Excess Enthalpy, Density, and Speed of Sound for the Ternary Mixture Methyl *tert*-Butyl Ether (1) + Butan-1-ol (2) + Octane (3)[†]

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Excess molar enthalpies, $H^E(x, T)$, at $T = 298.15$ K, densities, $\rho(x, T)$, and speeds of sound, $u(x, T)$, at temperatures $T = (288.15$ to $308.15)$ K and atmospheric pressure have been measured for the ternary system methyl *tert*-butyl ether (MTBE) (1) + butan-1-ol (2) + octane (3). Also, densities, $\rho(x, T)$, and speeds of sound, $u(x, T)$, for the binary mixture MTBE (1) + octane (3) and excess molar enthalpies, $H^E(x, T)$, $T = 298.15$ K, for the binary mixture butan-1-ol (2) + octane (3) have been measured. From experimental data, excess molar volumes, $V^E(x, T)$, and excess isentropic compressibility, $\kappa_S^E(x, T)$, were calculated. The Cibulka equation was used to correlate the ternary contribution to the experimental excess molar volume and excess isentropic compressibility. Additionally, excess molar enthalpies were correlated with the Nagata and Tamura equation, and the experimental results are compared with the estimations obtained by applying the group-contribution models of UNIFAC and DISQUAC.

Introduction

As noted in previous works,[1−4] the mixtures containing ethers, alkanes, and alkanols are a family of solutions of technological importance because tertiary-alkyl ethers, either pure or mixed with alkanols, have been recommended as octane blending agents for gasolines.

This work contributes to the series of ternary mixtures of methyl *tert*-butyl ether (MTBE) + butan-1-ol + *n*-alkane reported in previous works,[1−3] where the third component of the mixture was hexane and decane, respectively. So, experimental measurements of density and speed of sound for the ternary mixture MTBE (1) + butan-1-ol (2) + octane (3) at $T = (288.15, 293.15, 298.15, 303.15,$ and $308.15)$ K and atmospheric pressure over the whole composition range and excess molar enthalpy at $T = 298.15$ K are reported. Additionally, density and speed of sound values for the binary mixture MTBE (1) + octane (3) and excess molar enthalpies, at $T = 298.15$ K, for the binary mixture butan-1-ol (2) + octane (3) are reported.

From the experimental data, excess molar volumes, $V^E(x, T)$, and excess isentropic compressibilities, $\kappa_s^E(x, T)$, were computed. To adequately correlate these quantities, the Cibulka[6] equation was used to correlate the ternary contribution to the experimental excess molar volume and excess isentropic compressibility, and for excess molar enthalpy, the Nagata and Tamura[7] equation was used. Also, to estimate excess molar enthalpies, the group contribution models UNIFAC (in the versions of Dang and Tassios,[8] Larsen et al.,[9] Gmehling et al.,[10]) and DISQUAC[11,12] have been applied.

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Table 1. Properties of Octane at Several Temperatures

T	ρ/kg·m^{-3}		u/m·s^{-1}		α/k·K^{-1}		C_p/J·K^{-1}·mol^{-1}
K	exptl	lit.	exptl	lit.	calcd	lit.	lit.
288.15	706.58	706.6[a]	1213.6	1214[a]	1.142		250.84[e]
293.15	702.57	702.56[b]	1193.0	1193[a]	1.151		252.96[e]
298.15	698.55	698.54[b]	1171.9	1172[a]	1.148	1.164[d]	255.11[e]
303.15	694.48	694.5[c]	1151.0	1151.6[c]	1.160		257.29[e]
308.15	690.42	690.4[c]	1130.3	1132.9[c]	1.185		259.48[e]

[a] Ref 13. [b] Ref 14. [c] Ref 15. [d] Ref 16. [e] Ref 17.

Experimental Section

Methyl *tert*-butyl ether, which is also referred to as methyl 2−2 dimethylethyl ether according to IUPAC recommendations (mass fraction purity > 99.8 %), and butan-1-ol (mass fraction purity > 98.8 %) were supplied by Aldrich, and octane (mass fraction purity > 99.5 %) was supplied by Fluka. The substances were partially degassed in an ultrasound bath and dried over molecular sieves (Sigma, 0.4 nm).

Experimental densities, $\rho(T)$, and speeds of sound, $u(T)$, of octane agree satisfactorily with the literature data, as shown in Table 1. The experimental data of pure MTBE and butan-1-ol were reported in a previous work.[1]

The mixtures were prepared by mass with an accuracy of $\pm 5 \cdot 10^{-8}$ kg using an electronic balance (Mettler AE-240), with an uncertainty in mole fraction estimated to be lower than $\pm 1 \cdot 10^{-4}$.

