J. Chem. Eng. Data **2000,** *45*, 536−539

Density, Refractive Index, and Speed of Sound for 2-Ethoxy-2-Methylbutane + Ethanol + Water at 298.15 K

Alberto Arce,* Alberto Arce Jr., Eva Rodil, and Ana Soto

Department of Chemical Engineering, University of Santiago de Compostela,
E-15706 Santiago de Compostela, Spain

The density, refractive index, and speed of sound at 298.15 K and atmospheric pressure were measured in the miscibility range for 2-ethoxy-2-methylbutane + ethanol + water. From these results, excess molar volumes and molar refraction and isentropic compressiblity changes of mixing were calculated and satisfactorily correlated with the corresponding composition data using the Redlich−Kister polynomial.

Introduction

This contribution is a study on the behavior of alcohol and ether mixtures used as octane-enhancing components in gasoline (Arce et al., 1998, 1999). 2-Ethoxy-2-methylbutane (*tert*-amyl ethyl ether or TAEE) is a heavy tertiary ether which, if ethanol is elaborated by fermentation from renewable resources, seems to be an attractive solution for the insufficient supply of methyl *tert*-butyl ether (MTBE).

In this paper densities (ρ), refractive indices (n_D), and speeds of sound (u) have been determined over the complete concentration range of miscible mixtures of TAEE + ethanol + water at 298.15 K and atmospheric pressure. Excess molar volumes (V^E) and molar refraction and isentropic compressiblity changes of mixing were calculated from the measured properties and correlated with composition using the Redlich−Kister polynomial. No comparable data for the binary system ethanol + TAEE and for the ternary system TAEE + ethanol + water have been found in the surveyed literature.

Experimental Section

Materials. Water was purified using a Milli-Q Plus system. TAEE was supplied by the Yarsintez Research Institute (Yaroslav, Russia), and ethanol (Gradient grade) was supplied by Merck, both with nominal purity of 99.8 mass % and water content (determined with a Metrohm 737 KF coulometer) of 0.04 and 0.05 mass %, respectively. The purities were verified chromatographically. Materials were used without further purification.

Table 1 lists the densities, refractive indices, and sound speeds measured for the pure components, together with the published values for these parameters (Riddick et al., 1986; Bruun and Hvidt, 1977; Aminabhavi et al., 1993).

Apparatus and Procedure. The mixtures were prepared by filling well-stoppered flasks with the liquids and weighing on a Mettler AE 240 balance that measured to within ±0.000 01 g for calculating the mass. Densities were measured to within ±0.000 01 g·cm^{-3} in an Anton Paar DMA 60/602 densimeter, and sound speeds were measured to within ±1 m·s^{-1} in an Anton Paar DSA 48 densimeter and sound analyzer. Both instruments were calibrated with air and water. Refractive indices were measured to an accuracy of ±0.000 04 in an ATAGO RX-5000 refractometer. A Hetoterm thermostat was used to maintain the temperature at (298.15 ± 0.02) K.

Table 1. Densities (ρ), Refractive Indices (n_D), and Speeds of Sound (u) for Pure Components at 298.15 K and Atmospheric Pressure

	ρ/g·cm^{-3}		n_D		u/m·s^{-1}	
component	exptl	lit.	exptl	lit.	exptl	lit.
water	0.997 04	0.997 04[a]	1.332 50	1.332 50[a]	1497	1497[b]
ethanol	0.785 22	0.784 93[a]	1.359 20	1.359 41[a]	1143	1145[c]
TAEE	0.760 50	*d*	1.388 57	*d*	1096	*d*

[a] Riddick et al., 1986. [b] Bruun and Hvidt, 1977. [c] Aminabhavi et al., 1993. [d] Not found.

