Densities, Refractive Indices, Speeds of Sound, and Isentropic Compressibilities of Water + Methanol + 2-Methoxy-2-methylbutane at 298.15 K

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The densities, refractive indices, and speeds of sound of homogeneous mixtures of water + methanol + 2-methoxy-2-methylbutane at 298.15 K were determined and used to calculate excess molar volumes (V^E), molar refractions (R), and isentropic compressibilities (k_S). The V^E data and the deviations of $R(\Delta R)$ and $k_S(\Delta k_S)$ from mole fraction and volume fraction averages, respectively, of these properties of the pure components, were satisfactorily correlated with the composition data using the Redlich−Kister polynomial.

Introduction

Due to the importance of 2-methoxy-2-methylbutane (TAME or *tert*-amyl methyl ether) as a gasoline additive, recent years have seen a considerable increase in the amount of published work involving this ether. Nevertheless, while selected physical properties of the binary system TAME + methanol are available in the literature (Cervenková and Boublík, 1984), we found no such data for the ternary system water + methanol + TAME. To redress this, we now report densities (ρ), refractive indices (n_D), speeds of sound (u), and isentropic compressibilities (k_S) for the range of homogeneous mixtures of water + metha- + 2-methoxy-2-methylbutane, for which LLE data were obtained previously (Arce *et al.*, 1994). In addition, the corresponding excess molar volumes (V^E) and deviations of molar refractions (ΔR) and isentropic compressibilities $_S$) from mole fraction and volume fraction averages, respectively, of these properties of the pure components were correlated with the composition data using the Redlich−Kister polynomial.

Experimental Section

Materials. Water was purified using a Milli-Q Plus system. Methanol was supplied by Merck and had a nominal purity >99.7 mass %. 2 Methoxy-2 methylbutane (TAME) was supplied by Fluka Chemika with nominal purity >98.9 mass %. Water contents of the methanol and TAME were 0.03 and 0.02 mass %, respectively (determined with a Metrohm 737 KF coulometer).

Apparatus and Procedure. The mixtures were prepared by mass using a Mettler AE 240 balance that measured to within ±0.000 01 g. Their densities and the speed of sound in them were measured to within ±0.0001 g·cm^{-3} and ±1 m·s^{-1}, respectively, in an Anton Paar DSA-48 densimeter and sound analyzer calibrated with air and water (calibration values taken from Riddick *et al.*, 1986). Refractive indices were measured to within ±0.0001 in an ATAGO RX-1000 refractometer. A Hetotherm thermostat was used to maintain the temperature at (298.15 ± 0.02) K.

Table 1 lists the densities and refractive indices measured for the pure components, together with published values for these parameters (Riddick *et al.*, 1986; Cervenková and Boublík, 1984).

Table 1. Densities ρ and Refractive Indices n_D of the Pure Components at 298.15 K

	ρ/g·cm^{-3}		n_D	
component	exptl	lit	exptl	lit
methanol	0.7866	0.786 64[b]	1.3264	1.326 52[b]
TAME[a]	0.7705	0.770 74[c]	1.3884	1.388 48[c]

[a] At 293.15. [b] Riddick *et al.*, 1986. [c] Cervenková and Boublík, 1984.

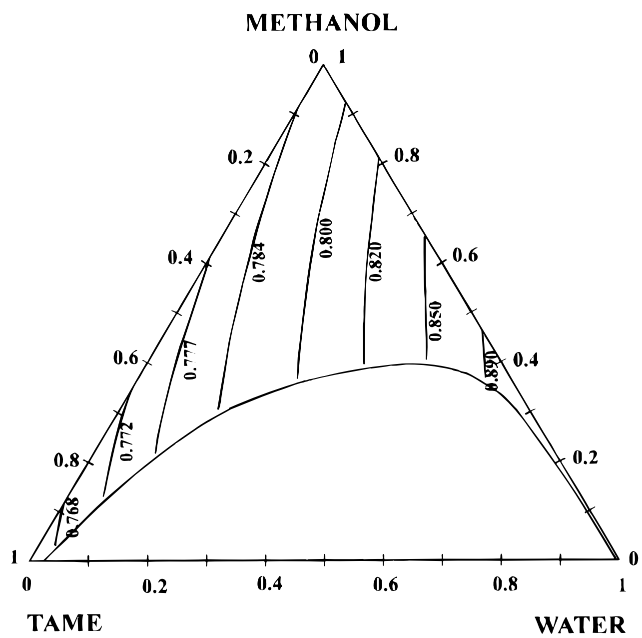

Figure 1. Density (g·cm^{-3}) isolines for water + methanol + TAME at 298.15 K and atmospheric pressure (system compositions in mole fractions).

