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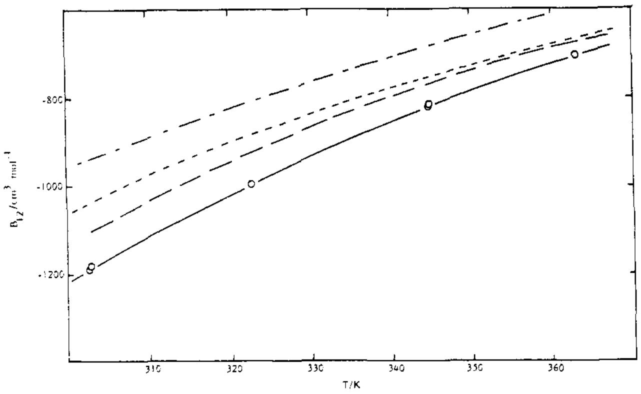

Figure 3. Unlike-interaction second virial coefficient for methyl acetate + diethyl ether: (- - -) Hayden and O'Connell (*5*); (- -) Hayden and O'Connell using T^c_{12}; (—) Tsonopoulos (*6*); (O) this work.

Second Virial Coefficients. In Tables III and IV, the results obtained and the prediction of the two correlations are tabulated.

Attempting to predict ϵ_{12} values is a demanding test of correlating functions for second virial coefficients and, as illustrated in Figure 1, neither equation is particularly successful.

Prediction of B_{12} is what the equations were devised to do, but again, as evidenced in Figure 3, neither provides a satisfactory representation of the data obtained. As has been observed for other systems (*1*), the Hayden and O'Connell correlation is improved by incorporating the independent T^c_{12} value but not sufficiently. The Tsonopoulos equation is only marginally better.

Notation

B_{11},B_{22}	pure-substance second virial coefficients
B_{12}	unlike-interaction second virial coefficient
ϵ_{12}	excess second virial coefficient
P	pressure
ΔP	pressure change of mixing
T	temperature
T^c_{11},T^c_{22}	pure-substance critical temperatures
T^c_{12}	unlike-interaction critical temperature
T^c_m	mixture critical temperature
y	mole fraction
V^c_{ii}	critical volume
V^c_{ij}	unlike-interaction critical volume
ω	accentric factor
P^c	critical pressure

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Received for review October 6, 1989. Accepted May 14, 1990.

Vapor Pressures of the Water-Lithium Bromide-Lithium Iodide System

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The vapor pressures of the water-lithium bromide-lithium iodide system (salt mole ratio 4:1) were measured in the range of temperatures from 280.85 to 383.05 K and in the range of absorbent concentrations from 10.0 to 64.5 wt %. The vapor pressure measurements were made with separate experimental apparatuses by a boiling point method for pressure above 2800 Pa and a static method for pressure below 2800 Pa. The experimental data measured with two experimental apparatuses were separately correlated by means of two Antoine-type equations. The calculated values from these equations were in good agreement with the experimental data.

Introduction

The vapor pressure data for the working medium-absorbent system are one of the important properties for the research and the design of absorption refrigerating machines, absorption heat pumps, and absorption heat transformers. The vapor pressures of the water-lithium bromide-lithium iodide system (salt mole ratio 4:1) were measured with separate experimental apparatuses by a boiling point method and a static method at various temperatures and absorbent concentrations. The vapor pressure measurements above 2800 Pa were made with the usual experimental apparatus (*1*) used for a boiling point method. It is difficult to measure low vapor pressure below 2800 Pa with the usual experimental apparatus used for a boiling point method. Therefore, the vapor pressure measurements below 2800 Pa were made with a special apparatus devised for low-pressure measurements (*2*) by a static method. Accurate vapor pressure data for the working medium-absorbent system at low temperatures are particularly important for the design of the absorber. The experimental data measured with two experimental apparatuses were separately correlated by means of two Antoine-type equations.

