

Measurement and Correlation of Phase Equilibria for Water + Hydrocarbon Systems near the Critical Temperature and Pressure of Water

Masashi Haruki, Yoshio Iwai,* Seiji Nagao, Yukihiro Yahiro, and Yasuhiko Arai

Department of Chemical Systems and Engineering, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

An experimental apparatus based on a flow method was constructed in order to measure the phase equilibria for water + hydrocarbon systems near and above the critical temperature of water in the high-pressure region. The phase equilibria were measured for the water + decane system at 573.2 K from 12.1 to 30.3 MPa and at 593.2 K from 15.4 to 25.1 MPa and for the water + toluene system at 553.2 K from 15.1 to 30.1 MPa and at 573.2 K from 17.2 to 30.5 MPa. The phase equilibria of the water + decane system at 573.2 and 593.2 K and of the water + toluene system at 553.2 and 573.2 K are correlated by a modified SRK (MSRK) equation of state, which is modified in the attractive term of the SRK equation of state to calculate well the saturated vapor pressures of many organic and inorganic compounds. An exponent-type mixing rule, which uses empirical exponential parameters showing deviations from random mixing, is applied to the energy parameter a , and a conventional mixing rule is applied to the size parameter b . Good correlation results are obtained.

Introduction

Mixtures of water and hydrocarbons, which are highly nonideal solutions, are treated frequently in oil refining processes and oil reservoirs. Moreover, processes using supercritical water as a reaction solvent have recently been considered. The hydrolysis processes of plastics are the focus of much attention from the standpoint of recycling of resources and environmental conservation. Knowledge of the phase equilibria for water + hydrocarbon systems at high temperatures and pressures is very important for designing such chemical processes.

To date, phase equilibria for water + hydrocarbon binary systems in the high-temperature and -pressure region have been reported in the literature.^{1–4} The critical loci have also been studied.^{5,6} However, the accumulation of data is still limited.

In this work, an experimental apparatus based on a flow method was constructed. The phase equilibria for the water + decane and water + toluene systems were measured to confirm the validity of the apparatus and the experimental technique and to present the new experimental data. Moreover, the data were correlated by using a modified Soave–Redlich–Kwong (MSRK) equation of state (EOS)⁷ with an exponent-type mixing rule⁸ applied to the attractive term.

Experiment

Materials. Ultrapure water was used. Distilled water was purified by MilliQ-Labo (Millipore Corporation) in order to obtain ultrapure water. Decane (>99%, supplied by Wako Pure Chem. Ind.), toluene (>99.5%, supplied by Wako Pure Chem. Ind.), 1-propanol (>99.5%, supplied by Wako Pure Chem. Ind.), and ethanol (>99.5%, supplied by Wako Pure Chem. Ind.) were used without further purification.

Apparatus and Procedure. A flow-type apparatus was used in order to reduce the thermal decomposition of hydrocarbon and the fluctuation in pressure caused by sampling. The schematic diagram of the apparatus is shown in Figure 1. It consists of a feed system, an equilibrium cell (13), and a sampling effluent system. Initially, a preheating coil (11), a linemixer (12), the equilibrium cell (13), and the collecting effluent lines were heated to the desired temperature by electric heaters. Then, the stop valves I (9) were closed, and pure water and pure hydrocarbon were supplied from each feed reservoir (1, 2) by feed pumps (4). The pressure in the system was controlled by back-pressure regulators (5). The stop valves I were opened. Only pressurized water was heated by the preheating coil. Both feeds were well mixed through the linemixer, and the mixed fluid was supplied to the equilibrium cell equipped with sapphire windows. The phase behaviors in the cell were observed by a video camera with a microscope. The deviations among the temperatures of the entrance (TC 1), top (TC 2), and bottom (TC 3) of the cell were controlled to within ± 1 K from the equilibrium temperature. The fluctuations of pressure from the equilibrium pressure were within ± 0.1 MPa. The effluents from the top and bottom phases in the cell were depressurized through expansion valves (15). Then, they were cooled by water baths (16) and collected in bottles (17). A subsidiary line was equipped to maintain the position of the phase interface at the center of cell. The feed rate was also controlled to maintain the position of the interface by changing the flow speed of the feed pumps. The residential time in the equilibrium cell was about 6–15 min.