Densities and speeds of sound of the pure liquids and mixtures were measured with a digital densimeter and sound analyzer Anton-Paar DSA-48. The apparatus was automatically thermostatted within a temperature uncertainty of $\pm 2 \cdot 10^{-2}$ K, with an estimated uncertainty of $\pm 5 \cdot 10^{-2}$ kg·m^{-3} and ± 0.5 m·s^{-1}

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Table 2. Densities (ρ) and Speeds of Sound (u) for the Binary Mixture MTBE (1) + Octane (3) and Ternary Mixture MTBE (1) + Butan-1-ol (2) + Octane (3) at Several Temperatures

		T/K							T/K				
x_1	x_2	288.15	293.15	298.15	303.15	308.15	x_1	x_2	288.15	293.15	298.15	303.15	308.15
				ρ/kg·m^{-3}							u/m·s^{-1}		
0.0681	0.0000	708.15	704.08	700.01	695.91	691.79	0.0681	0.0000	1205.4	1184.6	1163.5	1142.6	1121.8
0.1226	0.0000	709.47	705.36	701.24	697.10	692.93	0.1226	0.0000	1198.4	1177.6	1156.3	1135.4	1114.7
0.2056	0.0000	711.65	707.48	703.29	699.07	694.83	0.2056	0.0000	1187.6	1166.7	1145.4	1124.3	1103.4
0.3046	0.0000	714.48	710.23	705.96	701.64	697.30	0.3046	0.0000	1174.2	1153.1	1131.8	1110.5	1089.4
0.4001	0.0000	717.54	713.19	708.81	704.40	699.96	0.4001	0.0000	1161.4	1140.2	1118.7	1097.1	1075.9
0.4535	0.0000	719.37	714.96	710.53	706.06	701.56	0.4535	0.0000	1154.3	1132.9	1111.2	1089.6	1068.2
0.4947	0.0000	720.85	716.40	711.92	707.40	702.84	0.4947	0.0000	1148.7	1127.2	1105.4	1083.8	1062.3
0.5442	0.0000	722.73	718.21	713.67	709.09	704.48	0.5442	0.0000	1142.0	1120.6	1098.7	1077.0	1055.3
0.5996	0.0000	724.94	720.36	715.75	711.10	706.42	0.5996	0.0000	1134.7	1113.0	1091.0	1069.1	1047.5
0.6916	0.0000	728.91	724.20	719.47	714.70	709.89	0.6916	0.0000	1122.5	1100.6	1078.4	1056.2	1034.3
0.8001	0.0000	734.16	729.30	724.41	719.47	714.49	0.8001	0.0000	1108.1	1085.8	1063.2	1040.8	1018.6
0.9007	0.0000	739.68	734.66	729.60	724.50	719.35	0.9007	0.0000	1095.1	1072.6	1049.6	1026.9	1004.2
0.9487	0.0000	742.54	737.44	700.01	727.10	721.86	0.9487	0.0000	1089.0	1066.2	1043.1	1020.1	997.3
0.0668	0.0504	710.98	706.89	702.77	698.62	694.45	0.0668	0.0504	1203.6	1183.0	1162.1	1141.1	1120.4
0.0560	0.8928	800.22	796.34	792.42	788.46	784.49	0.0560	0.8928	1255.4	1237.9	1219.5	1201.1	1183.6
0.1149	0.0988	715.58	711.44	707.29	703.08	698.85	0.1149	0.0988	1197.8	1177.2	1156.3	1135.4	1114.6
0.1125	0.1968	722.58	718.44	714.26	710.04	705.8	0.1125	0.1968	1199.0	1178.5	1157.7	1136.9	1116.3
0.1094	0.2933	730.25	726.10	721.93	717.71	713.46	0.1094	0.2933	1201.6	1181.3	1160.7	1140.1	1119.6
0.1123	0.3915	739.26	735.12	730.95	726.73	722.49	0.1123	0.3915	1205.1	1185.0	1164.6	1144.2	1124.0
0.1082	0.4831	748.29	744.17	740.02	735.82	731.58	0.1082	0.4831	1210.3	1190.5	1170.4	1150.2	1130.3
0.1037	0.5963	761.06	756.96	752.85	748.69	744.49	0.1037	0.5963	1218.5	1199.1	1179.5	1159.8	1140.3
0.1066	0.6951	774.15	770.1	766.03	761.93	757.77	0.1066	0.6951	1227.4	1208.6	1189.4	1170.4	1150.4
