Table V. Standard Deviations for Molar Excess Volumes for the Tetrachloroethene (1) + 1,4-Dioxane (2) + Tetrahydrofuran (3) System at 298.15 and 308.15 K

	$\sigma(V^E) \times 10^9/(m^3\ mol^{-1})$	
eq	298.15 K	308.15 K
4	8.6	7.1
6	7.2	6.9
7	7.9	5.7
8	6.7	5.3
10	7.5	7.2
11	8.7	6.4

and $C = 5.37 \times 10^{-8}$ m^3 mol^{-1} and for 308.15 K are $A = 3.87 \times 10^{-8}$ m^3 mol^{-1}, $B = -1.8482 \times 10^{-6}$ m^3 mol^{-1}, and $C = -1.354 \times 10^{-7}$ m^3 mol^{-1}.

Table V shows the standard deviations calculated from applications of eq 4 of Rastogi, eq 6 of Radojkovič, eq 7 of Kohler, eq 8 of Jacob and Fitzner, eq 10 of Tsao and Smith, and eq 11 of Singh et al. for molar excess volumes for the ternary system at different temperatures.

Examination of Table V reveals that eq 8 of Jacob and Fitzner shows the best agreement with the experimental data.

Registry No. $Cl_2C{=}CCl_2$, 127-18-4; 1,4-dioxane, 123-91-1; tetrahydrofuran, 109-99-9.

Literature Cited

(1) Rastogi, R. P.; Nath, J.; Das, S. S. *J. Chem. Eng. Data* **1977**, *22*, 249.
(2) Radojkovič, N.; Tesič, A.; Grozdanič, D.; Djordjevič, B.; Malič, M. J. *Chem. Thermodyn.* **1977**, *9*, 349.
(3) Kohler, F. *Monatsh. Chem.* **1960**, *91*, 738.
(4) Jacob, K. T.; Fitzner, K. *Thermochim. Acta* **1977**, *18*, 197.
(5) Tsao, C. C.; Smith, J. M. *Chem. Eng. Prog., Symp. Ser.* **1953**, *7*, 107.
(6) Singh, P. P.; Niigam, R. K.; Sharma, S. P.; Aggarwal, S. *Fluid Phase Equilib.* **1984**, *18*, 333.
(7) Weissberger, A. *Organic Solvents*, 4th ed.; Interscience: New York, 1986.
(8) Papanastasiou, G. E.; Papoutsis, A. D.; Kokknidis, G. I. *J. Chem. Eng. Data* **1987**, *32*, 377.
(9) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 345.

Received for review July 22, 1991. Accepted November 4, 1991.

Densities and Viscosities of 2-Butanone/Dibutyl Ether, 2-Picoline/2-Butanone, and 2-Picoline/Water Mixtures

Ming-Jer Lee* and Ming-Chi Wei

Department of Chemical Engineering, National Taiwan Institute of Technology, Taipei 106, Taiwan

Densities and viscosities of the binary mixtures including 2-butanone/dibutyl ether, 2-picoline/2-butanone, and 2-picoline/water are measured at 303.15, 313.15, and 323.15 K over the entire molar fraction range. The excess volumes, viscosities, and Gibbs energies of activation of flow are calculated from the experimental data, and are correlated by a Redlich-Kister-type function in terms of molar fraction. McAllister's three-body and four-body interaction models are also used to correlate the kinematic viscosities.

Introduction

Densities and viscosities of fluids and fluid mixtures are essential for engineering applications. The variations of these properties with temperature and composition for mixtures containing polar and/or hydrogen-bonding components may be complex due to strongly polar and/or hydrogen-bonding effects in the mixtures. In this work, three binary systems containing 2-butanone, dibutyl ether, 2-picoline, and water were investigated at atmospheric pressure (nominal value 0.1 MPa) and at 303.15, 313.15, and 323.15 K over the entire range of molar fraction.

Experimental Section

Dibutyl ether (99+ wt %), 2-butanone (99.7+ wt %), methanol (99+ wt %), and toluene (99+ wt %) were purchased from Aldrich. Ethanol (99.8+ wt %, Ferak) and 2-picoline (98 wt %, Janssen) were also used in this work. Deionized distilled water (conductivity better than 2×10^{-6} Ω^{-1} cm^{-1}) was prepared in our laboratory. All the substances were used without further purification.

