

ΔS	entropy of activation for viscous flow, J/(mol K)
t	flow time, s
T	temperature, K
V	flowing volume, m ³
X_A	alcohol mole fraction
Δz	total liquid height, m
η	absolute viscosity, Pa s
ν	kinematic viscosity, m ² /s
ρ	density, kg/m ³

Literature Cited

- (1) Velo, E.; Pulgjaner, L.; Recasens, F. *Ind. Eng. Chem. Res.* **1988**, *27*, 2224.

- (2) Cáceres, E.; Pulgjaner, L.; Recasens, F. *Chem. Eng. J.* **1988**, *37*, 43.
 (3) Leung, P.; Zorrilla, C.; Recasens, F.; Smith, J. M. *AIChE J.* **1988**, *32*, 1839.
 (4) Kenttämä, J.; Tommila, E.; Martti, M. *Ann. Acad. Sci. Fenn.* **1959**, *93A*, 3.
 (5) Dinsdale, A.; Moore, F. *Viscosity and Its Measurement*; Chapman and Hall: London, 1962.
 (6) Weast, R. C. *Handbook of Chemistry and Physics*, 61st ed.; CRC Press: Boca Raton, FL, 1980.
 (7) Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport Phenomena*; J. Wiley & Sons: New York, 1960.

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Vapor-Liquid Equilibria for Three Binary Systems Made of Methyl Ethyl Ketone with Acetone, Methyl Acetate, or *N*-Amyl Alcohol

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Vapor-liquid equilibria were measured for the three binary systems made of methyl ethyl ketone with acetone, methyl acetate, or *n*-amyl alcohol at 100 kPa of pressure by the dew-point-bubble-point temperature method. The dew-point-bubble-point temperature apparatus previously proposed by the authors was modified in the present study. Combining the experimental dew-point and bubble-point temperature curves, vapor-liquid equilibria were obtained without using any analytical instrument. The experimental vapor-liquid equilibrium data were correlated with the Wilson equation and further with the pseudocubic equation of state previously proposed by the authors.

Introduction

Vapor-liquid equilibrium relations are required for practical use, such as in the design and operation of distillation equipment. The dew-point-bubble-point temperature method (1, 2) is one way for measuring vapor-liquid equilibria (VLE). The dew-point-bubble-point temperature apparatus previously proposed by the authors (1, 3) was modified in the present study. The VLE were obtained for the three binary systems of methyl ethyl ketone with acetone, methyl acetate, or *n*-amyl alcohol at 100 kPa of pressure by the dew-point-bubble-point temperature method.

Experimental Section

The dew-point-bubble-point temperature apparatus previously proposed by the authors (1, 4, 5) was modified as shown in Figure 1. In the present modification, the liquid volume in the dew- and bubble-point stills was changed from 15 to 33 cm³ to improve the accuracy of temperature measurements. The constructions of the feeder and condenser were further modified to prevent the contamination with water from the air. The experimental procedures are the same as in the previous papers (1, 3). Temperature was measured by means of a Hewlett-Packard 2804A quartz thermometer with an accuracy of

0.01 K. The solutions of desired composition were prepared with an accuracy of 0.001 in mole fraction by use of an automatic balance.

Special-grade reagents were supplied by the Wako Pure Chemical Industries, Ltd. All reagents were purified by fractional distillation in a 30-plate Oldershaw column. The physical properties of the materials used are listed in Table I.

Results

The experimental dew- and bubble-point data are given in Tables II-IV and shown in Figures 2-4. After the experimental dew-point temperature curve and the bubble-point one were combined, smoothed VLE data were obtained, as given in Tables V-VII and shown in Figures 5-7. For the acetone + methyl ethyl ketone system, the present experimental data lie between the data of Othmer et al. (6) and Babich et al. (7), as shown in Figures 2 and 5. For the methyl acetate + methyl ethyl ketone system, substantial differences are seen when the liquid-phase results of this study are compared with the data of Babich et al. (7), as shown in Figure 3. For the methyl ethyl ketone + *n*-amyl alcohol system, large differences are observed between the present experimental data and the data of Miller et al. (8), as shown in Figures 4 and 7. On the vapor-liquid equilibrium measurements, Miller et al. (8) and Othmer et al. (6) determined the equilibrium composition with the refractive index measurements. Babich et al. (7) analyzed chromatographically. The present experimental data were obtained without using any analytical instrument. Figures 8-10 give the calculation results of the conventional area test on consistency. The VLE data reported in the present study seem most reliable when compared with the previous data (6-8), as shown in Figures 8-10.

