Measurement and Prediction of Liquid−Liquid Equilibria for Water + Hexane + Hexadecane, Water + Toluene + Decane, and Water + Toluene + Ethylbenzene Ternary Systems at High Temperatures and Pressures

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An experimental apparatus based on a flow method was used to measure the liquid−liquid equilibria for three ternary systems: water + hexane + hexadecane at 573 K and 20 MPa, water + toluene + decane at 553 and 573 K and 20 MPa, and water + toluene + ethylbenzene at 553 K and 20 MPa. Furthermore, the phase equilibria for water + toluene + decane and water + toluene + ethylbenzene were predicted by the modified SRK equation of state. An exponent-type and conventional mixing rules were applied for the energy and size parameters of the equation of state, respectively. The predicted results are in good agreement with the experimental results.

Introduction

Recently, chemical processes using sub- and supercritical water as a reaction solvent have been considered for application in various fields. Among them, hydrolysis processes of waste plastics have received much attention in the framework of the recycling of resources and environmental conservation. In these processes, low molecular weight hydrocarbons such as paraffins and aromatic hydrocarbons are produced as decomposed products. Therefore, knowledge of the phase equilibria for water + hydrocarbon mixtures at high temperatures and pressures is required to design such chemical processes.

In previous works,[1,2] phase equilibria for water + hydrocarbon binary systems at high temperatures and pressures were measured and correlated. The liquid−liquid equilibrium data for water + hydrocarbon + hydrocarbon ternary systems at high temperatures and pressures have been reported by Brunner et al.[3] and O'Grady.[4] However, there are few phase equilibrium data of such ternary systems.

In this work, a previously designed apparatus, based on a flow method, was modified to measure liquid−liquid equilibria for ternary systems at high temperatures and pressures. First of all, the liquid−liquid equilibria for the water + hexane + hexadecane system were measured to determine the correct operation of the new apparatus and the measurement procedure. Then, water + toluene + decane and water + toluene + ethylbenzene systems were measured. The phase equilibria were predicted by using the SRK equation of state modified by Sandarusi et al.[5] An exponent-type mixing rule proposed by Higashi et al.[6] was applied to the energy parameter, and a conventional mixing rule was applied to the size parameter.

Experiment

Materials. Hexane, acetone, toluene, decane, 1-propanol, *p*-xylene, and ethylbenzene used in this work were supplied by Wako Pure Chem. Ind., and their reported purities were more than 96.0%, 99.5%, 99.5%, 99.0%, 99.5%, 98.0%, and 98.0%, respectively, which were determined by gas chromatography (GC). Ethanol was also supplied by Wako Pure Chem. Ind., and its reported purity was more than 99.5 vol. %, which was determined by a density measurement. Hexadecane was supplied by Aldrich Chem. Co. Inc., and its reported purity was more than 99.0%. 1,2,4,5-Tetramethylbenzene was supplied by Tokyo Kasei Kogyo Co., Ltd. Its purity was reported to be 99.0%, which was determined by GC. Moreover, the purities of these materials were checked by the authors with GC. The peak area percentages of the main compounds were more than 99.9%, 99.9%, 99.6%, 99.9%, 99.8%, 99.8%, 99.7%, 99.8%, 99.8%, and 99.9% for hexane, hexadecane, acetone, 1,2,4,5-tetramethylbenzene, toluene, decane, 1-propanol, *p*-xylene, ethanol, and ethylbenzene, respectively. Acetone and 1-propanol were dehydrated with molecular sieves 4A ($^1/_8$, Wako Pure Chem. Ind.). The other materials were used without further purification. Ultrapure water was used. It was purified by MILLIQ LABO (MILLIPORE Corporation) from distilled water.

Apparatus. A flow-type apparatus was adopted to avoid thermal decomposition of hydrocarbons and pressure fluctuation caused by sampling. The schematic diagram of the experimental apparatus is shown in Figure 1. The apparatus is quite similar to that used in previous works[1,2] and consists of a feed system, an equilibrium cell (12), pressure and temperature measurement and control systems, and a sampling effluent system. The diameter of the tube in the apparatus was about 0.16 cm. 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 water rich and hydrocarbon rich phases, and a subsidiary line. The subsidiary line was equipped with a back-pressure-regulator (15) which controlled the pressure in the system. The line was also used to maintain the position of the phase interface at the center of the cell.

