Liquid-Liquid Extraction of Ethanol from Aqueous Solutions with Amyl Acetate, Benzyl Alcohol, and Methyl Isobutyl Ketone at 298.15 K

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Experimental mutual solubility and tie-line data were determined for three ternary liquid-liquid systems containing water, ethanol, and (i) amyl acetate, (ii) benzyl alcohol, and (iii) methyl isobutyl ketone at 298.15 K in order to obtain their complete phase diagrams and to determine which is the most suitable solvent for extraction of ethanol from aqueous solutions. Tie lines were determined correlating the density of the binodal curve as a function of composition and the plait points using the Othmer and Tobias method. The experimental data were also correlated with the UNIFAC group contribution method. A qualitative agreement was obtained. Experimental results showed that amyl acetate is a better solvent than methyl isobutyl ketone and benzyl alcohol.

The development of any liquid extraction process and the design of the corresponding equipment require the knowledge of the phase equilibrium data. Moreover, the experimental measurements of these equilibrium data can be used to estimate new interaction parameters involved in several group contribution methods, such as the UNIFAC.

The traditional ethanol fermentation process leads to the production of diluted alcohol solutions which can be processed by liquid-liquid extraction to obtain enriched alcoholic mixtures and, in this way, to gain an important reduction of energy consumption in the overall process.

Esters, alcohols, and ketones are among the most suitable solvents (*1*, *2*) for extraction of ethanol. Keeping this fact in mind, three ternary liquid-liquid systems—(i) water-ethanol-amyl acetate (AA), (ii) water-ethanol-benzyl alcohol (BA), and (iii) water-ethanol-methyl isobutyl ketone (MIK)—were studied at 298.15 K in order to obtain their complete phase diagrams and to determine which is the most suitable solvent for extraction of ethanol from aqueous solutions.

The binodal curves were calculated by using the UNIFAC group contribution method (*3*) and the liquid-liquid equilibrium (LLE) interaction parameters reported by Magnussen, Rasmussen, and Fredenslund (*4*). A computer program (termed LLECAL) has been operated by using the manual provided by Magnussen (*5*).

Several tie lines were determined for each system. The correlation of mutual solubility with tie-line data (Othmer and Tobias' method) permitted the estimation of the plait point coordinates.

Experimental Section

All chemicals were from Merck (analytical reagent grade). Absolute ethanol was obtained by the following procedure (*6*): 0.5 g of iodine, 5 g of magnesium and 50-70 mL of anhydrous ethanol were warmed until the iodine disappeared. If vigorous evolution of hydrogen did not occur, an additional 0.5-g portion of iodine was added and the mixture heated until all magnesium has been converted into ethylate. Then, 900 mL of anhydrous ethanol was added and the mixture boiled for half an hour under reflux. The product was fractionally distilled and the middle fraction collected. The last traces of water were removed by passing the ethanol through a glass column (3 × 200 cm), packed with 0.3-nm molecular sieves. Benzyl alcohol was purified by a similar procedure. Methyl isobutyl ketone was dried over anhydrous K_2CO_3 and fractionally distilled under nitrogen atmosphere, and the middle fraction was collected. Amyl acetate was purified similarly to methyl isobutyl ketone.

All organic purified chemicals were conserved over activated molecular sieves to prevent water absorption. Water was bidistilled in an all-glass apparatus.

Procedures. Ternary liquid-liquid equilibrium data were determined by stirring weighted water-solvent mixtures in an equilibrium cell equipped with magnetic stirring and a jacket for circulation of the isothermal fluid (25 ± 0.05 °C). The third component was added from a microburet until transition from turbidity to a clear solution was observed. In this way, the central portions of the binodal curves were obtained. Taking into account that the accuracy with which the transition point can be observed is better as the angle between the tangent to the binodal curve in the transition point and the line passing through the composition of the binary system is nearer to a right angle, water-ethanol and ethanol-solvent mixtures were titrated with the remaining component to obtain the end portions of the binodal curves.

The quantities of the third component were determined by weighing the mixture after the transition point was reached.

The uncertainty in the observed values was determined by the accuracy of the observation of the transition point, since the quantities of titrating component and titrated mixtures were accurately determined by weighing. The uncertainty through the whole curve was less than 0.05 weight fraction % ethanol for all systems.

