Density and Viscosity for a Binary Mixture of Ethyl Valerate and Hexyl Acetate with 1-Pentanol and 1-Hexanol at 293.15 K, 303.15 K, and 313.15 K

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Density and viscosity for a binary mixture of ethyl valerate and hexyl acetate with 1-pentanol and 1-hexanol were measured in this experiment at three different temperatures (293.15, 303.15, and 313.15 K) and at atmospheric pressure. The measurements were carried out over the whole range of composition. Density values were used in the determination of the excess molar volume, V^E, and the viscosity deviations, $\Delta\eta_L$. The latter were fitted to the Redlich−Kister polynomial equation.

Introduction

In the flavor and fragrance industries, aliphatic and acrylic esters are important materials in the manufacturing processes. Several studies of the thermodynamic behavior, such as excess volume and excess enthalpy,[1−5] and physical properties[6,7] of their binary mixtures have been performed. The density and viscosity data of a binary mixture are important from practical and theoretical points of view, to understand liquid theory. However, detailed investigations of these physical properties of the esters in a binary mixture with alcohol over a wide range of temperatures and compositions are scarce in the literature. Therefore, this study was undertaken to obtain reliable density and viscosity data for binary mixtures of ethyl valerate and hexyl acetate with 1-pentanol and 1-hexanol at 293.15 K, 303.15 K, and 313.15 K. From these data, excess molar volume and the viscosity deviations were calculated.

Experimental Section

Materials. High purity and AR grade samples of ethyl valerate, hexyl acetate, 1-pentanol, and 1-hexanol were purchased from Merck, Germany. The purity of all the chemicals was analyzed by gas chromatography (Shimadzu, GC-17A) using a flame ionization detector with a DB-5 column. Since the purity of all compounds was >99.6 mol %, these chemicals were used without further purification. The binary mixture samples were prepared by mass in airtight stoppered glass bottles using a Mettler Toledo AE 240 balance with a precision of $\pm 10^{-5}$ g. The possible error of the mole fraction for each binary mixture is $<\pm 0.0001$.

Density Measurements. The measurements of the densities of the pure components and the binary mixtures were carried out using a Mettler Toledo density meter type DE50 with the precision 10^{-5} g·cm^{-3}. Prior to use, the instrument was calibrated with double-distilled water. The temperature of the measuring cell was maintained at 293.15 K, 303.15 K, and 313.15 K using Julabo refrigerated and heating circulators model F12-MD with stability up to ±0.01 K.

Viscosity Measurements. For the viscosity measurement, an automated microviscosimeter Anton Paar type AMVn, equipped with an automatic timer (±0.01 s), was used. This instrument uses the rolling ball principle according to DIN 53015 and ISO/DIS 12058, where gold-covered steel balls roll down inside an inclined, sample-filled glass capillary. The uncertainty in time in the range (0 to 250) s is <0.02 s with a resolution of ±0.01 s. The temperature range of this viscosimeter is from 283.15 K

Table 1. Comparison of Experimental Density (ρ_L), Viscosity (η_L), and Refractive Index (n_D) of Pure Liquid with Literature Values at 293.15 K, 303.15 K, and 313.15 K

		ρ_L/(g·cm^{-3})		η_L/(mPa·s)	
compound	T/K	exp	lit.	exp	lit.
ethyl valerate	293.15	0.876 80	0.8770[8]	0.846	0.847[8]
					0.840[9]
	303.15	0.866 90	n.a	0.694	0.698[9]
	313.15	0.856 81	n.a	0.629	0.603[9]
hexyl acetate	293.15	0.873 09	0.8726[10]	1.078	0.860[8]
					1.170[10]
	303.15	0.863 22	0.8636[10]	0.782	n.a
	313.15	0.853 53	0.8546[10]	0.672	n.a
1-pentanol	293.15	0.814 12	0.8144[10]	4.109	4.400[9]
	303.15	0.807 11	0.8072[10]	2.933	3.202[9]
			0.8068[11]		2.909[10]
					2.961[11]
	313.15	0.799 78	0.8000[10]	2.299	2.422[9]
1-hexanol	293.15	0.818 41	0.8187[10]	4.993	5.022[9]
	303.15	0.811 60	0.8118[10]	3.792	3.872[8]
			0.8119[11]		3.765[10]
					3.781[11]
	313.15	0.804 60	0.8048[10]	2.812	2.779[9]