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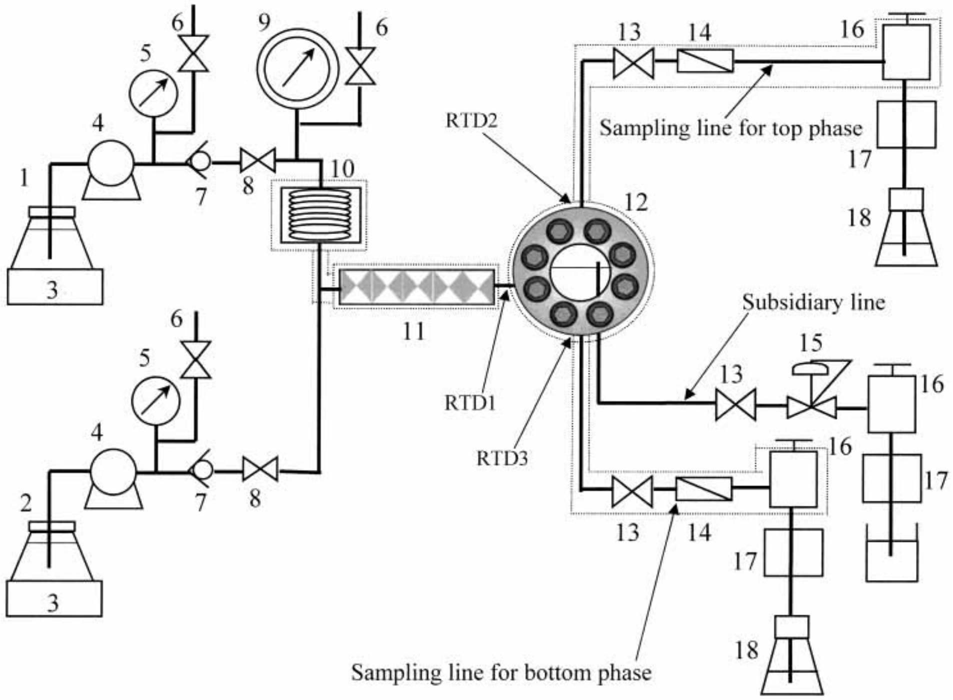

Figure 1. Schematic diagram of experimental apparatus: (1) water reservoir; (2) hydrocarbon reservoir; (3) electronic balance; (4) feed pump; (5) pressure gauge; (6) safety valve; (7) check valve; (8) stop valve; (9) precision pressure gauge; (10) preheating coil; (11) line mixer; (12) equilibrium cell; (13) stop valve; (14) filter; (15) back-pressure-regulator; (16) expansion valve; (17) water bath; (18) collecting bottle; (RTD1 to RTD3) resistance temperature detectors, (···) heater.

Procedure. The system was heated to the desired temperature by electric heaters. Pure water and hydrocarbon mixture were supplied by pumps (4). The pumps were nonbeat flow pumps of HPLC grade (PUS/PUD, GL sciences). The feed rates were measured by electronic balances (3) and confirmed to be constant during measurement. The feed rates of water and the hydrocarbon mixture were about 3.7 and 5.1 $g \cdot min^{-1}$. Only pressurized water was heated by a preheating coil (10). Pressurized water and the hydrocarbon mixture were sufficiently mixed through a line mixer (11) before entering the equilibrium cell. The line mixer was made of Hastelloy equipped with 10 elements inside. Supplied water and hydrocarbon mixture were sufficiently mixed by clashing with these elements. The phase behavior in the cell was observed with a video camera attached to a telescope of 42 modifications (CCD-TR3300, SONY). The residential time in the equilibrium cell was about 3 to 5 min. The temperatures of entrance, top, and bottom of the cell were controlled within ±1 K. The pressure fluctuation was held to ±0.2 MPa. The effluents from the top and bottom phases were depressurized through expansion valves (16) and cooled with a water bath (17). Samplings of each phase were carried out after the phase interface was well stabilized. Samples were collected into bottles (18) containing solvents such as ethanol, 1-propanol, and acetone to obtain homogeneous solutions, because water and hydrocarbon mixtures show phase separation at room temperature at atmospheric pressure. The tube exits were soaked in the solvents to prevent a volatilization of water and hydrocarbons during sampling. Large volumes (about 30 mL) of samples were collected to reduce experimental errors in determination of compositions. Acetone, 1-propanol, and ethanol were used for water + hexane + hexadecane, water + toluene + decane, and water + toluene + ethylbenzene systems as solvents, respectively. Acetone and 1-propanol were dehydrated with molecular sieves 4A before use. The concentrations of water in the solvents were adequately low. It was very difficult to dehydrate ethanol with molecular sieves 4A. So, the concentration of water in ethanol was analyzed by a Karl Fischer moisture titrator (Kyoto Elec. Manu. Co., Ltd.) prior to use. The compositions of samples were analyzed by GC with a thermal conductivity detector (GL sciences). An internal standard method was adopted to analyze the compositions. 1,2,4,5-Tetramethylbenzene, *p*-xylene, and decane were used for water + hexane + hexadecane, water + toluene + decane, and water + toluene + ethylbenzene systems as internal standards, respectively.

