# Property Changes of Mixing for the 1-Butanol + Methanol + 2-Methoxy-2-methylbutane System at 298.15 K and Atmospheric Pressure

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Densities, refractive indices, and speeds of sound at 298.15 K and atmospheric pressure for the 1-butanol + methanol + 2-methoxy-2-methylbutane ternary system have been measured. Excess molar volumes, molar refraction, and isentropic compressibility changes of mixing were determined from experimental measurements. The results were fitted to the Redlich−Kister equation to obtain the coefficients. These property changes were also predicted using several empirical equations from the values of their constituent binary subsystems, and the best results were obtained with the Kohler equation.

## Introduction

Reformulated gasolines generally require high proportions of oxygenated compounds. Most of those oxygenates are alcohols or ethers containing one to six carbons. 2-Methoxy-2-methylbutane (TAME) has a high blending octane number and appears to be a good candidate for use in gasolines. As part of an ongoing study of the thermophysical properties of mixtures containing TAME, we present some data for the ternary system 1-butanol + methanol + TAME.

Molar volume, molar refraction, and isentropic compressibility changes of mixing were calculated from experimental measurements of densities, refractive indices, and speeds of sound at 298.15 K and atmospheric pressure for the 1-butanol + methanol + 2-methoxy-2-methylbutane (TAME) ternary system and for the 1-butanol + TAME binary system. No comparable data in the surveyed literature for the ternary and this binary system have been found. In previous works we have published these properties for TAME + methanol and 1-butanol + methanol systems.[1,2]

We will also evaluate several empirical equations that allow the prediction of the properties of the ternary system from the corresponding properties of the constituent binary subsystems. If this approach works, an enormous experimental effort could be saved.

## Experimental Section

***Materials.*** Methanol was supplied by Merck with nominal purity >99.8 mass %. 1-Butanol was supplied by Aldrich with nominal purity >99.9 mass %, and TAME was supplied by Fluka with nominal purity >98.9 mass %. They were degassed using ultrasound. The water contents of the methanol, 1-butanol, and TAME (determined with a Metrohm 737 KF coulometer) were 0.03, 0.1, and 0.02 mass %, respectively.

Table 1 lists the densities, speeds of sound, and refractive indices measured for the pure components, together with published values for these properties.[3−5]

***Apparatus and Procedure.*** The mixtures were prepared by mass, using a Mettler AE240 balance, having a repeatibility of ±0.0001 g. The densities and speeds of sound of the mixtures 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. 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. Densities $\rho$, Refractive Indices $n_D$, and Speeds of Sound $u$ of the Pure Components at 298.15 K and Atmospheric Pressure**

| component | $\rho$/g·cm$^{-3}$ | | $n_D$ | | $u$/m·s$^{-1}$ | |
|---|---|---|---|---|---|---|
| | exptl | lit. | exptl | lit. | exptl | lit. |
| 1-butanol | 0.8060 | 0.805 75[3] | 1.3975 | 1.397 41[3] | 1241 | 1240[3] |
| methanol | 0.7866 | 0.786 37[3] | 1.3264 | 1.326 52[3] | 1102 | 1102[4] |
| TAME | 0.7658 | 0.765 77[5] | 1.3858 | 1.385 80[5] | 1115 | not found |

## Results

The measured densities ($\rho$), speeds of sound ($u$), and refractive indices ($n_D$) of the 1-butanol + methanol + TAME ternary system and the 1-butanol + TAME binary system at 298.15 K and atmospheric pressure are listed in Table 2, together with the quantities calculated from them: excess molar volumes ($V^E$), molar refraction ($\Delta R$), and isentropic compressibility changes of mixing ($\Delta\kappa_s$).

Excess molar volumes were calculated using the expression

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

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 $i$.

The molar refractions ($R$) were calculated using the Lorentz−Lorenz equation

$$R = \frac{n_D^2 - 1}{n_D^2 + 2} V \tag{2}$$

with $n_D$ and $V$ being the refractive indices and the molar volume, respectively, and the molar refraction changes of mixing ($\Delta R$) were obtained from

$$\Delta R = R - \sum_i x_i R_i \tag{3}$$

where $R_i$ is the molar refraction of pure component $i$.

