MEASUREMENT AND CORRELATION OF PHASE EQUILIBRIA FOR WATER + 2-PROPANOL + ALKANE TERNARY SYSTEMS AT HIGH TEMPERATURES AND PRESSURES

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The phase equilibria for the water + 2-propanol + alkane ternary systems were measured at high temperatures and pressures by an apparatus based on a flow method. The systems measured in this work show the phase behavior in which one liquid pair is partially miscible and both liquid pairs are fully miscible. The phase equilibrium data obtained were correlated by a modified SRK equation of state. An exponent-type mixing rule was applied to the attractive term of the equation of state. The correlated results show good agreement with the experimental results.

INTRODUCTION

Hydrolysis and cracking processes of heavy hydrocarbons and waste plastics utilizing sub- and supercritical water have been received much attention from the point of view of recycling of resources and conservation of environment. In these processes, low molecular weight hydrocarbons as well as alcohols, ketones and acids are produced as decomposed products. Therefore, the knowledge of phase equilibria of the mixtures containing these compounds at high temperatures and pressures is very useful for process design. In previous work [1]-[3], the authors measured and correlated the phase equilibria for the water + hydrocarbon binary systems and the water + hydrocarbon + hydrocarbon ternary systems near the critical point of water. Few literature data are available for the phase equilibria of the mixtures containing water, hydrocarbon and alcohol at high temperatures and pressures. In this work, therefore, the phase equilibria for water + 2-propanol + decane at 573, 593 K and 15.0, 20.0 MPa and water + 2-propanol + hexane systems at 573 K and 20.0 MPa were measured by an apparatus based on a flow method. Furthermore, the experimental data obtained were correlated by the modified SRK equation of state [4]. An exponent-type mixing rule [5] was applied for the attractive term of the equation of state.

EXPERIMENT

Materials

Ultrapure water was used. It was purified from distilled water. 2-propanol, decane, hexane, ethylbenzene and ethanol used in this work were analytical grade reagent and were supplied by Wako Pure Chem. Ind. Their purities were checked with gas chromatograph. The peak percentages of the main compounds were more than 99.8 %, 99.8 %, 99.9 %, 99.9 % and 99.8 %, respectively. These materials were used without further purification.

Apparatus and procedure

The apparatus based on a flow method used in previous work [3] was applied to measure the phase equilibria for the water + 2-propanol + alkane systems 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 (12) and a sampling effluent system. The equilibrium cell was 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 (14) which controlled pressure in the system. The line was used to maintain the position of the phase interface at the center of the cell.

The following experimental procedure was adopted. The system was heated to the desired temperature by electric heaters. Pure water and mixture of hydrocarbon and alcohol were supplied by each double plunger pump (4). The feed rates were measured by electronic balances and confirmed to be constant during measurements. The feed rates of water and the mixture were about 3.7 and 5.1 g min^{-1}. Pressurized water and the mixture were sufficiently mixed through a line mixer (11) and supplied to the equilibrium cell (12). The residential time in the equilibrium cell was about 3 to 5 min. The temperature of entrance, top and bottom of the cell was controlled ±1 K. The pressure fluctuation during the experiments was ±0.2 MPa. Samplings of each phase were carried out after the phase interface was well stabilized. The effluents from top and bottom phases were depressurised through expansion valves (15) and cooled with a water bath (16). Samples were trapped in sampling bottles (17) containing ethanol to obtain homogeneous solutions. The samples of each phase were analysed by gas chromatograph with thermal conductivity detector. The compositions of samples were determined by an internal standard method. Ethylbenzene was used as the internal standard.