0.1030	0.7987	789.45	785.46	781.46	777.4	773.33	0.1030	0.7987	1239.7	1221.4	1202.9	1184.5	1165.2
0.2079	0.0974	718.54	714.33	710.10	705.81	701.51	0.2079	0.0974	1188.1	1166.6	1145.5	1124.5	1103.9
0.2044	0.1957	726.11	721.88	717.64	713.35	709.04	0.2044	0.1957	1188.8	1168.2	1147.3	1126.5	1105.9
0.2052	0.2972	735.02	730.81	726.56	722.28	717.95	0.2052	0.2972	1191.7	1171.3	1150.5	1130.0	1109.6
0.2142	0.3922	744.88	740.66	736.42	732.13	727.81	0.2142	0.3922	1195.0	1174.8	1154.3	1134.0	1113.8
0.2072	0.4940	755.82	751.62	747.4	743.14	738.86	0.2072	0.4940	1201.8	1181.9	1161.8	1141.9	1122.2
0.2100	0.5926	768.56	764.40	760.21	755.97	751.7	0.2100	0.5926	1209.5	1190.3	1170.6	1151.0	1131.5
0.2060	0.6951	783.12	779.00	774.85	770.67	766.45	0.2060	0.6951	1220.9	1202.1	1182.9	1163.9	1145.0
0.2985	0.0980	721.81	717.51	713.21	708.85	704.46	0.2985	0.0980	1177.0	1155.6	1134.5	1113.4	1092.8
0.3011	0.1970	730.34	726.04	721.71	717.33	712.93	0.3011	0.1970	1179.1	1157.9	1137.0	1116.1	1095.6
0.3023	0.2975	739.97	735.68	731.35	726.96	722.56	0.3023	0.2975	1182.1	1162.1	1140.9	1120.1	1100.1
0.3037	0.3946	750.53	746.24	741.93	737.55	733.15	0.3037	0.3946	1186.2	1166.3	1145.9	1125.6	1105.4
0.3017	0.4935	762.43	758.16	753.86	749.52	745.14	0.3017	0.4935	1193.3	1173.5	1153.3	1133.2	1113.4
0.3016	0.5984	777.17	772.93	768.66	764.35	760.01	0.3016	0.5984	1203.2	1183.9	1164.2	1144.6	1125.2
0.4026	0.0951	725.61	721.22	716.81	712.33	707.85	0.4026	0.0951	1163.8	1142.8	1121.4	1100.1	1079.0
0.4008	0.1978	735.07	730.67	726.25	721.77	717.26	0.4008	0.1978	1166.8	1146.1	1124.8	1103.7	1082.9
0.4075	0.2953	745.61	741.21	736.78	732.29	727.77	0.4075	0.2953	1170.1	1149.6	1128.6	1107.9	1087.4
0.4067	0.3914	756.93	752.53	748.10	743.62	739.12	0.4067	0.3914	1175.8	1155.5	1134.9	1114.4	1095.2
0.4110	0.4865	770.09	765.71	761.30	756.83	752.34	0.4110	0.4865	1183.2	1163.3	1143.0	1122.8	1102.9
0.4943	0.0987	729.85	725.37	720.84	716.27	711.68	0.4943	0.0987	1152.8	1131.6	1110.1	1088.1	1067.0
0.4926	0.1999	740.00	735.50	730.97	726.4	721.79	0.4926	0.1999	1156.5	1135.7	1114.6	1093.6	1073.0
0.4921	0.3013	751.56	747.06	742.53	737.95	733.34	0.4921	0.3013	1161.5	1140.8	1119.8	1099.0	1078.5
0.4995	0.4003	765.05	760.55	756.02	751.44	746.82	0.4995	0.4003	1167.9	1147.5	1126.7	1106.1	1085.8
0.5949	0.0999	734.75	730.14	725.49	720.80	716.08	0.5949	0.0999	1140.7	1119.3	1096.5	1075.1	1053.9
0.5955	0.2006	746.01	741.38	736.73	732.02	727.27	0.5955	0.2006	1145.0	1123.9	1102.6	1081.4	1060.6
0.5999	0.3004	758.91	754.28	749.61	744.89	740.14	0.5999	0.3004	1150.6	1129.7	1108.6	1087.5	1066.9
0.6919	0.0998	739.86	735.11	730.34	725.51	720.66	0.6919	0.0998	1128.0	1106.3	1084.3	1062.4	1041.0
0.7003	0.1989	752.52	747.75	742.96	738.09	733.2	0.7003	0.1989	1133.2	1111.4	1089.6	1068.1	1046.6
0.8000	0.1005	746.31	741.42	736.48	731.49	726.48	0.8000	0.1005	1115.1	1092.8	1070.9	1048.0	1026.1
0.9016	0.0487	746.02	740.99	735.91	730.77	725.61	0.9016	0.0487	1098.6	1076.3	1053.2	1030.5	1008.1