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10.1021/je0001431 CCC: $20.00
Published on Web 12/09/2000

Table 2. Experimental Density (ρ_L), Viscosity (η_L), and Excess Molar Volume (V^E) for Binary Mixtures of Ethyl Valerate (1) + 1-Pentanol (2) at 293.15 K, 303.15 K, and 313.15 K

x_1	ρ_L/ (g·cm^{-3})	η_L/ (mPa·s)	V^E/ (cm^3·mol^{-1})
	293.15 K		
0.0000	0.814 08	4.109	0.0000
0.1037	0.821 71	3.302	0.1354
0.1921	0.827 50	2.761	0.2836
0.3001	0.834 20	2.241	0.4505
0.4089	0.841 13	1.841	0.5236
0.5015	0.846 81	1.575	0.5549
0.6062	0.853 52	1.340	0.4899
0.7081	0.859 94	1.163	0.3839
0.8013	0.865 58	1.036	0.2601
0.9029	0.871 51	0.927	0.1232
1.0000	0.876 80	0.846	0.0000
	303.15 K		
0.0000	0.807 10	2.933	0.0000
0.1037	0.814 50	2.379	0.1130
0.1921	0.820 30	2.008	0.2198
0.3001	0.826 72	1.651	0.3803
0.4089	0.833 19	1.377	0.4626
0.5015	0.838 72	1.195	0.4822
0.6062	0.845 11	1.033	0.4156
0.7081	0.851 11	0.912	0.3269
0.8013	0.856 53	0.825	0.2102
0.9029	0.861 94	0.749	0.1127
1.0000	0.866 90	0.694	0.0000
	313.15 K		
0.0000	0.799 78	2.299	0.0000
0.1037	0.806 91	1.887	0.1057
0.1921	0.812 70	1.610	0.1713
0.3001	0.818 81	1.344	0.3273
0.4089	0.825 01	1.139	0.4061
0.5015	0.830 24	1.004	0.4308
0.6062	0.836 31	0.884	0.3647
0.7081	0.842 12	0.793	0.2631
0.8013	0.846 96	0.728	0.1891
0.9029	0.852 13	0.672	0.1003
1.0000	0.856 81	0.629	0.0000

Table 3. Experimental Density (ρ_L), Viscosity (η_L), and Excess Molar Volume (V^E) for Binary Mixtures of Ethyl Valerate (1) + 1-Hexanol (2) at 293.15 K, 303.15 K, and 313.15 K

x_1	ρ_L/ (g·cm^{-3})	η_L/ (mPa·s)	V^E/ (cm^3·mol^{-1})
	293.15 K		
0.0000	0.818 40	4.993	0.0000
0.1071	0.824 71	3.938	0.1601
0.2022	0.830 21	3.209	0.2682
0.3018	0.836 02	2.610	0.3479
0.3929	0.841 19	2.177	0.3913
0.5117	0.848 31	1.740	0.4066
0.6028	0.853 60	1.483	0.3872
0.7035	0.859 50	1.258	0.3349
0.8025	0.865 30	1.086	0.2528
0.9053	0.871 30	0.946	0.1358
1.0000	0.876 81	0.846	0.0000
	303.15 K		
0.0000	0.811 61	3.792	0.0000
0.1071	0.818 01	3.004	0.0820
0.2022	0.823 27	2.460	0.1808
0.3018	0.828 81	2.012	0.2594
0.3929	0.833 81	1.688	0.3074
0.5117	0.840 41	1.362	0.3165
0.6028	0.845 44	1.170	0.3030
0.7035	0.851 00	1.002	0.2458
0.8025	0.856 52	0.873	0.1599
0.9053	0.862 21	0.769	0.0414
1.0000	0.866 77	0.694	0.0000
	313.15 K		
0.0000	0.804 60	2.812	0.0000
0.1071	0.810 82	2.257	0.0562
0.2022	0.816 13	1.873	0.1046
0.3018	0.821 28	1.558	0.1793
0.3929	0.826 01	1.329	0.2287
0.5117	0.832 22	1.100	0.2418
0.6028	0.837 00	0.964	0.2142
0.7035	0.842 20	0.846	0.1721
0.8025	0.847 44	0.755	0.0859
0.9053	0.852 81	0.682	−0.0345
1.0000	0.856 78	0.629	0.0000

to 343.15 K with an accuracy of <0.05 K. The calibrations of the apparatus were performed periodically with double-distilled water. The accuracy in the viscosity measurement was estimated as better than 0.004 mPa·s. The measuring temperature was kept at 293.15 K, 303.15 K, and 313.15 K by placing the sample-filled glass capillary in a block controlled with a Julabo refrigerated and heating circulator.

