Physical and excess properties of binary and ternary mixtures of 1,1-dimethylethoxy-butane, methanol, ethanol and water at 298.15 K

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Abstract

The ternary systems 1,1-dimethylethoxy-butane (BTBE) + methanol + water and BTBE + ethanol + water have large heterogeneous zones. Experimental densities, refractive indices and speeds of sound have been measured at 298.15 K for mixtures of these systems within the homogeneous zone, and also for methanol + BTBE and ethanol + BTBE binary systems over the entire range of compositions. Excess molar volumes and molar refraction and isentropic compressibility changes of mixing were calculated from the experimental physical properties and were satisfactorily correlated with the corresponding composition data using the Redlich–Kister polynomial. Fitted coefficients and mean standard deviations of correlations have been reported.
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1. Introduction

This paper completes a study on thermophysical properties of alcohol and ether mixtures used as octane-enhancing components in gasoline. On previous works [1–4], physical and other thermodynamic properties of binary and ternary systems containing tertiary ethers, such as MTBE or TAEE, with methanol or ethanol, and with water have been published. All these ternary mixtures show a large heterogeneous region due to the immiscibility between the ethers and the water.

In this work, densities (ρ), refractive indices (n_D), speeds of sound (u) and isentropic compressibilities (κ_s) are reported for complete miscible mixtures of the ternary systems 1,1-dimethylethoxy-butane (butyl *tert*-butyl ether or BTBE) + methanol + water and BTBE + ethanol + water, and for methanol + BTBE and ethanol + BTBE binary systems at 298.15 K. The results for excess molar volumes (V^E) and molar refraction (ΔR) and isentropic compressibility ($\Delta \kappa_s$) changes of mixing, calculated from the measured properties and correlated with composition data using the Redlich–Kister [5] polynomial, are also reported. No comparable data were found in the surveyed literature for the binary or ternary systems studied in this work.

2. Experimental

2.1. Materials

BTBE was supplied by Yarsintez (Yaroslav, Russia) with nominal purity >99.9 mass%. Methanol and ethanol were supplied by Merck (Madrid, Spain) and had a nominal purity >99.5 mass%. Water is purified using a Mili-Q Plus system. The water contents of BTBE was 0.1 mass%, and for methanol and ethanol were 0.05 and 0.04 mass%, respectively, determined with a Metrohm 737 KF coulometer. Information about pure components, i.e. experimental densities, refractive indices at 298.15 K, along with values published for other authors [6–8] is stated in Table 1.

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Table 1
Densities (ρ), refractive indices (n_D) and speeds of sound (u) for pure components at 298.15 K

Component	ρ (g cm^{-3})		n_D		u (m s^{-1})	
	Experimental	Literature	Experimental	Literature	Experimental	Literature
Water	0.99704	0.99704 [6]	1.33250	1.33250 [6]	1497	1497 [7]
Methanol	0.78663	0.78664 [6]	1.3264[(+)]	1.32652 [6]	1101	1102 [8]
Ethanol	0.78522	0.78493 [6]	1.35920	1.35941 [6]	1143	1145 [8]
BTBE	0.75757	–	1.39170	–	1113	–

(–): not found; (+): see Section 2.2.

2.2. Apparatus and procedure

The samples were prepared by filling glass vials with the liquids and weighing at once in a Mettler AE 240 balance, that measured to within ±0.00001 g, for calculating the composition by weight difference. Vials were closed with screw caps to ensure a secure seal and to prevent evaporation. Additions were made with syringe through a Teflon PTFE-faced silicone septum. Densities were measured to within ±0.00001 g cm^{-3} in an Anton Paar DMA 60/602 densimeter, calibrated with air and ultra purified water. Speeds of sound were measured to within ±1 m s^{-1} in an Anton Paar DSA 48 densimeter and sound analyser calibrated with air and ultra purified water (calibration values taken from Riddick et al. [6]). An ATAGO RX-5000 refractometer with an accuracy of ±0.00004 in the range 1.32700–1.58000 was used to measure refractive indices. Refractive index of pure methanol was measured with an ATAGO RX-1000 that measures to within ±0.0001. The temperature is controlled with a Hetotherm thermostat to maintain the temperature at 298.15 ± 0.02 K.

