

using on the one hand eq 3, and on the other, the empirical relationships previously mentioned and derived from ref 1 and 2. The data represented have been evaluated at every 0.05 units of the molar fraction of benzene, x .

The analysis of the figures permits us to establish the following: while for benzene + heptan-1-ol, the distribution of the $\bar{\alpha}$ values presented a negative deviation in relation to the straight line $\bar{\alpha}_1x + \bar{\alpha}_2(1-x)$, now, for benzene + pentan-1-ol and benzene + pentan-2-ol, the deviation is positive. Likewise, it is interesting to observe the shift that has taken place in the distribution of the points empirically and in a direction totally contrary to that of the $\bar{\alpha}$ -values. The shifting of $\bar{\alpha}_{G-D}$, $\bar{\alpha}_{L-L}$, and $\bar{\alpha}_E$ has the same order in both systems as those of the benzene + heptan-1-ol mixture (see ref 1), giving the impression of having moved $\bar{\alpha}$ -axis. While for the system $C_6H_6 + C_7H_{15}(OH)$ the empirical equation that produced the least deviation from experimental data was that derived from Lorentz-Lorenz, in this work that equation was that which caused the greatest differences due to the translation of the $\bar{\alpha}$ -axis previously mentioned. These differences are due to the particular behavior of each mixture. The mean errors obtained from the empirical equa-

tions in relation to the experimental ones are respectively for benzene + pentan-1-ol and benzene + pentan-2-ol 9.73% and 12.21% with $\bar{\alpha}_{G-D}$; 15.05% and 16.41% with $\bar{\alpha}_E$; 21.46% and 22.59% with $\bar{\alpha}_{L-L}$.

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Densities, Viscosities, and Refractive Indexes for the Methyl Isobutyl Ketone + Pentanols Systems. Measurements and Correlations

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In order to facilitate interpolation of the data, empirical single equations for density, viscosity, and refractive index as functions of composition and temperature were obtained by using the experimental results for the methyl isobutyl ketone + 1-pentanol, + 2-pentanol, + isoamyl alcohol, and + *tert*-amyl alcohol binary systems at 25, 30, 35, and 40 °C. The properties calculated through the empirical relations are in fairly good agreement with the experimental data.

Many industrial chemical processes or laboratory works need experimental data of density, viscosity, and refractive index at any given temperature and composition for binary liquid mixtures. Keeping in mind this problem, we are developing equations in which temperature and composition are incorporated to facilitate the interpolation data for these properties of the methyl isobutyl ketone (MIK) + 1-pentanol (P_1), + 2-pentanol (P_2), + isoamyl alcohol (IA), and + *tert*-amyl alcohol (TA) systems.

Experimental Section

Materials. The components were supplied by Merck-Darmstadt (A.R. grade). All species were dried with anhydrous K_2CO_3 and fractionally distilled. The middle fraction was collected in each case and kept out from humidity with 3 Å molecular sieves for the pentanols and 4 Å for the methyl isobutyl ketone. The samples were maintained over molecular sieves to prevent water absorption. The physical properties of chem-

icals used here are compared with those reported in the literature in Table I.

Procedure. Mixtures were prepared by mixing accurately weighed quantities of pure liquids. Caution was taken to prevent evaporation. The Anton Paar DMA 46 calculating density meter with a built-in thermostat, a Cannon-Fenske viscosimeter, and a Jena dipping refractometer were used to obtain the density, viscosity, and refractive index, respectively. The accuracy of the measurements of these properties reported here is reproducible to within $\pm 0.0001 \text{ g cm}^{-3}$, $\pm 0.5\%$, and ± 0.00002 , respectively. In all cases, a thermostatically controlled bath to $\pm 0.01 \text{ }^\circ\text{C}$ was used.

Results and Discussion

The experimental results of densities, viscosities, and refractive indexes at several temperatures and compositions for the systems (MIK + P_1), (MIK + P_2), (MIK + IA), and (MIK + TA) are summarized in Tables II, III, IV, and V, respectively.