The VLE data were correlated with the Wilson (9) equation. The vapor-phase correction was made with that given by Hayden and O'Connell (10-12), with use of the parameters shown in Table VIII. The association parameters of unlike molecules were evaluated as the arithmetic mean of the constituent pure components. Wilson parameters Λ_{12} and Λ_{21} were determined to minimize the sum of squares of the deviations in bubble-point temperatures, all points weighted equally.

Table I. Normal Boiling Points T_b , Densities ρ , and Refractive Indexes n_D of the Materials Used

material	T_b /K		$\rho(298.15\text{ K})/(\text{g cm}^{-3})$		$n_D(298.15\text{ K})$	
	exptl	lit. (23)	exptl	lit. (23)	exptl	lit. (23)
acetone	329.28	329.44	0.7849	0.78440	1.3564	1.35596
methyl ethyl ketone	352.75	352.79	0.7996	0.79968	1.3764	1.3764
methyl acetate	330.02	330.09	0.9268	0.9273	1.3589	1.3589
<i>n</i> -amyl alcohol	410.92	410.95	0.8107	0.8112	1.4079	1.4079

Table II. Experimental Dew-Point T_d and Bubble-Point T_b Data for the Acetone (1) + Methyl Ethyl Ketone (2) System at 100 kPa as a Function of the Mole Fraction x_1 of Acetone

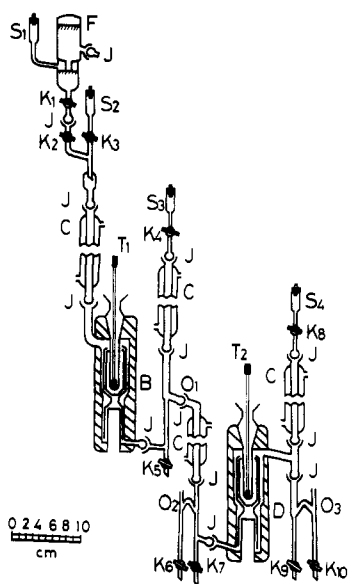
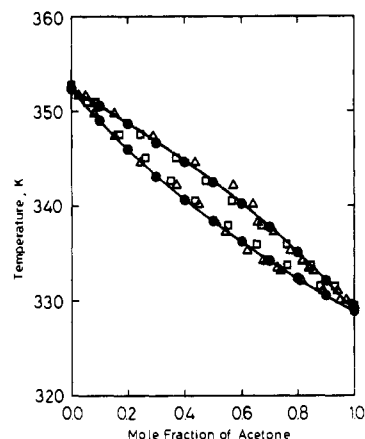
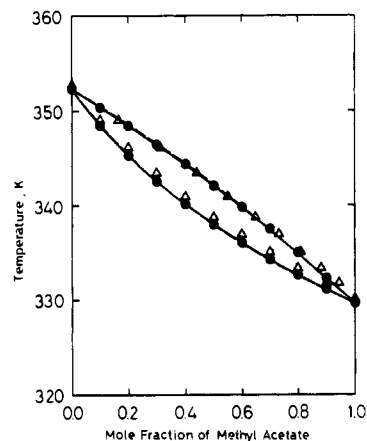
x_1	T_d /K	T_b /K	x_1	T_d /K	T_b /K
0.000		352.34	0.600	340.22	336.25
0.100	350.57	349.00	0.700	337.77	334.23
0.200	348.68	345.97	0.800	335.12	332.38
0.300	346.64	343.09	0.900	332.13	330.58
0.400	344.61	340.64	1.000		328.89
0.500	342.48	338.39			