3. Results

The experimental values of densities (ρ), speeds of sound (u) and refractive indices (n_D) for the binary and ternary mixtures of BTBE + methanol + water and BTBE + ethanol + water are listed in Supplementary data. This appendix also includes the values calculated for isentropic compressibility (κ_s), excess molar volumes (V^E) and molar refraction (ΔR) and in isentropic compressibility ($\Delta\kappa_s$) changes of mixing. Corresponding data for water + methanol and water + ethanol binary systems were reported in previous works [9,10].

V^E and ΔR are calculated as a function of mole fraction, x_i, using the following expressions:

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

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

Table 2
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 indicated binary systems (for $\Delta\kappa_s$, system compositions are in volume fractions, ϕ_i)

Property	A_0	A_1	A_2	A_3	A_4	σ
Methanol (1) + BTBE (2)						
V^E (cm^3 mol^{-1})	−2.1704	0.5536	−0.8192	0.5280	–	0.003
$\Delta\kappa_s$ (TPa^{-1})	−18.535	28.795	78.467	−32.300	−264.37	0.8
ΔR (cm^3 mol^{-1})	−0.0215	0.0128	–	–	–	0.002
Ethanol (1) + BTBE (2)						
V^E/cm^3 mol^{-1}	−1.5733	0.3437	−0.7062	0.3724	–	0.004
$\Delta\kappa_s$/TPa^{-1}	−24.525	−1.6546	37.693	20.080	−109.16	0.4
ΔR/cm^3 mol^{-1}	−0.0454	–	–	–	–	0.003

Table 3
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 indicated ternary systems (for $\Delta\kappa_s$, system compositions are in volume fractions, ϕ_i)

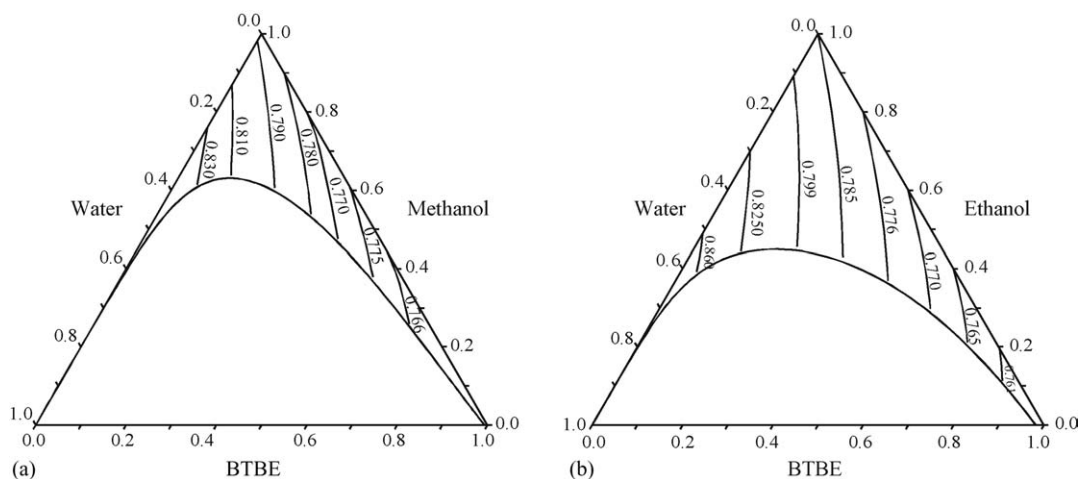| Property	A	B	C	D	E	F	G	σ
BTBE (1) + methanol (2) + water (3)								
V^E (cm^3 mol^{-1})	1.0159	−5.8899	25.552	−10.662	−13.205	39.420	−33.929	0.006
$\Delta\kappa_s$ (TPa^{-1})	1694.9	−2780.1	8534.7	−9861.3	−5708.4	11325	−383.12	2
ΔR (cm^3 mol^{-1})	−1.1662	3.2521	1.7332	1.4879	–	–	–	0.003
BTBE (1) + ethanol (2) + water (3)								
V^E (cm^3 mol^{-1})	−7.8743	−67.989	−71.233	−76.618	−8.6476	3.2619	−10.301	0.005
$\Delta\kappa_s$ (TPa^{-1})	1367.0	−2192.4	1733.6	−782.84	−564.32	−3474.8	−11456	2
ΔR (cm^3 mol^{-1})	−0.6297	−4.9393	−5.1000	−5.2475	–	–	–	0.002

Fig. 1. Isolines of density for the ternary systems: (a) BTBE (1) + methanol (2) + water (3); and (b) BTBE (1) + methanol (2) + water (3) at 298.15 K and atmospheric pressure (system compositions in mole fraction).