Density was measured with three 25 cm^3 pycnometers (products of Kimax, Japan). The internal volumes of the pycnometers were calibrated with pure water (*1*) at each of the measured temperatures. All mixtures were prepared metrically with an accuracy better than ±0.5 mg, and the nominal mass of the mixtures prepared was about 150 g. To minimize the errors in composition that arise from evaporation during the solution preparation, we charged the heavier component first. The loaded pycnometers were immersed in a thermostat (Neslab, RTE-220D) controlled within ±0.01 K. The temperature readings were calibrated with a Hart Scientific Microtherm 1006 (accuracy ±0.02 K) to ±0.1 K. The readings from three pycnometers were averaged to determine the density. The accuracy of the reported densities was better than ±0.1%. The change of composition due to evaporation during the measurement was minor according to the analysis by gas chromatography.

Viscosity was measured with a HAAKE falling-ball viscometer. The measuring tube was immersed in an insulated jacket wherein constant-temperature water (controlled within ±0.1 K) was circulated. The temperature was measured by a platinum resistance temperature detector (RTD) probe with a DP86-R display (Omega product) calibrated to ±0.1 K. The falling time (t, s) can be converted into dynamic viscosity (η, Pa s) by

$$\eta = K(\rho_b - \rho_m)t \qquad (1)$$

where ρ_b is the density of the ball. In this work, a borosilicate glass ball with a density of 2.219×10^3 kg m^{-3} was used for the full range of the experimental conditions. The notation of ρ_m refers to the density of the liquid determined at the measuring temperature, and K in eq 1 is the ball constant. To ensure the results are accurate to better than ±1%, the ball constant

* To whom correspondence should be addressed.

0021-9568/92/1737-0209$03.00/0

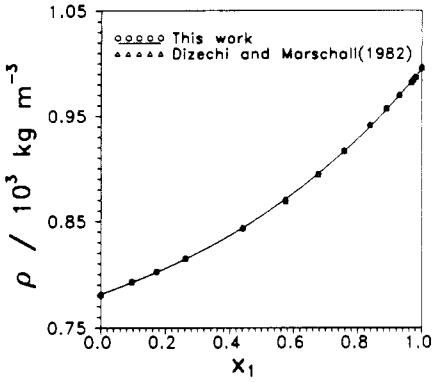

Figure 1. Comparison of density measurements of water (1)/ethanol (2) mixtures.

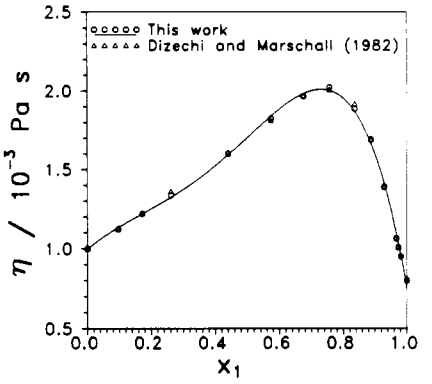

Figure 2. Comparison of viscosity measurements of water (1)/ethanol (2) mixtures.

Table I. Densities (ρ) and Viscosities (η) of Pure Liquids

		$\rho/(10^3$ kg m$^{-3})$			$\eta/(10^{-3}$ Pa s)		
substance	T/K	this work	lit.	ref	this work	lit.	ref
water	303.15	0.9957	0.9957	1	0.8002	0.8005	2
						0.7971	3
	313.15	0.9929	0.9923	1	0.6554	0.6568	2
						0.6513	3
	323.15	0.9889	0.9881	1	0.5498	0.5514	2
						0.5441	3
methanol	303.15	0.7826	0.7816	2	0.5147	0.5151	2
ethanol	303.15	0.7801	0.7807	2	0.9997	0.9993	2
toluene	303.15	0.8579	0.8576	3	0.5219	0.5220	3

should be calibrated with respect to fluid density. The literature data of water (*2*, *3*), ethanol (*2*), methanol (*2*), and toluene (*3*) were used to determine the ball constants, and the ball constants were correlated by the following equation:

$$K/(\mathrm{m^2\ s^{-2}}) = 0.815\,82 \times 10^{-6} + 0.107\,08 \times 10^{-12}(\rho_m/(\mathrm{kg\ m^{-3}})) \quad (2)$$

Five or more replications were made for each sample. Three readings of falling time were averaged to obtain the viscosity of the mixture from eq 1. The reproducibility was better than ±0.5%, and the accuracy was better than ±1%.

