective function shown below.

$$F_1 = w\sum_{k=1}^{N}\left|x_{1,k}^{\mathrm{I,exp}} - x_{1,k}^{\mathrm{I,calc}}\right| + \sum_{k=1}^{N}\left|x_{1,k}^{\mathrm{II,exp}} - x_{1,k}^{\mathrm{II,calc}}\right| \tag{7}$$

where N is the number of experimental data points. The superscripts I and II refer to the water and hydrocarbon rich phases, respectively. The concentrations of decane in the water rich phase are very low. So, the w factor was introduced in the water rich phase for the water + decane system. As the w factor is increased, the calculated results in the water rich phase become accurate, and those in the hydrocarbon rich phase become inaccurate. The w factor was selected so that the calculated results in both water and hydrocarbon rich phases agreed satisfactorily with the experimental results, and it was set to 7.0. For the other binary systems, it was set to 1.0.

The parameters between water and 2-propanol were also used for the parameters between water and 2-butanol. The interaction parameters for water + 2-butanol could not be determined because there are no phase equilibirium data for water + 2-butanol at high temperatures and pressures. However, the difference of hydrophobicity between 2-propanol and 2-butanol can be expressed even if interaction parameters for water + 2-propanol are used because the binary interaction parameters for hydrocarbon (2) + 2-alcohol (3) were determined by the experimental data for water (1) + hydrocarbon (2) + 2-alcohol (3) systems.

Table 7. Deviations between Mole Fractions of Experiment and Correlation for Water + Hydrocarbon + Alcohol Systems[a]

hydrocarbon	alcohol	T/K	p/MPa	δ^{I}	δ^{II}
decane	2-propanol	573	20.0	0.005	0.005
		573	15.0	0.006	0.017
		593	20.0	0.005	0.005
hexane	2-propanol	573	20.0	0.007	0.007
decane	2-butanol	573	20.0	0.003	0.004

[a] δ = averaged deviation between mole fractions of experiment and correlation. Superscripts: I, water rich phase; II, hydrocarbon rich phase.

The following objective function was adopted to determine the remaining binary parameters between hydrocarbon (2) + secondary alcohol (3) using the data for the water (1) + hydrocarbon (2) + alcohol (3) system.

$$F = F_1 + F_2 + F_3 \tag{8}$$

$$F_1 = \sum_{k=1}^{N}\left|x_{1,k}^{\mathrm{I,exp}} - x_{1,k}^{\mathrm{I,calc}}\right| + \sum_{k=1}^{N}\left|x_{1,k}^{\mathrm{II,exp}} - x_{1,k}^{\mathrm{II,calc}}\right| \tag{9}$$

$$F_2 = \sum_{k=1}^{N}\left|x_{2,k}^{\mathrm{I,exp}} - x_{2,k}^{\mathrm{I,calc}}\right| \tag{10}$$

$$F_3 = \sum_{k=1}^{N}\left|x_{3,k}^{\mathrm{I,exp}} - x_{3,k}^{\mathrm{I,calc}}\right| + \sum_{k=1}^{N}\left|x_{3,k}^{\mathrm{II,exp}} - x_{3,k}^{\mathrm{II,calc}}\right| \tag{11}$$

Table 6 lists the data sources for optimization of interaction parameters and the values determined.

Results and Discussion

Phase equilibrium calculations were carried out by fixing temperatures, pressures, and mole fractions of hydrocarbon in the hydrocarbon rich phase, x_2^{II}. Figures 1−5 and Table 7 show the correlated results of the phase equilibria for water + hydrocarbon + secondary alcohol systems at high temperatures and pressures. As shown in Figures 1−3, the correlated results are improved for the water + decane + 2-propanol system by using the interaction parameters newly optimized in this work, and they are in good agreement with experimental results, especially near the plait point. Good correlated results are obtained for water + hexane + 2-propanol and water + decane + 2-butanol systems, as shown in Figures 4 and 5.

Conclusion

The phase equilibria for water + decane + 2-propanol, water + hexane + 2-propanol, and water + decane + 2-butanol ternary systems were measured at high temperatures and pressures with a flow type apparatus. The phase behavior for water + hydrocarbon + secondary alcohol systems has been examined by changing the temperature, the pressure, the number of carbon atoms in the hydrocarbon, and the kind of secondary alcohol, and new phase equilibrium data were accumulated.

The phase equilibrium data were correlated by the modified SRK equation of state. The exponent type mixing rule was applied for the energy parameter of the equation of state. The correlated reslults are in good agreement with the experimental results for all ternary systems measured.

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