Results

The experimental values obtained of densities (ρ), sound speeds (u), and refractive indices (n_D) for the single-phase mixtures of TAEE + ethanol + water and for the binary mixture ethanol + TAEE are listed in Table 2. Data for a binary water + ethanol system have already been published (Arce et al., 1997). The same table includes the calculated values of isentropic compressibilities (κ_s), excess molar volumes (V^E), and molar refraction and isentropic compressibility changes of mixing (ΔR, $\Delta\kappa_s$).

The excess molar volumes (V^E) and molar refraction changes of mixing (ΔR) are calculated as a function of mole fraction, x_i, using the following expressions:

$$V^E = V_M - \sum_i x_i V_i \tag{1}$$

$$\Delta R = R_M - \sum_i x_i R_i \tag{2}$$

where V_M is the molar volume of the mixture, R_M is the molar refraction of the mixture obtained from the Lorentz−Lorenz equation, and V_i and R_i are the molar volume and the molar refraction, respectively, for component i.

Isentropic compressibilities (κ_s) and their changes of mixing ($\Delta\kappa_s$) are calculated using the relationships

$$\kappa_s = u^{-2}\rho^{-1} \tag{3}$$

$$\Delta\kappa_s = \kappa_s - \sum_i \phi_i \kappa_{si} \tag{4}$$

where κ_s and κ_{si} are the isentropic compressibilities of the mixture and component i, respectively, and ϕ_i are the

10.1021/je000009g CCC: $19.00

Table 2. Densities (ρ), Speeds of Sound (u), Isentropic Compressibilities (κ_S), Refractive Indices (n_D), Excess Molar Volumes (V^E), and $\Delta\kappa_s$ and ΔR Changes of Mixing for Mixtures of TAEE (1) + Ethanol (2) + Water (3) at 298.15 K and Atmospheric Pressure