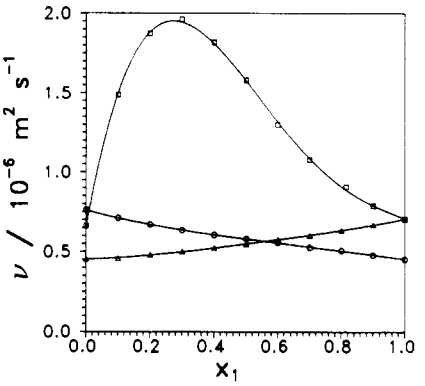

Figure 3. Variation of the kinematic viscosity with molar fraction at 313.15 K (O, 2-butanone (1)/dibutyl ether (2); Δ, 2-picoline (1)/2-butanone (2); □, 2-picoline (1)/water (2)).

The measured densities and viscosities of pure fluids are compared with literature values in Table I. Additionally, the densities and viscosities of water/ethanol mixtures are also investigated. The observed densities and viscosities are in good

Table II. Density (ρ) and Viscosity (η) for 2-Butanone (1)/Dibutyl Ether (2) Mixtures

T = 303.15 K			T = 313.15 K			T = 323.15 K		
x_1	$\rho/(10^3$ kg m$^{-3})$	$\eta/(10^{-3}$ Pa s)	x_1	$\rho/(10^3$ kg m$^{-3})$	$\eta/(10^{-3}$ Pa s)	x_1	$\rho/(10^3$ kg m$^{-3})$	$\eta/(10^{-3}$ Pa s)
0.0000	0.7600	0.6460	0.0000	0.7522	0.5715	0.0000	0.7432	0.5079
0.1005	0.7611	0.6078	0.1005	0.7532	0.5347	0.1005	0.7433	0.4826
0.2000	0.7626	0.5656	0.2000	0.7544	0.5046	0.2000	0.7446	0.4547
0.3000	0.7643	0.5411	0.3000	0.7546	0.4801	0.3000	0.7463	0.4348
0.4000	0.7669	0.5123	0.4000	0.7585	0.4584	0.4000	0.7482	0.4173
0.5000	0.7698	0.4882	0.5000	0.7610	0.4403	0.5000	0.7504	0.3980
0.6000	0.7732	0.4677	0.6000	0.7650	0.4254	0.6000	0.7535	0.3829
0.7000	0.7773	0.4480	0.7000	0.7681	0.4039	0.7000	0.7572	0.3693
0.8002	0.7818	0.4330	0.8002	0.7724	0.3920	0.8002	0.7614	0.3587
0.8998	0.7874	0.4036	0.8998	0.7806	0.3713	0.8998	0.7668	0.3465
1.0000	0.7944	0.3820	1.0000	0.7854	0.3560	1.0000	0.7748	0.3327

Table III. Density (ρ) and Viscosity (η) for 2-Picoline (1)/2-Butanone (2) Mixtures

T = 303.15 K			T = 313.15 K			T = 323.15 K		
x_1	$\rho/(10^3$ kg m$^{-3})$	$\eta/(10^{-3}$ Pa s)	x_1	$\rho/(10^3$ kg m$^{-3})$	$\eta/(10^{-3}$ Pa s)	x_1	$\rho/(10^3$ kg m$^{-3})$	$\eta/(10^{-3}$ Pa s)
0.0000	0.7944	0.3820	0.0000	0.7854	0.3560	0.0000	0.7748	0.3327
0.1000	0.8112	0.4017	0.1000	0.8011	0.3667	0.1000	0.7908	0.3457
0.2000	0.8259	0.4296	0.2000	0.8177	0.3917	0.2000	0.8071	0.3572
0.3000	0.8420	0.4565	0.3000	0.8327	0.4160	0.3000	0.8237	0.3813
0.4000	0.8571	0.4877	0.4000	0.8476	0.4445	0.4000	0.8378	0.4009
0.5000	0.8710	0.5193	0.5000	0.8618	0.4702	0.5000	0.8522	0.4264
0.6000	0.8846	0.5612	0.6000	0.8758	0.5038	0.6000	0.8663	0.4523
0.7000	0.8979	0.5978	0.7000	0.8893	0.5356	0.7000	0.8793	0.4827
0.7999	0.9111	0.6425	0.7999	0.9022	0.5718	0.7999	0.8929	0.5104
0.9000	0.9236	0.6942	0.9000	0.9153	0.6118	0.9000	0.9053	0.5528
1.0000	0.9359	0.7406	1.0000	0.9271	0.6537	0.1000	0.9182	0.5843

