Physical Properties and Their Changes on Mixing at 298.15 K and Atmospheric Pressure for the 2-Ethoxy-2-methylbutane + Methanol + Water System

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

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

Densities, refractive indices, and speeds of sound were measured at 298.15 K and atmospheric pressure for the ternary system 2-ethoxy-2-methylbutane + methanol + water. Excess molar volumes and molar refraction and isentropic compressibility changes of mixing have been calculated from the obtained values of measured physical properties and satisfactorily correlated with the corresponding composition data using the Redlich−Kister polynomial.

Introduction

The work described in this paper is a part of an ongoing study on thermophysical properties of alcohol and ether mixtures used as octane-enhancing components in gasoline.[1−4] 2-Ethoxy-2-methylbutane (*tert*-amyl ethyl ether or TAEE) is a higher molecular weight tertiary ether, which suggests, besides the 2-methoxy-2-methylbutane (*tert*-amyl methyl ether or TAME) and 2-ethoxy-2-methylpropane (ethyl *tert*-butyl ether or ETBE), it could be an alternative to 2-methoxy-2-methylpropane (methyl *tert*-butyl ether or MTBE), the largest additive employed as an octane-enhancer of unleaded gasoline.

Densities (ρ), refractive indices (n_D), speeds of sound (u) and isentropic compressibilities (κ_s) have been measured for completely miscible mixtures of 2-ethoxy-2-methylbutane + methanol + water at 298.15 K. Excess molar volumes (V^E), molar refraction changes of mixing (ΔR), and isentropic compressibility changes of mixing ($\Delta\kappa_s$) have been calculated from the measured properties and correlated with composition data using the Redlich−Kister polynomial. Some physical properties are available in several publications for the binary system water + methanol, but no comparable data have been found in the surveyed literature for the binary system methanol + TAEE and for the ternary system TAEE + methanol + water.

Experimental Section

Materials. 2-Ethoxy-2-methylbutane (TAEE) was supplied by Yarsintez Research Institute (Yaroslav, Russia) with nominal purity >99.9 mass %. Methanol was supplied by Merck (Madrid, Spain) and had a nominal purity >99.5 mass %. Water was purified using a Milli-Q Plus system. The water contents of methanol and TAEE were 0.05 and 0.02 mass %, respectively, determined with a Metrohm 737 KF coulometer.

Apparatus and Procedure. The samples were prepared by filling flasks with the liquids and weighing, immediately, on a Mettler AE 240 balance. Samples were measured with an accuracy of ±0.0001 g, and the compositions were determined by mass difference. Sample preparation flasks were stoppered by using a septum to prevent evaporative losses. Sample additions were made by extending a syringe through the septum. Densities were measured to an accuracy of ±0.000 01 g·cm^{-3} in an Anton Paar DMA 60/602 densimeter, and speeds of sound were measured to an accuracy of ±1 m·s^{-1} in an Anton Paar DSA 48 densimeter and sound analyzer. Both densimeters were calibrated with air and water. Refractive indices were measured to an accuracy of ±0.000 04 in an ATAGO RX-5000 refractometer. The temperature was controlled with a Hetoterm thermostat to maintain the temperature at (298.15 ± 0.02) K.

* Corresponding author. Phone: +34-981-563100 Ext. 14280. Fax: +34-981-595012. E-mail address: eqaaarce@usc.es.

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

	ρ/g·cm^{-3}		n_D		u/m·s^{-1}	
component	exptl	lit.	exptl	lit.	exptl	lit.
water	0.997 04	0.997 04[5]	1.332 50	1.332 50[5]	1497	1497[6]
methanol	0.786 63	0.786 64[5]	1.326 40	1.326 52[5]	1101	1102[7]
TAEE	0.760 57	−	1.388 57	−	1096	−

[a] (−) means not found.

The pure component densities, refractive indices, and speed of sound values obtained are listed in Table 1 and compared with published values[5−7] for these parameters.