Experimental Section

Materials. The lithium bromide and lithium iodide used in this work were from the Honjo Chemical Co., Ltd., analytical reagent

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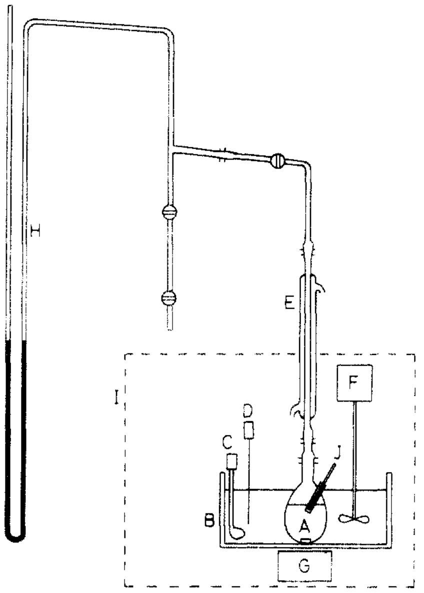

Figure 1. Experimental apparatus 1 for measurements of vapor pressure above 2800 Pa: A, sample vessel; B, constant-temperature bath; C, heater; D, temperature controller; E, condenser; F, stirrer; G, magnetic stirrer; H, U-tube manometer; I, air bath; J, standard thermometer.

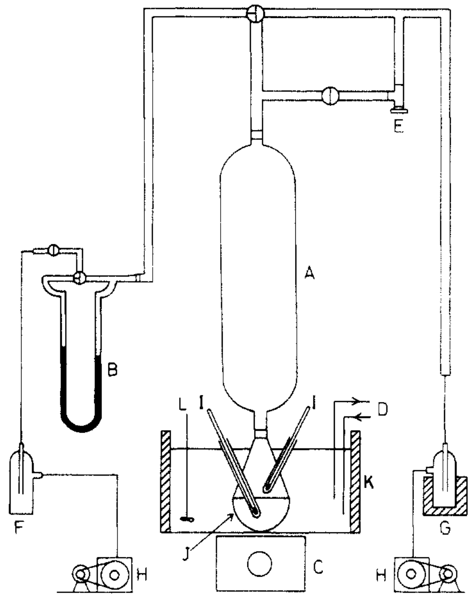

Figure 2. Experimental apparatus 2 for measurements of vapor pressure below 2800 Pa: A, buffer tank; B, U-tube manometer; C, magnetic stirrer; D, coolant; E, needle valve; F, trap; G, cold trap; H, vacuum pump; I, standard thermometer; J, sample vessel; K, constant-temperature bath; L, stirrer.

grade. The analytical results of the lithium bromide aqueous solution were as follows: concentration, 55.0 wt %; Ca, 0.0002 wt %; Mg, 0.00002 wt %; Cl, 0.01 wt %; SO_4, 0.01 wt %. The analytical results of the lithium iodide aqueous solution were as follows: concentration, 56.2 wt %; Ca, 0.0023 wt %; Fe, 0.0001 wt %; SO_4, 0.012 wt %. The *n*-butyl alcohol used in this work was from the Wako Pure Chemical Industries, Ltd., analytical reagent with a minimum purity of 99.8 wt %. The major impurity of *n*-butyl alcohol was water. All the reagents were used without further purification. The absorbent concentrations of the lithium bromide–lithium iodide aqueous solutions were determined by the Fajans method (*3*) with use of dichlorofluorescein as an adsorption indicator. The solution was titrated by using a microburet of 10-mL total delivery, with divisions of 0.02 mL.

The optimum mixing ratio of lithium bromide and lithium iodide was determined by measuring the crystallization temperature of sample solutions at constant absorbent concentration. Crystallization temperatures were obtained by changing the mixing ratio of lithium bromide in 1 mol of lithium iodide aqueous solutions. Consequently, the most suitable mixing ratio of lithium bromide and lithium iodide was found to be 4 and 1 mol, respectively (*4*).

Apparatus and Procedure. The schematic diagram of experimental apparatus 1 used for vapor pressure measurements above 2800 Pa of lithium bromide–lithium iodide aqueous solutions is shown in Figure 1. It consists primarily of a sample vessel with a volume of about 500 cm^3, a constant temperature bath, a heater, a temperature controller, two stirrers, a U-tube manometer, and an air bath. The equilibrium still was made of Pyrex glass. The four glass pieces were connected by ground-glass joints sealed with Dow Corning high-vacuum grease. The constant-temperature bath was maintained to within ±0.01 K. The temperature inside the sample vessel was measured by using a standard thermometer. The vapor pressure was measured with a mercury U-tube manometer. The pressure differences were read to 0.05 mm with a cathetometer.

A sample solution (250 cm^3) at various absorbent concentrations was placed in the sample vessel, and it was stirred well with a magnetic stirrer to prevent superheating. After thermal equilibrium was reached, the temperature of the sample solution and the pressure in the apparatus were measured. The absorbent concentration of the sample solution was analyzed after the vapor pressure measurements.