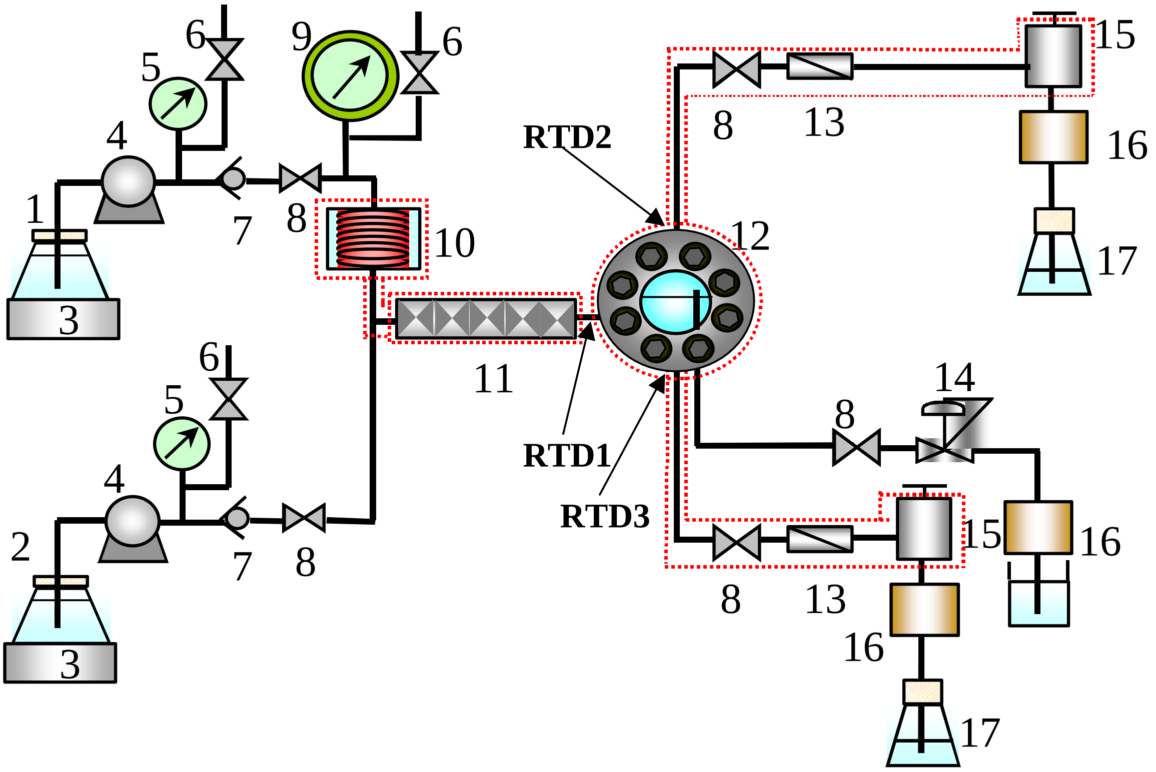

Figure 1. Schematic diagram of experimental apparatus: (1) water reservoir; (2) hydrocarbon + 2-propanol reservoir; (3) electronic balance; (4) feed pump; (5) pressure gauge; (6) safety valve; (7) check valve; (8) stop valve; (9) precision pressure gauge; (10) preheating coil; (11) line mixer; (12) equilibrium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

Results and discussion

According to the classification by Treybal [6], the phase equilibria for the systems measured in this work belong to type I. In type I, one liquid pair, such as water + decane or water + hexane, is partially miscible. On the other hand, both liquid pairs, such as water + 2-propanol and decane + 2-propanol or hexane + 2-propanol, are fully miscible.

The experimental results are shown in Figures 2-4. The mole fractions of water in hydrocarbon rich phase and water rich phase increase and decrease with increasing the mole fraction of 2-propanol, respectively. Furthermore, the mole fractions in hydrocarbon rich phase increase dramatically near the plait point. As shown in Figure 2, when the pressure decreases from 20.0 MPa to 15.0 MPa, the mole fractions of water in hydrocarbon rich phase and water rich phase increase. The solubility curves at 20.0 and 15.0 MPa come close each other at the mole fraction of 2-propanol in hydrocarbon rich phase is about 0.15. As shown in Figure 3, when the temperature increases from 573 K to 593 K, the mole fractions of water in hydrocarbon rich phase and water rich phase increase and decrease, respectively and two phase region reduces. As shown Figures 2 and 4, at 573 K and 20.0 MPa, two phase region reduces slightly compared with the case of the water + 2-propanol + decane system.

CORRELATION

Equation of state

The phase equilibrium data obtained in this work were correlated by a modified SRK equation of state (MSRK) [4]. An energy parameter of the original SRK equation of state [7] was modified by Sandarusi et al. to represent better vapor pressures especially for polar substances. MSRK is given as follows.