Table III. Experimental Dew-Point T_d and Bubble-Point T_b Data for the Methyl Acetate (1) + Methyl Ethyl Ketone (2) System at 100 kPa as a Function of the Mole Fraction x_1 of Methyl Acetate

x_1	T_d /K	T_b /K	x_1	T_d /K	T_b /K
0.000		352.34	0.600	339.84	336.04
0.100	350.38	348.45	0.700	337.52	334.27
0.200	348.44	345.30	0.800	335.01	332.63
0.300	346.47	342.57	0.900	332.30	331.11
0.400	344.42	340.15	1.000		329.64
0.500	342.10	337.99			

Table IV. Experimental Dew-Point T_d and Bubble-Point T_b Data for the Methyl Ethyl Ketone (1) + *n*-Amyl Alcohol (2) System at 100 kPa as a Function of the Mole Fraction x_1 of Methyl Ethyl Ketone

x_1	T_d /K	T_b /K	x_1	T_d /K	T_b /K
0.000		410.44	0.600	389.24	365.07
0.100	408.18	398.47	0.700	383.89	361.30
0.200	405.14	388.65	0.800	377.21	358.05
0.300	401.90	380.95	0.900	367.65	355.08
0.400	398.38	374.67	1.000		352.34
0.500	394.02	369.28			

**Figure 1. Experimental apparatus for measuring isobaric dew points–bubble points: (B) bubble-point still; (C) condenser; (D) dew-point still; (F) feeder; (J) ball joint; (K) cock; (O) overflow tube; (S) silica gel tube; (T) thermometer.****Figure 2. Experimental dew-point–bubble-point temperatures for the acetone + methyl ethyl ketone system: (●) this work, 100 kPa; (—) Wilson equation; (---) pseudocubic equation of state; (Δ) Othmer et al. (6), 101.33 kPa; (□) Babich et al. (7), 101.33 kPa.****Figure 3. Experimental dew-point–bubble-point temperatures for the methyl acetate + methyl ethyl ketone system: (●) this work, 100 kPa; (—) Wilson equation; (---) pseudocubic equation of state; (Δ) Babich et al. (7), 101.33 kPa.****Table V. Smoothed Vapor–Liquid Equilibrium Data, Temperatures T and Liquid-Phase x_1 and Vapor-Phase y_1 Mole Fractions, for Acetone (1) + Methyl Ethyl Ketone (2) at 100 kPa**

T /K	x_1	y_1	T /K	x_1	y_1
352.34	0.000	0.000	337.50	0.541	0.710
350.00	0.068	0.132	335.00	0.662	0.805
347.50	0.148	0.258	332.50	0.795	0.889
345.00	0.232	0.381	330.00	0.933	0.967
342.00	0.344	0.522	328.89	1.000	1.000
340.00	0.428	0.608			

Table VI. Smoothed Vapor–Liquid Equilibrium Data, Temperatures T and Liquid-Phase x_1 and Vapor-Phase y_1 Mole Fractions, for Methyl Acetate (1) + Methyl Ethyl Ketone (2) at 100 kPa

T /K	x_1	y_1	T /K	x_1	y_1
352.34	0.000	0.000	337.00	0.550	0.720
350.00	0.057	0.120	334.50	0.685	0.818
347.50	0.128	0.248	332.50	0.808	0.892
345.00	0.210	0.371	330.50	0.939	0.967
342.50	0.303	0.485	329.64	1.000	1.000
340.00	0.408	0.593			

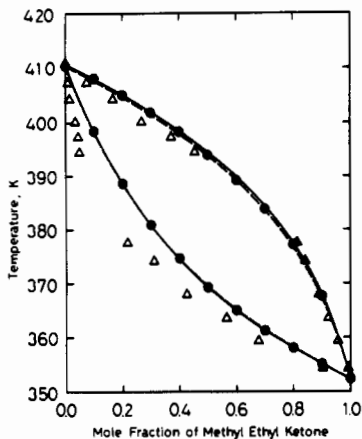


Figure 4. Experimental dew-point–bubble-point temperatures for the methyl ethyl ketone + *n*-amyl alcohol system: (●) this work, 100 kPa; (—) Wilson equation; (---) pseudocubic equation of state; (Δ) Miller et al. (8), 101.33 kPa.