for density and speed of sound measurements, respectively. The calibration was performed periodically using air and double distilled Millipore quality water.

Experimental excess molar enthalpies were measured using a Calvet microcalorimeter equipped with a Philips PM 2525 microvoltimeter and an automatic data acquisition system. The calibration was carried out electrically, with a Setaram EJP 30 stabilized current source. The uncertainty of experimental results for excess molar enthalpies was estimated, according to periodical comparison with IUPAC recommended data for hexane + cyclohexane binary mixtures, to be lower than ± 1 J·mol^{-1}. Details of the experimental procedure have been described previously.[1,4]

Results and Discussion

Experimental densities and speeds of sound for the ternary mixture MTBE (1) + butan-1-ol (2) + octane (3) and the binary mixture MTBE (1) + octane (3), measured at the temperatures cited previously, are listed in Table 2. Densities and speed of sound for the binary mixtures MTBE (1) + butan-1-ol (2) and butan-1-ol (2) + octane (3) were reported in earlier papers.[18,19]

Experimental values of excess molar enthalpies at $T = 298.15$ K for the binary mixtures butan-1-ol (2) + octane (3) and the ternary mixture MTBE (1) + butan-1-ol (2) + octane (3) are reported in Table 3. Excess molar enthalpies at 298.15 K for binary MTBE (1) + octane (3) have been presented by Mato et al.[5] Mascato et al.[1] have published excess molar enthalpies at $T = 298.15$ K for binary MTBE (1) + butan-1-ol (2).

Excess molar volumes, $V^E(x, T)$, and excess isentropic compressibility, $\kappa_s^E(x, T)$, were calculated using eqs 1 and 2, respectively, for the binary mixture MTBE (1) + octane (3) and the ternary mixture MTBE (1) + butan-1-ol (2) + octane (3), and they are reported as Supporting Information.

$$V^{E} = V - V_{id} = V - \sum_{i=1}^{n} x_i M_i/\rho_i \tag{1}$$

where V is the molar volume; x_i, M_i, and ρ_i stand for the mole fraction, molar mass, and density of component i, respectively; and n is the number of components in the mixture.

$$\kappa_s^{E} = \kappa_s - \kappa_s^{id} = \kappa_s - \sum_{i=1}^{n} \phi_i(\kappa_{s,i} + TV_i\alpha_i^2/C_{p,i}) - T\left(\sum_{i=1}^{n} x_iV_i\right)\left(\sum_{i=1}^{n}\phi_i\alpha_i\right)^2\Big/\sum_{i=1}^{n} x_iC_{p,i} \tag{2}$$

where κ_s, calculated as $\kappa_s = \rho^{-1}u^{-2}$, is the isentropic compressibility of the mixture; κ_s^{id} is the isentropic compressibility for an ideal mixture and was evaluated using the expression suggested by Benson and Kiyohara;[20] n represents the number of components of the mixture; and T is the temperature. ϕ_i, x_i, $\kappa_{s,i}$, V_i, α_i, and $C_{p,i}$ are the volume fraction, mole fraction, isentropic compressibility, molar volume, isobaric thermal expansivity, and molar heat capacity of component i, respectively. The values of α_i, calculated from a correlation function of density values at different temperatures by analytical differentiation (Mascato et al.[21]), and the $C_{p,i}$ values, found in the literature (Zabransky et al.[17]), are also reported in Table 1.

The estimated uncertainties, calculated analytically through the usual error propagation procedures, are $\pm 6\cdot10^{-9}$ m$^3\cdot$mol^{-1} for V^E and 3 TPa^{-1} for κ_s^E.

The ternary mixture derived properties, excess molar volume, excess isentropic compressibility, and excess molar enthalpy, were correlated using eq 3

$$Q_{123}^{E} = \sum_{i=1}^{3}\sum_{\substack{j=1\\j>i}}^{3} Q_{ij}^{E} + x_1x_2x_3\Delta_{123} \tag{3}$$

where Q_{ij}^E corresponds to the binary contributions and $(x_1x_2x_3\Delta_{123})$ is the so-called ternary contribution.

The binary contributions were correlated using eq 4

$$Q_{ij}^{E} = x_ix_j\sum_{p=1}^{m} A_p(x_i - x_j)^{p-1}/[1 + B_0(x_i - x_j)] \tag{4}$$

where A_p and B_0 are the adjustable fitting parameters, computed using an unweighted least-squares method, using the optimization F-test[22] to determine the number of parameters m. For the three binary systems, the adjustable fitting parameters A_p and B_0 and the corresponding standard deviations, calculated with eq 7, are given in Table 4.

For excess molar volume and excess isentropic compressibility, the ternary contribution was correlated using eq 5, suggested by Cibulka[6]

$$\Delta_{123} = C_0 + C_1x_1 + C_2x_2 \tag{5}$$

For excess molar enthalpy, the ternary contribution was correlated using the combination of the expression proposed by Nagata−Tamura[7] with a dividing skewing factor, eq 6, because the ternary representation of H^E is markedly asymmetric and the correlation results obtained with eq 5 were not completely satisfactory.