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 the component i, the κ_s and its 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 volume fraction of component i in the mixture given by:

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

and j refers to all the components in the mixture.

4. Data reduction

The V^E, ΔR and $\Delta\kappa_s$ calculated are correlated with composition data by means of the Redlich–Kister [5] polynomial, which for binary mixtures takes the shape:

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

where Q_{ij} is V^E or ΔR and x_i is the mole fraction of component i, or Q_{ij} is $\Delta\kappa_s$, being x_i the volume fraction of component i. A_k is the polynomial coefficient, and k is the number of the polynomial coefficient. For the ternary systems, the resulting equation as a function of the compositions, x_i (in mole or volume fraction), in order to correspond to the component subscripts stated is:

$$
\begin{aligned}
Q_{123} = {} & Q_{21} + Q_{32} + Q_{13} + x_1 x_2 x_3 (A + B(x_2 - x_1) \\
& + C(x_3 - x_2) + D(x_1 - x_3) + E(x_2 - x_1)^2 \\
& + F(x_3 - x_2)^2 + G(x_1 - x_3)^2 + \ldots) \tag{7}
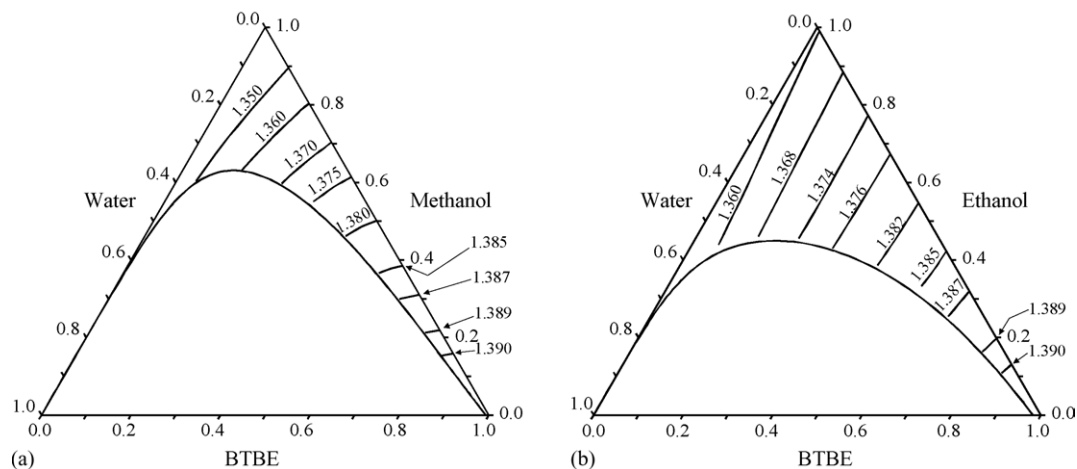\end{aligned}
$$