Table IV. Density (ρ) and Viscosity (η) for 2-Picoline (1)/Water (2) Mixtures

T = 303.15 K			T = 313.15 K			T = 323.15 K		
x_1	$\rho/(10^3$ kg m$^{-3})$	$\eta/(10^{-3}$ Pa s)	x_1	$\rho/(10^3$ kg m$^{-3})$	$\eta/(10^{-3}$ Pa s)	x_1	$\rho/(10^3$ kg m$^{-3})$	$\eta/(10^{-3}$ Pa s)
0.0000	0.9957	0.8002	0.0000	0.9923	0.6554	0.0000	0.9881	0.5502
0.1000	0.9918	1.9161	0.1000	0.9860	1.4666	0.1000	0.9792	1.1681
0.2000	0.9872	2.5060	0.2000	0.9810	1.8390	0.2000	0.9713	1.4201
0.3000	0.9819	2.5945	0.3000	0.9736	1.9091	0.3000	0.9646	1.4648
0.3999	0.9756	2.3638	0.3999	0.9670	1.7573	0.3999	0.9576	1.3621
0.4997	0.9682	1.9818	0.4997	0.9595	1.5151	0.4997	0.9501	1.2006
0.5999	0.9606	1.5541	0.5999	0.9522	1.2368	0.5999	0.9426	1.0079
0.7000	0.9531	1.2336	0.7000	0.9448	1.0165	0.7000	0.9354	0.8611
0.8146	0.9463	0.9988	0.8146	0.9378	0.8497	0.8146	0.9286	0.7336
0.8999	0.9402	0.8499	0.8999	0.9319	0.7339	0.8999	0.9227	0.6501
1.0000	0.9359	0.7406	1.0000	0.9271	0.6534	1.0000	0.9182	0.5843

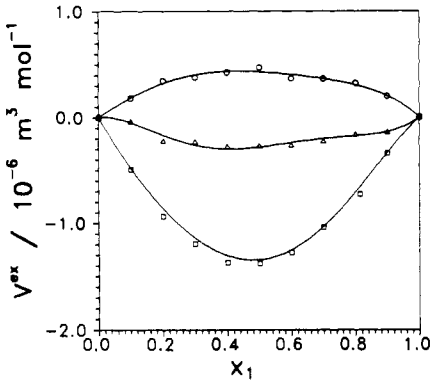

Figure 4. Variation of the excess volume with molar fraction at 313.15 K (O, 2-butanone (1)/dibutyl ether (2); Δ, 2-picoline (1)/2-butanone (2); □, 2-picoline (1)/water (2)).

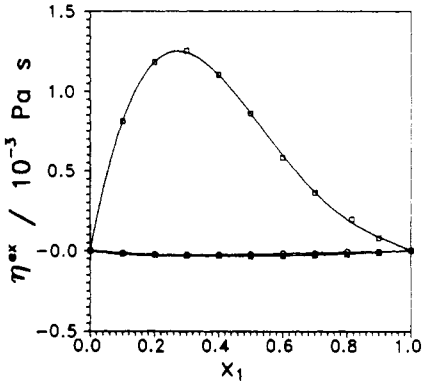

Figure 5. Variation of the excess viscosity with molar fraction at 313.15 K (O, 2-butanone (1)/dibutyl ether (2); Δ, 2-picoline (1)/2-butanone (2); □, 2-picoline (1)/water (2)).

agreement with the literature values (*2*) as illustrated in Figures 1 and 2, respectively.

Results and Discussion

The experimental results of density and viscosity measurements for 2-butanone/dibutyl ether, 2-picoline/2-butanone, and 2-picoline/water are listed in Tables II, III, and IV, respectively. Figure 3 illustrates the variations of the kinematic viscosity with molar fraction at 313.15 K. The excess volume and viscosity are calculated from the observed data with the following equations:

$$V^{ex} = V_m - (x_1V_1 + x_2V_2) \quad (3)$$

$$\eta^{ex} = \eta_m - (x_1\eta_1 + x_2\eta_2) \quad (4)$$

where V, x, and η are the molar volume, molar fraction, and dynamic viscosity. The subscripts 1 and 2 refer to the corresponding properties of pure components 1 and 2, respectively. The subscript m represents the corresponding properties of the mixture, and V_m is computed from the measured density (ρ_m) via

$$V_m = (x_1M_1 + x_2M_2)/\rho_m \quad (5)$$

The excess Gibbs energy of activation of flow can be calculated from eq 6 based on the Eyring viscosity equation (*4*, *5*):

$$\Delta G^{*ex} = RT\{\ln (\eta_m V_m) - [x_1 \ln (\eta_1 V_1) + x_2 \ln (\eta_2 V_2)]\} \quad (6)$$