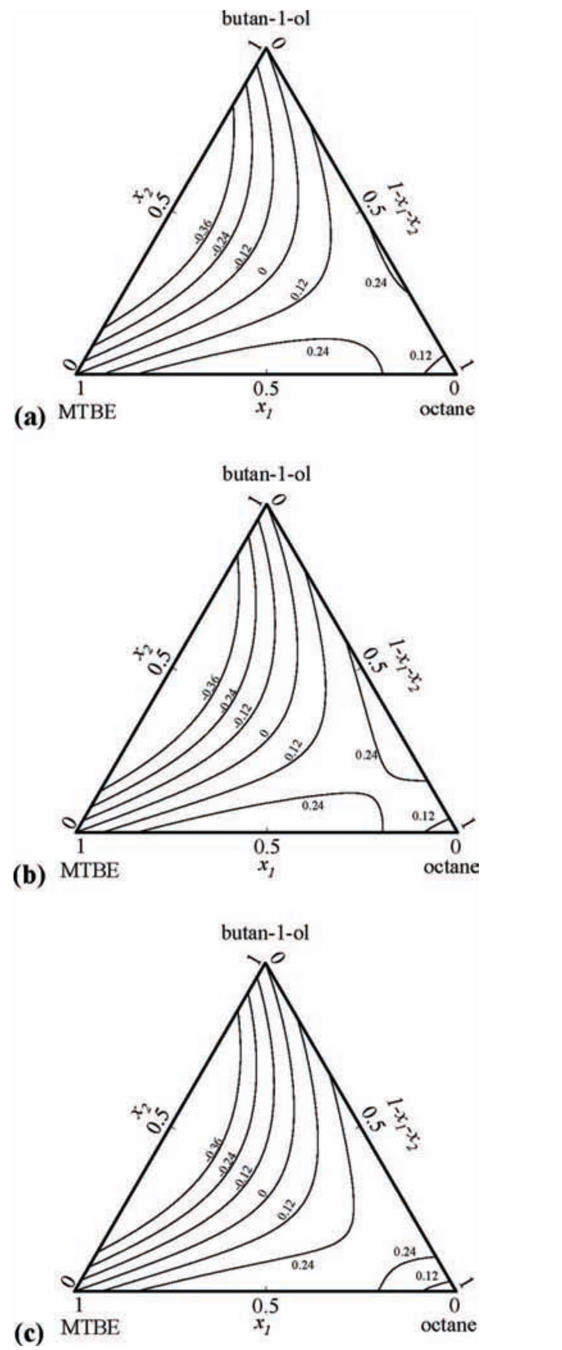

Figure 1. Excess molar volume, $V^E/10^{-6}$ m$^3\cdot$mol^{-1}, isolines correlated with eq 5 for the ternary system MTBE (1) + butan-1-ol (2) + octane (3) at: (a) T = 288.15 K, (b) T = 298.15 K, and (c) T = 308.15 K.

Table 3. Excess Molar Enthalpies (H^E) for the Binary Mixture Butan-1-ol (2) + Octane (3) and the Ternary Mixture MTBE (1) + Butan-1-ol (2) + Octane (3) at T = 298.15 K

x_1	x_2	H^E / J·mol^{-1}	x_1	x_2	H^E / J·mol^{-1}	x_1	x_2	H^E / J·mol^{-1}
0.0000	0.03632	323	0.0000	0.29898	682	0.0000	0.69876	470
0.0000	0.06450	427	0.0000	0.34501	687	0.0000	0.79786	342
0.0000	0.11819	537	0.0000	0.40282	680	0.0000	0.90052	182
0.0000	0.15683	575	0.0000	0.44991	668	0.0000	0.94925	94
0.0000	0.20312	637	0.0000	0.50289	635			
0.0000	0.24881	662	0.0000	0.60341	561			
0.0274	0.0822	518	0.0495	0.0500	463	0.0737	0.0248	373
0.0488	0.1465	655	0.0929	0.0939	638	0.1327	0.0447	530
0.0673	0.2020	729	0.1314	0.1329	747	0.1881	0.0634	660
0.0890	0.2671	785	0.1698	0.1717	840	0.2463	0.0830	764
0.1091	0.3274	806	0.2072	0.2095	892	0.2982	0.1005	831
0.1262	0.3786	828	0.2404	0.2430	923	0.3453	0.1163	863
0.1408	0.4224	832	0.2687	0.2716	944	0.3966	0.1336	882
0.1568	0.4705	799	0.2997	0.3029	959	0.4429	0.1492	881
0.1701	0.5105	784	0.3303	0.3339	944	0.4881	0.1645	874
0.1839	0.5519	754	0.3574	0.3612	932	0.5280	0.1779	869
0.1960	0.5882	709	0.3810	0.3852	903	0.5700	0.1921	844
0.2074	0.6222	658	0.4003	0.4047	868	0.6052	0.2039	819
0.2200	0.6600	599	0.4329	0.4375	821	0.6447	0.2172	769
0.2303	0.6909	541	0.4561	0.4610	766	0.6805	0.2293	716
0.2393	0.7179	479	0.4744	0.4795	707	0.7124	0.2401	652

$$\frac{\Delta_{123}}{RT} = \frac{D_0 - D_1x_1 - D_2x_2 - D_3x_1^2 - D_4x_2^2 - D_5x_1x_2 - D_6x_1^3 - D_7x_2^3 - D_8x_1^2x_2}{1 + (x_2 - x_3)} \tag{6}$$