The vapor pressure measurements at various temperatures were also made on pure water to examine the accuracy of the experimental apparatus and procedure. The results agreed well with literature values (*5*), with a maximum deviation of less than 0.3%.

The vapor pressures of lithium bromide–lithium iodide aqueous solutions at low temperatures were measured with an apparatus similar to that devised by Matsuda et al. (*2*) for low-pressure measurements. The schematic diagram of experimental apparatus 2 used for vapor pressure measurements below 2800 Pa of this system is shown in Figure 2. It consists primarily of a sample vessel with a volume of about 500 cm^3, a buffer tank with a volume of about 5000 cm^3, a constant-temperature bath, two traps, two vacuum pumps, and a U-tube manometer. The volume of the buffer tank was determined as follows (*2*):

$$V = v\theta/bp_{\min} = (6.7 \times 1800)/(0.03 \times 67) = 6000 \text{ cm}^3 \quad (1)$$

where V is the volume of the apparatus (cm^3), v is the volumetric air-flow rate leaked on the vacuum side in the apparatus (6.7 cm^3 Pa s^{-1}), θ is the time of the measurement (1800 s), b is the allowable pressure elevation (3%), and $p_{\min}$ is the minimum pressure of the measurement (67 Pa). Therefore, the volume (5000 cm^3) of the buffer tank was determined by considering the volume of the sample vessel and the connecting glass tube. The equilibrium still was made of Pyrex glass. The equilibrium still consists of four glass sections: a sample vessel, a buffer tank, a T-shaped piece, and a U-tube manometer. The four glass pieces were connected by ground-glass joints sealed with Dow Corning high-vacuum grease. The constant-temperature bath was maintained to within ±0.01 K. The temperature inside the sample vessel was measured with a standard thermometer. The measurements of pressure were carried out with a U-tube manometer. The manometer liquids were mercury and isobutyl phthalate with a density of 1034 kg m^{-3} at 313.15 K. Pressures below 666 Pa were read with a isobutyl phthalate U-tube manometer, and readings above 666

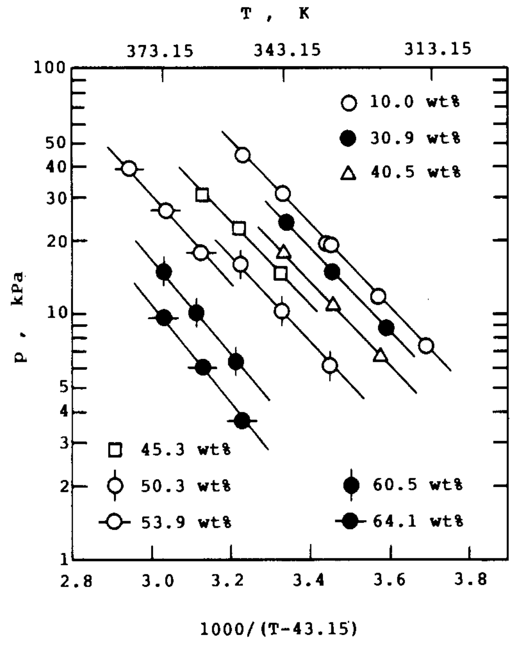

Figure 3. Vapor pressures of the H_2O–LiBr–LiI system measured with experimental apparatus 1.

Pa were made with a mercury U-tube manometer. The heights of the mercury and isobutyl phthalate meniscuses in the manometer limbs were measured by means of a cathetometer fitted with a vernier scale, capable of readings to 0.01 mm.

A sample solution (250 cm^3) at various absorbent concentrations was placed in the sample vessel, and the extraneous gases in the apparatus were then removed with a vacuum pump. The sample solution was stirred well with a magnetic stirrer to prevent superheating. After thermal equilibrium was reached, the temperature of the sample solution and the pressure in the apparatus were measured. The temperatures and pressures were measured three times at 5-min intervals for each data point to verify the reproducibility of the apparatus. Absorbent concentration of the sample solution was analyzed after the vapor pressure measurements.

The vapor pressure measurements at various temperatures were also made on pure water and *n*-butyl alcohol to examine the accuracy of the experimental apparatus and procedure. The results agreed well with literature values (*5*, *6*) with an average absolute deviation of less than 0.60%.

