

# Measurement and Correlation of Liquid–Liquid Equilibria for Water + Aromatic Hydrocarbon Binary Systems at High Temperatures and Pressures

Masashi Haruki, Yoshio Iwai,\* Seiji Nagao, and Yasuhiko Arai

Department of Chemical Engineering, Faculty of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Liquid–liquid equilibria for water + aromatic hydrocarbon binary systems were measured by a flow method at high temperatures and pressures. The measured systems and conditions are as follows: water + toluene system, (573.2 and 583.2) K from (10.5 to 28.1) MPa; water + ethylbenzene system, (553.2 and 583.2) K from (10.4 to 26.4) MPa; water + *p*-xylene system, (553.2 and 583.2) K from (10.2 to 26.5) MPa. The experimental results were correlated by the SRK equation of state. An exponent-type mixing rule was used for the energy parameter. The experimental data are fitted well by the correlation.

## Introduction

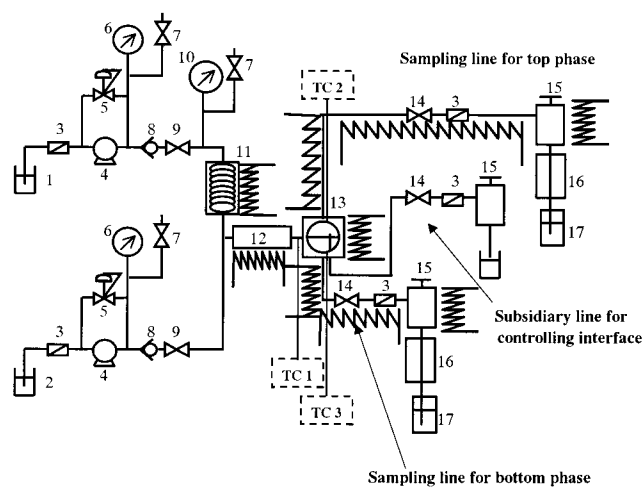
The knowledge of phase equilibria for water + hydrocarbon systems in the high-temperature and -pressure region is important for designing supercritical water processes, such as liquefying process of coals and decomposition processes of waste polymers. To date, the phase equilibrium data for water + hydrocarbon binary systems<sup>1–4</sup> and water + hydrocarbon + hydrocarbon ternary systems<sup>5,6</sup> in the high-temperature and -pressure region have been reported in the literature. However, the data reported are still limited. In a previous work,<sup>7</sup> a new apparatus based on a flow method was designed and liquid–liquid equilibria (LLE) for water + decane and water + toluene systems were measured. The measured data were correlated by the Soave–Redlich–Kwong equation of state modified by Sandarusi et al.<sup>8</sup> (SRK-EOS) with the exponent-type mixing rule proposed by Higashi et al.,<sup>9</sup> and a good fit was achieved.

In this work, high-temperature and -pressure LLE for water + toluene, water + ethylbenzene, and water + *p*-xylene systems were measured with the apparatus. The measured LLE data were correlated with the SRK-EOS with the exponent-type mixing rule.

## Experiment

**Materials.** The toluene, ethylbenzene, *p*-xylene, and ethanol used in this work were supplied by Wako Pure Chem. Ind. The toluene, ethylbenzene, and *p*-xylene used were more than 99.5%, 98%, and 98% pure, analyzed by gas chromatograph (GC), respectively. Ethanol is more than 99.5 vol % pure, analyzed by a density test. The purities of them were analyzed by Wako Pure Chem. Ind. Moreover, the purities were checked by the authors with GC, and the area % values of the main compounds were more than 99.8%, 99.8%, 99.9%, and 99.8% for toluene, ethylbenzene, *p*-xylene, and ethanol, respectively. They were used without further purification. Distilled water was purified by MILLIQ-LABO (MILLIPORE Corporation) in order to obtain ultrapure water which was used in this experiment.

\* To whom correspondence should be addressed. E-mail: iwai@chem-eng.kyushu-u.ac.jp. Telephone and fax: +81 92 642 3496.



**Figure 1.** Schematic diagram of experimental apparatus: (1) water reservoir; (2) hydrocarbon reservoir; (3) filter; (4) feed pump; (5) back-pressure-regulator; (6) pressure gauge; (7) safety valve; (8) check valve; (9) stop valve; (10) precision pressure gauge; (11) preheating coil; (12) line mixer; (13) equilibrium cell; (14) stop valve; (15) expansion valve; (16) water bath; (17) collecting bottle; (TC1–TC3) resistance temperature detector.