x_1	x_2	ρ/g·cm^{-3}	u/m·s^{-1}	κ_S/TPa^{-1}	n_D	V^E/cm^3·mol^{-1}	$\Delta\kappa_S$/TPa^{-1}	ΔR/cm^3·mol^{-1}
0.0987	0.9013	0.782 00	1136	990	1.366 66	−0.198	−11	−0.007
0.0934	0.8527	0.787 95	1152	956	1.367 38	−0.413	−37	−0.014
0.0807	0.7367	0.802 72	1192	877	1.368 53	−0.793	−93	−0.026
0.0734	0.6698	0.811 89	1214	835	1.368 88	−0.943	−119	−0.030
0.0642	0.5866	0.824 37	1242	786	1.368 98	−1.074	−146	−0.034
0.0561	0.5123	0.836 83	1268	743	1.368 74	−1.144	−165	−0.036
0.0454	0.4143	0.855 87	1309	682	1.367 78	−1.169	−188	−0.036
0.1974	0.8026	0.779 00	1130	1005	1.372 12	−0.342	−16	−0.013
0.1889	0.7681	0.783 21	1141	981	1.372 60	−0.510	−35	−0.018
0.1657	0.6737	0.795 15	1171	917	1.373 47	−0.861	−80	−0.029
0.1488	0.6052	0.804 46	1192	875	1.373 71	−1.029	−106	−0.034
0.1253	0.5093	0.819 01	1219	821	1.373 48	−1.166	−132	−0.039
0.1063	0.4323	0.832 55	1242	778	1.372 72	−1.201	−147	−0.040
0.2991	0.7009	0.776 10	1124	1020	1.376 32	−0.436	−17	−0.016
0.2667	0.6247	0.785 68	1147	967	1.377 11	−0.801	−56	−0.030
0.2626	0.6150	0.786 96	1150	960	1.377 19	−0.840	−60	−0.031
0.2196	0.5144	0.801 21	1179	897	1.377 52	−1.134	−99	−0.040
0.1946	0.4558	0.810 30	1192	869	1.377 11	−1.200	−109	−0.043
0.3998	0.6002	0.773 50	1118	1033	1.379 59	−0.494	−17	−0.019
0.3750	0.5630	0.778 47	1130	1006	1.380 03	−0.723	−37	−0.027
0.3541	0.5316	0.782 78	1140	983	1.380 28	−0.878	−53	−0.032
0.3333	0.5004	0.787 20	1149	962	1.380 41	−1.001	−66	−0.037
0.3165	0.4751	0.790 88	1155	947	1.380 41	−1.077	−74	−0.040
0.2982	0.4477	0.795 04	1161	933	1.380 31	−1.139	−81	−0.043
0.4928	0.5072	0.771 30	1115	1044	1.381 96	−0.518	−16	−0.020
0.4589	0.4723	0.776 34	1126	1016	1.382 36	−0.761	−36	−0.028
0.4295	0.4421	0.780 87	1135	994	1.382 56	−0.926	−50	−0.034
0.4083	0.4202	0.784 27	1141	980	1.382 62	−1.020	−59	−0.038
0.3939	0.4054	0.786 64	1144	972	1.382 60	−1.073	−63	−0.040
0.5939	0.4061	0.769 20	1111	1054	1.384 09	−0.531	−15	−0.020
0.5477	0.3745	0.774 38	1122	1027	1.384 41	−0.789	−34	−0.030
0.5450	0.3727	0.774 69	1122	1025	1.384 43	−0.802	−35	−0.031
0.5271	0.3604	0.776 82	1126	1016	1.384 51	−0.888	−41	−0.034
0.6950	0.3050	0.767 10	1107	1063	1.385 71	−0.491	−13	−0.029
0.6756	0.2970	0.768 79	1110	1055	1.385 84	−0.593	−19	−0.024
0.6373	0.2802	0.772 30	1117	1038	1.386 06	−0.780	−31	−0.030
0.7949	0.2051	0.765 10	1105	1071	1.387 02	−0.414	−12	−0.017
0.7760	0.2002	0.766 46	1107	1065	1.387 15	−0.506	−16	−0.018
0.7536	0.1945	0.768 12	1110	1057	1.387 28	−0.609	−21	−0.020
0.9252	0.0748	0.762 26	1100	1083	1.388 20	−0.194	−7	−0.004
0.8782	0.1218	0.763 29	1102	1078	1.387 86	−0.286	−9	−0.007
0.8192	0.1808	0.764 53	1104	1073	1.387 32	−0.374	−12	−0.010
0.7825	0.2175	0.765 28	1105	1070	1.386 91	−0.416	−13	−0.012
0.7264	0.2736	0.766 41	1107	1065	1.386 20	−0.465	−13	−0.015
0.7017	0.2983	0.766 91	1107	1063	1.385 85	−0.481	−14	−0.016
0.6460	0.3540	0.768 03	1109	1059	1.384 97	−0.506	−14	−0.018
0.6010	0.3990	0.768 95	1110	1055	1.384 18	−0.518	−15	−0.020
0.5321	0.4679	0.770 41	1113	1048	1.382 80	−0.522	−16	−0.021
0.4918	0.5082	0.771 29	1115	1044	1.381 90	−0.518	−16	−0.022
0.4362	0.5638	0.772 57	1117	1037	1.380 51	−0.505	−17	−0.022
0.3954	0.6046	0.773 56	1119	1032	1.379 39	−0.490	−18	−0.022
0.3424	0.6576	0.774 90	1122	1025	1.377 76	−0.464	−18	−0.022
0.2999	0.7001	0.776 03	1124	1020	1.376 30	−0.437	−18	−0.021
0.2414	0.7586	0.777 67	1127	1012	1.374 02	−0.389	−17	−0.019
0.2014	0.7986	0.778 84	1129	1007	1.372 25	−0.348	−16	−0.017
0.1400	0.8600	0.780 71	1133	997	1.369 11	−0.270	−14	−0.013
0.0988	0.9012	0.782 00	1136	990	1.366 65	−0.206	−12	−0.010
0.0517	0.9483	0.783 49	1139	983	1.363 41	−0.118	−7	−0.005

volume fraction of component i in the mixture, given by

$$\phi_i = x_i V_i / \sum_j x_j V_j \qquad (5)$$

and j refers to all the components in the mixture.