Results and Discussion

The vapor pressures above 2800 Pa of lithium bromide–lithium iodide aqueous solutions were measured with experimental apparatus 1 by a boiling point method in the range of temperatures from 313.45 to 383.05 K and in the range of absorbent concentrations from 10.0 to 64.1 wt %. The vapor pressures below 2800 Pa of this system were also measured with experimental apparatus 2 by a static method in the range of temperatures from 280.85 to 343.15 K and in the range of absorbent concentrations from 47.7 to 64.5 wt %. The experimental results of this system at various temperatures and absorbent concentrations are shown in Tables I and II. These experimental data were used to determine the constants for the empirical formulas by using a least-squares method. A part of the experimental results measured with experimental apparatus 1 are plotted in the form of log *p* vs 1000/(T − 43.15) in Figure 3. The experimental results measured with experimental apparatus 2 are plotted in Figure 4. In these figures, the log *p* vs 1000/(T − 43.15) relationships for the absorbent concentration over the temperature and pressure measured were linear. The experimental data measured with experimental apparatuses 1 and 2 were separately correlated by means of Antoine-type eqs 2 and 3, which express vapor pressure as a

$$\log p = \sum_{n=0}^{6} \{A_n + [1000B_n/(T - 43.15)]\}X^n \qquad (2)$$

$$\log p = \sum_{n=0}^{4} \{A_n + [1000B_n/(T - 43.15)]\}X^n \qquad (3)$$

function of temperature and absorbent concentraion and where p is the vapor pressure (Pa), T is the absolute temperature (K), and X is absorbent concentration (wt %). Values of the constants A_n and B_n in eqs 2 and 3 are given in Tables III and IV. Maximum and average absolute deviations between the experimental data in Table I and the calculated values from eq 2 were −1.02% and 0.50%, respectively. Maximum and average absolute deviations between the experimental data in

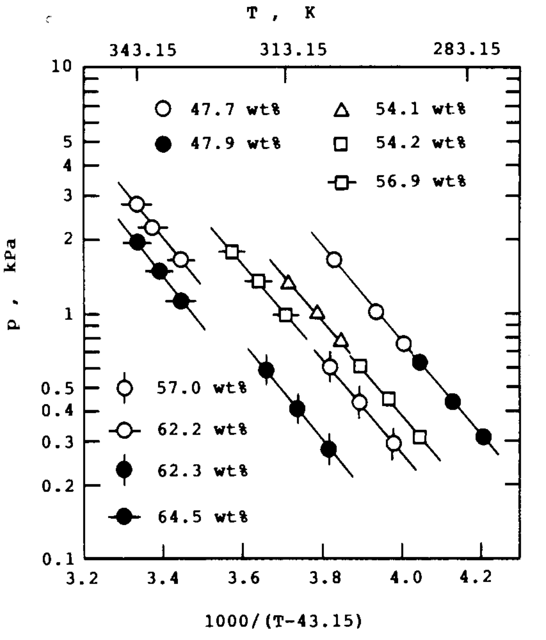

Figure 4. Vapor pressures of the H_2O–LiBr–LiI system measured with experimental apparatus 2.

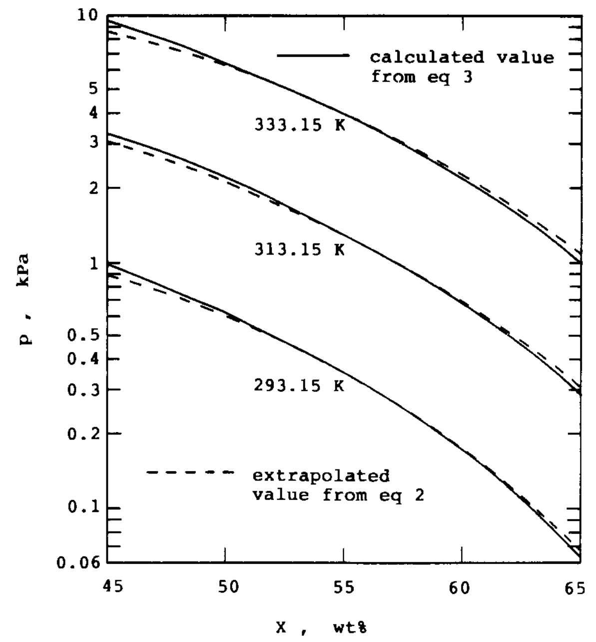

Figure 5. Comparison of vapor pressures for the H_2O–LiBr–LiI system at 293.15, 313.15, and 333.15 K.