After equilibrium was reached, the densities of the ternary mixtures were measured with a vibrating tube densimeter Anton Paar DMA 46 at 25 ± 0.01 °C with an accuracy of ±0.1 kg m^{-3}, and with these values a calibrating curve density vs weight fraction of ethanol was drawn.

For determination of tie-line data, different weighted ternary mixtures with compositions within the heterogeneous region were shaken vigorously in the equilibrium cell for at least 2 h at constant temperature. Then, the magnetic stirrer was turned off and samples of each phase were taken off. Samples were analyzed by measuring their densities, and the compositions were obtained with the aid of the calibrating curve. In this way, the two end points of a tie line were obtained. An independent material-balance checking was provided by the fact that the

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Table I. Physical Properties of Pure Components at 298.15 K

chemicals	density, kg m^{-3} exptl	density, kg m^{-3} lit.	refractive index (n_D) exptl[a]	refractive index (n_D) lit.
water	997.0	997.07 (*7*)	1.332 85	1.332 87 (*7*)
ethanol	785.1	785.06 (*6*)	1.359 39	1.359 41 (*6*)
AA	868.6	870.7 (*6*)	1.400 13	1.400 (*7*)
MIK	796.3	796.1 (*6*)	1.393 60	1.393 30 (*6*)
BA	1041.2	1041.27 (*6*)	1.537 14	1.537 1 (*6*)

[a] Measured with a Jena dipping refractometer with an accuracy of ±0.000 02.

Table II. Binodal Curve Data for Water (1)–Ethanol (2)–AA (3) System at 298.15 K

water-rich layer			AA-rich layer		
W_{11}%	W_{21}%	W_{31}%	W_{13}%	W_{23}%	W_{33}%
99.78	0.00	0.22	38.59	38.77	22.64
94.60	5.00	0.40	36.32	38.80	24.88
89.23	10.17	0.60	33.91	38.50	27.59
84.10	15.10	0.80	30.18	37.44	32.38
78.96	20.07	0.97	23.61	35.56	40.83
74.17	24.71	1.12	19.60	34.33	46.07
68.85	29.59	1.56	16.53	32.32	51.15
62.17	34.24	3.59	11.60	26.46	61.88
56.50	36.99	6.51	8.82	22.71	68.47
46.94	38.91	14.15	6.99	19.93	73.08
43.12	39.36	17.52	4.67	14.68	80.65
40.06[a]	39.12[a]	20.82[a]	3.00	10.00	87.00
			1.68	5.90	93.42
			1.20	0.00	98.80

[a] Estimated PP by Othmer and Tobias' method.

Table III. Binodal Curve Data for Water (1)–Ethanol (2)–MIK (3) System at 298.15 K

water-rich layer			MIK-rich layer		
W_{11}%	W_{21}%	W_{31}%	W_{13}%	W_{23}%	W_{33}%
98.24	0.00	1.76	46.65[a]	30.57[a]	22.78[a]
96.76	1.29	1.93	42.80	30.60	26.60
95.50	2.49	1.99	38.20	30.80	31.00
93.00	4.96	2.04	31.00	30.00	39.00
90.40	7.52	2.08	25.00	29.00	46.00
87.80	9.95	2.25	20.00	27.00	53.00
82.53	14.83	2.64	17.60	25.00	57.40
81.20	16.02	2.78	15.35	23.00	61.65
79.50	17.51	2.99	13.45	21.00	65.55
76.30	20.09	3.61	11.98	19.00	69.02
73.50	22.50	4.00	10.40	17.00	72.60
70.90	23.99	5.11	8.48	13.81	77.69
69.30	25.00	5.70	6.08	9.48	84.43
67.50	26.04	6.40	5.46	7.46	87.08
63.90	27.51	8.59	4.32	4.75	90.92
58.45	28.98	12.56	3.29	1.91	94.78
54.03	29.97	16.00	1.74	0.00	98.26
49.45	30.40	20.15			

[a] Estimated PP by Othmer and Tobias' method.

overall composition of an equilibrium mixture must lie on the straight line joining the equilibrium layers.