When the interface of both phases was well stabilized, samplings were carried out after flow rates were measured. Water and hydrocarbon may not be homogeneous downstream from the equilibrium cell. Therefore, large volumes of samples, such as about 10 cm³, were collected from each phase in bottles containing alcohol to obtain

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

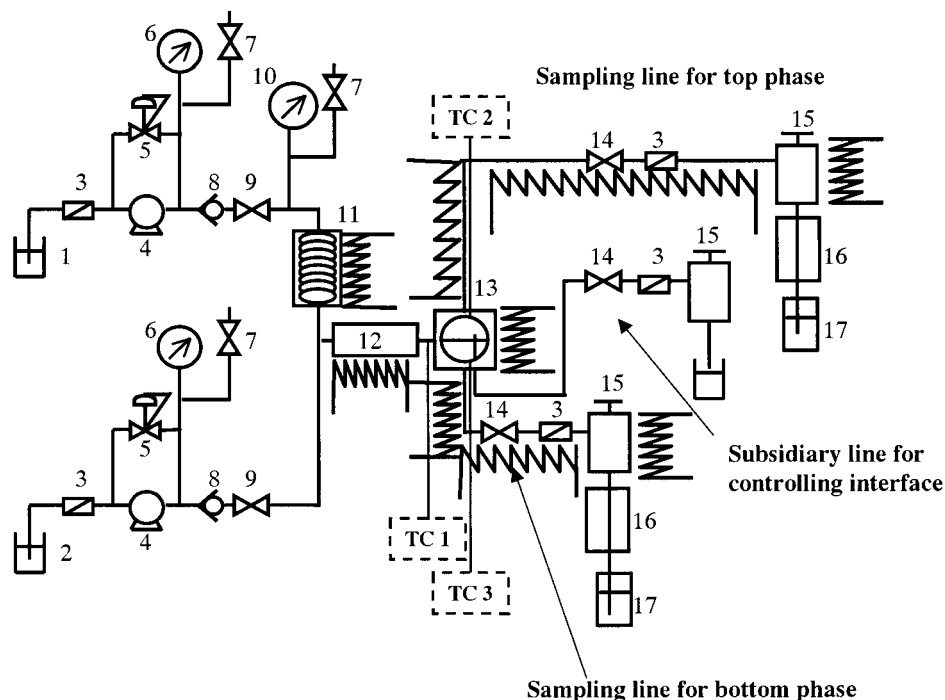


Figure 1. Schematic diagram of the experimental apparatus: (1) water reservoir, (2) hydrocarbon reservoir, (3) filter, (4) feed pump, (5) back-pressure regulator, (6) pressure gauge, (7) safety valve, (8) check valve, (9) stop valve I, (10) precision pressure gauge, (11) preheating coil, (12) linemixer, (13) equilibrium cell, (14) stop valve II, (15) expansion valve, (16) water bath, and (17) collecting bottle.

homogeneous solutions. The tube exits were soaked in alcohol to prevent the volatilization of water and hydrocarbon during sampling. 1-Propanol and ethanol were used for the water + decane and water + toluene systems, respectively. The volumes of alcohol used were about two times those of the samples. The samplings were carried out at least 6 times.

The compositions of the samples were analyzed by gas chromatograph (GC) (GL Science Inc.) with a thermal conductivity detector. The GC column used was 2.0 m in length and 2.2 mm in diameter and was made of SUS316.

The details of the equilibrium cell are shown in Figure 2. The cell was made of hastelloy. The inside diameter and volume of the cell were 20 mm and 31 cm³, respectively. Gaskets (4 mm in thickness) made of graphite were used to avoid leakage. Mica thin plates (0.3 mm in thickness) were used to prevent the sapphire windows from touching the cell fluid directly. Copper thin plates (0.3 mm in thickness) and inconel plates (6 mm in thickness) were attached between the sapphire windows and plate springs made of inconel (5 mm in thickness \times 3 for each side) to provide uniform pressure to the sapphire windows.