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**Table 2. Densities $\rho$, Speeds of Sound $u$, Isentropic Compressibilities $K_s$, Refractive Indices $n_D$, Excess Molar Volumes $V^E$, and Changes of Mixing $\Delta K_s$ and $\Delta R$ for Mixtures of 1-Butanol (1) + Methanol (2) + TAME (3) at 298.15 K and Atmospheric Pressure**

| $x_1$ | $x_2$ | $\rho$/g·cm$^{-3}$ | $u$/m·s$^{-1}$ | $\kappa_s$/T Pa$^{-1}$ | $n_D$ | $V^E$/cm$^3$·mol$^{-1}$ | $\Delta\kappa_s$/T Pa$^{-1}$ | $\Delta R$/cm$^3$·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 0.9267 | 0.0000 | 0.7691 | 1126 | 1026 | 1.3870 | −0.207 | −11 | −0.006 |
| 0.8825 | 0.0000 | 0.7710 | 1132 | 1013 | 1.3877 | −0.297 | −17 | −0.009 |
| 0.8392 | 0.0000 | 0.7727 | 1137 | 1001 | 1.3882 | −0.365 | −21 | −0.013 |
| 0.7855 | 0.0000 | 0.7748 | 1144 | 987 | 1.3889 | −0.428 | −25 | −0.017 |
| 0.7396 | 0.0000 | 0.7766 | 1149 | 975 | 1.3894 | −0.468 | −27 | −0.021 |
| 0.6731 | 0.0000 | 0.7792 | 1157 | 959 | 1.3902 | −0.508 | −29 | −0.025 |
| 0.6452 | 0.0000 | 0.7803 | 1160 | 953 | 1.3905 | −0.520 | −30 | −0.027 |
| 0.5751 | 0.0000 | 0.7830 | 1168 | 936 | 1.3913 | −0.537 | −31 | −0.031 |
| 0.5297 | 0.0000 | 0.7848 | 1173 | 926 | 1.3918 | −0.541 | −32 | −0.033 |
| 0.5243 | 0.0000 | 0.7869 | 1180 | 913 | 1.3924 | −0.537 | −32 | −0.035 |
| 0.4405 | 0.0000 | 0.7883 | 1184 | 904 | 1.3928 | −0.529 | −32 | −0.036 |
| 0.3827 | 0.0000 | 0.7907 | 1192 | 890 | 1.3934 | −0.508 | −31 | −0.036 |
| 0.3652 | 0.0000 | 0.7914 | 1194 | 886 | 1.3936 | −0.499 | −31 | −0.036 |
| 0.2994 | 0.0000 | 0.7941 | 1203 | 870 | 1.3943 | −0.454 | −29 | −0.034 |
| 0.2687 | 0.0000 | 0.7953 | 1207 | 863 | 1.3947 | −0.427 | −28 | −0.033 |
| 0.1904 | 0.0000 | 0.7985 | 1218 | 845 | 1.3955 | −0.337 | −23 | −0.027 |
| 0.1615 | 0.0000 | 0.7996 | 1221 | 838 | 1.3958 | −0.297 | −20 | −0.024 |
| 0.1135 | 0.0000 | 0.8015 | 1227 | 829 | 1.3963 | −0.221 | −15 | −0.019 |
| 0.0579 | 0.0000 | 0.8037 | 1234 | 817 | 1.3969 | −0.119 | −8 | −0.010 |
| 0.1034 | 0.8966 | 0.7899 | 1125 | 1001 | 1.3403 | 0.037 | 4 | 0.001 |
| 0.0929 | 0.8052 | 0.7867 | 1130 | 996 | 1.3529 | −0.163 | −14 | 0.001 |