Results

The experimental values of the measurements obtained for density (ρ), speed of sound (u), and refractive index (n_D) for single-phase mixtures of the methanol + TAEE binary system and the TAEE + methanol + water ternary system are listed in Tables 2 and 3, respectively. These tables also include the calculated values for isentropic compressibility (κ_s), excess molar volume (V^E), molar refraction changes of mixing (ΔR), and isentropic compressibility changes of mixing ($\Delta\kappa_s$). Corresponding data for the binary system water + methanol have already been published.[1]

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:

$$V^E = V_M - \sum_i x_i V_i \quad (1)$$

$$\Delta R = R_M - \sum_i x_i R_i \quad (2)$$

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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 on Mixing for the Methanol (1) + TAEE (2) Binary System at 298.15 K

x_1	ρ / g·cm^{-3}	u / m·s^{-1}	κ_s / T·Pa^{-1}	n_D	V^E / cm^3·mol^{-1}	$\Delta\kappa_s$ / T·Pa^{-1}	ΔR / cm^3·mol^{-1}
0.0558	0.762 05	1099	1087	1.388 13	−0.207	−7	−0.006
0.1008	0.763 14	1100	1083	1.387 65	−0.337	−11	−0.009
0.1470	0.764 19	1101	1079	1.387 03	−0.441	−14	−0.012
0.1901	0.765 11	1102	1076	1.386 35	−0.516	−16	−0.014
0.2216	0.765 76	1103	1074	1.385 79	−0.560	−18	−0.015
0.2598	0.766 53	1103	1072	1.385 02	−0.602	−19	−0.016
0.3024	0.767 38	1103	1070	1.384 06	−0.636	−20	−0.016
0.3604	0.768 52	1104	1068	1.382 57	−0.666	−20	−0.017
0.3813	0.768 94	1104	1068	1.381 97	−0.672	−20	−0.017
0.4423	0.770 18	1104	1066	1.380 02	−0.679	−21	−0.017
0.5017	0.771 44	1104	1064	1.377 80	−0.670	−21	−0.017
0.5356	0.772 19	1104	1062	1.376 37	−0.660	−22	−0.017
0.5950	0.773 57	1105	1059	1.373 51	−0.631	−23	−0.017
0.6534	0.775 02	1105	1056	1.370 16	−0.589	−23	−0.017
0.6972	0.776 18	1105	1055	1.367 23	−0.548	−23	−0.016
0.7454	0.777 54	1105	1054	1.363 48	−0.494	−21	−0.016
0.7865	0.778 77	1104	1054	1.359 75	−0.439	−18	−0.014
0.8407	0.780 50	1103	1054	1.353 90	−0.353	−14	−0.012
0.8901	0.782 21	1103	1051	1.347 35	−0.260	−12	−0.010
0.9438	0.784 25	1103	1048	1.338 47	−0.142	−9	−0.006

Table 3. 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 the TAEE (1) + Methanol (2) + Water (3) System at 298.15 K