Results and Discussion

Water + Decane System. In this work, the phase equilibria for the water + decane system were measured at 573.2 and 593.2 K for pressures up to 30.3 MPa. The results are listed in Table 1 and shown in Figure 3. The compositions listed in Table 1 were obtained from an arithmetic average of several measurements at each condition. The compositions of both phases were almost independent of the residential time. According to the classification of van Konynenburg and Scott,⁹ the phase behavior of the water + decane system belongs to type III. In type III, three phase equilibrium curves exist. The measurement range of this work exceeds the three-

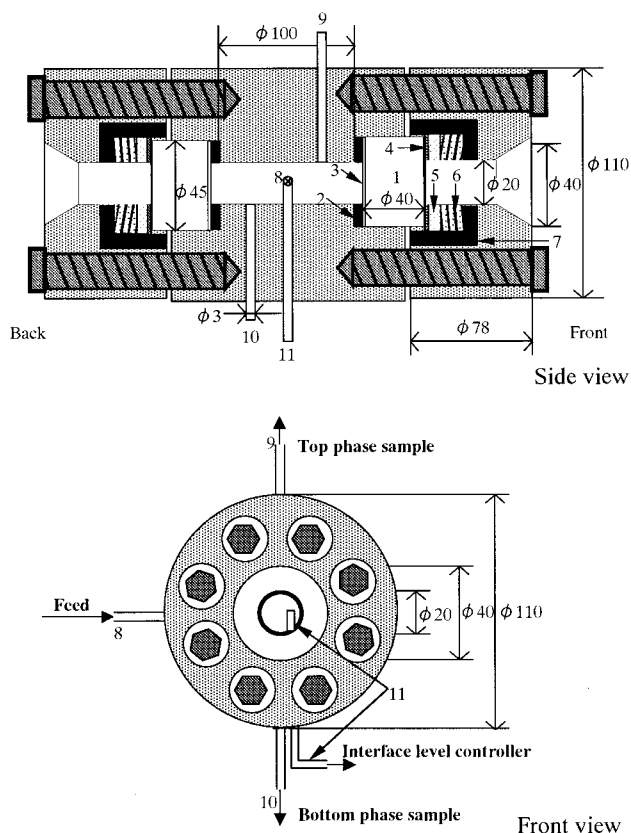


Figure 2. Details of the equilibrium cell: (1) sapphire window, (2) gasket, (3) mica plate, (4) copper plate, (5) inconel plate, (6) plate spring, (7) cap, (8) mixture fluid entrance tube, (9) top-phase exit tube, (10) bottom-phase exit tube, and (11) interface level control tube.

phase critical endpoint. Vapor-liquid equilibria (VLE) and liquid-liquid equilibria (LLE) may exist in the temperature range. In this work, LLE were measured. As shown in Figure 3, the data for the top phase

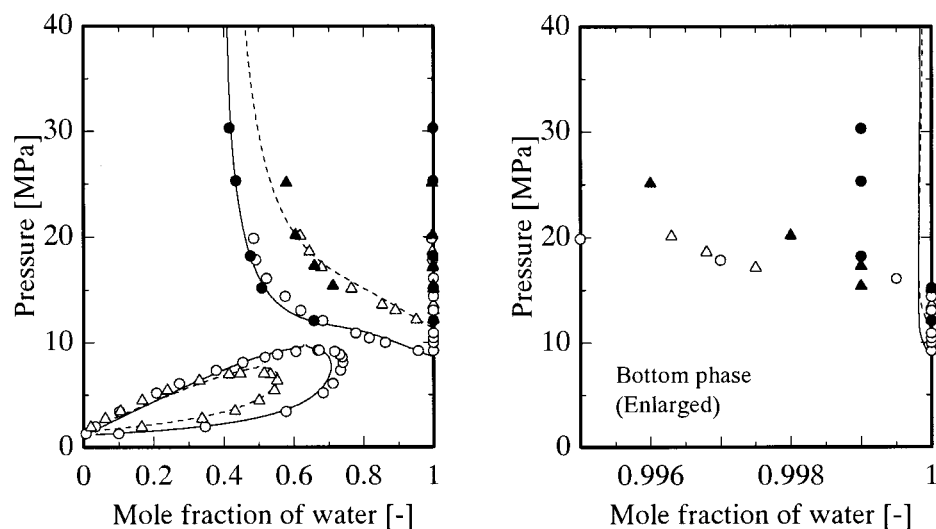


Figure 3. Phase equilibria of the water(1) + decane(2) system: (●, ▲), this work at (573.2, 593.2 K); (○, △), Wang and Chao³ at (573.2, 593.2 K); (—, - -), calculated results at (573.2, 593.2 K).