| 0.0832 | 0.7212 | 0.7840 | 1132 | 996 | 1.3611 | −0.298 | −23 | 0.001 |
| 0.0734 | 0.6366 | 0.7815 | 1132 | 999 | 1.3673 | −0.396 | −26 | 0.002 |
| 0.0641 | 0.5559 | 0.7792 | 1131 | 1003 | 1.3719 | −0.461 | −28 | 0.002 |
| 0.0555 | 0.4812 | 0.7773 | 1130 | 1007 | 1.3752 | −0.497 | −28 | 0.002 |
| 0.0442 | 0.3837 | 0.7750 | 1129 | 1012 | 1.3787 | −0.510 | −27 | 0.002 |
| 0.0354 | 0.3066 | 0.7732 | 1128 | 1017 | 1.3809 | −0.489 | −25 | 0.002 |
| 0.0263 | 0.2284 | 0.7714 | 1125 | 1024 | 1.3827 | −0.435 | −21 | 0.001 |
| 0.0167 | 0.1451 | 0.7695 | 1122 | 1032 | 1.3842 | −0.332 | −15 | 0.001 |
| 0.2000 | 0.8000 | 0.7926 | 1144 | 965 | 1.3510 | 0.062 | 5 | 0.002 |
| 0.1788 | 0.7153 | 0.7891 | 1145 | 966 | 1.3606 | −0.162 | −15 | 0.001 |
| 0.1603 | 0.6412 | 0.7862 | 1145 | 971 | 1.3667 | −0.302 | −24 | 0.001 |
| 0.1465 | 0.5861 | 0.7841 | 1143 | 976 | 1.3703 | −0.380 | −28 | 0.001 |
| 0.1233 | 0.4932 | 0.7808 | 1140 | 986 | 1.3750 | −0.469 | −30 | 0.000 |
| 0.1036 | 0.4144 | 0.7782 | 1137 | 994 | 1.3781 | −0.509 | −30 | −0.000 |
| 0.0900 | 0.3601 | 0.7766 | 1135 | 1000 | 1.3798 | −0.518 | −29 | −0.001 |
| 0.0771 | 0.3082 | 0.7751 | 1133 | 1005 | 1.3812 | −0.511 | −28 | −0.001 |
| 0.0559 | 0.2235 | 0.7726 | 1129 | 1015 | 1.3831 | −0.463 | −23 | −0.001 |
| 0.0380 | 0.1519 | 0.7706 | 1125 | 1025 | 1.3843 | −0.377 | −18 | −0.001 |
| 0.3131 | 0.6869 | 0.7954 | 1164 | 928 | 1.3614 | 0.074 | 5 | 0.004 |
| 0.2795 | 0.6132 | 0.7917 | 1162 | 936 | 1.3682 | −0.166 | −15 | −0.001 |
| 0.2496 | 0.5475 | 0.7883 | 1158 | 945 | 1.3725 | −0.314 | −26 | −0.004 |
| 0.2233 | 0.4898 | 0.7855 | 1154 | 956 | 1.3755 | −0.405 | −29 | −0.006 |
| 0.1926 | 0.4225 | 0.7825 | 1149 | 968 | 1.3783 | −0.477 | −31 | −0.008 |
| 0.1606 | 0.3524 | 0.7795 | 1144 | 980 | 1.3806 | −0.517 | −31 | −0.008 |
| 0.1359 | 0.2982 | 0.7774 | 1140 | 990 | 1.3820 | −0.525 | −30 | −0.009 |
| 0.1098 | 0.2408 | 0.7752 | 1136 | 999 | 1.3833 | −0.510 | −27 | −0.008 |
| 0.0855 | 0.1877 | 0.7732 | 1132 | 1009 | 1.3842 | −0.468 | −24 | −0.007 |
| 0.0511 | 0.1122 | 0.7704 | 1126 | 1024 | 1.3852 | −0.352 | −17 | −0.005 |
| 0.3907 | 0.6093 | 0.7971 | 1176 | 908 | 1.3676 | 0.074 | 4 | 0.004 |