Results

The physical properties of chemicals are listed in Table I along with literature values for comparison. The experimental values for the binodal curve of the three systems are given in Tables II–IV, and tie-line data are given in Table V.

Figures 1, 2, and 3 show the liquid–liquid equilibrium diagrams at 25 °C containing binodal curves, tie lines, and the plait points for the systems water–ethanol–AA, water–ethanol–MIK, and water–ethanol–BA, respectively. Predicted LLE data by the UNIFAC method are also shown.

The tie-line data for the three systems were satisfactorily correlated by the method of Othmer and Tobias (*8*), as can be seen in Figure 4. The plait points (PP) were determined by that method and their compositions are given in Tables II–IV for each system.

Table IV. Binodal Curve Data for Water (1)–Ethanol (2)–BA (3) System at 298.15 K

water-rich layer			BA-rich layer		
W_{11}%	W_{21}%	W_{31}%	W_{13}%	W_{23}%	W_{33}%
96.00	0.00	4.00	47.89	23.14	28.96
92.66	3.10	4.24	42.68	22.77	34.54
90.20	5.40	4.40	35.17	22.18	42.65
87.50	8.00	4.50	31.78	21.54	46.68
84.28	11.00	4.72	27.66	20.75	51.59
80.45	13.76	5.78	24.16	19.50	56.33
77.50	15.40	7.10	22.21	18.03	59.76
75.04	16.88	8.08	19.26	16.30	64.43
71.20	18.10	9.70	17.15	14.86	67.99
68.71	19.88	11.41	14.96	12.02	73.02
63.88	20.71	15.39	12.36	8.42	79.22
60.20	21.50	18.20	9.48	4.53	85.98
56.65	22.12	21.23	8.00	2.27	89.71
52.57	22.92	24.51	7.09	0.00	92.91
50.00[a]	23.00[a]	27.00[a]			

[a] Estimated PP by Othmer and Tobias' method.

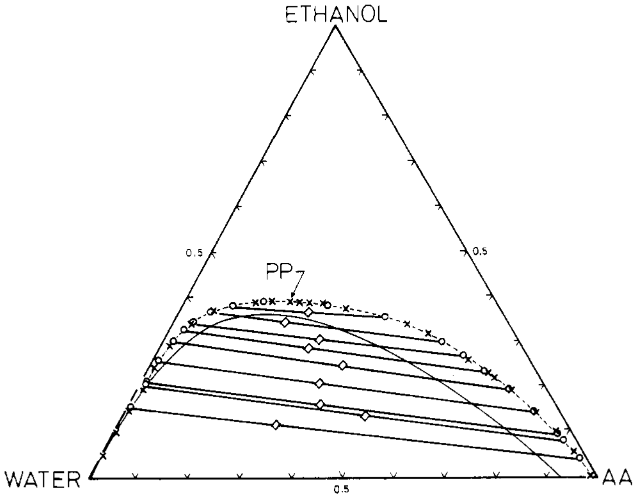

Figure 1. Liquid–liquid equilibria for the system water (1)–ethanol (2)–AA (3) at 298.15 K. PP = plait point. Continuous curve: LLE predicted by UNIFAC method. Dashed curve: experimental binodal curve. (×) Experimental binodal points. (○) Experimental tie line. (◇) Overall composition for tie line.

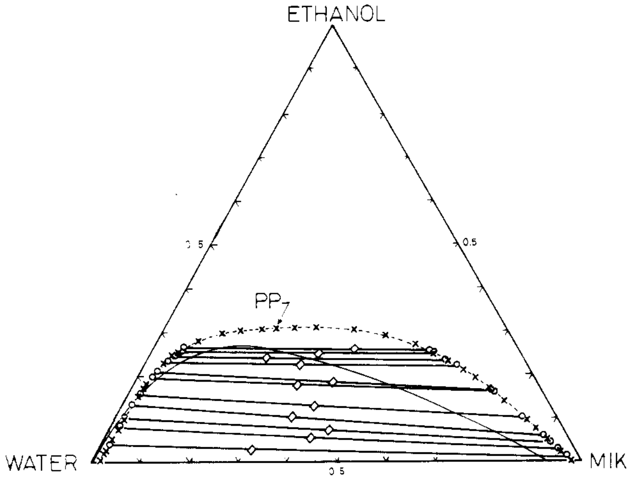

Figure 2. Liquid–liquid equilibria for the system water (1)–ethanol (2)–MIK (3) at 298.15 K. PP = plait point. Continuous curve: LLE predicted by UNIFAC method. Dashed curve: experimental binodal curve. (×) Experimental binodal points. (○) Experimental tie line. (◇) Overall composition for tie line.