The following functional relationships of density, viscosity, and refractive index of the mixtures with the temperature were assumed (4-6).

$$\rho = A_1 e^{\beta_1 t} \quad (1)$$

$$\eta = A_2 e^{\beta_2 t/T} \quad (2)$$

$$n_D = A_3 e^{\beta_3 t} \quad (3)$$

Table I. Physical Properties of the Pure Chemicals

components	$t, ^\circ\text{C}$	$\rho, \text{g cm}^{-3}$		η, cP		n_D	
		exptl	lit.	exptl	lit.	exptl	lit.
MIK	25	0.7963	0.7961 (1)	0.543	0.542 (1)	1.39360	1.39330 (1)
	30	0.7920		0.519		1.39124	
	35	0.7868		0.493		1.38875	
	40	0.7826		0.467		1.38674	
P_1	25	0.8110	0.8115 (1)	3.35	3.347 (1)	1.40783	1.40790 (1)
	30	0.8073		3.00	2.99 (3)	1.40573	
	35	0.8039		2.63		1.40354	
	40	0.7999		2.30		1.40180	
P_2	25	0.8055	0.8054 (1)	3.45	3.445 (2)	1.40418	1.40440 (1)
	30	0.8010		2.77	2.78 (1)	1.40201	
	35	0.7969	0.7977 (2)	2.32	2.392 (2)	1.39966	1.40001 (2)
	40	0.7928		1.92		1.39799	
IA	25	0.8071	0.8071 (1)	3.48		1.40523	1.40520 (1)
	30	0.8027		2.95	2.96 (1)	1.40347	
	35	0.7990	0.7975 (2)	2.53	2.80 (2)	1.40129	1.40061 (2)
	40	0.7949		2.21		1.39954	
TA	25	0.8050	0.8050 (1)	3.52	3.548 (2)	1.40237	1.40240 (1)
	30	0.8006		2.87	2.81 (1)	1.40002	
	35	0.7960	0.7962 (2)	2.37	2.377 (2)	1.39740	1.39775 (2)
	40	0.7912		1.96		1.39546	

Table II. Experimental Density, Viscosity, and Refractive Index at Several Temperatures for the MIK + P_1 System

X_{MIK}	$\rho, \text{g cm}^{-3}$				η, cP				X_{MIK}	n_D			
	25 $^\circ\text{C}$	30 $^\circ\text{C}$	35 $^\circ\text{C}$	40 $^\circ\text{C}$	25 $^\circ\text{C}$	30 $^\circ\text{C}$	35 $^\circ\text{C}$	40 $^\circ\text{C}$		25 $^\circ\text{C}$	30 $^\circ\text{C}$	35 $^\circ\text{C}$	40 $^\circ\text{C}$
0.0000	0.8110	0.8073	0.8039	0.7999	3.35	3.00	2.63	2.30	0.0000	1.40783	1.40573	1.40354	1.40180
0.1011	0.8095	0.8058	0.8021	0.7983	2.47	2.20	1.96	1.75	0.1020	1.40638	1.40424	1.40201	1.40027
0.1974	0.8082	0.8043	0.8005	0.7966	1.89	1.70	1.53	1.38	0.2026	1.40497	1.40278	1.40054	1.39874
0.3040	0.8066	0.8027	0.7986	0.7948	1.46	1.32	1.20	1.09	0.3006	1.40357	1.40139	1.39909	1.39722
0.4023	0.8051	0.8012	0.7970	0.7931	1.20	1.10	1.01	0.915	0.4042	1.40216	1.39991	1.39751	1.39571
0.5022	0.8037	0.7996	0.7953	0.7913	1.00	0.919	0.846	0.781	0.4992	1.40069	1.39843	1.39609	1.39423
0.6064	0.8020	0.7980	0.7936	0.7895	0.856	0.792	0.735	0.683	0.6015	1.39934	1.39696	1.39461	1.39275
0.7079	0.8006	0.7964	0.7918	0.7878	0.738	0.694	0.646	0.601	0.7005	1.39789	1.39559	1.39320	1.39120
0.7955	0.7993	0.7951	0.7903	0.7862	0.668	0.624	0.589	0.555	0.7995	1.39652	1.39410	1.39165	1.38972
0.8962	0.7978	0.7936	0.7886	0.7844	0.592	0.558	0.530	0.501	0.8996	1.39509	1.39271	1.39024	1.38824
1.0000	0.7963	0.7920	0.7868	0.7826	0.543	0.519	0.493	0.467	1.0000	1.39360	1.39124	1.38875	1.38674

Table III. Experimental Density, Viscosity, and Refractive Index at Several Temperatures for the MIK + P_2 System