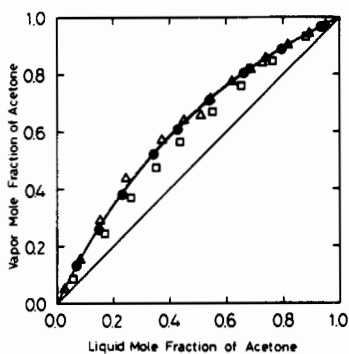


Figure 5. Vapor–liquid equilibria for the acetone + methyl ethyl ketone system: (●) this work, 100 kPa; (—) Wilson equation; (---) pseudocubic equation of state; (Δ) Othmer et al. (6), 101.33 kPa; (□) Babich et al. (7), 101.33 kPa.

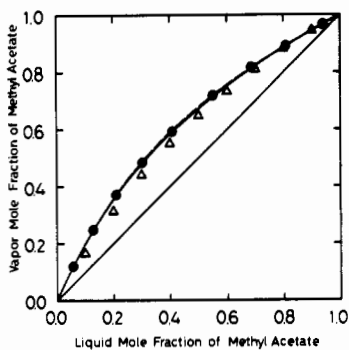


Figure 6. Vapor–liquid equilibria for the methyl acetate + methyl ethyl ketone system: (●) this work, 100 kPa; (—) Wilson equation; (---) pseudocubic equation of state; (Δ) Babich et al. (7), 101.33 kPa.

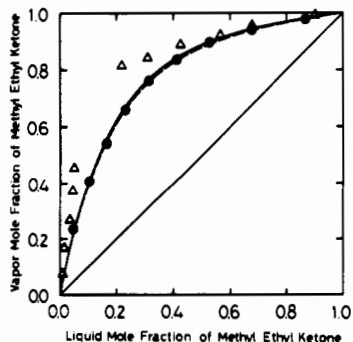


Figure 7. Vapor–liquid equilibria for the methyl ethyl ketone + *n*-amyl alcohol system: (●) this work, 100 kPa; (—) Wilson equation; (---) pseudocubic equation of state; (Δ) Miller et al. (8), 101.33 kPa.

Table VII. Smoothed Vapor–Liquid Equilibrium Data, Temperatures T and Liquid-Phase x_1 and Vapor-Phase y_1 Mole Fractions, for Methyl Ethyl Ketone (1) + *n*-Amyl Alcohol (2) at 100 kPa

T/K	x_1	y_1	T/K	x_1	y_1
410.44	0.000	0.000	374.00	0.412	0.836
404.00	0.047	0.235	368.00	0.526	0.897
398.00	0.103	0.408	362.00	0.678	0.941
392.00	0.164	0.542	356.00	0.868	0.978
386.00	0.231	0.661	352.34	1.000	1.000
380.00	0.314	0.762			

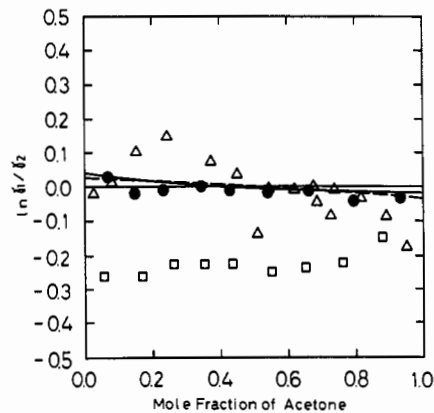


Figure 8. Calculation results of the conventional area test on consistency for the acetone + methyl ethyl ketone system: (●) this work; (—) Wilson equation; (---) pseudocubic equation of state; (Δ) Othmer et al. (6); (□) Babich et al. (7).

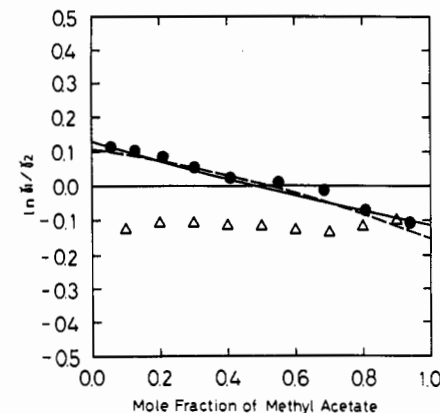


Figure 9. Calculation results of the conventional area test on consistency for the methyl acetate + methyl ethyl ketone system: (●) this work; (—) Wilson equation; (---) pseudocubic equation of state; (Δ) Babich et al. (7).