All measurements described above were performed at least as three, and the results were averaged to give the final values.

Results and Discussion

The experimental results of density and viscosity of the pure liquid and comparison with those from the literature are summarized in Table 1. The experimental values are generally in agreement with those from the literature.[8−11] The experimental results of density and viscosity of four binary mixtures, ethyl valerate (1) + 1-pentanol (2), ethyl valerate (1) + 1-hexanol (2), hexyl acetate (1) + 1-pentanol (2), and hexyl acetate (1) + 1-hexanol (2), at 293.15 K, 303.15 K, and 313.15 K are summarized in Tables 2−5.

The excess molar volume, V^E, was calculated from density measurements according to the following equation:

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho_L} - x_1V_1 - x_2V_2 \qquad (1)$$

where ρ_L is the density of the mixture and x_1, V_1, M_1, x_2, V_2, and M_2 are the mole fraction, molar volume, and molecular weight of pure compounds 1 and 2, respectively. The excess molar volume values calculated from eq 1 are also summarized in Tables 2−5. The excess molar volumes for all mixtures are positive and decrease with the increase of temperature from 293.15 K to 313.15 K. The positive excess molar volume values for ester + alkanols systems have been explained in terms of the declustering of alkanols

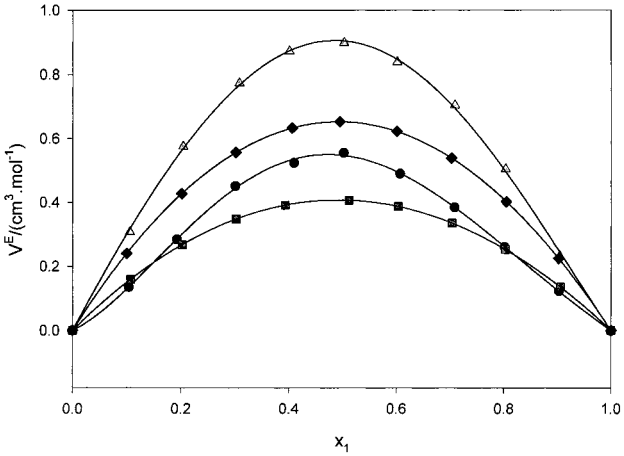

Figure 1. Excess molar volumes, V^E, at 293.15 K for (●) ethyl valerate (1) + 1-pentanol (2), (■) ethyl valerate (1) + 1-hexanol (2), (▲) hexyl acetate (1) + 1-pentanol (2), and (◆) hexyl acetate (1) + 1-hexanol (2).

Table 4. Experimental Density (ρ_L), Viscosity (η_L), and Excess Molar Volume (V^E) for Binary Mixtures of Hexyl Acetate (1) + 1-Pentanol (2) at 293.15 K, 303.15 K, and 313.15 K

x_1	ρ_L/ (g·cm^{-3})	η_L/ (mPa·s)	V^E/ (cm^3·mol^{-1})
	293.15 K		
0.0000	0.814 06	4.109	0.0000
0.1057	0.820 92	3.347	0.3080
0.2038	0.826 72	2.798	0.5754
0.3074	0.832 77	2.346	0.7730
0.4005	0.838 31	2.028	0.8722
0.5019	0.844 31	1.755	0.8986
0.6009	0.850 23	1.548	0.8384
0.7083	0.856 54	1.373	0.7038
0.8029	0.862 10	1.253	0.5038
0.9041	0.868 00	1.153	0.2326
1.0000	0.873 11	1.078	0.0000
	303.15 K		
0.0000	0.807 05	2.933	0.0000
0.1057	0.813 91	2.392	0.2536
0.2038	0.819 40	2.002	0.5146
0.3074	0.825 20	1.682	0.7057
0.4005	0.830 60	1.456	0.7736
0.5019	0.836 22	1.262	0.8142
0.6009	0.841 71	1.115	0.7725
0.7083	0.847 68	0.991	0.6378
0.8029	0.853 01	0.906	0.4456
0.9041	0.858 73	0.835	0.1622
1.0000	0.863 23	0.782	0.0000
	313.15 K		
0.0000	0.799 76	2.299	0.0000
0.1057	0.806 44	1.889	0.2364
0.2038	0.811 62	1.594	0.5019
0.3074	0.817 31	1.352	0.6660
0.4005	0.822 33	1.181	0.7596
0.5019	0.827 80	1.035	0.7759
0.6009	0.833 10	0.924	0.7279
0.7083	0.838 81	0.830	0.6025
0.8029	0.843 81	0.766	0.4267
0.9041	0.849 12	0.712	0.1779
1.0000	0.853 54	0.672	0.0000