x_1	x_2	ρ / g·cm^{-3}	u / m·s^{-1}	κ_s / T·Pa^{-1}	n_D	V^E / cm^3·mol^{-1}	$\Delta\kappa_s$ / T·Pa^{-1}	ΔR / cm^3·mol^{-1}
0.0201	0.9799	0.785 77	1099	1053	1.331 13	−0.053	1	−0.002
0.0188	0.9159	0.796 35	1132	979	1.333 01	−0.300	−55	−0.008
0.0170	0.8267	0.811 89	1181	883	1.335 59	−0.582	−126	−0.014
0.0150	0.7322	0.829 30	1236	789	1.338 15	−0.811	−188	−0.020
0.0131	0.6396	0.847 23	1292	707	1.340 34	−0.967	−235	−0.023
0.0113	0.5513	0.865 08	1348	636	1.342 00	−1.048	−267	−0.025
0.0987	0.9013	0.782 62	1103	1050	1.345 67	−0.237	−12	−0.009
0.0892	0.8141	0.796 44	1144	960	1.347 82	−0.585	−80	−0.016
0.0793	0.7245	0.811 63	1187	875	1.349 80	−0.864	−139	−0.022
0.0696	0.6360	0.827 65	1229	800	1.351 40	−1.055	−184	−0.027
0.0611	0.5576	0.842 73	1266	740	1.352 40	−1.148	−213	−0.029
0.1974	0.8026	0.779 20	1103	1054	1.358 10	−0.415	−17	−0.014
0.1853	0.7533	0.786 58	1124	1007	1.359 13	−0.635	−53	−0.019
0.1687	0.6858	0.797 15	1152	945	1.360 34	−0.890	−96	−0.025
0.1449	0.5892	0.813 42	1191	867	1.361 57	−1.144	−145	−0.032
0.2900	0.7100	0.776 46	1105	1054	1.366 25	−0.535	−22	−0.016
0.2722	0.6664	0.782 82	1122	1015	1.367 00	−0.747	−51	−0.022
0.2583	0.6324	0.788 01	1135	986	1.367 52	−0.891	−73	−0.027
0.2444	0.5984	0.793 36	1148	957	1.367 95	−1.015	−92	−0.031
0.2301	0.5633	0.799 01	1161	929	1.368 25	−1.119	−110	−0.034
0.2164	0.5297	0.804 50	1173	903	1.368 37	−1.195	−125	−0.036
0.3956	0.6044	0.773 77	1105	1059	1.372 99	−0.625	−23	−0.017
0.3697	0.5648	0.779 65	1119	1025	1.373 56	−0.847	−47	−0.025
0.3510	0.5363	0.784 05	1128	1002	1.373 88	−0.977	−63	−0.030
0.3344	0.5108	0.788 05	1138	981	1.374 07	−1.074	−77	−0.034
0.3129	0.4780	0.793 21	1149	954	1.374 11	−1.168	−93	−0.038
0.4965	0.5035	0.771 46	1104	1064	1.377 72	−0.670	−21	−0.017
0.4626	0.4691	0.776 90	1115	1036	1.378 17	−0.901	−40	−0.027
0.4397	0.4459	0.780 74	1122	1017	1.378 40	−1.018	−53	−0.032
0.4162	0.4220	0.784 76	1130	998	1.378 52	−1.108	−65	−0.037
0.5878	0.4122	0.769 57	1104	1067	1.381 03	−0.677	−21	−0.017
0.5431	0.3808	0.774 95	1113	1042	1.381 35	−0.930	−36	−0.028
0.5150	0.3611	0.778 41	1119	1027	1.381 43	−1.034	−46	−0.033
0.7024	0.2976	0.767 28	1103	1070	1.384 18	−0.633	−20	−0.016
0.6695	0.2837	0.770 22	1107	1060	1.384 36	−0.798	−26	−0.023
0.6449	0.2732	0.772 44	1110	1051	1.384 44	−0.886	−30	−0.027
0.7996	0.2004	0.765 33	1103	1075	1.386 17	−0.532	−17	−0.014
0.7698	0.1929	0.767 48	1104	1069	1.386 33	−0.650	−20	−0.018
0.7571	0.1898	0.768 42	1105	1066	1.386 38	−0.689	−21	−0.020

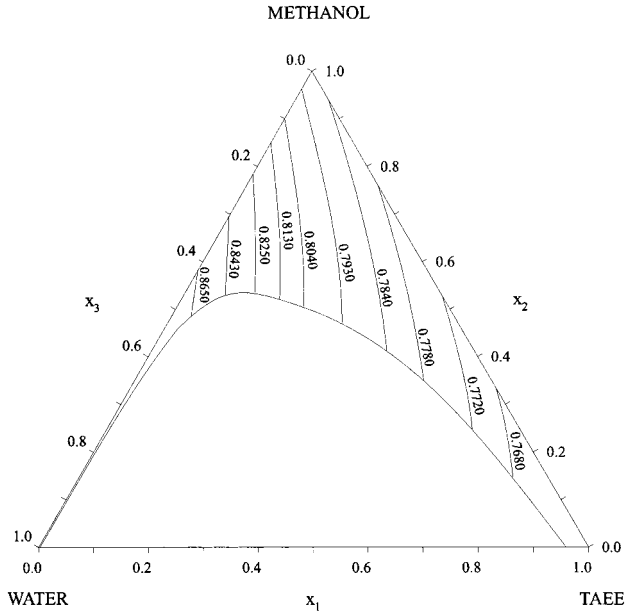

Figure 1. Density isolines for the TAEE (1) + methanol (2) + water (3) system at 298.15 K and atmospheric pressure.

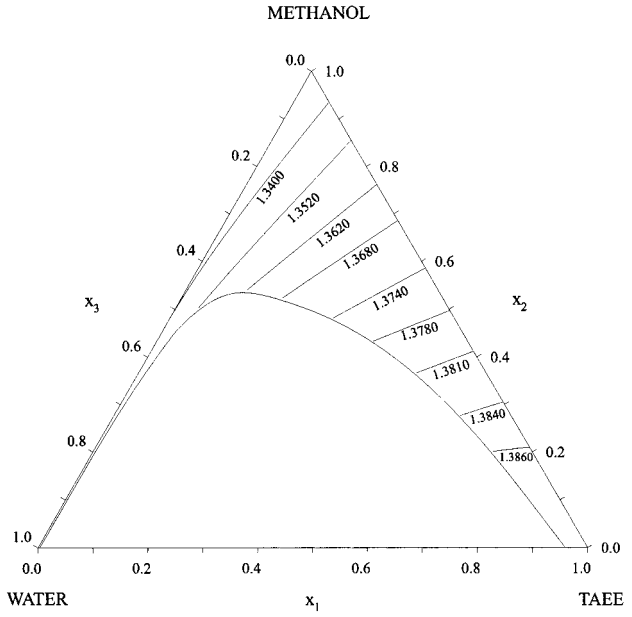

Figure 2. Refractive index isolines for the TAEE (1) + methanol (2) + water (3) system at 298.15 K and atmospheric pressure.