The excess properties are correlated by a Redlich–Kister-type equation:

$$Y^{ex} = x_1x_2\sum_{i=0}^{3} A_i(x_1 - x_2)^i \quad (7)$$

where Y^{ex} stands for V^{ex}, η^{ex}, or ΔG^{*ex}. The coefficients A_i were determined from fitting eq 7 to the experimental data, and the optimal values of A_i together with the average absolute deviations (AAD) of calculated densities, dynamic viscosities, and ΔG^{*ex} are reported in Table V. The variations of excess properties with molar fraction at 313.15 K are shown in Figures 4–6, and the values calculated from eq 7 are illustrated by the smooth curves.

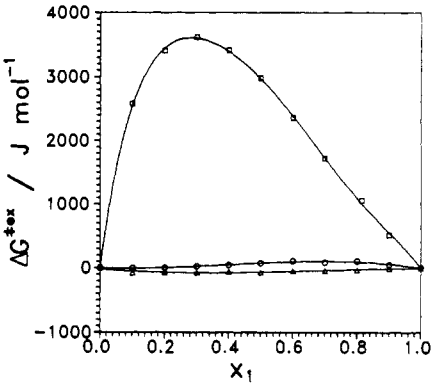

Figure 6. Variation of the excess Gibbs energy of activation of flow with molar fraction at 313.15 K (O, 2-butanone (1)/dibutyl ether (2); Δ, 2-picoline (1)/2-butanone (2); □, 2-picoline (1)/water (2)).

The kinematic viscosity data were correlated by using McAllister's three-body and four-body interaction models (*6*). The results are shown in Table VI. McAllister's three-body interaction model represents the viscosities of 2-butanone/dibutyl ether and 2-picoline/2-butanone mixtures satisfactorily, whereas it is not so successful for 2-picoline/water mixtures. For this mixture, the four-body interaction model substantially improves the accuracy of the correlations.

Glossary

A_i	coefficients in eq 7
K	ball constant
ΔG^*	Gibbs energy of activation of flow
M	molecular weight
r_i	molecular radius for component i
R	gas constant

Table V. Coefficients to Equation 7 for the Excess Properties

Excess Molar Volume

compd 1/compd 2	T/K	$A_0(10^{-6}$ Pa mol$^{-1})$	$A_1(10^{-6}$ Pa mol$^{-1})$	$A_2(10^{-6}$ Pa mol$^{-1})$	$A_3(10^{-6}$ Pa mol$^{-1})$	AAD[a]/%
2-butanone/dibutyl ether	303.15	1.4521	−0.7648	0.4487	0.6676	0.01
	313.15	1.7270	−0.3482	0.6596	0.7527	0.01
	323.15	2.4566	0.0384	2.2660	−0.6038	0.02
2-picoline/2-butanone	303.15	−1.0677	−0.0335	−0.1741	0.9039	0.03
	313.15	−1.1299	0.6871	0.1315	−2.0207	0.02
	323.15	−1.1680	0.7900	1.1054	−1.1344	0.03
2-picoline/water	303.15	−5.6437	0.8599	1.6709	0.5743	0.03
	313.15	−5.5891	0.7706	1.2394	0.3800	0.03
	323.15	−5.3847	0.5253	1.3124	0.8020	0.03

Excess Viscosity

compd 1/compd 2	T/K	$A_0(10^{-3}$ Pa s)	$A_1(10^{-3}$ Pa s)	$A_2(10^{-3}$ Pa s)	$A_3(10^{-3}$ Pa s)	AAD[b]/%
2-butanone/dibutyl ether	303.15	−0.0988	0.1352	0.0148	−0.1212	0.50
	313.15	−0.0916	0.0881	−0.0378	−0.0376	0.26
	323.15	−0.0903	0.0377	0.0350	−0.0109	0.22
2-picoline/2-butanone	303.15	−0.1617	−0.0347	0.0180	0.1077	0.24
	313.15	−0.1278	0.0208	−0.0642	0.1048	0.20
	323.15	−0.1375	−0.0098	0.0321	0.0764	0.47
2-picoline/water	303.15	4.9018	−8.2562	3.1515	1.8861	1.10
	313.15	3.4466	−5.2854	2.4108	0.3785	0.61
	323.15	2.5078	−3.5798	2.0178	−0.2871	0.52