Fig. 2. Isolines of refractive index for the ternary systems: (a) BTBE (1) + methanol (2) + water (3); and (b) BTBE (1) + methanol (2) + water (3) at 298.15 K and atmospheric pressure (system compositions in mole fraction).
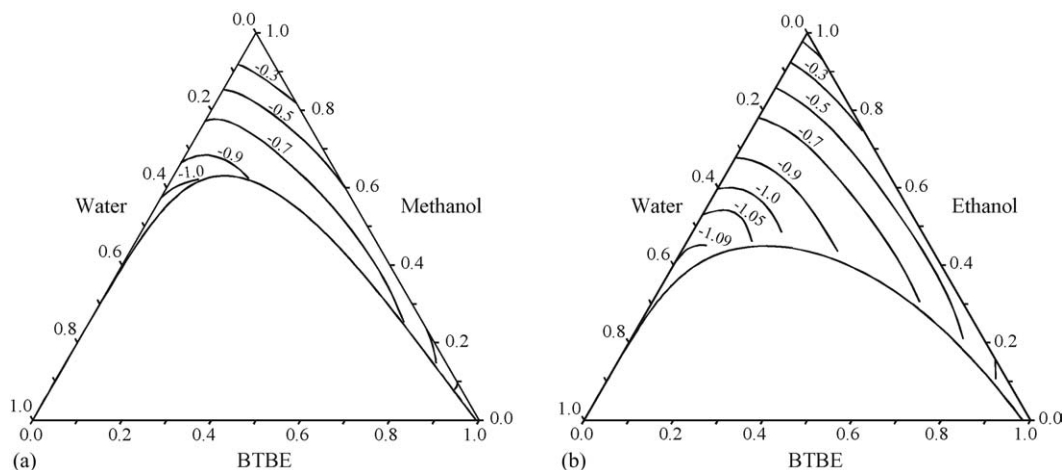
Fig. 3. Isolines of excess molar volume for the ternary systems: (a) BTBE (1) + methanol (2) + water (3); and (b) BTBE (1) + methanol (2) + water (3) at 298.15 K and atmospheric pressure (system compositions in mole fraction).
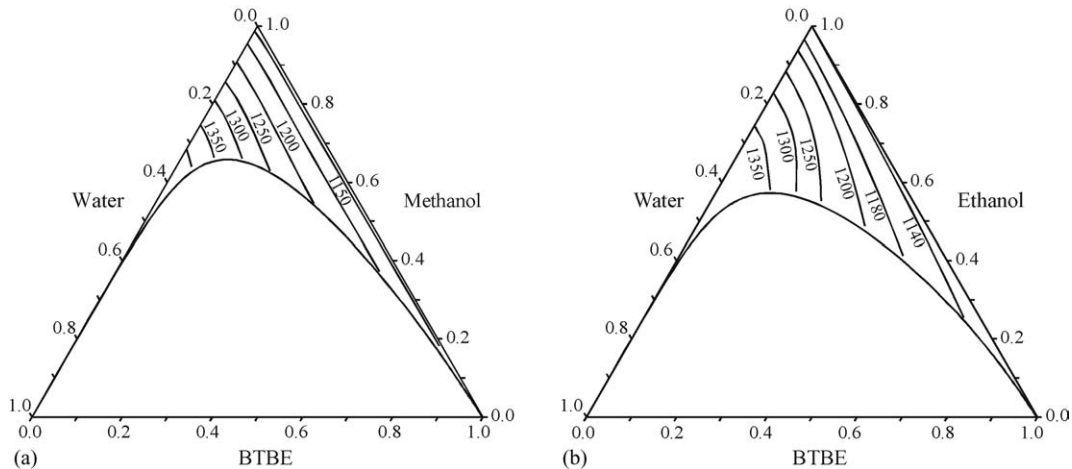

Fig. 4. Isolines of speed of sound for the ternary systems: (a) BTBE (1) + methanol (2) + water (3); and (b) BTBE (1) + methanol (2) + water (3) at 298.15 K and atmospheric pressure (system compositions in volume fraction).
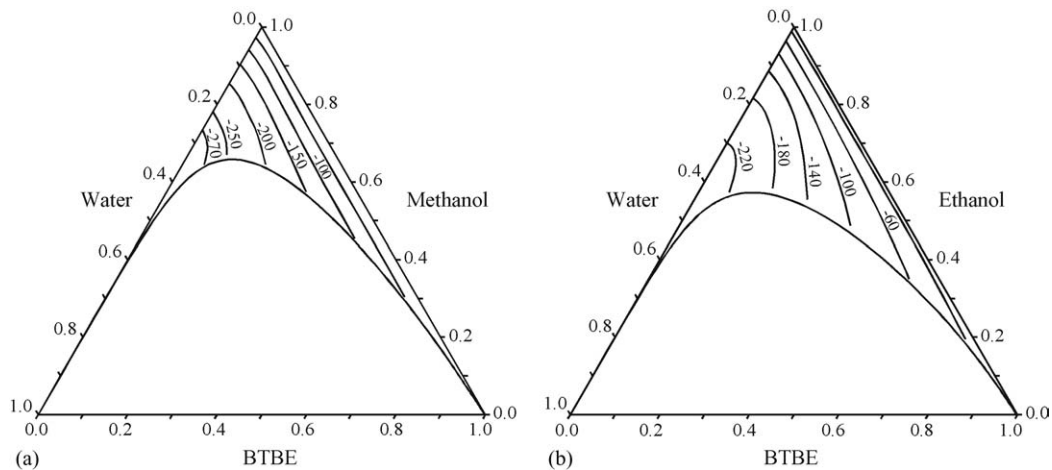

Fig. 5. Isolines of isentropic compressibility changes of mixing for the ternary systems: (a) BTBE (1) + methanol (2) + water (3); and (b) BTBE (1) + methanol (2) + water (3) at 298.15 K and atmospheric pressure (system compositions in volume fraction).

where Q_{123} represents V^E, ΔR or $\Delta \kappa_s$ for the ternary mixtures of BTBE (1) + methanol (2) + water (3) or BTBE (1) + ethanol (2) + water (3) and Q_{21}, Q_{32} and Q_{13} is the value of the Redlich–Kister polynomial for the same property of the binary systems involved, being in this case Q_{13} equal to zero because of the immiscibility of water and BTBE.