**Apparatus.** A flow-type apparatus was used to measure the phase equilibria at high temperatures and pressures. The schematic diagram of the apparatus is shown in Figure 1. The apparatus consists of a feed system, an equilibrium cell with sapphire windows, and a sampling effluent system. Four flow lines, which are the feed line, the sampling lines for the water- and hydrocarbon-rich phases, and a subsidiary line for maintaining the position of the phase interface at the center of the cell, were connected to the cell. The cell was made of Hastelloy. The inside diameter and volume of the cell were 20 mm and 31 cm<sup>3</sup>, respectively. A detailed description of the equipment was given in a previous work.<sup>7</sup>

**Procedure.** The experiment was carried out by the following procedures. At first, the system was heated to a desired temperature by electric heaters. Then, pure water and pure hydrocarbon were added. The pressure in the system was controlled by back-pressure-regulators. Pres-

**Table 1. Liquid–Liquid Equilibria for the Water (1) + Toluene (2) System**

<i>T</i> /K	<i>p</i> /MPa	water-rich phase			hydrocarbon-rich phase		
		$x_1^I$	$N_s^a$	$S_1^b (\times 10^3)$	$x_1^{II}$	$N_s^a$	$S_1^b (\times 10^3)$
573.2	10.5				0.871	12	19.0
	11.2				0.836	12	6.0
	12.3				0.740	12	13.0
	13.6	0.975	12	1.3	0.702	12	9.6
	15.3	0.975	12	1.1	0.694	12	6.7
583.2	11.4				0.920	12	8.3
	12.6				0.843	6	6.3
	13.6				0.787	12	11.9
	15.2				0.782	12	8.1
	18.3	0.953	17	1.2	0.790	18	8.3
	20.4	0.952	12	0.9	0.791	12	6.1
	22.2	0.952	12	1.9	0.782	12	8.0
	25.2	0.955	12	0.8	0.759	12	5.5
	28.1	0.956	12	1.1	0.745	12	7.6

<sup>a</sup>  $N_s$ : number of data points used for arithmetic average. <sup>b</sup>  $S_1$ : standard deviation of composition.  $S_1 = [(1/N_s)\sum_{n=1}^{N_s}(x_{1,n} - x_1)^2]^{1/2}$ .  $n$ : data point.

**Table 2. Liquid–Liquid Equilibria for the Water (1) + Ethylbenzene (2) System**

<i>T</i> /K	<i>p</i> /MPa	water-rich phase			hydrocarbon-rich phase		
		$x_1^I$	$N_s^a$	$S_1^b (\times 10^3)$	$x_1^{II}$	$N_s^a$	$S_1^b (\times 10^3)$
553.2	10.4	0.994	9	1.2	0.521	10	14.9
	14.4	0.994	9	1.2	0.508	11	11.7
	17.5	0.993	11	1.0	0.498	9	16.2
	20.4	0.993	11	0.9	0.469	10	24.1
	23.4	0.993	12	1.4	0.463	8	11.9
	26.4	0.993	12	0.9	0.453	12	19.8
583.2	12.6				0.809	10	8.0
	14.5				0.746	10	5.7
	17.1	0.978	12	2.0	0.719	12	7.6
	20.5	0.979	18	1.6	0.700	18	8.6
	23.4	0.979	12	1.1	0.680	11	3.4
	26.3	0.980	12	1.0	0.664	12	14.6

<sup>a</sup>  $N_s$ : number of data points used for arithmetic average. <sup>b</sup>  $S_1$ : standard deviation of composition.  $S_1 = [(1/N_s)\sum_{n=1}^{N_s}(x_{1,n} - x_1)^2]^{1/2}$ .  $n$ : data point.

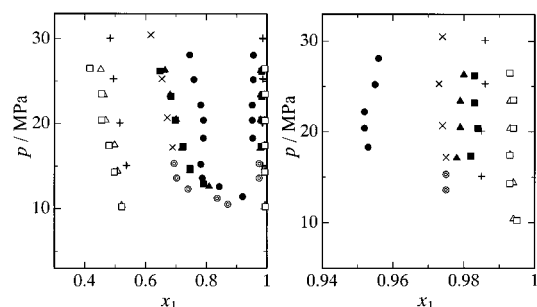
surized water was heated by a preheating coil, and both feeds were well mixed through the line mixer before entering the equilibrium cell. The phase behavior was observed with a video camera attached to a telescope. The temperatures of the entrance, top, and bottom of the cell were controlled within  $\pm 1$  K. The fluctuations of pressure were within  $\pm 0.1$  MPa. When the interface of both phases was well stabilized, samplings were made after flow rates were measured. The residential time in the equilibrium cell was about (6 to 15) min. About 10 cm<sup>3</sup> of samples were collected from each phase in bottles containing ethanol to obtain homogeneous solutions. The volumes of ethanol used were about twice the sample size for the water + toluene system and three times the size for the water + ethylbenzene and water + *p*-xylene systems, respectively. The compositions of the samples were analyzed by a gas chromatograph with a thermal conductivity detector.