| 0.3429 | 0.5348 | 0.7928 | 1171 | 919 | 1.3730 | −0.198 | −19 | −0.013 |
| 0.3073 | 0.4792 | 0.7895 | 1166 | 931 | 1.3760 | −0.338 | −28 | −0.019 |
| 0.2699 | 0.4208 | 0.7862 | 1160 | 945 | 1.3785 | −0.438 | −31 | −0.023 |
| 0.2367 | 0.3692 | 0.7834 | 1154 | 958 | 1.3802 | −0.495 | −32 | −0.023 |
| 0.2084 | 0.3250 | 0.7811 | 1150 | 968 | 1.3815 | −0.522 | −32 | −0.022 |
| 0.1720 | 0.2682 | 0.7783 | 1144 | 981 | 1.3829 | −0.529 | −31 | −0.019 |
| 0.1323 | 0.2063 | 0.7754 | 1138 | 995 | 1.3841 | −0.499 | −27 | −0.014 |
| 0.0951 | 0.1483 | 0.7727 | 1132 | 1009 | 1.3849 | −0.430 | −22 | −0.009 |
| 0.0667 | 0.1041 | 0.7707 | 1128 | 1021 | 1.3853 | −0.345 | −17 | −0.006 |
| 0.4812 | 0.5188 | 0.7988 | 1189 | 886 | 1.3738 | 0.069 | 2 | 0.002 |
| 0.4310 | 0.4647 | 0.7949 | 1183 | 899 | 1.3772 | −0.158 | −16 | −0.003 |
| 0.3768 | 0.4062 | 0.7908 | 1175 | 916 | 1.3799 | −0.340 | −28 | −0.008 |
| 0.3335 | 0.3596 | 0.7877 | 1168 | 931 | 1.3816 | −0.438 | −32 | −0.011 |
| 0.2937 | 0.3167 | 0.7848 | 1161 | 945 | 1.3827 | −0.494 | −33 | −0.012 |
| 0.2516 | 0.2713 | 0.7819 | 1155 | 959 | 1.3837 | −0.525 | −33 | −0.013 |
| 0.2136 | 0.2303 | 0.7794 | 1149 | 972 | 1.3845 | −0.529 | −31 | −0.013 |
| 0.1562 | 0.1684 | 0.7758 | 1140 | 991 | 1.3853 | −0.498 | −28 | −0.012 |
| 0.1254 | 0.1352 | 0.7739 | 1136 | 1001 | 1.3856 | −0.460 | −25 | −0.011 |
| 0.0663 | 0.0714 | 0.7703 | 1127 | 1022 | 1.3860 | −0.323 | −16 | −0.007 |
| 0.5975 | 0.4025 | 0.8010 | 1204 | 862 | 1.3807 | 0.055 | 1 | −0.001 |
| 0.5373 | 0.3620 | 0.7971 | 1196 | 878 | 1.3826 | −0.166 | −16 | −0.008 |
| 0.4638 | 0.3124 | 0.7923 | 1185 | 899 | 1.3841 | −0.349 | −28 | −0.015 |
| 0.4384 | 0.2953 | 0.7907 | 1181 | 907 | 1.3845 | −0.395 | −30 | −0.017 |
| 0.3593 | 0.2421 | 0.7858 | 1168 | 933 | 1.3855 | −0.492 | −33 | −0.021 |
| 0.2840 | 0.1913 | 0.7815 | 1157 | 956 | 1.3861 | −0.528 | −32 | −0.022 |
| 0.2411 | 0.1624 | 0.7791 | 1151 | 969 | 1.3863 | −0.523 | −31 | −0.021 |
| 0.1808 | 0.1218 | 0.7758 | 1142 | 988 | 1.3864 | −0.482 | −27 | −0.018 |
| 0.1339 | 0.0902 | 0.7733 | 1136 | 1002 | 1.3864 | −0.417 | −23 | −0.015 |
| 0.0804 | 0.0542 | 0.7704 | 1128 | 1020 | 1.3863 | −0.298 | −15 | −0.010 |