For the ternary system, Figures 1−3 show the density, refractive index, and excess molar volume isolines (system compositions in mole fraction, x_i), and Figures 4 and 5 show the sound speed and the isentropic compressibility changes of mixing isolines (system composition in volume fraction, ϕ_i).

Correlation

The V^E, ΔR, and $\Delta\kappa_S$ values were correlated with the composition by means of the Redlich−Kister polynomial (Redlich−Kister, 1948), which for binary mixtures is

$$Q_{ij} = x_i x_j \sum_k A_k (x_i - x_j)^k \qquad (6)$$

where Q_{ij} is V^E or ΔR and x_i is the mole fraction of component i, or Q_{ij} is $\Delta\kappa_S$, with x_i being the volume fraction of component i. A_k is the polynomial coefficient, and k is the number of the polynomial coefficient. For ternary

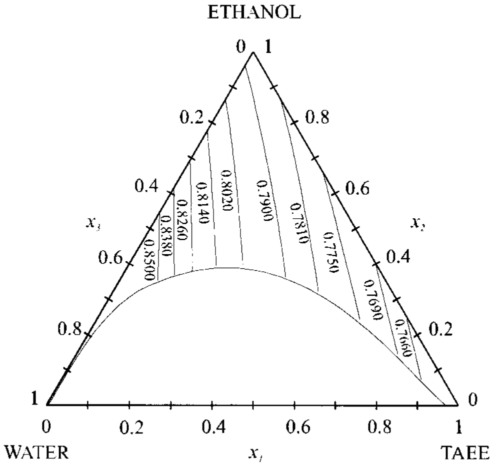

Figure 1. Density isolines for TAEE (1) + ethanol (2) + water (3) at 298.15 K and atmospheric pressure.

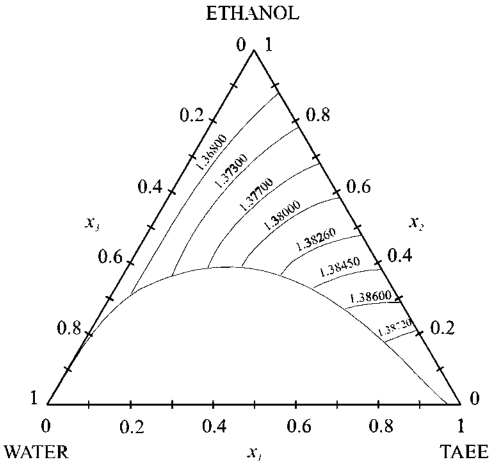

Figure 2. Refractive index isolines for TAEE (1) + ethanol (2) + water (3) at 298.15 K and atmospheric pressure.

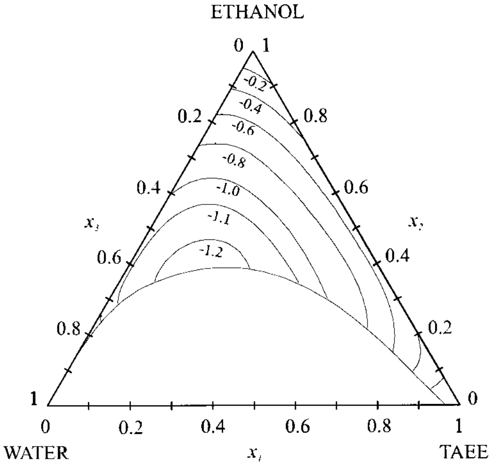

Figure 3. Excess molar volume isolines for TAEE (1) + ethanol (2) + water (3) at 298.15 K and atmospheric pressure (system compositions in mole fraction).