X_{MIK}	$\rho, \text{g cm}^{-3}$				η, cP				X_{MIK}	n_D			
	25 $^\circ\text{C}$	30 $^\circ\text{C}$	35 $^\circ\text{C}$	40 $^\circ\text{C}$	25 $^\circ\text{C}$	30 $^\circ\text{C}$	35 $^\circ\text{C}$	40 $^\circ\text{C}$		25 $^\circ\text{C}$	30 $^\circ\text{C}$	35 $^\circ\text{C}$	40 $^\circ\text{C}$
0.0000	0.8055	0.8010	0.7969	0.7928	3.45	2.77	2.32	1.92	0.0000	1.40418	1.40201	1.39966	1.39799
0.1036	0.8034	0.7989	0.7948	0.7906	2.26	1.93	1.65	1.41	0.1020	1.40265	1.40047	1.39810	1.39638
0.2131	0.8018	0.7972	0.7931	0.7888	1.61	1.41	1.25	1.10	0.2032	1.40113	1.39887	1.39652	1.39477
0.3003	0.8005	0.7960	0.7918	0.7874	1.32	1.16	1.05	0.965	0.3022	1.39975	1.39753	1.39515	1.39337
0.3959	0.7995	0.7950	0.7905	0.7863	1.12	1.01	0.910	0.837	0.4009	1.39869	1.39644	1.39406	1.39228
0.5098	0.7983	0.7938	0.7893	0.7850	0.924	0.848	0.780	0.718	0.5015	1.39763	1.39536	1.39297	1.39110
0.5963	0.7977	0.7932	0.7884	0.7843	0.821	0.760	0.705	0.658	0.6025	1.39662	1.39435	1.39192	1.39001
0.6924	0.7969	0.7924	0.7878	0.7833	0.712	0.664	0.620	0.601	0.7003	1.39567	1.39338	1.39090	1.38902
0.7942	0.7964	0.7918	0.7870	0.7827	0.646	0.607	0.571	0.553	0.7997	1.39488	1.39255	1.39009	1.38817
0.9001	0.7961	0.7917	0.7866	0.7824	0.589	0.557	0.527	0.502	0.9015	1.39410	1.39178	1.38930	1.38732
1.0000	0.7963	0.7920	0.7868	0.7826	0.543	0.519	0.493	0.467	1.0000	1.39360	1.39124	1.38875	1.38674

Table IV. Experimental Density, Viscosity, and Refractive Index at Several Temperatures for the MIK + IA System

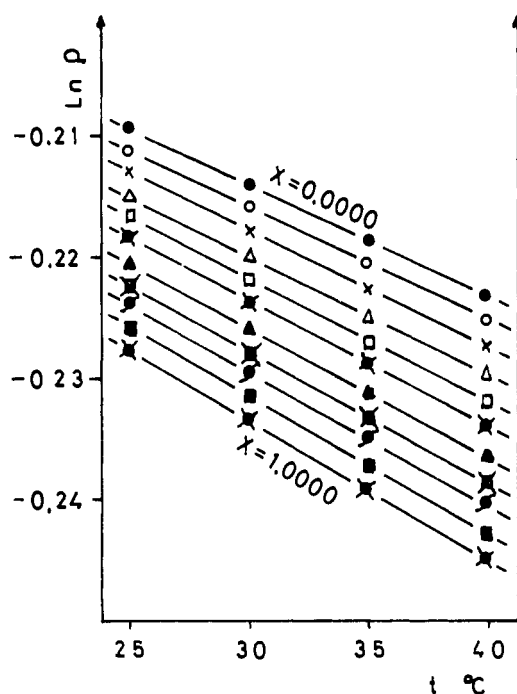
X_{MIK}	$\rho, \text{g cm}^{-3}$				η, cP				X_{MIK}	n_D			
	25 $^\circ\text{C}$	30 $^\circ\text{C}$	35 $^\circ\text{C}$	40 $^\circ\text{C}$	25 $^\circ\text{C}$	30 $^\circ\text{C}$	35 $^\circ\text{C}$	40 $^\circ\text{C}$		25 $^\circ\text{C}$	30 $^\circ\text{C}$	35 $^\circ\text{C}$	40 $^\circ\text{C}$
0.0000	0.8071	0.8027	0.7990	0.7949	3.48	2.95	2.53	2.21	0.0000	1.40523	1.40347	1.40129	1.39954
0.1006	0.8058	0.8014	0.7976	0.7934	2.58	2.26	1.99	1.75	0.1020	1.40400	1.40202	1.40004	1.39807
0.2027	0.8045	0.8002	0.7963	0.7921	1.89	1.69	1.51	1.36	0.2047	1.40272	1.40080	1.39856	1.39677
0.3201	0.8031	0.7988	0.7947	0.7906	1.40	1.28	1.17	1.05	0.3036	1.40148	1.39952	1.39725	1.39542
0.3948	0.8022	0.7979	0.7939	0.7896	1.20	1.10	1.01	0.926	0.4015	1.40026	1.39824	1.39594	1.39408
0.5073	0.8010	0.7967	0.7925	0.7882	0.965	0.903	0.837	0.766	0.5028	1.39900	1.39693	1.39460	1.39274
0.6072	0.7999	0.7957	0.7913	0.7870	0.839	0.781	0.728	0.681	0.6001	1.39796	1.39583	1.39347	1.39155
0.7013	0.7990	0.7948	0.7901	0.7859	0.728	0.682	0.640	0.602	0.7008	1.39681	1.39463	1.39221	1.39029
0.8032	0.7981	0.7938	0.7890	0.7848	0.648	0.617	0.579	0.545	0.8027	1.39561	1.39339	1.39097	1.38902
0.8927	0.7972	0.7930	0.7880	0.7838	0.595	0.566	0.534	0.506	0.9013	1.39450	1.39221	1.38976	1.38774
1.0000	0.7963	0.7920	0.7868	0.7826	0.543	0.519	0.493	0.467	1.0000	1.39360	1.39124	1.38875	1.38674