**Table 2. (Continued)**

| $x_1$ | $x_2$ | $\rho$/g·cm$^{-3}$ | $u$/m·s$^{-1}$ | $\kappa_s$/T Pa$^{-1}$ | $n_D$ | $V^E$/cm$^3$·mol$^{-1}$ | $\Delta\kappa_s$/T Pa$^{-1}$ | $\Delta R$/cm$^3$·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 0.6763 | 0.3237 | 0.8021 | 1212 | 848 | 1.3846 | 0.043 | 0 | −0.003 |
| 0.5892 | 0.2820 | 0.7971 | 1201 | 870 | 1.3860 | −0.221 | −20 | −0.013 |
| 0.5328 | 0.2550 | 0.7939 | 1192 | 886 | 1.3865 | −0.345 | −27 | −0.018 |
| 0.4730 | 0.2264 | 0.7906 | 1183 | 904 | 1.3869 | −0.443 | −32 | −0.021 |
| 0.3984 | 0.1907 | 0.7865 | 1172 | 926 | 1.3872 | −0.524 | −34 | −0.024 |
| 0.3364 | 0.1610 | 0.7833 | 1163 | 944 | 1.3874 | −0.558 | −34 | −0.024 |
| 0.2976 | 0.1425 | 0.7813 | 1158 | 955 | 1.3874 | −0.563 | −33 | −0.024 |
| 0.2242 | 0.1073 | 0.7776 | 1148 | 976 | 1.3873 | −0.535 | −30 | −0.021 |
| 0.1615 | 0.0773 | 0.7744 | 1139 | 995 | 1.3871 | −0.465 | −25 | −0.017 |
| 0.1090 | 0.0522 | 0.7717 | 1132 | 1011 | 1.3868 | −0.365 | −19 | −0.013 |
| 0.8014 | 0.1986 | 0.8038 | 1225 | 830 | 1.3901 | 0.023 | −0 | −0.006 |
| 0.7049 | 0.1747 | 0.7991 | 1212 | 852 | 1.3904 | −0.228 | −18 | −0.014 |
| 0.6303 | 0.1562 | 0.7954 | 1201 | 871 | 1.3903 | −0.362 | −26 | −0.018 |
| 0.5576 | 0.1382 | 0.7918 | 1191 | 891 | 1.3901 | −0.454 | −31 | −0.020 |
| 0.4779 | 0.1184 | 0.7879 | 1179 | 913 | 1.3898 | −0.518 | −32 | −0.022 |
| 0.4272 | 0.1059 | 0.7856 | 1172 | 927 | 1.3895 | −0.542 | −33 | −0.022 |
| 0.3473 | 0.0861 | 0.7819 | 1161 | 948 | 1.3891 | −0.553 | −32 | −0.021 |
| 0.3072 | 0.0761 | 0.7801 | 1156 | 959 | 1.3888 | −0.544 | −30 | −0.020 |
| 0.1926 | 0.0477 | 0.7749 | 1142 | 990 | 1.3880 | −0.457 | −25 | −0.015 |
| 0.1124 | 0.0278 | 0.7713 | 1131 | 1013 | 1.3872 | −0.326 | −17 | −0.001 |
| 0.8960 | 0.1040 | 0.8049 | 1233 | 818 | 1.3938 | 0.010 | −0 | −0.006 |
| 0.7943 | 0.0922 | 0.8004 | 1220 | 840 | 1.3934 | −0.215 | −16 | −0.013 |
| 0.7099 | 0.0824 | 0.7968 | 1208 | 859 | 1.3930 | −0.366 | −25 | −0.017 |
| 0.6243 | 0.0725 | 0.7930 | 1196 | 881 | 1.3924 | −0.471 | −30 | −0.020 |
| 0.5508 | 0.0639 | 0.7897 | 1186 | 900 | 1.3918 | −0.523 | −32 | −0.022 |
| 0.4659 | 0.0541 | 0.7859 | 1175 | 922 | 1.3910 | −0.546 | −32 | −0.022 |
| 0.3812 | 0.0442 | 0.7823 | 1164 | 944 | 1.3902 | −0.540 | −31 | −0.021 |
| 0.2774 | 0.0322 | 0.7779 | 1151 | 970 | 1.3892 | −0.501 | −28 | −0.018 |
| 0.2168 | 0.0252 | 0.7755 | 1144 | 985 | 1.3886 | −0.458 | −25 | −0.015 |
| 0.1182 | 0.0137 | 0.7714 | 1132 | 1013 | 1.3875 | −0.334 | −17 | −0.009 |

The speeds of sound through the mixtures ($u$) and the corresponding densities ($\rho$) were used to calculate isentropic compressibilities ($\kappa_s$) using the equation

$$\kappa_s = u^{-2}\rho^{-1} \tag{4}$$

and the isentropic compressibility changes of mixing ($\Delta\kappa_s$) were obtained using the expression

$$\Delta\kappa_s = \kappa_s - \sum_i \phi_i \kappa_{si} \tag{5}$$

where $\kappa_s$ and $\kappa_{si}$ are the isentropic compressibilities of the mixture and component $i$, respectively, and $\phi_i$ is the volume fraction of component $i$ in the mixture as given by

$$\phi_i = x_i V_i / \sum_j x_j V_j \tag{6}$$

where $j$ refers to all components of the mixture.

For the ternary system, Figure 1 shows the plotted density and refractive index isolines versus the mole fraction of the mixture and the plotted sound velocity isolines versus volume fraction. Figure 2 shows excess molar volume isolines versus mole fraction and isentropic compressibility changes of mixing isolines versus volume fraction.

***Correlation.*** The $V^E$, $\Delta R$, and $\Delta\kappa_s$ data were correlated with the composition data by means of the Redlich−Kister polynomial,[6] which for binary mixtures is

$$\Delta M = x_i x_j \sum_K A_K (x_i - x_j)^k \tag{7}$$

where $\Delta M$ is $V^E$ or $\Delta R$ and $x$ is the mole fraction, or $\Delta M$ is $\Delta\kappa_s$ and $x$ is the volume fraction, $A_K$ is the polynomial coefficient, and $K$ is the number of the polynomial coefficient. For ternary systems the corresponding equation is

$$\Delta M_{123} = \Delta M_{12} + \Delta M_{32} + \Delta M_{13} + x_1 x_2 x_3 (A + B(x_1 - x_2) + C(x_3 - x_2) + D(x_1 - x_3) + E(x_1 - x_2)^2 + F(x_3 - x_2)^2 + G(x_1 - x_3)^2 + \ldots \tag{8}$$

where $\Delta M_{123}$ is $V^E$, $\Delta\kappa_s$, or $\Delta R$; $x_i$ is the mole fraction or volume fraction of component $i$, according to the parameter being correlated as previously indicated; and $\Delta M_{ij}$ is the value of the Redlich−Kister polynomial for the same property fitted to the data for the binary system ($i$, $j$).