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 relations

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

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

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

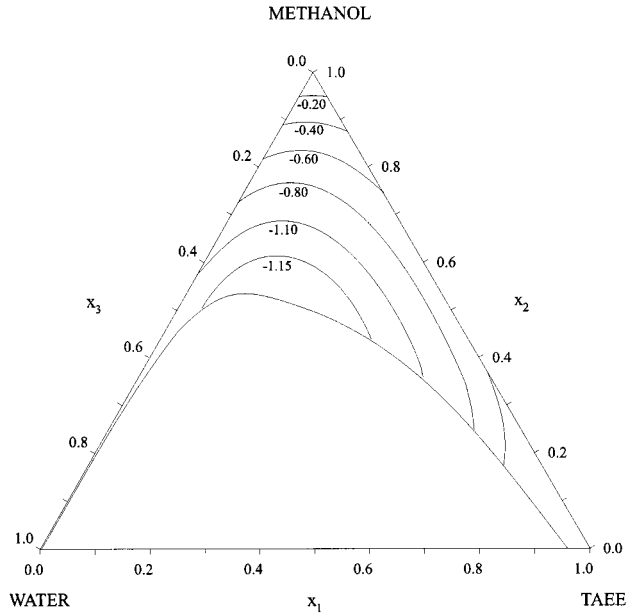

Figure 3. Excess molar volume isolines for the TAEE (1) + methanol (2) + water (3) system at 298.15 K and atmospheric pressure (system compositions in mole fraction).

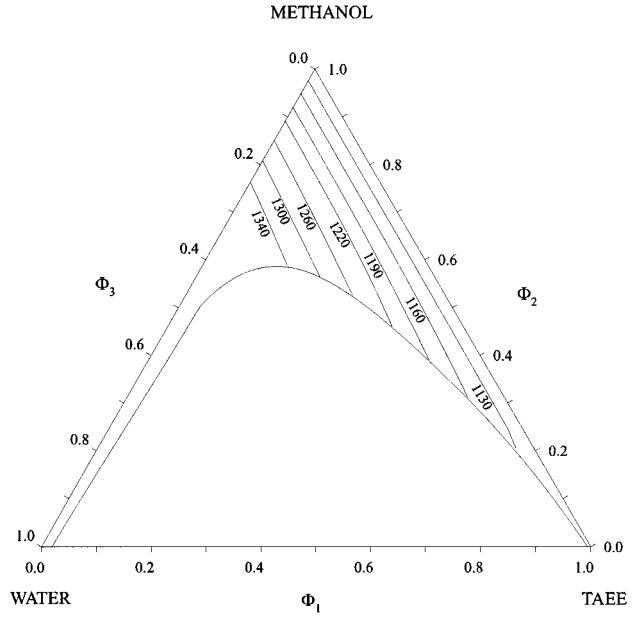

Figure 4. Speed of sound isolines for the TAEE (1) + methanol (2) + water (3) system at 298.15 K and atmospheric pressure (system compositions in volume fraction).

volume fractions of component i in the mixture given by

$$\phi_i = x_i V_i / \sum_j x_j V_j \tag{5}$$

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, respectively (system composition in mole fraction, x_i), and Figures 4 and 5 show the speed of sound isolines and the isentropic compressibility changes of mixing, respectively (system composition in volume fraction, ϕ_i). These isolines are limited to the miscible region of the ternary mixture, the boundaries of which were established previously.[8]

Table 4. 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 Composition Is in Volume Fractions, ϕ_i)

property	A_0	A_1	A_2	A_3	A_4	A_5	σ
			Methanol (1) + TAEE (2)				
V^E/cm^3·mol^{-1}	−2.6836	0.4881	−0.7925	−0.2690			0.003
$\Delta\kappa_s$/T·Pa^{-1}	−71.300	104.04	−72.675	337.87		578.86	0.7
ΔR/cm^3·mol^{-1}	−0.0698		−0.0503				0.002
			Water (1) + Methanol (2)				
V^E/cm^3·mol^{-1}	−4.1148	−0.1325	0.5078	0.6222			0.001
$\Delta\kappa_s$/T·Pa^{-1}	−1113.1	416.4	−228.7	239.9			0.3
ΔR/cm^3·mol^{-1}	−0.0952						0.001