Results and Discussion. According to the classification of Treybal,[7] the phase equilibria measured in this work belong to type II. In type II, both liquid pairs, such as water (1) + hydrocarbon (2) and water (1) + hydrocarbon (3), are partially miscible. On the other hand, hydrocarbon (2) and hydrocarbon (3) are fully miscible.

The experimental results of water + hexane + hexadecane systems at 573 K and 20 MPa are listed in Table 1 and shown in Figure 2. The values of mole fractions listed in Table 1 were obtained from the arithmetic average of several measurements. The number of data points and the deviation are shown in Table 1. In the water rich phase, hexadecane was not detected because of very small solubilities of hexadecane in water. As shown in Figure 2, the results of this work are in good agreement with the literature data.[3] Therefore, it was ascertained that the experimental apparatus and procedure were suitable to measure the phase equilibria for ternary systems at high temperatures and pressures.

The results of the water + toluene + decane system at 553 and 573 K and 20 MPa are listed in Table 1 and shown in Figures 3 and 4, respectively. As shown in Figures 3 and 4, the solubilities of water in the hydrocarbon rich phase increase dramatically with increase in the concentration of toluene. The solubilities of decane in the water rich phase are low at both 553 and 573 K.

Table 1. Phase Equilibria for Water (1) + Hydrocarbon (2) + Hydrocarbon (3) Systems at 20 MPa[a]

T/K	x_1^{I}	x_2^{I}	x_3^{I}	N^{I}	$S^{I} \times 10^3$	x_1^{II}	x_2^{II}	x_3^{II}	N^{II}	$S^{II} \times 10^3$
				Water (1) + Hexane (2) + Hexadecane (3)						
573	0.9996	0.0004	nd	4	0.35	0.495	0.338	0.167	4	12.0
	1.000	nd	nd	2	0	0.425	0.180	0.395	2	23.8
	1.000	nd	nd	2	0	0.447	0.041	0.512	2	33.6
				Water (1) + Toluene (2) + Decane (3)						
553	0.990	0.010	nd	4	1.42	0.428	0.462	0.110	2	7.11
	0.992	0.008	nd	3	1.80	0.398	0.346	0.256	2	3.16
	0.996	0.004	nd	4	0.54	0.387	0.248	0.365	4	5.28
	0.9974	0.0024	0.0002	4	0.36	0.378	0.125	0.497	3	2.13
	0.988	0.012	nd	4	1.74	0.472	0.503	0.025	3	12.2
	0.9989	0.0008	0.0003	4	0.26	0.380	0.038	0.582	3	4.38
573	0.993	0.007	nd	3	0.15	0.493	0.227	0.280	3	7.07
	0.987	0.013	nd	2	0.03	0.567	0.329	0.104	2	0.13
	0.987	0.013	nd	3	0.20	0.568	0.339	0.093	3	4.96
	0.983	0.017	nd	4	0.37	0.598	0.352	0.050	4	9.04
	0.980	0.020	nd	3	0.56	0.633	0.347	0.020	3	2.51
	0.999	0.001	nd	2	9.55	0.466	0.051	0.483	2	9.54
	0.9908	0.0088	0.0004	3	0.59	0.523	0.275	0.202	2	18.9
	0.9972	0.0022	0.0006	4	0.19	0.487	0.093	0.420	3	8.73
				Water (1) + Toluene (2) + Ethylbenzene (3)						
553	0.989	0.007	0.004	3	0.21	0.489	0.278	0.233	3	1.03
	0.986	0.013	0.001	3	0.18	0.514	0.435	0.051	3	1.56
	0.992	0.002	0.006	3	0.23	0.482	0.103	0.415	3	1.98
	0.992	0.001	0.007	3	0.27	0.473	0.027	0.500	3	3.00
	0.990	0.005	0.005	3	0.99	0.492	0.201	0.307	3	3.74
	0.987	0.010	0.003	3	0.65	0.503	0.346	0.151	3	1.66

[a] nd = not detected. N = number of data points used for arithmetic average. x_i = mole fraction of component i. $S = [(^1/_3N)\sum_{n=1}^{N}\sum_{i=1}^{3}|x_{i,n} - x_i|^2]^{1/2}$. n = data point. Superscripts: I, water rich phase; II, hydrocarbon rich phase.