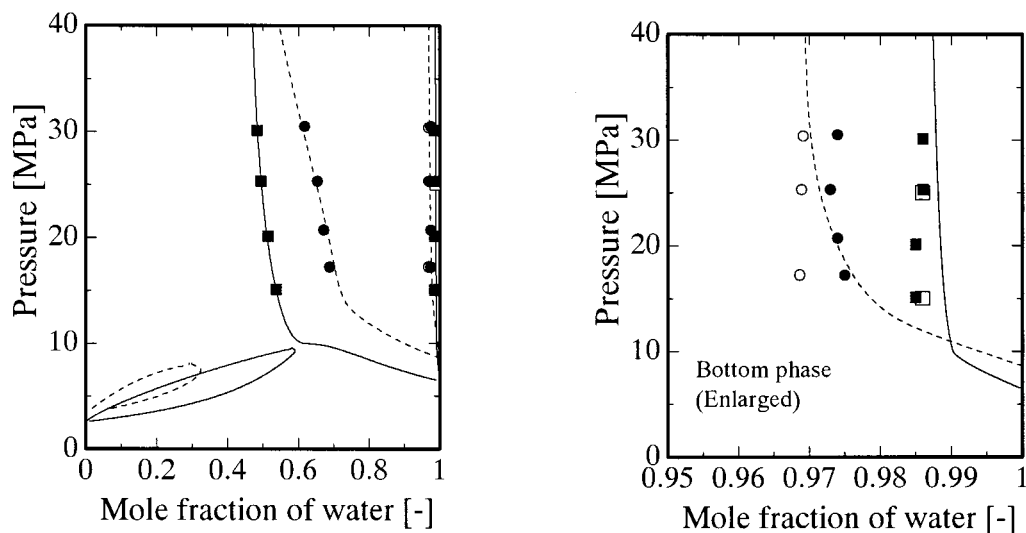


Figure 4. Phase equilibria of the water(1) + toluene(2) system: (■, ●), this work at (553.2, 573.2 K); (□, ○), Connolly¹² at (553.2, 573.2 K); (—, - -), calculated results at (553.2, 573.2 K).

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

<i>T</i> /K	<i>p</i> /MPa	bottom phase		top phase	
		<i>x</i> ₁	<i>S</i> ₁ ^a × 10 ³	<i>x</i> ₁	<i>S</i> ₁ ^a × 10 ³
573.2	12.1	1.0	0	0.657	19.7
	15.2	1.0	0	0.508	22.0
	18.2	0.999	0.3	0.476	11.7
	25.3	0.999	0.4	0.435	11.6
	30.3	0.999	0.3	0.417	12.3
593.2	15.4	0.999	0.4	0.712	2.5
	17.3	0.999	0.2	0.659	5.6
	20.2	0.998	0.5	0.605	9.4
	25.1	0.996	3.1	0.579	35.6

^a *S* = standard deviation of composition.

obtained are in good agreement with the literature data³ measured by a flow method. The measured mole fractions of water in the bottom phase are slightly higher than those of the literature data.

Water + Toluene System. The measurements were carried out at 553.2 and 573.2 K for the water + toluene system. The phase behavior of the water + toluene system belongs to type III, as does that of the water + decane system. The three-phase pressures for the

Table 2. Phase Equilibria for the Water(1) + Toluene(2) System

<i>T</i> /K	<i>p</i> /MPa	bottom phase		top phase	
		<i>x</i> ₁	<i>S</i> ₁ ^a × 10 ³	<i>x</i> ₁	<i>S</i> ₁ ^a × 10 ³
553.2	15.1	0.985	0.4	0.537	5.6
	20.1	0.985	1.1	0.515	3.8
	25.3	0.986	1.1	0.494	10.1
	30.1	0.986	0.8	0.483	8.2
573.2	17.2	0.975	0.8	0.688	9.6
	20.7	0.974	0.5	0.671	4.6
	25.3	0.973	1.7	0.654	6.5
	30.5	0.974	0.9	0.617	4.4