Table 5. 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) + Methanol (2) + Water (3) (for $\Delta\kappa_s$, System Composition Is in Volume Fractions, ϕ_i)

property	A	B	C	D	E	F	G	σ
V^E/cm^3·mol^{-1}	−12.297	1.3669	0.2185	−1.5854	−11.527	12.125	−11.664	0.006
$\Delta\kappa_s$/T·Pa^{-1}	−896.19	−1199.4	−1643.4	286.63	2842.8	−895.90	−9369.1	2
ΔR/cm^3·mol^{-1}	−0.7087	0.3246	−0.3165	−0.0081				0.002

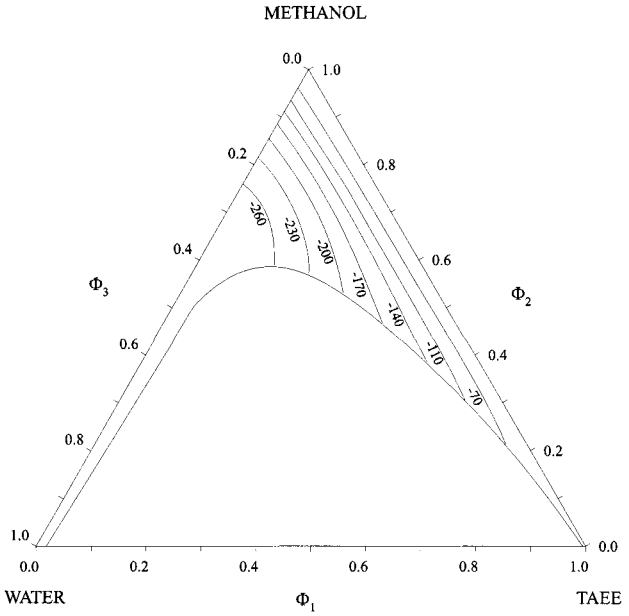

Figure 5. Isentropic compressibility changes of mixing isolines for the TAEE (1) + methanol (2) + water (3) system at 298.15 K and atmospheric pressure.

Correlation

The V^E, ΔR, and $\Delta\kappa_s$ calculated data were correlated with the composition data by means of the Redlich−Kister[9] polynomial, 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 $\Delta\kappa_s$, 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 systems the corresponding equation, as a function of the composition, x_i (in mole or volume fraction), is

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

where Q_{123} represents V^E, ΔR, or $\Delta\kappa_s$ for the ternary mixture TAEE (1) + methanol (2) + water (3) and Q_{21}, Q_{32}, and Q_{13} are the values of the Redlich−Kister polynomial for the same property fitted to the binary systems data; Q_{13} in this case is equal to zero because of the immiscibility of water and TAEE.

The values of the coefficients A_k for Q_{21} (methanol + TAEE) and Q_{32} (water + methanol) are summarized in Table 4 along with the standard deviations of the fit. For the binary system water + methanol the parameters of the fitted polynomials were previously obtained by this group and have already been published.[3] The Redlich−Kister coefficients for the ternary system are listed in Table 5 together with the corresponding standard deviations of the fit. All of these coefficients were obtained fitting, to the appropriate parameters, eqs 6 and 7 by least-squares regression, and the Fisher's F-test was used to decide the degree of the polynomial.

Conclusions

For the binary system methanol + TAEE at 298.15 K and atmospheric pressure, excess molar volumes are negative, reaching a minimum around −0.68 cm^3·mol^{-1} for mixtures with methanol in around 0.45 mole fraction. The values of the isentropic compressibility changes of mixing are always negative, reaching values of −23 T·Pa^{-1}.

For the ternary system TAEE + methanol + water, excess molar volumes are relatively large and negative throughout the entire range of homogeneous mixtures, showing minimum values around −1.15 cm^3·mol^{-1}. Also the isentropic compressibility changes of mixing ($\Delta\kappa_s$) are negative and have large values with the minimum values those corresponding to the water + methanol binary system.

For binary and ternary systems, molar refraction changes of mixing (ΔR) are negative; however, this property did have small values.

It has been proved, for the calculated properties V^E, ΔR, and $\Delta\kappa_s$, that the Redlich−Kister polynomial suggests an appropriate correlation.

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