systems the corresponding equation, as a function of the composition, x_i (for $\Delta\kappa_s$, volume fraction ϕ_i instead of mole fraction x_i), is

$$Q_{123} = Q_{21} + Q_{32} + Q_{13} + x_1x_2x_3(A + B(x_2 - x_1) + C(x_3 - x_2) + D(x_1 - x_3) + E(x_2 - x_1)^2 + F(x_3 - x_2)^2 + G(x_1 - x_3)^2 + ... \quad (7)$$

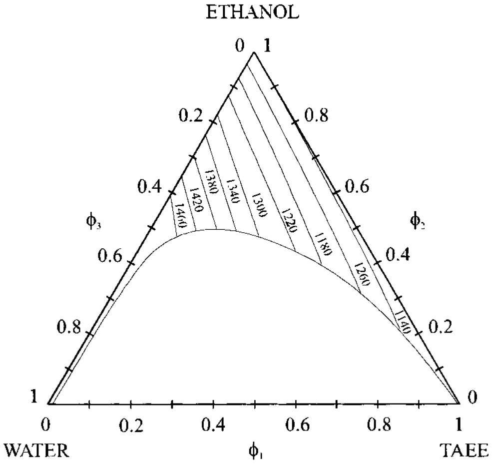

Figure 4. Speed of sound isolines for TAEE (1) + ethanol (2) + water (3) at 298.15 K and atmospheric pressure (system compositions in volume fraction).

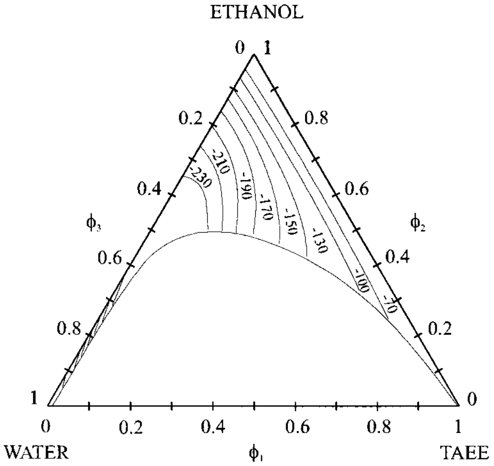

Figure 5. Isentropic compressibility changes of mixing isolines for TAEE (1) + ethanol (2) + water (3) at 298.15 K and atmospheric pressure.

Table 3. Polynomial Coefficients and Standard Deviations (σ) Obtained for Fits of Eq 6 to the V^E, $\Delta\kappa_s$, and ΔR Composition Data for the Binary Systems (for $\Delta\kappa_s$, System Compositions Were in Volume Fractions, ϕ_i)

property	A_0	A_1	A_2	A_3	A_4	σ
			Ethanol (1) + TAEE (2)			
V^E/cm^3·mol^{-1}	−2.0764	0.2644	−0.6934			0.003
$\Delta\kappa_s$/TPa^{-1}	−70.649	26.749	−98.173	−74.001	210.71	0.5
ΔR/cm^3·mol^{-1}	−0.0873	−0.0271				0.002
			Water (1) + Ethanol (2)			
V^E/cm^3·mol^{-1}	−4.296	−1.116	−1.235			0.001
$\Delta\kappa_s$/TPa^{-1}	−974.5	−28.0	−259.1	584.5		0.3
ΔR/cm^3·mol^{-1}	−0.092					0.001

where Q_{123} represents V^E, ΔR, or $\Delta\kappa_s$ for the ternary mixture TAEE (1) + ethanol (2) + water (3) and Q_{ij} is the Redlich−Kister polynomial for the same property fitted to the binary systems data, with, in this case, Q_{13} equal to zero because of the immiscibility of water and TAEE.