Table V. Tie-Line Data for Water (1)-Ethanol (2)-Solvent (3) Systems at 298.15 K

water-rich layer			solvent-rich layer		
W_{11}%	W_{21}%	W_{31}%	W_{13}%	W_{23}%	W_{33}%
Water-Ethanol-AA System					
83.80	15.80	0.40	1.30	4.40	94.30
78.40	20.74	0.86	2.62	8.56	88.82
77.60	21.60	0.80	3.00	9.50	87.50
72.60	26.50	0.90	4.70	14.40	80.90
67.80	30.70	1.50	7.00	20.00	73.00
64.53	32.91	2.56	9.58	23.81	66.61
62.13	34.21	3.66	12.13	27.11	60.76
56.60	37.20	6.20	15.32	30.08	54.60
51.72	38.20	10.08	23.60	35.40	41.00
45.12	39.03	15.85	33.38	38.15	28.47
Water-Ethanol-MIK System					
93.90	4.25	1.85	2.35	0.85	96.80
89.80	8.05	2.15	3.10	2.43	94.47
87.80	10.02	2.18	4.00	4.40	91.60
84.85	13.25	2.25	4.50	5.65	89.85
83.04	14.60	2.36	6.10	9.20	84.70
77.76	18.89	3.35	9.88	15.87	74.25
75.75	20.55	3.70	10.10	16.25	73.65
72.30	23.05	4.65	14.20	21.90	63.90
70.10	24.48	5.42	15.55	23.15	61.30
68.25	25.50	6.25	17.75	25.00	57.25
67.60	25.90	6.50	17.80	25.30	56.90
Water-Ethanol-BA System					
92.30	3.50	4.20	8.50	3.00	88.50
90.70	5.00	4.30	9.60	4.90	85.50
85.30	10.00	4.70	13.20	9.60	77.20
83.80	11.20	5.00	14.00	10.80	75.20
83.25	11.60	5.05	14.30	11.30	74.40
79.50	14.40	6.10	17.20	14.50	68.30
78.70	14.90	6.40	18.50	15.90	65.60
74.25	17.40	8.35	22.58	18.60	58.82
69.27	19.55	11.18	27.82	20.61	51.57
66.87	20.38	12.75	31.12	21.47	47.41

Figure 5 shows selectivity diagrams on a solvent-free basis for the three systems studied here (*9*), where ethanol is the distributed substance in each case. The selectivity follows the order $S_{AA} > S_{MIK} > S_{BA}$, indicating that AA is the best of the three solvents.

The solubility of these systems shows a normal temperature behavior, because solubility increases when temperature increases. The binodal UNIFAC estimated curves at higher temperatures than 298.15 K follow a similar trend in the range 298.15-313.15 K.

However, in the three systems studied the aqueous layer is richer in ethanol than the organic one (see Figures 1-3), except for water-ethanol-BA system up to 15% ethanol, because this system presents a slight solutropic behavior (*10*). So, the tie-line slope leads to the solvent layer being weaker in ethanol than aqueous one. Consequently, all distribution coefficients m_2 (defined as the ratio between the weight fraction of ethanol in both equilibrium phases) were less than 1 ($m_2 < 1$) except for water-ethanol-BA up to 15% ethanol.