**Results and Discussion.** The experimental results of the water + toluene, water + ethylbenzene, and water + *p*-xylene systems are listed in Tables 1, 2, and 3, respectively. The values listed in Tables 1–3 were obtained from arithmetic averages of several measurements at each pressure. As shown in Figure 2, the solubilities of water in ethylbenzene and *p*-xylene are quite close at 553.2 and 583.2 K. The solubilities of ethylbenzene in water are slightly larger than those of *p*-xylene at 583.2 K. The mutual solubilities of the water + toluene system are larger

**Table 3. Liquid–Liquid Equilibria for the Water (1) + *p*-Xylene (2) System**

<i>T</i> /K	<i>p</i> /MPa	water-rich phase			hydrocarbon-rich phase			
		$x_1^I$	$N_s^a$	$S_1^b (\times 10^3)$	$x_1^{II}$	$N_s^a$	$S_1^b (\times 10^3)$	
553.2	10.2	0.995	11	0.9	0.522	11	12.4	
	14.3	0.993	14	0.5	0.497	13	6.4	
	17.4	0.993	15	0.6	0.480	8	6.6	
	20.4	0.994	11	0.7	0.456	8	4.5	
	23.5	0.994	16	0.5	0.456	13	10.4	
	26.5	0.993	11	0.4	0.415	9	12.2	
	583.2	12.9				0.790	11	5.8
		14.7				0.746	8	7.4
17.3		0.982	15	1.0	0.723	12	5.2	
20.4		0.984	9	1.3	0.698	9	3.7	
23.2		0.983	10	1.3	0.684	12	8.5	
26.2		0.983	10	0.9	0.648	9	7.1	

<sup>a</sup>  $N_s$ : number of data points used for arithmetic average. <sup>b</sup>  $S_1$ : standard deviation of composition.  $S_1 = [(1/N_s)\sum_{n=1}^{N_s}(x_{1,n} - x_1)^2]^{1/2}$ .  $n$ : data point.



**Figure 2.** Experimental results for liquid–liquid equilibria of the water (1) + toluene (2), water (1) + ethylbenzene (2), and water (1) + *p*-xylene (2) systems: (○, ●) this work at (573.2 and 583.2 K); (+, ×) Haruki et al.<sup>7</sup> at (553.2 and 573.2 K) for the water + toluene system; (△, ▲) this work at (553.2 and 583.2 K) for the water + ethylbenzene system; (□, ■) this work at (553.2 and 583.2 K) for the water + *p*-xylene system.

than those of the water + ethylbenzene and water + *p*-xylene systems.

## Correlation

**Equation of State and Mixing Rules.** The SRK equation of state modified by Sandarusi et al.<sup>8</sup> (SRK-EOS) was adopted. Additionally, the exponent-type mixing rule proposed by Higashi et al.<sup>9</sup> for the energy parameter and the conventional mixing rule for the size parameter were applied to correlate the experimental results. The SRK-EOS is given by

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

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 by

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

$$b = \frac{0.08664RT_c}{p_c} \quad (3)$$

and

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

**Table 4. Critical Properties and Parameters  $m$  and  $n$  in the SRK-EOS<sup>8</sup>**

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
ethylbenzene	617.1	3.61	0.7458	0.2512
<i>p</i> -xylene	616.2	3.51	0.7941	0.2400

**Table 5. Interaction Parameters for the Water (1) + Hydrocarbon (2) Systems**

system	$k_{12}$	$l_{12}$	$\beta_{12}$
water + toluene	0.38	0.30	1.40
water + ethylbenzene	0.42	0.34	1.43
water + <i>p</i> -xylene	0.42	0.34	1.47

**Table 6. Correlated Results of the Water (1) + Hydrocarbon (2) Systems**

system	$T$ /K	$N^{a,c}$		deviation <sup>b,c</sup> ( $\times 10^3$ )		ref
		$p^I x^{II}$	$p x^{II}$	$x_1^I$	$x_1^{II}$	
water + toluene	553.2	4		3.3	2.4	7
	573.2	6	3	4.6	9.1	7, this work
	583.2	5	4	5.0	22.4	this work
water + ethylbenzene	553.2	6		0.4	8.2	this work
	583.2	4	2	2.1	11.4	this work
water + <i>p</i> -xylene	553.2	6		0.6	10.8	this work
	583.2	4	2	0.9	12.6	this work

<sup>a</sup> Number of data points. <sup>b</sup> deviation =  $(1/N)\sum_{i=1}^N |x_{1,calc} - x_{1,exp}|_n$ .  
<sup>c</sup> The superscripts I and II denote the water- and hydrocarbon-rich phases, respectively.

where  $m$  and  $n$  are the parameters obtained from a fit to the vapor pressure curve, and the subscripts c and r denote the critical and reduced properties, respectively. The critical properties and the parameters  $m$  and  $n$  for water, toluene, ethylbenzene, and *p*-xylene are listed in Table 4.