Results and Discussion

For single phase mixtures of water + methanol + TAME at 298.15 K, and also for binary mixtures of methanol + TAME, Table 2 lists the measured densities and refractive indices, together with excess molar volumes calculated using the expression

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

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Table 2. Densities ρ, Speeds of sound u, Isentropic Compressibilities k_S, Refractive Indices n_D, Excess Molar Volumes V^E, and Deviations Δk_S and ΔR for Mixtures of Water (1) + Methanol (2) + TAME (3) at 298.15 K

x_1	x_2	ρ/g·cm^{-3}	u/m·s^{-1}	k_S/TPa^{-1}	n_D	V^E/cm^3·mol^{-1}	Δk_S/TPa^{-1}	ΔR/cm^3·mol^{-1}	x_1	x_2	ρ/g·cm^{-3}	u/m·s^{-1}	k_S/TPa^{-1}	n_D	V^E/cm^3·mol^{-1}	Δk_S/TPa^{-1}	ΔR/cm^3·mol^{-1}
0.0000	1.0000	0.7866	1102	1047	1.3264	0.000	0	0.000	0.1772	0.7147	0.8079	1184	884	1.3505	−0.772	−121	−0.023
0.0000	0.9505	0.7850	1106	1041	1.3354	−0.084	−7	−0.004	0.1576	0.6357	0.7988	1168	918	1.3606	−0.833	−99	−0.029
0.0000	0.9004	0.7836	1110	1036	1.3429	−0.162	−12	−0.008	0.1394	0.5622	0.7923	1156	944	1.3671	−0.847	−81	−0.032
0.0000	0.8468	0.7822	1113	1032	1.3495	−0.235	−17	−0.011	0.1202	0.4849	0.7867	1147	966	1.3722	−0.827	−66	−0.031
0.0000	0.8004	0.7810	1115	1029	1.3543	−0.290	−20	−0.014	0.0991	0.3995	0.7817	1140	984	1.3764	−0.771	−53	−0.023
0.0000	0.7427	0.7797	1117	1027	1.3594	−0.348	−22	−0.016	0.0789	0.3181	0.7778	1135	999	1.3796	−0.688	−42	−0.013
0.0000	0.6979	0.7787	1119	1026	1.3627	−0.384	−23	−0.018	0.0592	0.2388	0.7744	1130	1012	1.3820	−0.578	−32	−0.001
0.0000	0.6456	0.7776	1120	1026	1.3661	−0.418	−23	−0.020	0.0409	0.1650	0.7716	1125	1024	1.3837	−0.445	−22	0.008
0.0000	0.6034	0.7767	1120	1026	1.3685	−0.438	−24	−0.021	0.0211	0.0853	0.7687	1120	1037	1.3850	−0.259	−12	0.011
0.0000	0.5508	0.7757	1121	1026	1.3712	−0.455	−24	−0.021	0.3006	0.6994	0.8412	1271	736	1.3357	−0.845	−212	−0.020
0.0000	0.5056	0.7748	1122	1026	1.3732	−0.463	−24	−0.021	0.2691	0.6262	0.8216	1222	815	1.3532	−0.998	−166	−0.031
0.0000	0.4559	0.7739	1122	1026	1.3752	−0.465	−23	−0.021	0.2415	0.5619	0.8093	1195	865	1.3625	−1.040	−133	−0.035
0.0000	0.4055	0.7730	1122	1027	1.3770	−0.459	−23	−0.021	0.2189	0.5094	0.8015	1178	899	1.3678	−1.035	−110	−0.036
0.0000	0.3553	0.7721	1122	1028	1.3786	−0.444	−22	−0.020	0.1788	0.4160	0.7910	1158	943	1.3744	−0.972	−80	−0.031
0.0000	0.3144	0.7714	1122	1029	1.3798	−0.427	−21	−0.018	0.1511	0.3516	0.7854	1149	965	1.3777	−0.898	−65	−0.025
0.0000	0.2538	0.7704	1122	1032	1.3813	−0.388	−18	−0.016	0.1187	0.2761	0.7800	1140	986	1.3806	−0.784	−50	−0.017
0.0000	0.2054	0.7696	1121	1034	1.3824	−0.346	−16	−0.014	0.0896	0.2084	0.7760	1133	1004	1.3825	−0.650	−37	−0.010
0.0000	0.1576	0.7687	1120	1037	1.3834	−0.293	−13	−0.011	0.0634	0.1474	0.7727	1128	1018	1.3839	−0.499	−26	−0.005
0.0000	0.1126	0.7679	1119	1041	1.3842	−0.230	−10	−0.009	0.0327	0.0760	0.7692	1121	1034	1.3850	−0.280	−13	0.001
0.0000	0.0591	0.7669	1117	1045	1.3850	−0.135	−6	−0.005	0.4024	0.5976	0.8617	1336	651	1.3380	−0.980	−255	−0.023
0.0000	0.0000	0.7657	1115	1051	1.3858	0.000	0	0.000	0.3719	0.5523	0.8411	1274	732	1.3523	−1.119	−211	−0.028
0.1011	0.8989	0.8042	1155	932	1.3297	−0.364	−84	−0.009	0.3371	0.5006	0.8240	1229	803	1.3622	−1.178	−168	−0.033
0.0956	0.8504	0.7997	1151	944	1.3396	−0.447	−78	−0.014	0.2779	0.4128	0.8043	1184	887	1.3719	−1.141	−113	−0.038
0.0809	0.7197	0.7905	1144	967	1.3572	−0.592	−65	−0.021	0.2449	0.3637	0.7966	1168	920	1.3754	−1.088	−91	−0.038
0.0710	0.6313	0.7858	1138	983	1.3649	−0.639	−54	−0.023	0.4968	0.5032	0.8814	1398	580	1.3399	−1.028	−281	−0.024
0.0606	0.5386	0.7817	1134	995	1.3708	−0.652	−46	−0.022	0.4738	0.4799	0.8644	1340	644	1.3497	−1.153	−251	−0.034
0.0510	0.4537	0.7786	1132	1003	1.3749	−0.636	−40	−0.020	0.4462	0.4520	0.8477	1285	715	1.3578	−1.221	−211	−0.040
0.0411	0.3659	0.7757	1129	1011	1.3782	−0.591	−34	−0.016	0.4246	0.4301	0.8367	1253	761	1.3625	−1.222	−182	−0.039
0.0311	0.2769	0.7731	1127	1019	1.3809	−0.514	−27	−0.011	0.5929	0.4071	0.9020	1461	519	1.3411	−0.994	−290	−0.023
0.0218	0.1936	0.7709	1123	1028	1.3828	−0.409	−20	−0.007	0.5786	0.3973	0.8902	1418	558	1.3469	−1.080	−277	−0.032
0.0125	0.1113	0.7687	1120	1037	1.3843	−0.268	−12	−0.004	0.5624	0.3861	0.8789	1368	608	1.3523	−1.170	−252	−0.042
0.1987	0.8013	0.8218	1210	831	1.3328	−0.635	−153	−0.015									