Table I. Vapor Pressures of the H_2O–LiBr–LiI System Measured with Experimental Apparatus 1

T, K	p_{exp}, kPa	p_{cal}, kPa	ϵ, %
	10.0 wt %		
314.15	7.38	7.44	-0.81
323.35	11.82	11.93	-0.93
333.05	19.02	19.00	0.11
333.55	19.28	19.45	-0.89
343.85	30.51	30.79	-0.92
352.85	44.50	44.87	-0.83
	19.1 wt %		
313.45	6.60	6.60	0
323.15	10.95	10.91	0.37
333.05	17.63	17.60	0.17
	20.0 wt %		
322.75	10.61	10.60	0.09
332.95	17.38	17.37	0.06
343.25	27.70	27.64	0.22
	30.8 wt %		
343.35	23.94	23.98	-0.17
352.95	35.99	36.12	-0.36
362.55	53.02	53.08	-0.11
	30.9 wt %		
321.85	8.64	8.63	0.12
332.75	14.68	14.75	-0.48
342.95	23.42	23.51	-0.38
	40.5 wt %		
323.05	6.68	6.66	0.30
332.85	10.92	10.88	0.37
343.35	17.76	17.77	-0.06
	45.3 wt %		
343.95	14.42	14.30	0.83
353.95	22.41	22.26	0.67
363.05	32.68	32.50	0.55
	50.3 wt %		
333.25	6.07	6.05	0.33
343.85	10.19	10.14	0.49
353.75	15.99	15.91	0.50
	51.5 wt %		
343.65	9.13	9.12	0.11
353.65	14.32	14.44	-0.84
364.35	22.86	22.86	0
	53.9 wt %		
363.35	17.89	18.07	-1.01
372.75	26.42	26.65	-0.87
383.05	39.39	39.79	-1.02
	60.5 wt %		
354.65	6.35	6.30	0.79
364.55	10.08	9.99	0.89
373.35	14.82	14.71	0.74
	64.1 wt %		
353.05	3.67	3.70	-0.82
362.85	6.06	6.02	0.66
373.15	9.67	9.72	-0.52

Table II and the calculated values from eq 3 were 2.59% and 1.02%, respectively.

Table II. Vapor Pressures of the H_2O–LiBr–LiI System Measured with Experimental Apparatus 2

T, K	p_{exp}, Pa	p_{cal}, Pa	ϵ, %
	47.7 wt %		
292.75	750	752	-0.27
297.45	1022	1023	-0.10
304.65	1606	1607	-0.06
	47.9 wt %		
280.85	315	319	-1.27
285.35	439	442	-0.68
290.35	631	627	0.63
	54.1 wt %		
303.15	773	753	2.59
307.45	1014	989	2.47
312.25	1338	1327	0.82
	54.2 wt %		
290.55	316	317	-0.32
295.35	443	443	0
300.05	607	608	-0.16
	56.9 wt %		
312.75	982	986	-0.41
317.95	1352	1349	0.22
322.95	1780	1802	-1.24
	57.0 wt %		
294.55	295	294	0.34
300.05	433	430	0.69
305.05	609	599	1.64
	62.2 wt %		
333.35	1641	1613	1.71
339.75	2263	2294	-1.37
343.15	2765	2749	0.58
	62.3 wt %		
305.35	280	277	1.07
310.85	411	402	2.19
316.45	589	578	1.87
	64.5 wt %		
333.45	1138	1117	1.85
338.05	1480	1454	1.76
343.15	1953	1930	1.18

Table III. Values of A_n and B_n in Equation 2

n	A_n	B_n
0	10.11413	-1.68571
1	9.48411×10^{-5}	2.86650×10^{-4}
2	1.88232×10^{-5}	-1.66734×10^{-4}
3	-4.44823×10^{-6}	1.06604×10^{-5}
4	3.01686×10^{-7}	-3.48593×10^{-7}
5	-7.70012×10^{-9}	5.09598×10^{-9}
6	6.73478×10^{-11}	-3.20049×10^{-11}

Table IV. Values of A_n and B_n in Equation 3

n	A_n	B_n
0	11.23260	-6.99580
1	-2.14457×10^{-1}	4.52919×10^{-1}
2	1.02083×10^{-2}	-1.42931×10^{-2}
3	-1.86969×10^{-4}	1.98091×10^{-4}
4	1.19595×10^{-6}	-1.04250×10^{-6}

The vapor pressures of this system measured with experimental apparatus 2 were compared with the extrapolated values from eq 2 at 293.15, 313.15, and 333.15 K. The results are shown in Figure 5. The solid and broken lines indicate the calculated values from eq 3 and the extrapolated values from eq 2, respectively. The deviations between the calculated values and the extrapolated values were large, especially except for absorbent concentrations from 50 to 60 wt %. The deviations for 293.15, 313.15, and 333.15 K at 45 wt % were 10.1%, 9.3%, and 8.5%, respectively. The deviations for those at 65 wt % were 5.8%, 6.6%, and 7.3%, respectively. Therefore, we separately correlated the data by means of two Antoine-type equations, because the experimental data measured with experimental apparatuses 1 and 2 are difficult to correlate by means of a single equation.