The values of the coefficients A_k values for Q_{21} (methanol or ethanol + BTBE) and Q_{32} (water + methanol or ethanol) are summarised in Table 2 along with the standard deviations of the fits. For the binary system water + methanol and water + ethanol, the parameters of the fitted polynomials are already published in previous works [9,10]. The Redlich–Kister coefficients for the ternary systems are listed in Table 3 together with the corresponding standard deviations of the fits. All of these coefficients are derived by fitting to the appropriate parameters Eqs. (6) and (7) by least-squares regression. The Fisher's F-test is used to check the statistical significance of the polynomial coefficients, thus deciding the degree of the polynomial.

For the ternary systems, Figs. 1–3 show the density, refractive index, and excess molar volume isolines, respectively (system composition in mole fraction, x_i) and Figs. 4 and 5 show the speed of sound isolines and the deviations in isentropic compressibility, respectively (system composition in volume fraction, ϕ_i). Isolines for direct and calculated properties are built from the correlations of the calculated properties.

5. Conclusions

At 298.15 K and atmospheric pressure, for binary system methanol + BTBE, excess molar volumes are negative with a minimum of about $-0.56\,cm^3\,mol^{-1}$ at 0.61 in mole fraction of BTBE, for the binary ethanol + BTBE, a minimum value of $-0.40\,cm^3\,mol^{-1}$ is found at 0.60 in mole fraction of BTBE. The values of isentropic compressibility changes of mixing are relatively small and very similar for both binaries, these values are always negative and they did not exceed -7 or $-6\,TPa^{-1}$ for systems with methanol and ethanol, respectively. The deviations in molar refraction for both binaries yields scattered and small negative values.

The excess molar volumes of the ternary systems are large and negative throughout the entire range of homogeneous mixtures. The ternary BTBE + methanol + water yields minimum values around $-1.00\,cm^3\,mol^{-1}$ corresponding to the water + methanol binary system, whereas for the

ternary BTBE + ethanol + water are slightly smaller, around $-1.10\,cm^3\,mol^{-1}$ also corresponding to the water + ethanol binary system. The values of the isentropic compressibility changes of mixing are always negative, corresponding highest deviations, similar to excess volumes, to the binaries water + alcohol with a minimum of $-290\,TPa^{-1}$ for system with methanol and around $-240\,TPa^{-1}$ for system with ethanol. The molar refraction changes of mixing have small and negative values.

It has been proved, for the calculated properties, the molar excess volume, and the isentropic compressibility and molar refraction changes of mixing, that the Redlich–Kister polynomial provides a good correlation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2005.04.030.

References

[1] A. Arce, J. Martinez-Ageitos, J. Mendoza, A. Soto, J. Chem. Eng. Data 40 (1995) 647–649.
[2] A. Arce, A. Blanco, J. Mendoza, A. Soto, J. Chem. Eng. Data 40 (1995) 1285–1287.
[3] A. Arce, A. Arce Jr., E. Rodil, A. Soto, J. Chem. Eng. Data 45 (2000) 536–539.
[4] A. Arce, A. Arce Jr., E. Rodil, A. Soto, J. Chem. Eng. Data 46 (2001) 1261–1265.
[5] O. Redlich, A.T. Kister, Ind. Eng. Chem. 40 (1948) 345–348.
[6] J.A. Riddick, B.W. Bunger, T. Sakano, Organic Solvents, fourth ed., John Willey, New York, 1986.
[7] S.G. Bruun, A. Hvidt, Ber. Bunsen-Ges. Phys. Chem. Chem. Phys. 81 (1977) 930–933.
[8] T.M. Aminabhavi, M.I. Aralaguppi, S.B. Harogoppad, R.H. Balundgi, J. Chem. Eng. Data 38 (1993) 31–39.
[9] A. Arce, J. Martinez-Ageitos, A. Soto, J. Chem. Eng. Data 41 (1996) 718–723.
[10] A. Arce, J. Martinez-Ageitos, J. Mendoza, A. Soto, Fluid Phase Equilib. 141 (1997) 207–220.