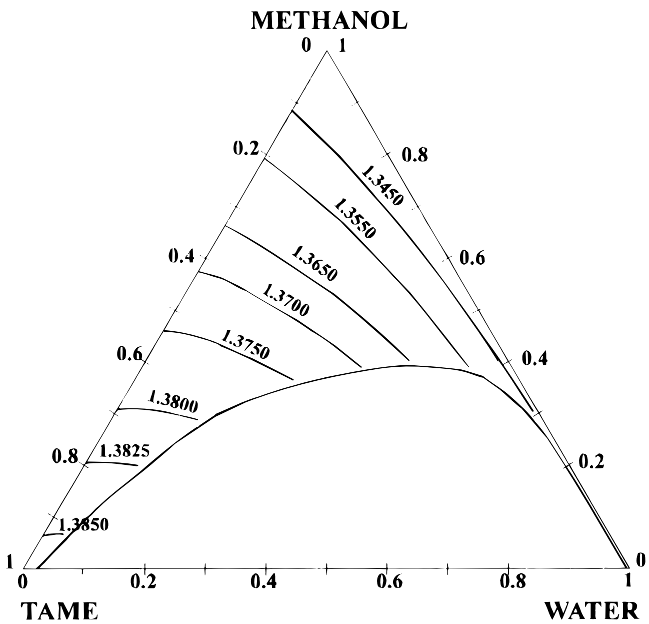

Figure 2. Refractive index isolines for water + methanol + TAME at 298.15 K and atmospheric pressure (system compositions in mole fractions).