The experimental data were also correlated with the UNIFAC group contribution method (*11*, *12*) using the isoactivity conditions as restraint equations. The LLE data for a given system

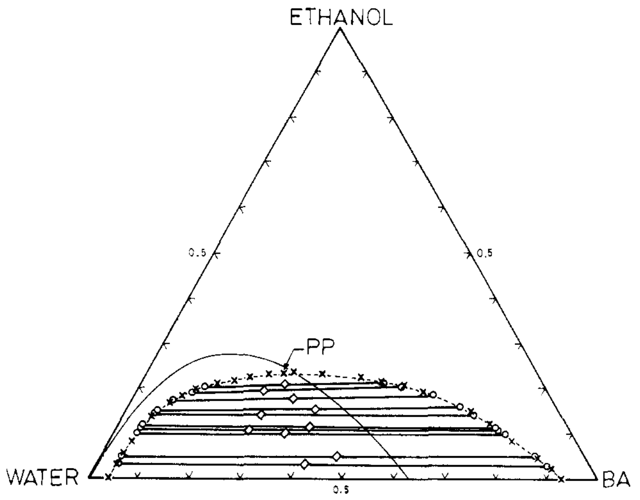

Figure 3. Liquid-liquid equilibria for the system water (1)-ethanol (2)-BA (3) at 298.15 K. PP = plait point. Continuous curve: LLE predicted by UNIFAC method. Dashed curve: experimental binodal curve. (×) Experimental binodal points. (○) Experimental tie line. (◇) Overall composition for tie line.

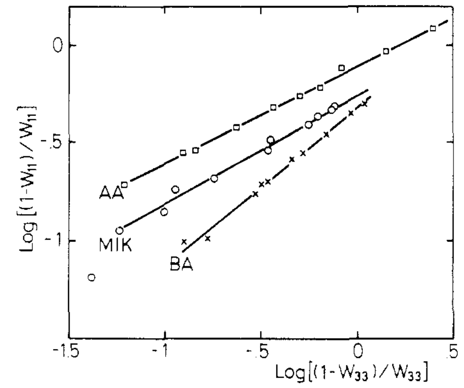

Figure 4. Correlation of the liquid-liquid equilibrium data at 298.15 K by the method of Othmer and Tobias.

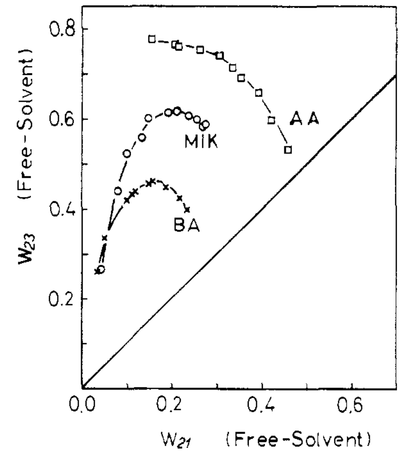

Figure 5. Selectivity diagrams at 298.15 K: (□) water-ethanol-AA; (○) water-ethanol-MIK; (×) water-ethanol-BA systems.

Table VI. UNIFAC Interaction Parameters[a]

	main group	1	3	4	5	8	10	14
1	CH_2	0.0	-114.8	-115.7	644.6	1300	472.6	972.4
3	ACH	156.5	0.0	167.0	703.9	859.4	593.7[b]	6.0[b]
4	$ACCH_2$	104.4	-146.8	0.0	4000	5695	916.7[b]	5688.0[b]
5	OH	328.2	-9.21	1.27	0.0	28.73	67.07	195.6
8	H_2O	342.4	372.8	203.7	-122.4	0.0	-171.8	-6.32
10	CH_2CO	66.56	-78.31[b]	-73.87[b]	216.0	634.8	0.0	258.7[b]
14	COOC	-320.1	114.8[b]	-170.0[b]	180.6	385.9	58.84[b]	0.0

[a] From ref *4*. [b] Not applicable to this work.

can be estimated by minimizing the Gibbs free energy by the UNIFAC method.

Table VI shows all interaction parameter values used in the LLE estimation. Prediction of the LLE on these systems by the UNIFAC method showed a correct qualitative behavior regarding mutual solubilities, but gave a poor quantitative agreement with the experimental data. This is more evident for the system containing BA (see Figure 3), probably due to inappropriate figures for the interaction parameters used for the calculation and the fact that the UNIFAC model had not taken into account the interaction between the OH groups of both alcohols in the solution for LLE calculation.