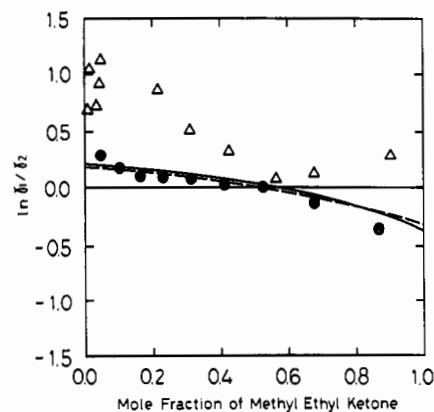


Figure 10. Calculation results of the conventional area test on consistency for the methyl ethyl ketone + *n*-amyl alcohol system: (●) this work; (—) Wilson equation; (---) pseudocubic equation of state; (Δ) Miller et al. (8).

Table VIII. Parameters Used for Vapor-Phase Correction

material	P_c /MPa	T_c /K	$V/(10^{-3}$ $\text{m}^3 \text{mol}^{-1})$	$R'/\text{\AA}$	μ/D	η
acetone (11)	47.0	509.1	0.0740	2.740	2.88	0.90
methyl ethyl ketone (11)	41.0	535.0	0.0902	3.139	2.70	0.90
methyl acetate (11)	46.3	506.9	0.0799	2.862	1.72	0.85
<i>n</i> -amyl alcohol (12)	38.0	586.0	0.1087	3.504 ^a	1.70	2.20 ^b

^a Evaluated from its parachor. ^b Assumed as 2.20.

Table IX. Wilson Parameters Λ_{ij} , Interaction Parameter of Pseudocubic Equation of State k_{ij} , Mean Absolute Deviations in Temperature ΔT , and Vapor-Phase Composition Δy_1 Obtained from the VLE Data^a

system	Wilson equation				pseudocubic equation		
	Λ_{12}	Λ_{21}	$\Delta T/\text{K}$	Δy_1	k_{ij}	$\Delta T/\text{K}$	Δy_1
I	0.6360	1.4101	0.04	0.002	0.001	0.04	0.004
II	0.8119	1.0751	0.02	0.002	0.014	0.07	0.001
III	1.3571	0.4826	0.17	0.007	0.015	0.15	0.005

^a Systems: I, acetone (1) + methyl ethyl ketone (2); II, methyl acetate (1) + methyl ethyl ketone (2); III, methyl ethyl ketone (1) + *n*-amyl alcohol (2). Λ_{ij} is defined in ref 9. $\Delta T = \sum |T_{\text{calc}} - T_{\text{exptl}}|/N$. $\Delta y_1 = \sum |y_{1,\text{calc}} - y_{1,\text{exptl}}|/N$ (N , number of experimental points).

Table X. Relative Percentage Densities $\delta_{\text{rel}}(\rho)$ between Calculated and Experimental Liquid Densities at 101.33 kPa and 298.15 K^a

substance	$\rho_{\text{exptl}}/(\text{g cm}^{-3})$	$\delta_{\text{rel}}(\rho)$		
		PC	SRK	PR
acetone	0.7849	1.2	21.7	11.9
methyl ethyl ketone	0.7996	5.3	18.3	8.2
methyl acetate	0.9268	2.8	15.3	4.7
<i>n</i> -amyl alcohol	0.8107	4.3	12.2	1.6
average		3.4	16.9	6.6

^a $\delta_{\text{rel}}(\rho) = 100(|\rho_{\text{exptl}} - \rho_{\text{calc}}|/\rho_{\text{exptl}})$. Abbreviations: PC, pseudocubic equation of state; SRK, Soave-Redlich-Kwong equation of state; PR, Peng-Robinson equation of state.

Table IX shows the Wilson parameters obtained and their accuracies. The solid lines in Figures 2–10 show the calculated results with the Wilson equation. The vapor pressures of the pure components have been calculated by using the Antoine equation, with coefficients estimated by Boublik et al. (13) from the experimental data of Ambrose et al. (14–17).