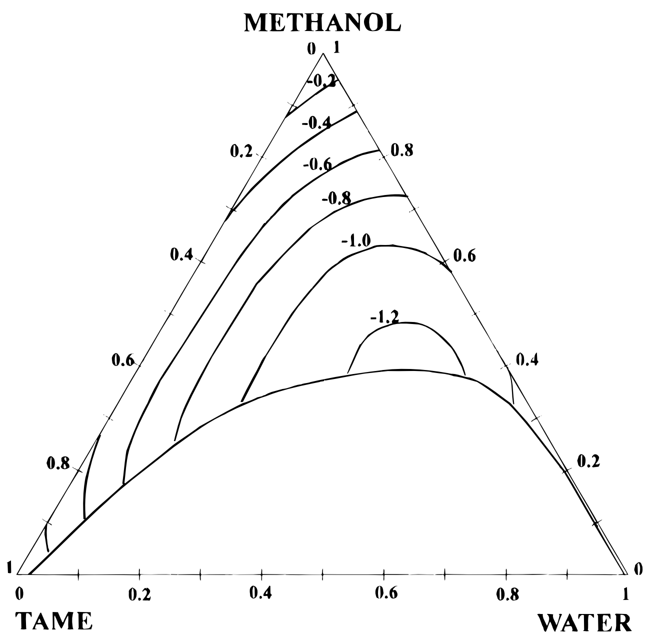

Figure 3. Excess molar volume (cm^3·mol^{-1}) isolines for water + methanol + TAME at 298.15 K and atmospheric pressure (system compositions in mole fractions).

where V is the molar volume of the mixture and V_i and x_i are the molar volume and mole fraction, respectively, of component i. From V and the refractive indices, the molar refraction, R, was obtained using the Lorentz−Lorenz equation, and the deviation in R (Table 2) was calculated as

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

where R is the molar refraction of the mixture and R_i is the molar refraction of component i. All these data for binary water + methanol mixtures have already been published (Arce *et al.*, 1993).

Also included in Table 2 are the speeds of sound in the ternary and the TAME + methanol mixtures; these values, together with the corresponding densities, were used to calculate isentropic compressibilities using the equation

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

The deviations in isentropic compressibility (Table 2) were then obtained using the expression

Table 3. Polynomial Coefficients (A_k) and Standard Deviations (σ) Obtained for the Fits of Equation 6 to the V^E, ΔR, and Δk_S Composition data for the Binary Systems (for Δk_S, System Compositions Were in Volume Fractions, ϕ_i)

property	A_0	A_1	A_2	A_3	A_4	σ
			Water (1) + Methanol (2)			
V^E/cm^3·mol^{-1}	−4.1148	−0.1325	0.5078	0.6222		0.001
ΔR/cm^3·mol^{-1}	−0.0952					0.001
Δk_S/TPa^{-1}	−1113.1	416.4	−228.7	239.9		0.30
			TAME (1) + methanol (2)			
V^E/cm^3·mol^{-1}	−1.8559	−0.1787	−0.3252	−0.2319		0.001
ΔR/cm^3·mol^{-1}	−0.0857					0.001
Δk_S/TPa^{-1}	−84.6	−52.6		−62.4	−128.4	0.20

Table 4. Polynomial Coefficients and Standard Deviations (σ) Obtained for Fits of Equation 7 to the V^E, ΔR, and Δk_S Composition Data for the Ternary System Water (1) + Methanol (2) + TAME (3) (for Δk_S, System Compositions Were in Volume Fractions, ϕ_i)

property	A	B	C	D	E	F	G	σ
V^E/cm^3·mol^{-1}	−14.465	−11.318	−7.890	3.428	−6.325	−12.899	−6.510	0.009
ΔR/cm^3 ·mol^{-1}	−0.452	−0.374	0.414	0.788				0.003
Δk_S/TPa^{-1}	−1726.0	1993.5	−76.1	−2069.6	1098.6	−2752.8	−4932.0	2.00

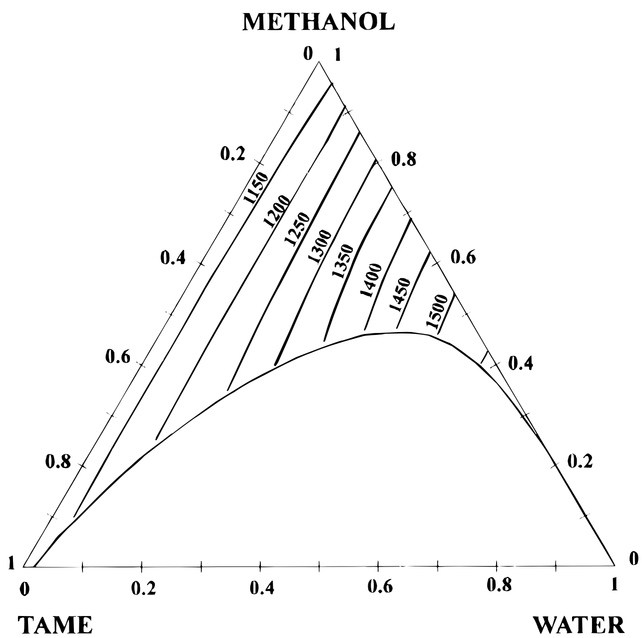

Figure 4. Speed of sound (m·s^{-1}) isolines for water + methanol TAME at 298.15 K and atmospheric pressure (system compositions in volume fractions).