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

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

$$a(T) = \frac{0.42747 R^2 T_\mathrm{c}^2}{p_\mathrm{c}} a(T) \tag{2}$$

$$b = \frac{0.08664 R T_\mathrm{c}}{p_\mathrm{c}} \tag{3}$$

and

$$a(T) = 1 + (1 - T_\mathrm{r})\left(m + \frac{n}{T_\mathrm{r}} \right) \tag{4}$$

where the subscript 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, decane and hexane cited from the literature are listed in Table 1.

Mixing and combing rule

An exponent-type mixing rule proposed by Higashi et al. [5] was applied for the energy parameter a. The mixing and combining rules for the energy parameter a are given as follows.

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

Introduction of exponential parameter b_{ij} may express the contact probability of molecule i with molecule j. This means that non-randomness in the mixture can be evaluated empirically. The mixture in this work shows very complex behavior caused by strong interaction. This mixing rule is effective for the mixture. b_{12}, b_{23} and b_{13} strongly affect the calculation of the phase equilibria for the water(1) + 2-propanol(2) + alkane(3) systems, compared with the case of the parameter b_{21}, b_{32} and b_{31}. So, the values of b_{21}, b_{32} and b_{31} were set to be unity. The value of b_{ii} is also unity, because the parameter is for pure compound i.

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

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

The interaction parameters k_{ij}, l_{ij} and b_{ij} are determined using phase equilibrium data for binary and ternary systems. Table 2 shows the data source for determination of interaction parameters. Marquardt method [8] was adopted to optimize the interaction parameters. The determined interaction parameters are listed in Table 3.

Results and discussion

Figures 2-4 show the correlated results. As shown in Figures 2 and 3, the correlated results for the water + 2-propanol + decane system are in good agreement with the experimental results except for the results near the plait points. As shown in Figure 4, the correlated results for the water + 2-propanol + hexane system are in good agreement with the experimental results.

Table 1 Critical properties and parameters m and n in MSRK [4]

Substance	T_c [K]	p_c [MPa]	m	n
water	647.3	22.1	0.9499	0.1630
2-propanol	508.3	4.76	0.6434	0.7854
decane	617.6	2.10	0.8905	0.3863
hexane	507.4	3.01	0.7446	0.2476

Table 2 Data source for determination of interaction parameters

i	j	System	T [K]	Ref.
water	2-propanol	water + 2-propanol	573	[9]
water	decane	water + decane	573, 593	[1]
water	hexane	water + hexane	573	[10], [11]
2-propanol	decane	water + 2-propanol + decane	573, 593	this work
2-propanol	hexane	water + 2-propanol + hexane	573	this work

Table 3 Interaction parameters for water + 2-propanol + decane and water + 2-propanol + hexane systems

i	j	T [K]	k_{ij}	l_{ij}	b_{ij}
water	decane	573, 593	0.48	0.27	1.48
water	hexane	573	0.49	0.28	1.55
water	2-propanol	573, 593	0.04	0.15	0.98
2-propanol	decane	573	0.40	0.26	0.55
2-propanol	decane	593	0.49	0.35	0.41
2-propanol	hexane	573	0.66	0.72	0.45