Table V. Experimental Density, Viscosity, and Refractive Index at Several Temperatures for the MIK + TA System

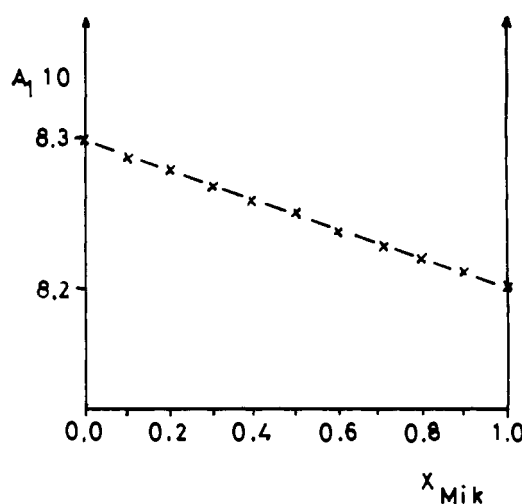
X_{MIK}	ρ , g cm ⁻³				η , cP				X_{MIK}	n_D			
	25 °C	30 °C	35 °C	40 °C	25 °C	30 °C	35 °C	40 °C		25 °C	30 °C	35 °C	40 °C
0.0000	0.8050	0.8006	0.7960	0.7912	3.52	2.87	2.37	1.96	0.0000	1.40237	1.40002	1.39740	1.39546
0.1053	0.8036	0.7993	0.7946	0.7897	2.50	2.11	1.79	1.52	0.1029	1.40123	1.39890	1.39657	1.39424
0.1952	0.8024	0.7981	0.7934	0.7884	1.77	1.52	1.32	1.15	0.2045	1.40017	1.39784	1.39551	1.39318
0.3050	0.8010	0.7967	0.7920	0.7871	1.37	1.21	1.07	0.951	0.3052	1.39901	1.39668	1.39435	1.39203
0.4324	0.7995	0.7952	0.7906	0.7856	1.05	0.946	0.856	0.776	0.4040	1.39798	1.39563	1.39331	1.39099
0.4950	0.7988	0.7945	0.7898	0.7851	0.950	0.866	0.786	0.721	0.5112	1.39702	1.39470	1.39238	1.39007
0.6000	0.7978	0.7934	0.7885	0.7840	0.813	0.747	0.690	0.640	0.6061	1.39602	1.39370	1.39138	1.38907
0.7004	0.7970	0.7926	0.7875	0.7832	0.719	0.671	0.627	0.587	0.7036	1.39503	1.39271	1.39039	1.38805
0.7937	0.7965	0.7921	0.7870	0.7828	0.641	0.603	0.569	0.538	0.7991	1.39437	1.39205	1.38974	1.38744
0.9001	0.7961	0.7917	0.7866	0.7824	0.589	0.558	0.529	0.503	0.9028	1.39380	1.39149	1.38918	1.38687
1.0000	0.7963	0.7920	0.7868	0.7826	0.543	0.519	0.493	0.467	1.0000	1.39360	1.39124	1.38875	1.38674