^a *S* = standard deviation of composition.

system were reported by Chandler et al.¹⁰ The three-phase endpoint of the water + toluene system is 558.2 K and 10.1 MPa.¹¹ Therefore, a three-phase equilibrium exists at 553.2 K, and both VLE and LLE regions can be observed at 573.2 K. The measurements of LLE at 553.2 K were carried out above the three-phase pressure. The phase equilibria in the LLE region were measured at 573.2 K. The results are listed in Table 2 and shown in Figure 4. The results for this system were also compared with the literature data¹² measured by

Table 3. Critical Properties and Parameters m and n in MSRK EOS⁷

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

a cloud-point method. The data of this work are in good agreement with the literature data at 553.2 K. However, slight deviations between the present data and the literature data are shown at 573.2 K.

Correlation

MSRK EOS and Exponent-Type Mixing Rule. The experimental results were correlated by the MSRK EOS.⁷ The EOS is given as follows:

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

where

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

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

and

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

The MSRK EOS is characterized by using eq 4 in order to calculate well the saturated vapor pressures of pure substances. The critical properties and the parameters m and n for water, decane, and toluene are listed in Table 3.

Water + hydrocarbon systems are nonideal mixtures because of the hydrogen bonding interactions of water. Therefore, an unsymmetrical mixing rule is needed to apply the EOS to the mixtures. In this work, an exponent-type mixing rule,⁸ characterized by an empirical exponent parameter, was applied for the energy parameter. The mixing rule and combining rule are given as follows:

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

The conventional mixing rule and combining rule given by the following equations were applied for the size parameter.

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

Results and Discussion

The performance of the cubic EOS for the calculation of the phase equilibria for water + hydrocarbon systems in the high-temperature and -pressure region was shown in a previous work.¹³ The parameters k_{12} , l_{12} , and β_{12} are adjusted to give precise fits to the experimental

Table 4. Interaction Parameters for Water(1) + Hydrocarbon(2) Systems

system	T/K	k_{12}	l_{12}	β_{12}
water(1) + decane(2)	573.2	0.48	0.36	1.93
	593.2	0.46	0.27	1.78
water(1) + toluene(2)	553.2	0.38	0.28	1.30
	573.2	0.34	0.24	1.58

data and the following expressions are assumed for simplicity:¹³

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

The VLE and LLE data for the water + decane system at 573.2 and 593.2 K were correlated. The literature data³ in the VLE region were cited. In the LLE region, only the present data were used to obtain optimum parameters. The correlation results are shown in Table 4 and Figure 3. Good agreement is obtained by adjusting the parameters. However, the solubilities of decane in water are so small that deviations between the calculated results and the experimental data still remain in water-rich phase.

The data for the water + toluene system measured in this work were correlated at 553.2 and 573.2 K. The results are shown in Figure 4 with good agreement. The values of the adjustable parameters are listed in Table 4.

The optimum parameters were determined with the data in the high-pressure region at 553.2 K, which is far from the three-phase pressure. In addition, the temperature is only 5 K lower than the three-phase endpoint. The calculated three-phase endpoint is slightly different from the literature data. Therefore, the three-phase coexistence does not appear at 553.2 K according to the calculation.

As shown in Table 4, the values of the parameter β_{12} are larger than unity. The parameter β_{12} is the exponent of the composition of water in eq 5. The results seem to imply that the effective mole fraction of water is reduced because of the self-association of water.

Conclusions

In this work, an experimental apparatus based on a flow method was constructed to measure the phase equilibria for water + hydrocarbon systems in the high-temperature and -pressure region. Phase equilibria for the water + decane and the water + toluene systems were measured to confirm the validity of the apparatus and technique. Moreover, new data were added in the high-pressure region for the water + decane system. Data for the toluene-rich phase were accumulated for the water + toluene system. The phase equilibria of the water + decane system at 573.2 and 593.2 K and of the water + toluene system at 553.2 and 573.2 K were correlated by the MSRK EOS with an exponent-type mixing rule, and good correlation results are obtained.