in the presence of ester.[11] The V^E values of ester (ethyl valerate or hexyl acetate) + 1-pentanol systems are higher than those of ester (ethyl valerate or hexyl acetate) + 1-hexanol systems, indicating that interstitial accommodation becomes important with the increasing alkanol size.[12] Interstitial accommodation and orientational ordering lead to a more compact structure and tend to decrease V^E values.[11] Figure 1 depicts the excess molar volumes for all systems at 293.15 K.

The experimental values of viscosity listed in Tables 2−5 were used to calculate viscosity deviations using the following equation

$$\Delta\eta_L = \eta_L - (x_1\eta_{L1} + x_2\eta_{L2}) \qquad (2)$$

where η_L is the viscosity of the mixture and η_{L1} and η_{L2} are the viscosities of pure components 1 and 2, respectively. The viscosity deviations of all systems at 293.15 K are graphically presented in Figure 2 with a minimum located near $x_1 \approx 0.4$. The $\Delta\eta_L$ values at all concentration ranges of the mixtures were affected by the molecular size of alkanols, as shown in Figure 2.

The well-known Redlich−Kister[13] polynomial equation, which has the following form,

$$V^E = x_1x_2\sum_{i=0}^{n} b_i(x_1 - x_2)^i \qquad (3)$$

Table 5. Experimental Density (ρ_L), Viscosity (η_L), and Excess Molar Volume (V^E) for Binary Mixtures of Hexyl Acetate (1) + 1-Hexanol (2) at 293.15 K, 303.15 K, and 313.15 K

x_1	ρ_L/ (g·cm^{-3})	η_L/ (mPa·s)	V^E/ (cm^3·mol^{-1})
	293.15 K		
0.0000	0.818 40	4.993	0.0000
0.0998	0.823 90	4.012	0.2405
0.2013	0.829 40	3.281	0.4275
0.3012	0.834 91	2.721	0.5560
0.4056	0.840 60	2.266	0.6326
0.4937	0.845 42	1.964	0.6521
0.6002	0.851 24	1.677	0.6218
0.7021	0.856 78	1.464	0.5384
0.8045	0.862 38	1.299	0.4022
0.9018	0.867 70	1.176	0.2251
1.0000	0.873 10	1.078	0.0000
	303.15 K		
0.0000	0.811 61	3.792	0.0000
0.0998	0.817 29	3.073	0.1460
0.2013	0.822 69	2.502	0.2989
0.3012	0.827 91	2.065	0.4135
0.4056	0.833 30	1.710	0.4827
0.4937	0.837 90	1.474	0.4898
0.6002	0.843 41	1.249	0.4563
0.7021	0.848 63	1.083	0.3828
0.8045	0.853 90	0.954	0.2446
0.9018	0.858 70	0.858	0.1114
1.0000	0.863 22	0.782	0.0000
	313.15 K		
0.0000	0.804 61	2.812	0.0000
0.0998	0.810 20	2.301	0.1111
0.2013	0.815 41	1.895	0.2458
0.3012	0.820 33	1.584	0.3613
0.4056	0.825 52	1.332	0.4134
0.4937	0.829 68	1.164	0.4478
0.6002	0.834 88	1.005	0.4167
0.7021	0.839 89	0.887	0.3309
0.8045	0.844 55	0.795	0.2566
0.9018	0.849 00	0.726	0.1554
1.0000	0.853 51	0.672	0.0000