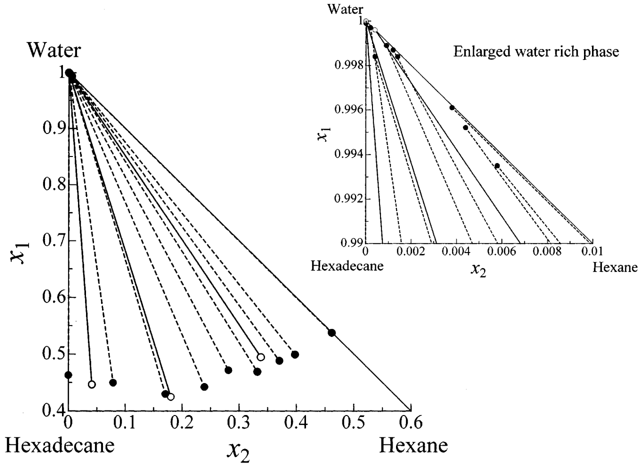

Figure 2. Experimental results for liquid−liquid equilibria of the water (1) + hexane (2) + hexadecane (3) system at 573 K and 20 MPa: (○) this work; (●) Brunner et al.[3]

The results of the water + toluene + ethylbenzene system at 553 K and 20 MPa are listed in Table 1 and shown in Figure 5. As shown in Figure 5, the coexisting curves are flat. Figures 2−5 show that the solubilities of hydrocarbon in water for the water + toluene + ethylbenzene system are higher than those of the other systems.

Prediction

Equation of State and Mixing Rules. The SRK equation of state modified by Sandarusi et al.[5] (modified-SRK EOS) was used to predict the phase equilibria for the ternary systems. The modified-SRK EOS is given by the following equations

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

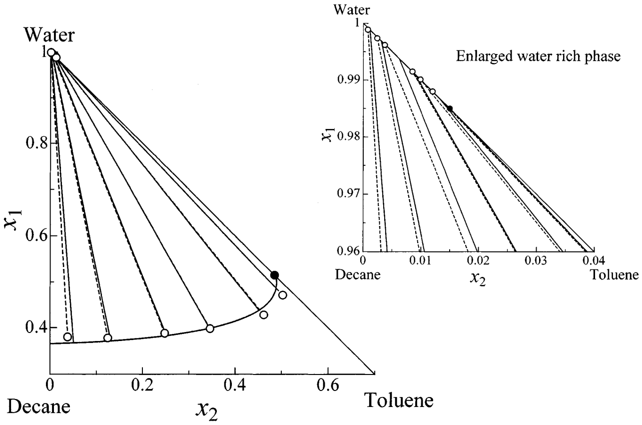

Figure 3. Phase equilibria for the water (1) + toluene (2) + decane (3) system at 553 K and 20 MPa: (○) experimental results; (—) predicted results; (●) data for the water + toluene binary system.[1]

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 $a(T)$ and the size parameter b are expressed as follows.

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

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

and

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

where the subscripts c and r denote the critical and reduced

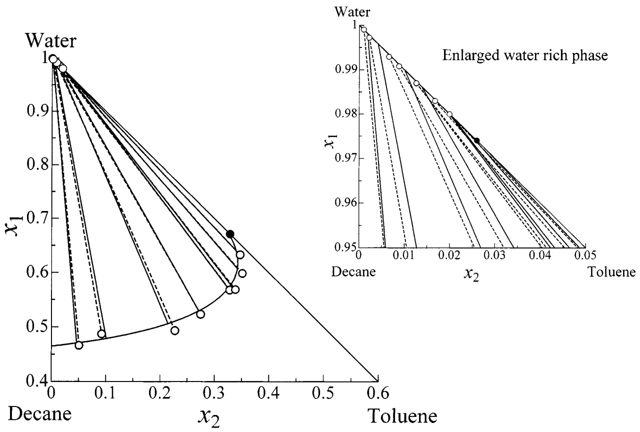

Figure 4. Phase equilibria for the water (1) + toluene (2) + decane (3) system at 573 K and 20 MPa: (○) experimental results; (—) predicted results; (●) data for the water + toluene binary system.[1]