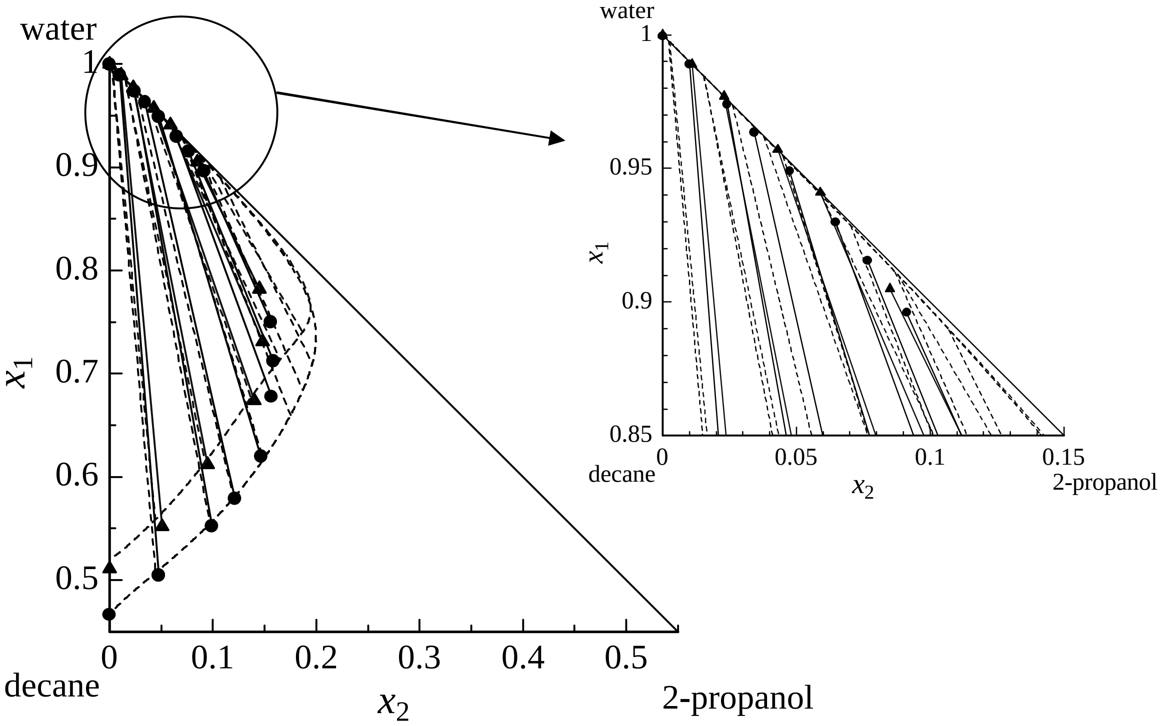

Figure 2 Phase equilibria for water(1) + 2-propanol(2) + decane(3) system at 573 K; (●——●) experimental results at 20.0 MPa; (▲——▲) experimental results at 15.0 MPa ; (-------) correlated results by MSRK