Table VI. Equations for Density, Viscosity, and Refractive Index as a Function of the Temperature and Composition for the MIK + Pentanols Systems^a

system	equations	D
MIK + P ₁	$\rho = (0.8296 - 0.0097X) \exp[(-9.054 - 2.607X)10^{-4}t]$ (4) $\eta = (12.86 + 62.76X - 59.05X^2 + 220.33X^3)10^{-4} \exp[(2338.05 - 1966.49X + 886.04X^2 - 332.20X^3)/T]$ (5) $n_D = (1.41802 - 0.01272X) \exp[(-28.82 - 5.610X + 1.093X^2)10^{-5}t]$ (6)	1.2×10^{-2} 2.15 7.7×10^{-3}
MIK + P ₂	$\rho = (0.8268 - 0.0166X + 0.0101X^2) \exp[(-10.55 - 1.35X)10^{-4}t]$ (7) $\eta = \exp(-10.99 + 24.29X - 40.37X^2 + 35.08X^3 - 11.75X^4) \exp[(3647.3 - 8702.7X + 14295.9X^2 - 12684.2X^3 + 4379.1X^4)/T]$ (8) $n_D = (1.41461 - 0.01471X + 0.00524X^2) \exp[(-29.88 - 3.28X)10^{-5}t]$ (9)	1.3×10^{-2} 0.99 8.6×10^{-3}
MIK + IA	$\rho = (0.8276 - 0.0118X + 0.0042X^2) \exp[(-10.068 - 0.891X - 0.763X^2)10^{-4}t]$ (10) $\eta = \exp(-8.26 + 12.97X - 18.90X^2 + 15.87X^3 - 5.45X^4) \exp[(2829.6 - 4805.7X + 5890.7X^2 - 4362.7X^3 + 1388.1X^4)/T]$ (11) $n_D = (1.41502 - 0.01122X + 0.00128X^2) \exp[(-27.54 - 5.62X)10^{-5}t]$ (12)	1.3×10^{-2} 0.68 5.9×10^{-3}
MIK + TA	$\rho = (0.8291 - 0.0167X + 0.0073X^2) \exp[(-11.62 - 0.12X)10^{-4}t]$ (13) $\eta = \exp(-10.97 + 16.32X - 19.57X^2 + 19.96X^3 - 9.49X^4) \exp[(3638.8 - 5977.7X + 6560.3X^2 - 6019.3X^3 + 2738.0X^4)/T]$ (14) $n_D = (1.41424 - 0.01301X + 0.00367X^2) \exp[(-33.39 + 0.19X)10^{-5}t]$ (15)	2.6×10^{-2} 1.36 9.2×10^{-3}

^a Units: ρ , g cm⁻³; η , cP.**Figure 1.** MIK + P₁ mixture densities vs. temperature.

Density and refractive index data of the mixtures are plotted vs. t , while the viscosity data are plotted vs. $1/T$. Then the parameter pairs ($A_1; B_1$), ($A_2; B_2$), and ($A_3; B_3$) are plotted as a function of the molar fraction of MIK.

**Figure 2.** Constant A_1 in eq 1 vs. molar fraction of methyl isobutyl ketone.

Smoothed ($\ln \rho$) data of the mixtures are plotted vs. t for the (MIK + P₁) system (see Figure 1), keeping X_{MIK} as a parameter. All systems show straight lines for each of the integral values of composition as stated above. Then the parameter pair ($A_1; B_1$) was determined for all straight lines (see Figures 2 and 3). For the other properties and systems, the plots are similar, but they are not presented here. However, the functional relationship between A_2 's and X_{MIK} is replaced by $\ln A_2$'s vs. X_{MIK} , except for the MIK-P₁ system.