Acknowledgment

We gratefully acknowledge the financial support provided by "Research for the Future" Program (96P00401), The Japan Society for the Promotion of Science.

Nomenclature

a = energy parameter of the EOS, Pa m⁶ mol⁻²
 b = size parameter of the EOS, m³ mol⁻¹

k = interaction energy parameter
 l = interaction size parameter
 m, n = parameters in eq 4
 p = pressure, Pa
 R = gas constant, $\text{m}^3 \text{Pa mol}^{-1} \text{K}^{-1}$
 S = standard deviation
 T = temperature, K
 v = molar volume, $\text{m}^3 \text{mol}^{-1}$
 x = mole fraction
 β = exponential parameter

Subscripts

c = critical property
 i, j = components i, j
 r = reduced property

Literature Cited

- (1) Rebert, C. J.; Kay, W. B. The Phase Behavior and Solubility Relations of the Benzene–Water System. *AIChE J.* **1959**, *5*, 285.
- (2) de Loos, T. W.; Penders, W. G.; Lichtenthaler, R. N. Phase Equilibria and Critical Phenomena in Fluid (*n*-Hexane + Water) at High Pressures and Temperatures. *J. Chem. Thermodyn.* **1982**, *14*, 83.
- (3) Wang, Q.; Chao, K. C. Vapor–Liquid and Liquid–Liquid Equilibria and Critical States of Water + *n*-Decane Mixtures. *Fluid Phase Equilib.* **1990**, *59*, 207.
- (4) Stevenson, R. L.; LaBracio, D. S.; Beaton, T. A.; Thies, M. C. Fluid Phase Equilibria and Critical Phenomena for the Dodecane–Water and Squalane–Water Systems at Elevated Temperatures and Pressures. *Fluid Phase Equilib.* **1994**, *93*, 317.
- (5) Rebert, C. J.; Hayworth, K. E. The Gas and Liquid Solubility Relations in Hydrocarbon–Water Systems. *AIChE J.* **1967**, *13*, 118.
- (6) Brunner, E. Fluid Mixture at High Pressures. IX. Phase Separation and Critical Phenomena in 23 (*n*-Alkane + Water) Mixtures. *J. Chem. Thermodyn.* **1990**, *22*, 335.
- (7) Sandarusi, J. A.; Kidnay, A. J.; Yesavage, V. F. Compilation of Parameters for a Polar Fluid Soave–Redlich–Kwong Equation of State. *Ind. Eng. Chem. Process Des. Dev.* **1986**, *25*, 957.
- (8) Higashi, H.; Furuya, T.; Ishidao, T.; Iwai, Y.; Arai, Y. An Exponent-Type Mixing Rule for Energy Parameters. *J. Chem. Eng. Jpn.* **1994**, *27*, 677.
- (9) van Konynenburg, P. H.; Scott, R. L. Critical Lines and Phase Equilibria in Binary van der Waals Mixtures. *Philos. Trans. R. Soc. London, Ser. A* **1980**, *298*, 495.
- (10) Chandler, K.; Eason B.; Liotta, C. L.; Eckert, C. A. Phase Equilibria for Binary Aqueous Systems from a Near-Critical Water Reaction Apparatus. *Ind. Eng. Chem. Res.* **1998**, *37*, 3515.
- (11) Roof, J. G. Three-Phase Critical Point in Hydrocarbon–Water Systems. *J. Chem. Eng. Data* **1970**, *15*, 301.
- (12) Connolly, J. F. Solubility of Hydrocarbons in Water Near the Critical Solution Temperatures. *J. Chem. Eng. Data* **1966**, *11*, 13.
- (13) Haruki, M.; Yahiro, Y.; Higashi, H.; Iwai, Y.; Arai, Y. Correlation of Phase Equilibria for Water + Hydrocarbon Systems at High Temperatures and Pressures by Cubic Equation of State. *J. Chem. Eng. Jpn.* **1999**, *32*, 535.

Received for review February 4, 2000

Revised manuscript received June 23, 2000

Accepted June 23, 2000

IE000185I