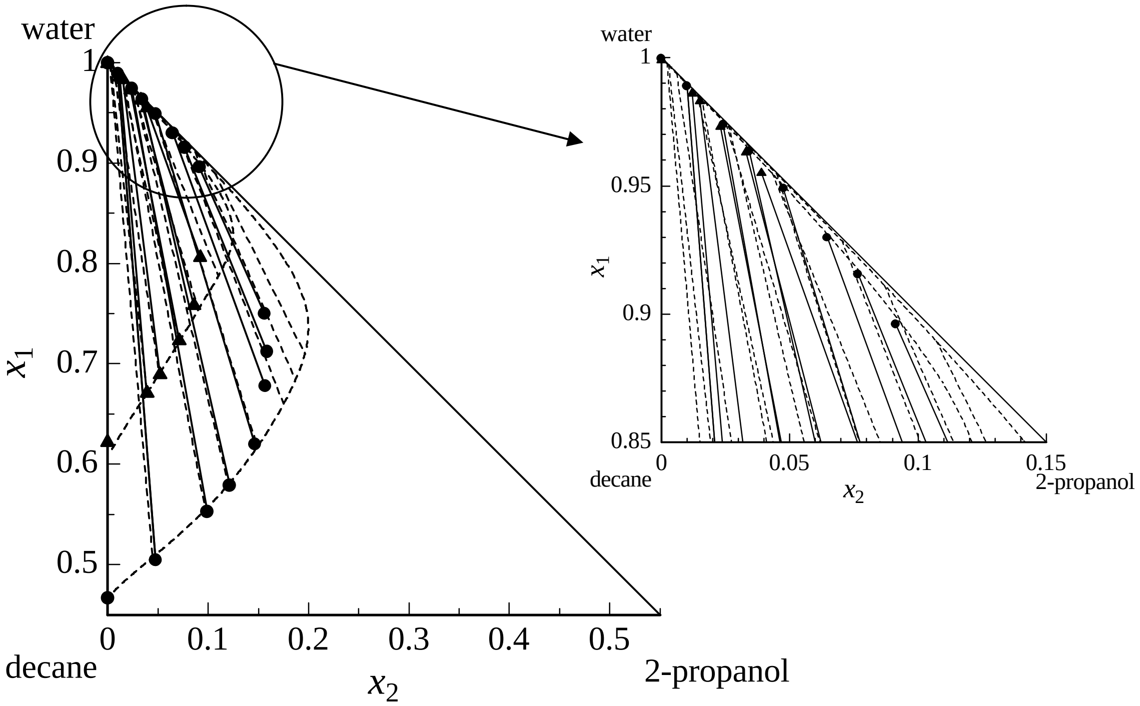

Figure 3 Phase equilibria for water(1) + 2-propanol(2) + decane(3) at 20.0 MPa ; (●——●) experimental results at 573 K ; (▲——▲) experimental results at 593 K; (-------) correlated results by MSRK

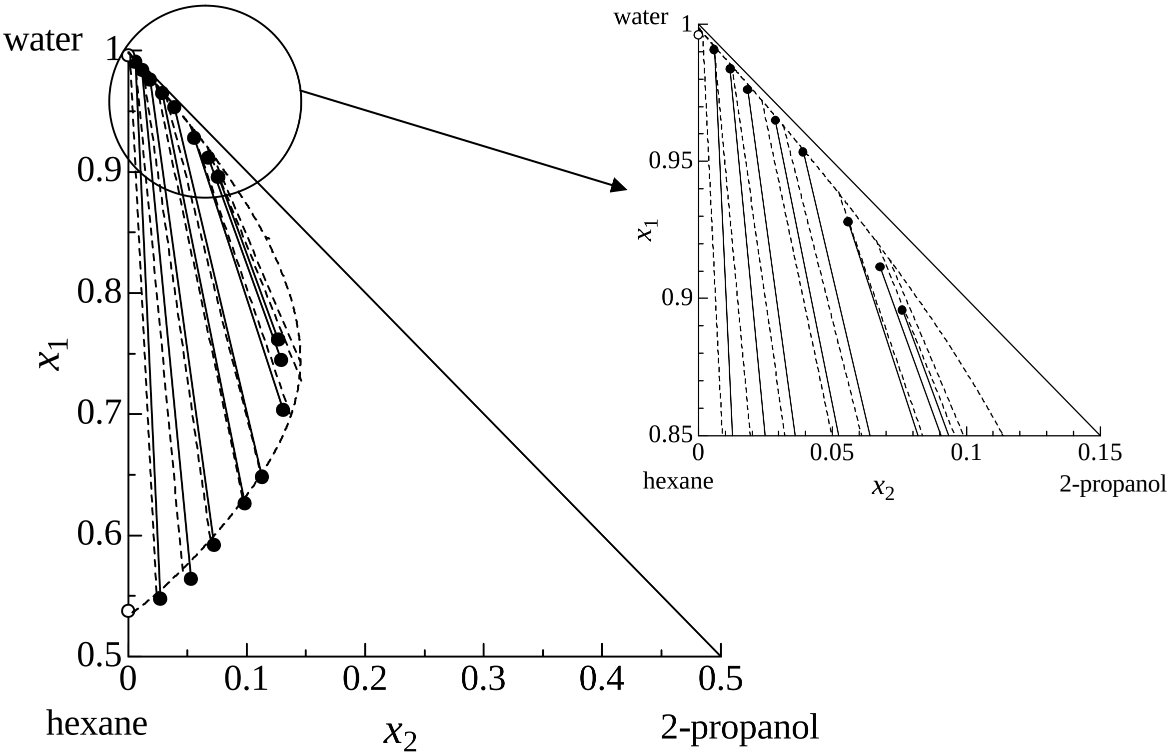

Figure 4 Phase equilibria for water(1) + 2-propanol(2) + hexane(3) at 573 K and 20.0 MPa (●——●) experimental results; (○) Literature data [10]; (------) correlated results by MSRK

CONCLUSION

The phase equilibria for water + 2-propanol + decane and water + 2-propanol + hexane systems were measured at high temperatures and pressures by a flow type apparatus in order to accumlated new data. The phase equilibrium data obtained were correlated by the modified SRK equation of state. The exponent type mixing rule was applied for the energy parameter of the equation. The correlated reslults are in good agreement with the experimental results except for the results near the plait point for the water + 2-propanol + decane system.

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