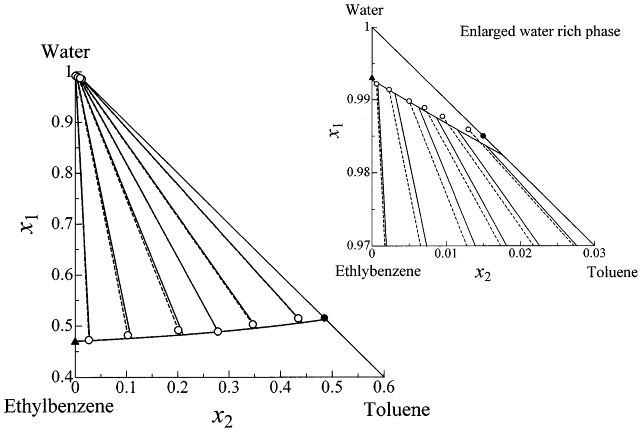

Figure 5. Phase equilibria for the water (1) + toluene (2) + ethylbenzene (3) system at 553 K and 20 MPa: (○) experimental results; (—) predicted results; (●) data for the water + toluene binary system;[1] (▲) data for the water + ethylbenzene binary system.[2]

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, toluene, decane, and ethylbenzene cited from the literature[5] are listed in Table 2.

The exponent-type mixing rule proposed by Higashi et al.[6] was applied to the energy parameter a. The mixing and the combining rules for the energy parameter a are given as follows.

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

Introducing exponential parameter β_{ij} may express the contact probability of molecule i with molecule j.[6] This means that nonrandomness in the mixture can be evaluated empirically. The value of β_{ii} is unity, because the parameter is for pure compound i.

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

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

Results and Discussion. The liquid−liquid equilibria for the water (1) + hexane (2) + hexadecane (3) system could not be predicted, because the liquid−liquid equilibrium data of the water (1) + hexadecane (3) binary system were not available. The liquid−liquid equilibria for water (1) + toluene (2) + decane (3) and water (1) + toluene (2) + ethylbenzene (3) systems were predicted. The binary parameters for water + toluene and water + ethylbenzene systems were cited from the literature.[2] They are listed in Table 3. As pointed out in the previous work,[2] the parameter β_{12} strongly affects the calculation of the phase equilibria for the water (1) + hydrocarbon (2) system, compared with the case of the parameter β_{21}. So, the value of β_{21} was set at unity, and the binary parameters of k_{12}, l_{12}, and β_{12} for the water + decane system were determined by fitting the phase equilibrium data[1] at 573 and 593 K. They are shown in Table 3. The values of k_{23} and l_{23} are set at 0.00, and β_{23} and β_{32} are set at 1.00 for the hydrocarbon (2) + hydrocarbon (3) system because the interactions between hydrocarbons are weak and the local composition would be almost the same as the bulk composition. The predicted results for the ternary systems by using the binary parameters are shown in Figures 3−5. In the calculations, temperature, pressure, and mole fraction of decane and ethylbenzene in the hydrocarbon rich phase were fixed as the experimental values. The predicted results are in good agreement with the experimental results.

Table 2. Critical Properties and Parameters *m* and *n*[5]

substance	T_c/K	p_c/MPa	m	n
water	647.3	22.1	0.9500	0.1630
toluene	591.8	4.11	0.7117	0.2242
decane	617.6	2.11	0.8905	0.3863
ethylbenzene	617.1	3.61	0.7458	0.2512

Table 3. Interaction Parameters for Water (1) + Hydrocarbon (*j*) Systems

j	k_{1j}	l_{1j}	β_{1j}	β_{j1}
toluene	0.38[2]	0.30[2]	1.40[2]	1.00[2]
decane	0.48	0.27	1.48	1.00
ethylbenzene	0.42[2]	0.34[2]	1.43[2]	1.00[2]

Conclusion

The liquid−liquid equilibria for water + hydrocarbon + hydrocarbon ternary systems were measured at high temperatures and pressures by a flow-type apparatus in order to accumulate new data. Moreover, the phase equilibria were predicted using the modified SRK equation of state in which the exponential mixing rule was applied to the energy parameter. The predicted results are in good agreement with the experimental results. The model would be used in calculation of phase equilibria for water + hydrocarbon + hydrocarbon ternary systems at high temperatures and pressures.

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