Equations 7 and 8 were fitted to the appropriate 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 (data for TAME + methanol and 1-butanol + methanol systems were taken from previously papers[1,2]) and in Table 4 for the ternary system.

***Prediction.*** Although it would be desirable to be able to estimate the thermodynamic properties of multicomponent systems from the properties of their pure components, in practice such estimates are often inaccurate due to the effects of mixing. An attractive alternative that limits experimental work to binary mixtures is to evaluate the property changes of mixing of the multicomponent system from the properties of its constituent binary subystems. To assess the viability of this approach for the ternary system studied here, their $V^E$, $\Delta R$, and $\Delta\kappa_s$ values were predicted from the properties of their constituent binary subsystems by means of empirical equations available in the literature. The equations used were from refs 7−14. These equations are common in the bibliography, have been used in previous papers,[15] and are not therefore repeated unnecessarily.

For each ternary system, Table 5 lists the standard deviations in the values of $V^E$, $\Delta R$, and $\Delta\kappa_s$ predicted by each equation.

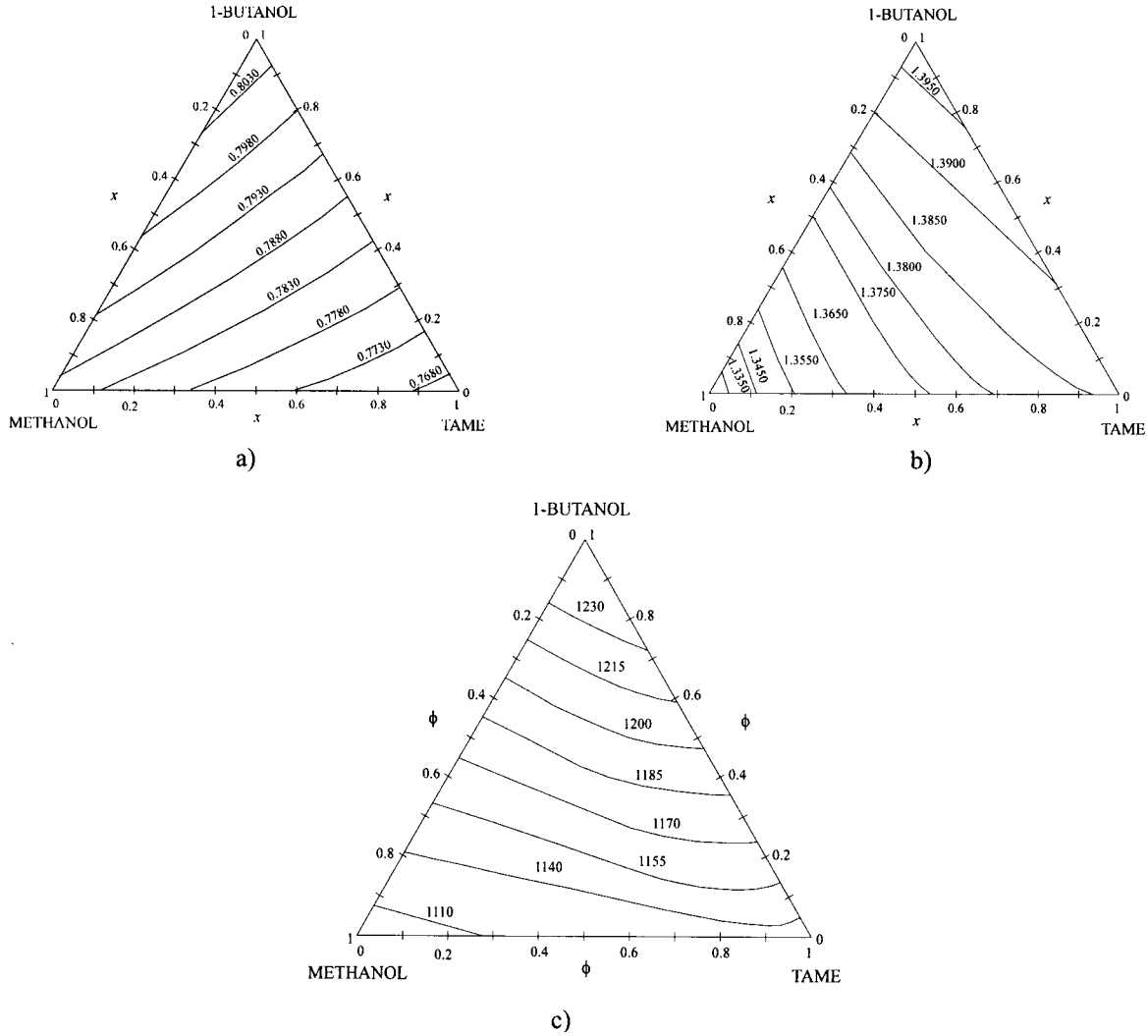


**Figure 1.** Density ($g \cdot cm^{-3}$)−mole fraction (a), refractive index−mole fraction (b), and speed of sound ($m \cdot s^{-1}$)−volume fraction (c) isolines for 1-butanol + methanol + TAME mixtures at 298.15 K and atmospheric pressure.

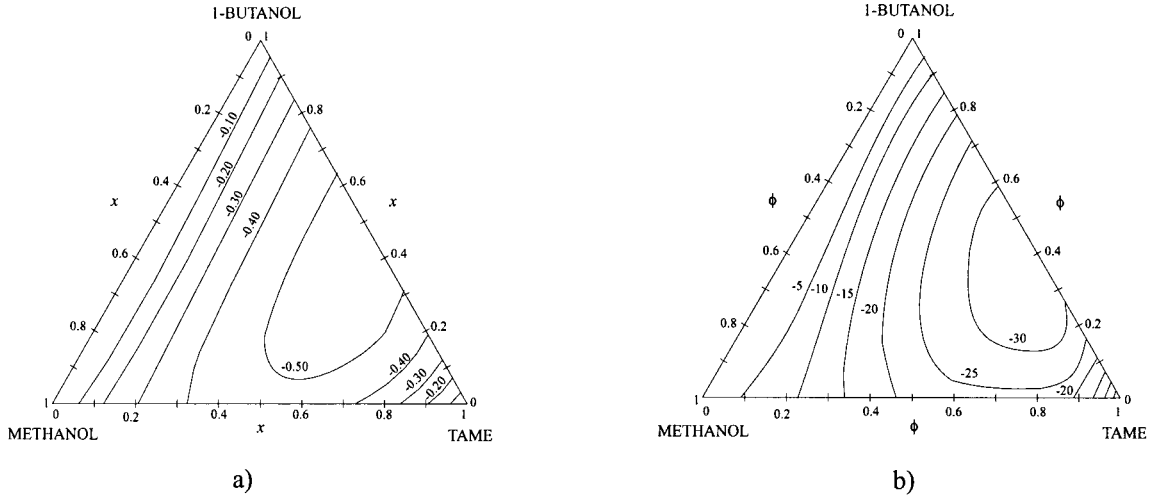


**Figure 2.** Excess molar volumes ($cm^{-3} \cdot mol^{-1}$)−mole fraction (a) and isentropic compressibility ($T\ Pa^{-1}$) changes of mixing (b) isolines for 1-butanol + methanol + TAME mixtures at 298.15 K and atmospheric pressure.

## Conclusions

A thermodynamic contribution to the study of 1-butanol + methanol + TAME mixtures has been carried out with the determination of molar volume, molar refraction, and isentropic compressibility changes of mixing from experimental measurements of densities, refractive indices, and speeds of sound at 298.15 K and atmospheric pressure.

Excess molar volumes were negative, reaching a minimum around $-0.56\ cm^3 \cdot mol^{-1}$; only the binary system 1-butanol + methanol shows positive but very low values