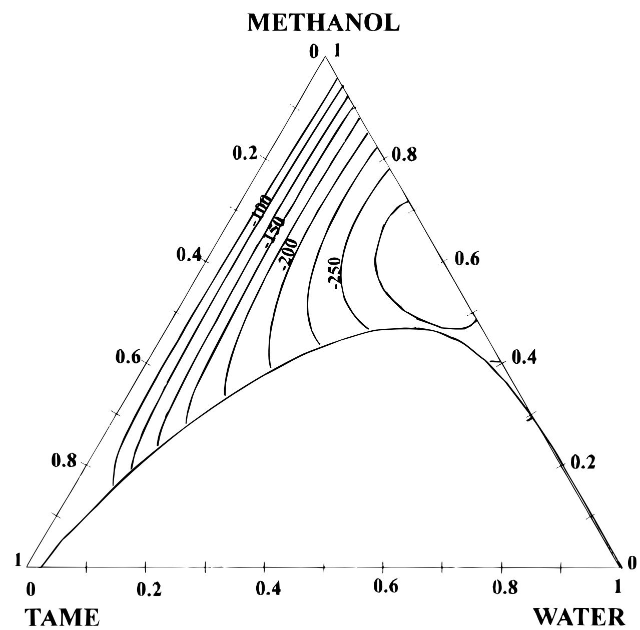

Figure 5. Isentropic compressibility deviation (TPa^{-1}) isolines for water + methanol + TAME at 298.15 K and atmospheric pressure (system compositions in volume fractions).

$$\Delta k_S = k_S - \sum_i \phi_i k_{Si} \tag{4}$$

where k_S and k_{Si} are the isentropic compressibilities of the mixture and component i, respectively, and ϕ_i is the volume fraction of component i in the mixture as given by

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

where j refers to all the components of the mixture.

For the ternary system, Figures 1−3 show the density, refractive index, and excess volume isolines, respectively (system compositions in mole fractions, x_i), and Figures 4 and 5 show the isolines for the speeds of sound and the deviations in isentropic compressibility, respectively (system compositions in volume fraction, ϕ_i).

For the entire range of homogeneous mixtures, the excess molar volume (V^E) has relatively large, negative values, the minimum lying around −1.2 cm^3·mol^{-1}. Generally, the deviation in molar refraction (ΔR) is small and negative, except for compositions rich in TAME that lie close to the binodal curve, for which it has small, positive values. The deviation in isentropic compressibility (Δk_S) is always negative and has larger values for mixtures poor in TAME.

The V^E, ΔR, and Δk_S data were correlated with the composition data by means of the Redlich−Kister polynomial (Redlich−Kister, 1948), which for binary mixtures is

$$Q_{ij} = x_i x_j \sum_k A_k (x_i - x_j)^k \qquad k = 0, 1, 2, ... \tag{6}$$

where Q_{ij} is V^E or ΔR and x_i is the mole fraction of component i, or Q_{ij} is Δk_S and x_i is the volume fraction of component i, and k is the number of the polynomial coefficient. For ternary systems the corresponding equation is

$$Q_{123} = Q_{12} + Q_{32} + Q_{31} + x_1 x_2 x_3 (A + B(x_1 - x_2) + C(x_3 - x_2) + D(x_3 - x_1) + E(x_1 - x_2)^2 + F(x_3 - x_2)^2 + G(x_3 - x_1)^2) \tag{7}$$

where x_i is the mole or volume fraction, depending on the parameter being correlated, as previously indicated.

Equations 6 and 7 were fitted to the appropiate parameter−composition data for the binary and ternary systems by least-squares regression, applying Fisher's *F*-test to establish the number of coefficients. These coefficients and their mean standard deviations are listed in Table 3 for the binary systems, and in Table 4 for the ternary system. In all cases, the Redlich−Kister polynomial allowed satisfactory correlation of the data.

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