The VLE data were further correlated with the pseudocubic equation of state previously proposed by the authors (18–20). The interaction parameter a_{ij} between unlike molecules is expressed by

$$a_{ij} = (1 - k_{ij})(a_i a_j)^{1/2} \quad (1)$$

where k_{ij} was determined to minimize the sum of squares of the deviations in bubble-point temperatures, all points weighted equally. The mean absolute deviation of equilibrium vapor composition and equilibrium temperature between the experimental data and calculated ones are shown in Table IX. In the present calculations, the critical values T_c , P_c , and V_c were obtained from Reid et al. (12). The broken lines in Figures 2–10 show the results calculated with the pseudocubic equation of state. The activity coefficient γ_i was evaluated with the following equation.

$$\gamma_i = \hat{\phi}_i / \phi_i^\circ \quad (2)$$

where the fugacity coefficients ϕ_i° and $\hat{\phi}_i$ were calculated with the equation of state. As shown in Figures 8–10, reasonable values were obtained. Table X gives the accuracies of the

liquid densities calculated with several equations of state. The pseudocubic equation of state gives better results than the conventional equations of Soave (21) and Peng-Robinson (22).

The VLE data obtained in the present study were successfully correlated with the Wilson equation and with the pseudocubic equation of state, as shown in Table IX.

Acknowledgment

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Literature Cited

- (1) Kato, M. *J. Chem. Eng. Data* **1988**, *33*, 499.
- (2) Kato, M.; Konishi, H.; Hirata, M. *J. Chem. Eng. Data* **1970**, *15*, 435.
- (3) Kato, M.; Konishi, H.; Hirata, M. *J. Chem. Eng. Data* **1970**, *15*, 501.
- (4) Kato, M.; Yamaguchi, M.; Yoshikawa, H. *J. Chem. Eng. Data* **1990**, *35*, 85.
- (5) Kato, M.; Yoshikawa, H.; Yamaguchi, M. *Fluid Phase Equilib.* **1990**, *54*, 47.
- (6) Othmer, D. F.; Chudgar, M. M.; Levy, S. L. *Ind. Eng. Chem.* **1952**, *44*, 1872.
- (7) Babich, S. V.; Ivanchikova, R. A.; Serafimov, L. A. *Zh. Prikl. Khim. (Leningrad)* **1969**, *42*, 1354.
- (8) Miller, K. J.; Huang, H. S. *J. Chem. Eng. Data* **1972**, *17*, 77.
- (9) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
- (10) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
- (11) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.
- (12) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.
- (13) Boublik, T.; Fried, V.; Hala, E. *The Vapor Pressures of Pure Substances*; Elsevier: Amsterdam, 1984.
- (14) Ambrose, D.; Sprake, C. H. S. *J. Chem. Thermodyn.* **1970**, *2*, 631.
- (15) Ambrose, D.; Sprake, C. H. S.; Townsend, R. *J. Chem. Thermodyn.* **1974**, *6*, 693.
- (16) Ambrose, D.; Ellender, J. H.; Lees, E. B.; Sprake, C. H. S.; Townsend, R. *J. Chem. Thermodyn.* **1975**, *7*, 453.
- (17) Ambrose, D.; Ellender, J. H.; Gundry, H. A.; Lee, D. A.; Townsend, R. *J. Chem. Thermodyn.* **1981**, *13*, 795.
- (18) Kato, M.; Tanaka, H. *Adv. Cryog. Eng.* **1988**, *31*, 1169.
- (19) Kato, M.; Tanaka, H.; Kiuchi, T.; Zhu, Z.-R. *Distillation and Absorption. Inst. Chem. Eng. Symp. Ser.* **1988**, No. 104B, 347.
- (20) Kiuchi, T.; Kato, M. *J. Jpn. Pet. Inst.* **1989**, *32*, 92.
- (21) Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197.
- (22) Peng, D. Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
- (23) TRC—Thermodynamic Tables—Non-Hydrocarbons. Thermodynamics Research Center, The Texas A&M University System: College Station, TX, extant 1965, 1966, 1969 (loose-leaf data sheets).

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