Equations that resulted from the analyses of these data are

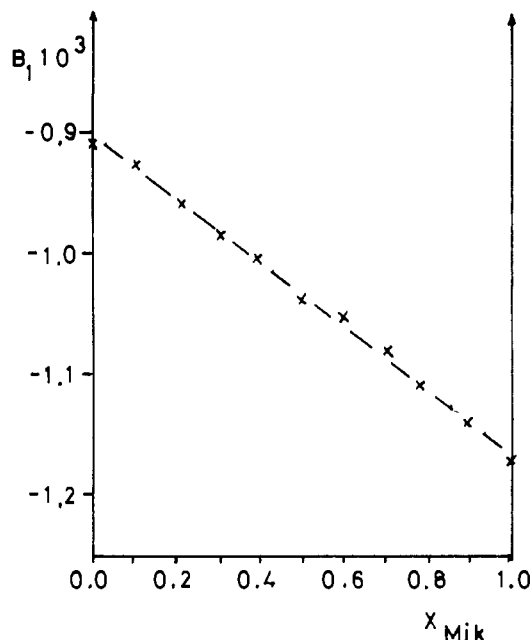


Figure 3. Constant B_1 in eq 1 vs. molar fraction of methyl isobutyl ketone.

listed in Table VI. By means of eq 4-15, density, viscosity, and refractive index data for the studied systems in this paper at any temperature and composition, within the experimental ranges, can be predicted. The calculated values through these equations compared well with the experimental data, and the

average percent deviation (D) for each property and system is also listed in Table VI.

Glossary

A_1, B_1	constants in eq 1
A_2, B_2	constants in eq 2
A_3, B_3	constants in eq 3
ρ	density of the mixture, g cm^{-3}
η	viscosity of the mixture, cP
n_D	refractive index of the mixture for the sodium D line.
X_{Mik}, X	molar fraction of the MIK
T	temperature, K
t	temperature, $^{\circ}\text{C}$
D	average percent deviation

Registry No. MIBK, 108-10-1; P₁, 71-41-0; P₂, 6032-29-7; IA, 123-51-3; TA, 75-85-4.

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Isentropic Compressibilities of Binary Liquid Mixtures at 303.15 and 313.15 K

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Isentropic compressibilities for the binary mixtures of methyl ethyl ketone with benzene, toluene, chlorobenzene, bromobenzene, and nitrobenzene have been determined at 303.15 and 313.15 K, using ultrasonic velocity and density data. Excess isentropic compressibility, k_s^E , values are negative over the entire range of composition for all the systems and at both temperatures. The behavior of k_s^E as a function of composition and temperature has been studied. The results have been discussed in terms of dipole-induced dipole and dipole-dipole interactions between dissimilar components.

Excess isentropic compressibilities have been determined for binary mixtures of methyl ethyl ketone with benzene, toluene, chlorobenzene, bromobenzene, and nitrobenzene in order to study the effect that group substitution on a benzene ring has on the molecular interaction in the presence of a polar component. A literature survey revealed that the excess isentropic compressibilities for these systems have not been reported.

Table I. Pure Component Parameters

component	T/K	$V/(\text{cm}^3 \text{mol}^{-1})$	$K_s/(\text{TPa}^{-1})$	$10^3 \alpha/\text{K}^{-1}$	$C_p/(\text{J K}^{-1} \text{mol}^{-1})$
MEK	303.15	90.77	915	1.256	162.2
	313.15	91.72	1002	1.271	169.1
C_6H_6	303.15	89.81	707	1.242	137.4
	313.15	91.08	770	1.258	140.6
$\text{C}_6\text{H}_5\text{CH}_3$	303.15	107.44	699	1.079	159.9
	313.15	108.61	757	1.091	163.4
$\text{C}_6\text{H}_5\text{Cl}$	303.15	102.75	589	0.985	150.6
	313.15	103.76	634	1.005	152.2
$\text{C}_6\text{H}_5\text{Br}$	303.15	105.98	514	0.896	155.9
	313.15	106.95	554	0.992	157.3
$\text{C}_6\text{H}_5\text{NO}_2$	303.15	103.16	395	0.818	177.3
	313.15	104.01	426	0.865	173.6

Experimental Section

Ultrasonic velocities were measured by using a single-crystal interferometer at a frequency of 2 MHz, and the values were accurate to $\pm 0.1\%$. Density data for the pure components were measured by using a bicapillary pycnometer, and in the