The A_k values for Q_{21} (ethanol + TAEE) and Q_{32} (water + ethanol) are summarized in Table 3 together with the corresponding standard deviations of the fit. The parameters of the fitted polynomials for the binary water + ethanol system have been published (Arce et al, 1997). The Redlich−Kister coefficients for the ternary system are listed in Table 4 together with the corresponding standard deviations of fit. All of these coefficients were obtained fitting, to the appropriate parameters, eqs 6 and 7 by least-

Table 4. Polynomial Coefficients and Standard Deviations (σ) Obtained for Fits of Eq 7 to the V^E, $\Delta\kappa_s$, and ΔR Composition Data for the Ternary System TAEE (1) + Ethanol (2) + Water (3) (for $\Delta\kappa_s$, System Compositions Are in Volume Fractions, ϕ_i)

property	*A*	*B*	*C*	*D*	*E*	*F*	*G*	σ
V^E/cm^3·mol^{-1}	−13.480	7.7748	−5.9383	−1.8365	−13.698	−0.6950	−3.6215	0.006
$\Delta\kappa_s$/TPa^{-1}	−791.18	−1068.1	−732.46	1800.6	3491.8	−7961.7	−14697	1.45
ΔR/cm^3·mol^{-1}	−0.7904	0.1839	−0.4203	0.2347				0.002

squares regression; the Fisher's F-test were used to decide the degree of the polynomial.

Conclusions

Excess molar volumes at 298.15 K and atmospheric pressure for binary mixtures of ethanol + TAEE were negative, reaching a minimum around −0.52 cm^3·mol^{-1} in the neighborhood of $x = 0.5$. Isentropic compressibility changes of mixing are also negative, reaching a minimum of aproximately −18 TPa^{-1}. Values of molar refraction changes of mixing are likewise negative, but the absolute value of the change is never more than about 0.022 cm^3·mol^{-1}.

The ternary system TAEE + ethanol + water exhibits relatively large and negative excess molar volumes for the entire range of homogeneous mixtures, reaching a minimum around −1.2 cm^3·mol^{-1}. Isentropic compressibility changes of mixing are also negative; the lower values corresponding to the ethanol + water system which reaches a minimum of approximately −243 TPa^{-1} (Arce et al., 1997). Values of molar refraction changes of mixing are so small that it is difficult to establish any conclusion.

Literature Cited

Aminabhavi, T. M.; Aralaguppi M. Y.; Harogoppad, Sh. B.; Balundgi, R. H. Densities, viscosities, refractive indices, and speeds of sound for methyl acetoacetate + aliphatic alcohols (C1−C8). *J. Chem. Eng. Data* **1993**, *38*, 31−39.

Arce, A.; Martínez-Ageitos, J.; Mendoza, J.; Soto, A. Densities, refractive indices, speeds of sound and isentropic compresibilities of water + ethanol + 2-methoxy-2-methylbutane at 298.15 K. *Fluid Phase Equilib.* **1997**, *141*, 207−220.

Arce, A.; Rodil, E.; Soto, A. Molar volume, molar refraction and isentropic compressibility changes of mixing at 25 °C for the system ethanol + methanol + dibutyl ether. *J. Solution Chem.* **1998**, *27*, 911−923.

Arce, A.; Rodil, E.; Soto, A. Physical Properties of the Ternary System 1-Butanol + of Methanol + 2-Methoxy-2-methylpropane at 298.15 K: Measurement and Prediction. *J. Chem. Eng. Data* **1999a**, *44*, 1028−1033.

Arce, A.; Martínez-Ageitos, J.; Rodil, E.; Soto, A. Thermodynamic behaviour of ethanol + methanol + 2-ethoxy-2-methylpropane system. Physical properties and phase equilibria. *Fluid Phase Equilib.* **1999b**, *165*, 121−139.

Bruun, S. G.; Hvidt, A. *Ber. Bunsen-Ges. Phys. Chem.* **1977**, *81*, 930.

Redlich, O.; Kister A. T. Thermodynamics of Nonelectrolyte Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

Riddick, J. A.; Bunger, W. B.; Sakano, T. *Organic Solvents*, 4th ed.; John Wiley: New York, 1986.

Received for review January 14, 2000. Accepted March 2, 2000.

JE000009G