The adjustable fitting parameters C_i and D_i, of eqs 5 and 6, and the corresponding standard deviations, calculated with eq 7, are given in Table 5.

$$s = \left[\frac{\sum_{i=1}^{n_{\mathrm{Dsts}}} (Q^{\mathrm{E}}(\mathrm{exptl})_i - Q^{\mathrm{E}}(\mathrm{calcd})_i)^2}{(n_{\mathrm{d}} - n_{\mathrm{p}})}\right]^{1/2} \tag{7}$$

where n_{d} is the number of data and n_{p} is the number of parameters.

The isolines of Figures 1 and 2 represent V^{E} and $\kappa_{\mathrm{s}}^{\mathrm{E}}$, respectively, at T = (288.15, 298.15, and 308.15) K. From these figures, it can be noted that the ternary plots present, at all the temperatures studied, an ideal behavior isoline (zero value isoline). A temperature increment produces an increment of the absolute values in the negative region, while the positive ones are scarcely modified.

In Figure 3, the excess molar enthalpy, correlated with eq 6, at T = 298.15 K was plotted, and the H^{E} values show a maximum at an approximate concentration of $x_1 = x_2 = 0.3$. The positive H^{E} obtained for the ternary system may be explained qualitatively as the result of the breaking of alcohol hydrogen bonding autoassociation, added to two other effects as breaking of dipole−dipole interactions of MTBE, and the contribution due to the loss of orientation order of the alkane. These effects are more significant than the cross association

Table 4. Parameters (A_{p}) and (B_0) of Equation 4 and Standard Deviations (s), Equation 7, for Excess Molar Volume (V^{E}), Excess Isentropic Compressibility ($\kappa_{\mathrm{s}}^{\mathrm{E}}$), and Excess Molar Enthalpy (H^{E})

	T/K	B_0	A_1	A_2	A_3	A_4	A_5	s
			MTBE (1) + Butan-1-ol (2)					
$V^{\mathrm{E}}/10^{-6}$ m^3·mol^{-1} [a]	288.15	–	−2.620	−0.336	−0.256			0.005
	293.15	–	−2.740	−0.350	−0.301			0.005
	298.15	–	−2.858	−0.359	−0.319			0.004
	303.15	–	−2.955	−0.365	−0.275			0.005
	308.15	–	−3.058	−0.351	−0.219			0.006
$\kappa_{\mathrm{S}}^{\mathrm{E}}$/TPa^{-1} [a]	288.15	–	−278.9	−3.5	−40.8			0.6
	293.15	–	−311.0	−3.4	−38.5			0.6
	298.15	–	−346.1	−5.4	−41.5			0.6
	303.15	–	−384.3	−6.5	−42.2			0.7
	308.15	–	−427.0	−5.7	−36.7			0.8
H^{E}/J·mol^{-1} [b]	298.15	–	2519	779	213	442	–	7
			MTBE (1) + Octane (3)					
$V^{\mathrm{E}}/10^{-6}$ m^3·mol^{-1}	288.15	–	1.623	0.190	0.085	–	–	0.002
	293.15	–	1.616	0.201	0.095	–	–	0.002
	298.15	–	1.604	0.193	0.092	–	–	0.002
	303.15	–	1.587	0.216	0.064	–	–	0.002
	308.15	–	1.581	0.221	0.078	–	–	0.002
$\kappa_{\mathrm{S}}^{\mathrm{E}}$/TPa^{-1}	288.15	–	45.5	24.5	–	–	–	0.2
	293.15	–	43.0	24.8	–	–	–	0.2
	298.15	–	38.4	24.4	–	–	–	0.2
	303.15	–	34.9	25.6	–	–	–	0.3
	308.15	–	32.3	26.4	–	–	–	0.3
H^{E}/J·mol^{-1} [c]	298.15	–	1867	−179	−277	414	326	3
			Butan-1-ol (2) + Octane (3)					
	288.15	0.902	0.926	0.302	−0.283	–	–	0.004
$V^{\mathrm{E}}/10^{-6}$ m^3·mol^{-1} [d]	293.15	0.930	1.008	0.356	−0.339	–	–	0.004
	298.15	0.946	1.094	0.396	−0.393	–	–	0.003
	303.15	0.942	1.192	0.431	−0.423	–	–	0.004
	308.15	0.949	1.304	0.476	−0.461	–	–	0.003
$\kappa_{\mathrm{S}}^{\mathrm{E}}$/TPa^{-1} [d]	288.15	–	36.3	−42.7	–	–	–	0.4
	293.15	–	41.7	−45.0	–	–	–	0.5
	298.15	–	48.1	−47.8	–	–	–	0.6
	303.15	–	52.4	−50.5	–	–	–	0.6
	308.15	–	57.0	−59.7	–	–	–	0.6
H^{E}/J·mol^{-1}	298.15	0.940	2572	1308	−208	–	–	5

[a] Ref 18. [b] Ref 1. [c] Ref 4. [d] Ref 19.