ΔG^{*ex}

compd 1/compd 2	T/K	A_0(J mol^{-1})	A_1(J mol^{-1})	A_2(J mol^{-1})	A_3(J mol^{-1})	AAD[c]
2-butanone/dibutyl ether	303.15	382.6	728.1	174.9	−590.8	13.2
	313.15	312.7	556.4	−102.0	−258.2	6.7
	323.15	435.0	278.0	1053.4	66.7	11.9
2-picoline/2-butanone	303.15	−220.4	−32.4	0.0	515.9	6.7
	313.15	−218.0	2.5	−460.6	675.4	5.9
	323.15	−438.2	166.5	143.3	297.2	12.4
2-picoline/water	303.15	12187.5	−10891.6	8490.9	−6088.7	46.4
	313.15	11545.4	−9796.5	8411.2	−6852.8	46.4
	323.15	10985.5	−9047.5	8721.0	−7186.8	49.3

[a] $\text{AAD}/\% = [\sum_{i=1}^{n}(|V_{cal} - V_{exp}|/V_{exp})_i \times 100]/n$. [b] $\text{AAD}/\% = [\sum_{i=1}^{n}(|\eta_{cal} - \eta_{exp}|/\eta_{exp})_i \times 100]/n$. [c] $\text{AAD} = \sum_{i=1}^{n}|\Delta G^{*ex}{}_{cal} - \Delta G^{*ex}{}_{exp}|_i/n$.

Table VI. Coefficients for Kinematic Viscosities with McAllister's Models

			three-body model			four-body model			
compd 1/compd 2	T/K	r_2/r_1	ν_{12}	ν_{21}	AAD/%	ν_{1112}	ν_{1122}	ν_{2221}	AAD/%
2-butanone/dibutyl ether	303.15	1.2361	0.6238	0.6699	0.46	0.6006	0.6117	0.7355	0.38
	313.15	1.2355	0.5716	0.6030	0.27	0.5047	0.5782	0.6388	0.28
	323.15	1.2348	0.5108	0.5675	0.35	0.5047	0.5085	0.6093	0.21
2-picoline/2-butanone	303.15	1.0311	0.6547	0.5394	0.29	0.6863	0.5933	0.5243	0.29
	313.15	1.0304	0.5939	0.4927	0.38	0.6092	0.5633	0.4703	0.28
	323.15	1.0291	0.5422	0.4517	0.40	0.5704	0.4862	0.4469	0.39
2-picoline/water	303.15	1.7651	0.7322	16.7598	7.75	1.2338	1.2843	13.9500	2.23
	313.15	1.7687	0.6494	10.5258	7.44	1.0742	1.0079	8.9503	2.27
	323.15	1.7719	0.5943	7.0370	7.47	0.9387	0.8102	6.3359	2.34

t	falling time
T	temperature
V	molar volume
x	molar fraction
Y	variables in eq 7
ρ	density
η	dynamic viscosity
ν	kinematic viscosity
ν_{ij}	coefficients in McAllister's three-body interaction model
ν_{ijkl}	coefficients in McAllister's four-body interaction model

Superscript

ex	excess properties

Subscripts

1,2	components 1 and 2
b	ball
cal	calculated value
exp	experimental value
m	mixture properties

Registry No. 2-Butanone, 78-93-3; dibutyl ether, 142-96-1; 2-picoline, 109-06-8; water, 7732-18-5.

Literature Cited

(1) Haar, L.; Gallagher, J. S.; Kell, G. S. *NBS/NRC Steam Tables: Thermodynamic and Transport Properties and Computer Programs for Vapor and Liquid States of Water in SI Units*; Hemisphere Publishers: New York, 1984; p 34.
(2) Dizechi, M.; Marschall, E. *J. Chem. Eng. Data* **1982**, *27*, 358.
(3) Vargaftik, N. B. *Tables on the Thermophysical Properties of Liquids and Gases*, 2nd ed.; Hemisphere: Washington, DC, 1975; pp 48 and 348.
(4) Singh, R. P.; Sinha, C. P. *J. Chem. Eng. Data* **1985**, *30*, 470.
(5) Pikkarainen, L. *J. Chem. Eng. Data* **1983**, *28*, 381.
(6) McAllister, R. A. *AIChE J.* **1960**, *6*, 427.

Received for review July 22, 1991. Accepted November 25, 1991. Financial support from the National Science Council, ROC, through Grant No. NSC80-0402-E011-02 is gratefully acknowledged.