Glossary

AA	amyl acetate
BA	benzyl alcohol
MIK	methyl isobutyl ketone
m_2	distribution coefficient of ethanol ($m_2 = W_{23}/W_{21}$)
PP	plait point
W_{11}	weight fraction of water (1) in the water-rich layer
W_{13}	weight fraction of water (1) in the solvent-rich layer
W_{21}	weight fraction of ethanol (2) in the water-rich layer
W_{23}	weight fraction of ethanol (2) in the solvent-rich layer
W_{31}	weight fraction of solvent (3) in the water-rich layer
W_{33}	weight fraction of solvent (3) in the solvent-rich layer

Registry No. AA, 628-63-7; MIK, 108-10-1; BA, 100-51-6; ethanol, 64-17-5.

Literature Cited

(1) Roddy, J. W. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 104–107.

(2) Roddy, J. W.; Coleman, C. F. *Ind. Eng. Chem. Fundam.* **1981**, *20*, 250–254.

(3) Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977; pp 27–64 and 243–249.

(4) Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 331–339.

(5) Magnussen, T. Phase Equilibria and Separation Process; Instituttet for Kemiteknik, Denmark; MAN 8001, 1980.

(6) Riddick, J. A.; Bunger, W. B. *Organic Solvents*; Weissberger, A., Ed. Wiley-Interscience: New York, 1970; Vol. II.

(7) Weast, R. C. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1980–1981.

(8) Othmer, D. F.; Tobias, P. E. *Ind. Eng. Chem.* **1942**, *34*, 690–700.

(9) Treybal, R. E. *Liquid Extraction*; McGraw-Hill: New York, San Francisco, Toronto, and London, 1963; pp 122–127.

(10) Sørensen, J.; Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Fluid Phase Equilib.* **1979**, *2*, 297.

(11) Sørensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Fluid Phase Equilib.* **1979**, *3*, 47.

(12) Sørensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Fluid Phase Equilib.* **1980**, *4*, 151.

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Vapor–Liquid Equilibria at 760 mmHg in the Binary Systems Cyclohexene–1,2-Dichloroethane and Cyclohexane–1,2-Dichloroethane

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Vapor–liquid equilibrium at 1 atm pressure has been determined for the title binary systems. Thermodynamic consistency was checked by Herington's area test. Both systems present moderate positive deviations from ideal behavior, and minimum boiling azeotropes were observed. The data were satisfactorily correlated by various equations, and appropriate parameters are reported.

Introduction

The vapor–liquid equilibria (VLE) for the three binary systems cyclohexene-1,2-dichloroethane, cyclohexane-1,2-dichloroethane, and cyclohexene-cyclohexane have been investigated by Mesnage and Marsan (*1*) inasmuch as the previously reported data (*2*, *3*) for the systems cyclohexane-1,2-dichloroethane and cyclohexene-cyclohexane showed an inadequate thermodynamic consistency. However, the data of Mesnage and Marsan (*1*) for the systems cyclohexene-1,2-dichloroethane and cyclohexane-1,2-dichloroethane also show a doubtful thermodynamic consistency according to the Herington (*4*) criterion; on the other hand, opposite to indications by Mesnage and Marsan, the van Laar equation correlates the experimental data as well as the Wilson equation.

The aim of this paper is to provide new VLE data for the systems cyclohexene-1,2 dichloroethane and cyclohexane-1,2 dichloroethane at the pressure of 1 atm. The experimental data of this work satisfy the consistency test of Herington and can be satisfactorily correlated by the van Laar, Mato, Wilson, and NRTL equations.

Experimental Section

Purity of Materials. All starting chemicals were distilled through a column (20 mm i.d. and 900 mm long) packed with 2 × 2 mm Dixon rings. The final purity level of all chemicals, estimated by gas–liquid chromatography, was better than 99.85%, and some significant physical properties (density, refractive index, and boiling point) are listed in Table I along with the literature values.

Apparatus and Procedure. The VLE data were obtained by use of an all-glass recirculation still connected to a constant-pressure system operated at 760 ± 0.1 mmHg. The equilibrium temperatures were measured with a certified mercury thermometer (PROTON). The accuracy in determination of temperature was ±0.1 °C. The apparatus and the experimental features have been described in detail elsewhere (*5*).

The liquid and condensed vapor compositions were obtained from density measurements at 25 °C by using a double leveling pycnometer. Previous calibration analysis was carried out with mixtures of known composition. Molar fractions of the mixtures

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