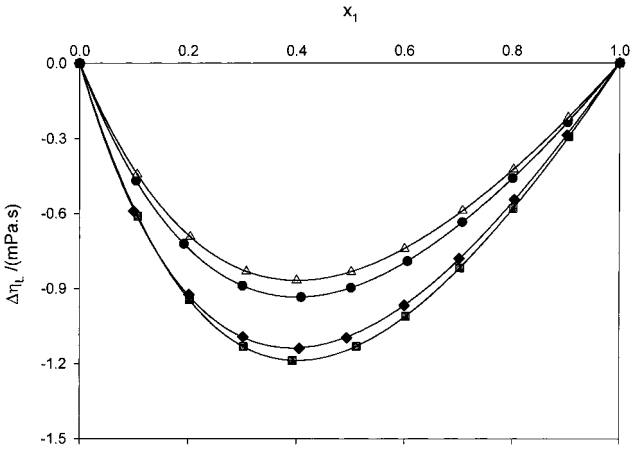

Figure 2. $\Delta\eta_L$ values at 293.15 K for (●) ethyl valerate (1) + 1-pentanol (2), (■) ethyl valerate (1) + 1-hexanol (2), (▲) hexyl acetate (1) + 1-pentanol (2), and (◆) hexyl acetate (1) + 1-hexanol (2).

or

$$\Delta\eta_L = x_1x_2\sum_{i=0}^{n} b_i(x_1 - x_2)^i \qquad (4)$$

was used to correlate the experimental data. The coefficients b_i were evaluated from a least-squares method, and

Table 6. Parameters and Standard Deviations of the Redlich−Kister Polynomial Equation for Ethyl Valerate (1) + 1-Pentanol (2), Ethyl Valerate (1) + 1-Hexanol (2), Hexyl Acetate (1) + 1-Pentanol (2), and Hexyl Acetate (1) + 1-Hexanol (2)

	T/K	b_0	b_1	b_2	b_3	σ
			Ethyl Valerate + 1-Pentanol			
V^E/(cm^3·mol^{-1})	293.15	2.1873	−0.3847	−1.2014	0.5602	0.0027
	303.15	1.8915	−0.3904	−1.2077	0.7356	0.0096
	313.15	1.6523	−0.3696	−1.1363	0.7657	0.0175
$\Delta\eta_L$/(mPa·s)	293.15	−3.5914	1.4104	−0.4327	0.1050	0.0020
	303.15	−2.4641	0.9670	−0.3000	0.0733	0.0017
	313.15	−1.8285	0.7211	−0.2049	0.0544	0.0018
			Ethyl Valerate + 1-Hexanol			
V^E/(xm^3·mol^{-1})	293.15	1.6285	−0.0567	0.0017	−0.0007	0.0009
	303.15	1.3117	−0.0162	−0.8110	−0.2589	0.0087
	313.15	0.9939	0.1160	−1.1967	−0.8963	0.0134
$\Delta\eta_L$/(mPa·s)	293.15	−4.5647	1.7920	−0.5578	0.1372	0.0012
	303.15	−3.4094	1.3379	−0.4143	0.1011	0.0010
	313.15	−2.4025	0.9438	−0.2917	0.0702	0.0007
			Hexyl Acetate + 1-Pentanol			
V^E/(cm^3·mol^{-1})	293.15	3.6170	−0.2655	−0.8173	−0.0877	0.0090
	303.15	3.3109	−0.0944	−1.1653	−0.5726	0.0206
	313.15	3.1547	−0.2840	−1.0151	0.0232	0.0161
$\Delta\eta_L$/(mPa·s)	293.15	−3.3348	1.3111	−0.4056	0.0951	0.0031
	303.15	−2.3670	0.9313	−0.2882	0.0664	0.0009
	313.15	−1.7876	0.7025	−0.2170	0.0535	0.0013
			Hexyl Acetate + 1-Hexanol			
V^E/(cm^3·mol^{-1})	293.15	2.6079	−0.0841	0.0022	−0.0004	0.0005
	303.15	1.9869	−0.1898	−0.7703	−0.0757	0.0062
	313.15	1.7498	−0.1994	−0.4672	0.7819	0.0088
$\Delta\eta_L$/(mPa·s)	293.15	−4.3516	1.7451	−0.7905	0.4895	0.0039
	303.15	−3.3125	1.3002	−0.4033	0.0986	0.0001
	313.15	−2.3547	0.9249	−0.2857	0.0689	0.0008

the results together with the standard deviations, σ, are presented in Table 6.