Table 5. Parameters C_i and D_i of Equations 5 and 6 and Standard Deviations, s, Equation 7, for Excess Molar Volume (V^{E}), Excess Isentropic Compressibility ($\kappa_{\mathrm{s}}^{\mathrm{E}}$), and Excess Molar Enthalpy (H^{E}) for the Ternary Mixture MTBE (1) + Butan-1-ol (2) + Octane (3)

	T/K	C_0	C_1	C_2	s
$V^{\mathrm{E}}/10^{-6}$ m^3·mol^{-1}	288.15	−2.556	1.561	3.437	0.006
	293.15	−2.645	1.926	3.652	0.005
	298.15	−2.661	2.143	3.596	0.005
	303.15	−2.391	1.923	2.995	0.005
	308.15	−2.177	1.513	2.627	0.005
$\kappa_{\mathrm{S}}^{\mathrm{E}}$/TPa^{-1}	288.15	−15.6	77.6	329.1	0.7
	293.15	3.1	60.2	302.4	0.8
	298.15	6.3	72.6	310.9	0.8
	303.15	34.5	42.6	287.7	0.8
	308.15	28.3	−52.1	358.7	0.9

	T/K	D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	s
H^{E}/J·mol^{-1}	298.15	2.6	−3	11	14	−20	−13	−17	11	8	5

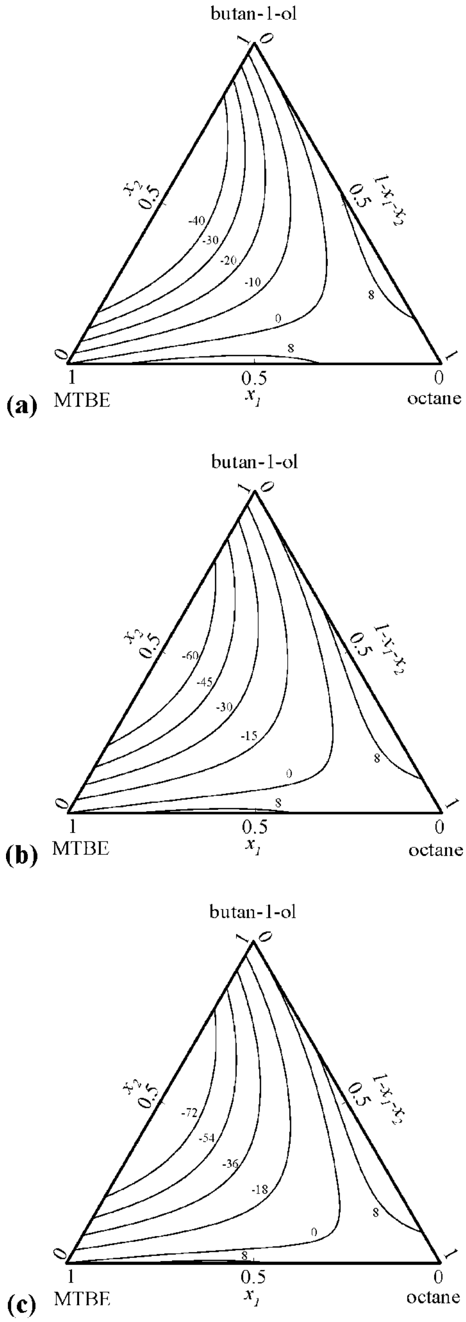

Figure 2. Excess isentropic compressibility, κ_S^E/TPa^{-1}, isolines correlated with eq 5 for the ternary system MTBE (1) + butan-1-ol (2) + octane (3) at: (a) T = 288.15 K, (b) T = 298.15 K, and (c) T = 308.15 K.

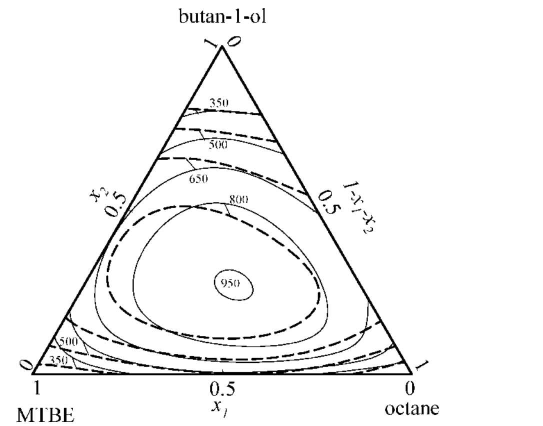

Figure 3. Excess molar enthalpy, H^E/J·mol^{-1}, for the ternary system MTBE (1) + butan-1-ol (2) + octane (3) at T = 298.15 K. —, isolines correlated with eq 6; and – – –, prediction with UNIFAC (Dang and Tassios version).