**Table 3. Polynomial Coefficients ($A_K$) and Standard Deviations ($\sigma$) Obtained for the Fits of Eq 7 to the $V^E$−, $\Delta\kappa_s$−, and $\Delta R$−Composition Data for the Binary Systems (for $\Delta\kappa_s$, System Compositions Were in Volume Fraction, $\phi_i$)**

| property | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\sigma$ |
|---|---|---|---|---|---|---|
| | | | 1-Butanol + Methanol | | | |
| $V^E$/cm$^3$·mol$^{-1}$ | 0.2673 | −0.2032 | | | | 0.001 |
| $\Delta\kappa_s$/T Pa$^{-1}$ | 18.9 | −19.7 | −7.2 | | | 0.1 |
| $\Delta R$/cm$^3$·mol$^{-1}$ | 0.0079 | 0.0445 | −0.0582 | | | 0.001 |
| | | | TAME + Methanol | | | |
| $V^E$/cm$^3$·mol$^{-1}$ | −1.8559 | −0.1787 | −0.3252 | −0.2319 | | 0.001 |
| $\Delta\kappa_s$/T Pa$^{-1}$ | −84.6 | −52.6 | | −62.4 | −128.4 | 0.2 |
| $\Delta R$/cm$^3$·mol$^{-1}$ | −0.0857 | | | | | 0.001 |
| | | | 1-Butanol + TAME | | | |
| $V^E$/cm$^3$·mol$^{-1}$ | −2.1579 | 0.1624 | −0.6287 | 0.4640 | | 0.001 |
| $\Delta\kappa_s$/T Pa$^{-1}$ | −126.1 | 19.0 | −52.2 | 67.0 | | 0.1 |
| $\Delta R$/cm$^3$·mol$^{-1}$ | −0.1366 | −0.0620 | | | | 0.001 |

**Table 4. Polynomial Coefficients and Standard Deviations ($\sigma$) Obtained for the Fits of Eq 8 to the $V^E$−, $\Delta\kappa_s$−, and $\Delta R$−Composition Data for the Ternary System 1-Butanol (1) + Methanol (2) + TAME (3) (for $\Delta\kappa_s$, System Compositions Were in Volume Fraction, $\phi_i$)**

| property | $A$ | $B$ | $C$ | $D$ | $\sigma$ |
|---|---|---|---|---|---|
| $V^E$/cm$^3$·mol$^{-1}$ | −1.2775 | 0.6392 | 0.5977 | 0.0415 | 0.008 |
| $\Delta\kappa_s$/T Pa$^{-1}$ | −60.64 | −12.04 | 23.84 | −35.88 | 0.54 |
| $\Delta R$/cm$^3$·mol$^{-1}$ | 0.3407 | −0.2812 | 0.0284 | −0.3096 | 0.005 |

**Table 5. Standard Deviations in the Excess Molar Volumes and Changes of Mixing in Molar Refraction and Isentropic Compressibility Predicted for the Ternary Mixture at 298.15 K and Atmospheric Pressure**

| | $V^E_{123}$ / cm$^3$·mol$^{-1}$ | $\Delta K^E_{s123}$ / T Pa$^{-1}$ | $\Delta R^E_{123}$ / cm$^3$·mol$^{-1}$ |
|---|---|---|---|
| Radojkovic | 0.027 | 1 | 0.010 |
| Rastogi | 0.165 | 10 | 0.006 |
| Kohler | 0.011 | 2 | 0.010 |
| Jacob and Fitzner | 0.030 | 2 | 0.009 |
| Tsao and Smith[a] | 0.063 | 5 | 0.013 |
| Tsao and Smith[b] | 0.071 | 6 | 0.014 |
| Tsao and Smith[c] | 0.087 | 5 | 0.011 |
| Colinet | 0.231 | 14 | 0.013 |
| Toop[a] | 0.036 | 3 | 0.011 |
| Toop[b] | 0.037 | 4 | 0.011 |
| Toop[c] | 0.080 | 5 | 0.011 |
| Scatchard[a] | 0.164 | 10 | 0.017 |
| Scatchard[b] | 0.197 | 10 | 0.021 |
| Scatchard[c] | 0.111 | 7 | 0.011 |

[a] 1-Butanol is the asymmetric component. [b] Methanol is the asymmetric component. [c] TAME is the asymmetric component.

of this property. Isentropic compressibility changes of mixing are also negative, reaching a minimum of approximately −34 T Pa$^{-1}$ except for the previously cited binary system. Values of molar refraction changes of mixing are so small that it is difficult to establish any conclusion.

In all cases the data were satisfactorily correlated with the composition data by the Redlich−Kister polynomial.

The equation of Kohler, followed by those of Radojkovic and Jacob and Fitzner, is the most adequate for the prediction of the properties considered in this paper and usable in the absence of ternary data. The equations of Colinet, Rastogi, and Scatchard produce high deviations and are not recommended. Limitations are found using the equations of Toop and Tsao and Smith. The conclusions obtained for the prediction of the property changes of mixing (and therefore for the direct physical properties also) from the constituent binary systems are repetitive for mixtures with ethers and alcohols.[2,15,16]

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