Conclusion

New experimental values of density and viscosity for the systems ethyl valerate (1) + 1-pentanol (2), ethyl valerate (1) + 1-hexanol (2), hexyl acetate (1) + 1-pentanol (2), and hexyl acetate (1) + 1-hexanol (2) were measured. The excess molar volume and viscosity deviations were correlated using the Redlich−Kister polynomial equation, and an excellent agreement was observed.

Literature Cited

(1) Grolier, J. P. E.; Ballet, D.; Viallard, D. Thermodynamics of Ester Containing Mixtures. Excess Enthalpies, Excess Volumes for Alkyl Acetates + Alkanes, + Benzene, + Toluene and + Ethyl Benzene. *J. Chem. Thermodyn.* **1974**, *6*, 895−908.

(2) Jimenez, E.; Romani, L.; Paz Andrade, M. I.; Roux-Desgranges, G.; Grolier, J. P. E. Molar excess Heat Capacities and Volumes for mixtures of Alkanoates with cyclohexane at 25 °C. *J. Solution Chem.* **1986**, *15*, 879−890.

(3) Katyal, R. C.; Sethi, B. P. S.; Raju, K. S. N. Enthalpies of Mixing of Binary Systems of Alkyl Esters with *o*-, *m*-, and *p*-Xylene at 298.15 K. *Ind. J. Technol.* **1990**, *28*, 191−196.

(4) Qin, A.; Hoffman, D. E.; Munk, P. Excess Volumes of Selected Alkyl Esters and Ketones with Aromatic Hydrocarbons. *J. Chem. Eng. Data* **1992**, *37* (7), 66−70.

(5) Ortega, J.; Matos, J. S.; Paz Andrade, M. I.; Fernandez, J.; Pias, L. Analysis of Excess Enthalpies of Ester+ 1-Chloroalkanes with Two Group Contibution Models. *Fluid Phase Equilib.* **1988**, *43*, 295−316.

(6) Sastry, N. V.; Dave, P. N. Thermodynamics of Methyl Methacrylate + Organic Solvent II. Viscosities of Methyl Methacrylate + *n*-Hexane, + *n*-Heptane, + Carbon Tetrachloride, + Chlorobenzene and + *o*-Dichlorobenzene at 303.15 K. *Thermochim. Acta* **1996**, *286*, 119−130.

(7) Sastry, N. V.; George, A.; Jain, N. J.; Bahadur, P. Densities, Relative Permittivities, Excess Volumes, and Excess Molar Polarization fro Alkyl Ester (Methyl Propanoate, Methyl Butanoate, Ethyl Propanoate, and Ethyl Butanoate) + Hydrocarbons (*n*-Heptane, Benzene, Chlorobenzene, and 1,1,2,2-Tetrachloroethane) at 308.15 K and 318.15 K. *J. Chem. Eng. Data* **1999**, *44*, 456−464.

(8) Dean, J. A. *Hand Book of Organic Chemistry*; McGraw-Hill: New York, 1987.

(9) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill International Editions: Singapore, 1987.

(10) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Methods of Purification*, 4th ed.; John Wiley & Sons: New York, 1986.

(11) Nikam, P. S.; Mahale, T. R.; Hasan, M. Densities and Viscosities for Ethyl Acetate + Pentan-I-ol, + Hexan-1-ol, + 3,5,5-Trimethylhexan-1-ol, + Heptan-1-ol, + Octan-I-ol, and + Decan-1-ol at (298.15, 303.15, and 308.15) K. *J. Chem. Eng. Data* **1998**, *43*, 436−440.

(12) Kiyohara, O.; Benson, G. C. Ultrasonic Speed and Isentropic Compressibilities of *n*-Alkanol + *n*-Heptane Mixtures at 298.15 K. *J. Chem. Thermodyn.* **1979**, *11*, 861−873.

(13) Redlich, O.; Kister, A. T. Algebric Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

Received for review May 11, 2000. Accepted October 16, 2000.

JE0001431