Table 6. Maxima (max) and Minima (min) Values of Excess Molar Volume (V^E) and Excess Molar Enthalpy (H^E) for Ternary Mixtures at T = 298.15 K

system		x_1	x_2	V^E / 10^{-6} m^3·mol^{-1}
MTBE + butan-1-ol + hexane[a]	min	0.49225	0.40605	−0.523
	max	0.20790	0.09221	0.200
MTBE + butan-1-ol + octane	min	0.49950	0.40027	−0.465
	max	0.29851	0.09801	0.251
MTBE + butan-1-ol + decane[b]	min	0.49794	0.40283	−0.416
	max	0.11609	0.29365	0.270
MTBE + propan-1-ol + octane[c]	min	0.4989	0.4020	−0.378
	max	0.0896	0.3085	0.293

system		x_1	x_2	H^E / J·mol^{-1}
MTBE + butan-1-ol + hexane[a]	max	0.28935	0.29133	863
MTBE + butan-1-ol + octane	max	0.29967	0.30292	959
MTBE + butan-1-ol + decane[b]	max	0.30189	0.30349	1065
MTBE + propan-1-ol + octane[c]	max	0.2803	0.2826	971

[a] Ref 1. [b] Ref 2 and 3. [c] Ref 5.

between MTBE/butan-1-ol, the crossed interactions dipole/induced dipole, and the weak butan-1-ol/octane interactions due to dispersive forces.

In Table 6, the maxima and minima values of V^E and H^E for the ternary system MTBE (1) + butan-1-ol (2) + octane (3) at T = 298.15 K with other ternary systems previously published[1−3,5] are compared. A significant increment in the V^E negative values and a diminution of the positive ones was observed with a reduction in the length of the alkyl chain of alkane. The position of the minimum is approximately x_1 = 0.5 and x_2 = 0.4 for all these systems, but the maximum value was located at a different composition for each system.

The compared maximum values of H^E for the systems of Table 6 lead to an increase of the maximum value with an increase in the length of the alkyl chain of alkane. There was no significant difference between the mixtures MTBE (1) + butan-1-ol (2) + octane (3) and MTBE (1) + propan-1-ol (2) + octane (3). The position of the maximum value is scarcely modified for the different systems.

Theoretical Predictions

The group contribution models UNIFAC (versions of Dang and Tassios,[8] Larsen et al.,[9] Gmehling et al.[10]) and DISQUAC[11,12] were applied to estimate excess molar enthalpies. The version of Dang and Tassios yielded the best fit for this ternary mixture, with a 5.1 % average relative deviation from experimental data vs 8.5 % for the Larsen et al. version and 7.7 % for the Gmehling et al. version. With the DISQUAC model, the average relative deviation obtained was 12 %. The results obtained by the Dang and Tassios version are displayed graphically in Figure 3. The figure shows the qualitative agreement between the experimental and estimated values, indicating that this type of model is suitable for prediction of this thermophysical property for practical purposes.

Conclusions

Densities, $\rho(x, T)$, and speeds of sound, $u(x, T)$, for the binary mixture MTBE (1) + octane (3) and for the ternary mixture of MTBE (1) + butan-1-ol (2) + octane (3) were measured at the temperatures of T = (288.15, 293.15, 298.15, 303.15, and 313.15) K and atmospheric pressure over the whole range of compositions. Excess molar volumes and excess isentropic compressibilities for the ternary mixture show a positive and a negative region in the mixtrure diagram at the five temperatures studied.

The excess molar enthalpies, $H^{E}(x, T)$, measured for the binary mixture butan-1-ol (2) + octane (3) and the ternary mixture of MTBE (1) + butan-1-ol (2) + octane (3) at T = 298.15 K were positive over the whole composition range, as a consequence of the breakage of molecular interactions of the pure components in the mixture process. The main contribution to this behavior may be attributed to the breaking of hydrogen bonds between alcohol molecules induced by the presence of the other components in the mixtures. Nevertheless, the dipole−dipole interaction between ether molecules must also be taken into account, as well as the volumetric influence of the orientational order between alkane linear molecules. The trends shown in the figures presented are a qualitative balance of these main contributions, but further conclusions about the molecular behavior of the mixture need more support than macroscopic thermophysical mixture data only.

The tested group contribution models UNIFAC and DISQUAC are in qualitative satisfactory agreement with the experimental excess molar enthalpy results, showing in every case average relative deviations lower than 12 %.

Supporting Information Available:

Calculated excess molar volumes and excess isentropic compressibility for the binary mixture MTBE (1) + octane (3) and the ternary mixture MTBE (1) + butan-1-ol (2) + octane (3). This material is available free of charge via the Internet at http://pubs.acs.org.

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