The exponent-type mixing rule and the combining rule for the energy parameter  $a$  are given by

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

The conventional mixing rule and combining rule for the size parameter  $b$  are given by

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

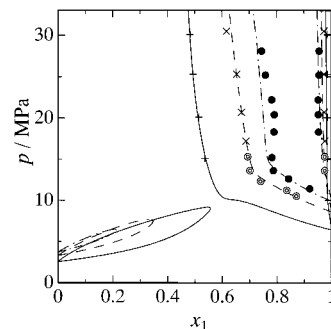
The parameter  $\beta_{12}$  strongly affects the calculation of the phase equilibria for the water (1) + hydrocarbon (2) system. So, the following expressions are assumed for the reduction of the calculation time.

$$\beta_{11} = \beta_{22} = \beta_{21} = 1 \quad (7)$$

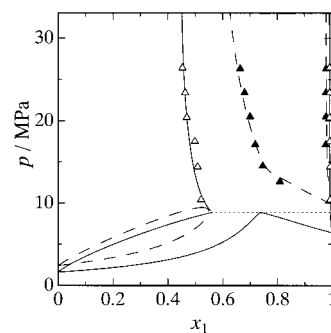
**Results and Discussion.** The parameters  $k_{12}$ ,  $l_{12}$ , and  $\beta_{12}$  were changed by 0.01 intervals, and the values of OF, which is defined by the following equation, were calculated.

$$OF = \frac{1}{N^I} \sum_1^M |x_{1,calc}^I - x_{1,exp}^I| + \frac{1}{N^{II}} \sum_1^M |x_{1,calc}^{II} - x_{1,exp}^{II}| \quad (8)$$

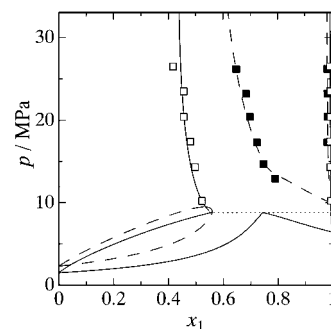
where  $N$  is the number of data and  $x_1$  is the mole fraction of water. The superscripts I and II denote the water-rich phase and the hydrocarbon-rich phase, respectively. The subscripts exp and calc are the experimental and calculated



**Figure 3.** Phase equilibria for the water (1) + toluene (2) system: (●, ○) this work at (573.2 and 583.2 K); (+, ×) Haruki et al.<sup>7</sup> at (553.2 and 573.2 K); (—, ---, - · -) correlated results at (553.2, 573.2, and 583.2 K).



**Figure 4.** Phase equilibria for the water (1) + ethylbenzene (2) system: (▲, △) this work at (553.2 and 583.2 K); (—, ---) correlated results at (553.2 and 583.2 K); (· · ·) three-phase equilibria at 553.2 K.



**Figure 5.** Phase equilibria for the water (1) + *p*-xylene (2) system: (■, □) this work at (553.2 and 583.2 K); (—, ---) correlated results at (553.2 and 583.2 K); (· · ·) three-phase equilibria at 553.2 K.

results, respectively. The optimized parameters which give the minimized value of OF are listed in Table 5. The calculated results of water + toluene, water + ethylbenzene, and water + *p*-xylene systems are shown in Figures 3, 4, and 5, respectively. The correlation results are summarized in Table 6.

The upper critical end points of the water + toluene and water + ethylbenzene systems are 558.2 K, 10.1 MPa and 574.3 K, 11.2 MPa, respectively.<sup>10</sup> Therefore, the three-phase equilibria for water + toluene and water + ethylbenzene systems exist at 553.2 K. The three-phase equilibria are calculated for the water + ethylbenzene system at 553.2 K as shown in Figure 4. On the other hand, the three-phase coexistence does not appear at 553.2 K in the calculation for the water + toluene system, since the temperature is only 5 K lower than the three-phase end point. The three-phase equilibria are also calculated for the water + *p*-xylene system at 553.2 K as shown in Figure 5.

The correlated results are in good agreement with the experimental data for all systems.

### Conclusion

The liquid–liquid equilibria for the water + toluene system at (573.2 and 583.2) K and from (10.5 to 28.1) MPa, for the water + ethylbenzene system at (553.2 and 583.2) K and from (10.4 to 26.4) MPa, and for the water + *p*-xylene system at (553.2 and 583.2) K and from (10.2 to 26.5) MPa were measured by a flow method. The solubilities of ethylbenzene in water are slightly larger than those of *p*-xylene at 583.2 K. The mutual solubilities of water + toluene are higher than those of the other systems. The experimental results are well correlated by the SRK-EOS with the exponent-type mixing rule for the energy parameter and the conventional mixing rule for the size parameter.

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