Conclusions

The vapor pressures of lithium bromide–lithium iodide aqueous solutions were measured with two experimental apparatuses at various temperatures and absorbent concentrations. The experimental data measured with experimental apparatuses 1 and 2 were separately correlated by means of two Antoine-type equations. The calculated values from these equations were in good agreement with the experimental data. The vapor pressure data of this system are available for the design of absorption refrigerating machines, absorption heat pumps, and absorption heat transformers. The vapor pressure data measured at low temperatures are particularly useful for the design of the absorber.

Glossary

A_n,B_n	constants in eqs 2 and 3
b	allowable pressure elevation in experimental apparatus 2, %
n	integer exponent in eqs 2 and 3
p	vapor pressure, Pa
T	absolute temperature, K
V	volume of experimental apparatus 2, cm^3
v	volumetric air-flow rate leaked on the vacuum side in experimental apparatus 2, cm^3 Pa s^{-1}
X	absorbent concentration, wt %

Greek Letters

ϵ	deviation, %
θ	time of measurement in experimental apparatus 2, s

Subscripts

cal	calculated value from eqs 2 and 3
exp	experimental data
min	minimum pressure of measurement in experimental apparatus 2

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Received for review October 24, 1989. Accepted June 11, 1990. We gratefully acknowledge the support for this research by the Yazaki Memorial Foundation for Science and Technology.

Liquid-Liquid Equilibria for the Ternary System Water-Acetone-Isooctane

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Liquid-liquid equilibrium data for the ternary system water-acetone-isooctane were measured at 283, 293, 303, and 313 K. The experimental data were correlated by the UNIQUAC model. The reliability of the experimental data was ascertained by the Ishida correlation.

Introduction

Liquid-liquid equilibrium (LLE) data are an essential element in the design of equipment for liquid extraction. Although a large volume of LLE data exists in the literature, it did not receive much attention in terms of theoretical interpretation until the mid-seventies. Much interest has been generated in this area since Sorensen (*1*, *2*) made a systematic study of the published LLE data and correlated these data using the UNIQUAC and NRTL models. The purpose of this study was to generate additional data for the water-acetone-alkane series to aid in the correlation and prediction of liquid-liquid equilibria. LLE data for the ternary system water-acetone-isooctane (2,2,4-trimethylpentane) were measured at 283, 293, 303, and 313 K, at atmospheric pressure, and were correlated by using the UNIQUAC model.

Experimental Section

Materials. All materials used in this study were obtained from Fisher Scientific. Acetone and water were HPLC grades, and isooctane was Fisher's Optima grade. Although all materials had a stated minimum purity of 99.5 wt %, the purities of water and isooctane were determined by chromatographic analysis to be greater than 99.9 wt %, and these chemicals were used directly without any further purification. The major impurity in the acetone was water (0.5 wt %), which was removed by freshly activated Union Carbide Type 4A molecular sieve.

Procedure. The experimental work was carried out by using Supelco sample bottles sealed with Teflon-lined septum caps. Sampling of the lower phase was accomplished through the use of a glass capillary tube, inserted through the cap and extending to near the bottom of the bottle. A Forma Scientific constant-temperature bath, with a range of 253-343 K, maintained the samples at a constant temperature ±0.02 K. The samples were mixed with an air-driven magnetic stirrer and a Teflon-coated stirring bar. After equilibrium was attained, the two phases were allowed to separate and settle for a minumum of 22 h. Samples of both phases were taken using Hamilton Gastight 1701 syringes. The sample analysis was performed using a Hewlett-Packard 5890A gas chromatograph equipped with a single-channel thermal conductivity detector and a Spectra-Physics SP4270 electronic integrator. The sample size was 2 μL. In all cases, an 8 ft × $^{1}/_{8}$ in. Hayesep Q column was used. The injector and detector temperatures were maintained at 423 and 540 K, respectively. The column temperature was programmed for an initial temperature of 448 K and a final temperature of 535 K. The heating rate was 35 K/min, and the flow rate of helium carrier gas was 60 mL/min. Calibration analyses were performed to convert the peak area ratio to the weight composition of the sample. The gas chro-

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