TEMPERATURE DEPENDENCE OF VOLUMETRIC BEHAVIOUR FOR METHYL *tert*-BUTYLETHER+1-BUTANOL SYSTEM

E. Mascato[1], L. Mosteiro[1], M. M. Piñeiro[1], B. E. de Cominges[1], M. M. Mato[2] and J. L. Legido[1]*

[1]Departamento de Física Aplicada, Facultade de Ciencias, Universidade de Vigo, E-36200 Vigo, Spain
[2]Departamento de Física Aplicada, Facultad de Física, Universidade de Santiago, E-15706 Santiago de Compostela, Spain

Abstract

Excess molar volumes and excess isoentropic compressibilities of methyl *tert*-butylether (MTBE)+1-butanol at 288.15, 293.15, 298.15, 303.15 and 308.15 K and atmospheric pressure have been studied. In order to analyse the temperature dependence of this mixture, isobaric expansibility α, $(\delta V_m^E/\delta T)_{P,x}$ and $(\delta H_m^E/\delta P)_{T,x}$, were computed by analytical differentiation of the density and excess molar volume fitting equations.

Cubic equation of state (Soave–Redlich–Kwong) has been applied to excess molar volume correlation obtaining binary interaction parameters using different mixing rules.

Keywords: 1-butanol, equation of state, excess isoentropic compressibilities, excess molar volume, MTBE

Introduction

Oxygenated compounds like branched ethers and alcohols are being used as additives for enhancing the octane number in lead-free petrol. Thermodynamic properties of these mixtures are of great interest in order to characterize the hydroxyl and ether groups specific interactions. Furthermore they are interesting for the design of chemical processes involving these oxygenating agents. This work provides excess molar volumes and excess isoentropic compressibilities from 288.15 to 308.15 K and atmospheric pressure for the mixture methyl *tert*-butylether (MTBE)+1-butanol, at different compositions. Soave–Redlich–Kwong [1] cubic equation of state has been applied to excess molar volumes correlation. The mixing rules parameters calculated should allow to make further estimations of multicomponent volumetric behaviour.

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*   Author for correspondence: E-mail: xllegido@uvigo.es

Experimental

MTBE (anhydrous) and 1-butanol (HPLC grade) with stated purities exceeding 99.8 mol% were obtained from Aldrich. The substances were degassed and stored over molecular sieves (Sigma, type 0.4 nm) and kept in argon (N-55) atmosphere. The mole fraction of water in each of the liquids was determined to be <0.01 mol% by Karl Fischer titration. All compounds were checked by GLC analysis and no significant impurities were found. Densities and speeds of sound were measured with a densimeter and sound analyser, Anton Paar DSA-48, with a precision of $\pm 3 \cdot 10^{-5}$ g cm^{-3} for density and $\pm 10^{-1}$ m s^{-1} for speed of sound. The details of the measuring apparatus and procedure have been described in a previous work [2]. Densities and speeds of sound of the pure components are in reasonable agreement with literature values [3, 4].

Data correlation and results

Densities ρ, speeds of sound u, and isentropic compressibilities $\kappa_S (\kappa_S = \rho^{-1} u^{-2})$, at the studied temperatures are reported in Table 1. Excess molar volumes V_m^E, and excess isentropic compressibilities κ_S^E were calculated with the following expressions:

$$V_m^E = \sum_{i=1}^{n} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right)$$ (1)

$$\kappa_S^E = \kappa_S - \sum_{i=1}^{n} \phi_i \left(\kappa_{S,i} + \frac{T V_i \alpha_i^2}{C_{p,i}} \right) - T \frac{\sum_{i=1}^{n} x_i V_i \left(\sum_{i=1}^{n} \phi_i \alpha_i \right)^2}{\sum_{i=1}^{n} x_i C_{p,i}}$$ (2)

where n is the number of components in the mixture, x_i, M_i, ρ_i, ϕ_i, $\kappa_{s,i}$, V_i, α_i and $C_{p,i}$ denote the mole fraction, molar mass, density, volume fraction, isentropic compressibility, molar volume, isobaric expansibility, and molar heat capacity of component i in the mixture, respectively, and T is the temperature. The values of V_i and α_i were calculated from densities, and $C_{p,i}$ was calculated from literature [5]. V_m^E were fitted as a function of mole fraction and temperature to a polynomial of the form:

$$V_m^E / \text{cm}^3 \text{ mol}^{-1} = x(1-x) \sum_{i=1}^{m} \sum_{j=1}^{3} B_{ij} 10^{1-j} (2x-1)^{i-1} (T-T_0)^{j-1}$$ (3)

The fitting coefficients B_{ij}, (Table 2) were obtained by using Marquardt's optimization method [6]. κ_S^E were fitted to the Redlich–Kister [7] equation:

$$\kappa_S^E / \text{TPa}^{-1} = x(1-x) \sum_{p=0}^{M} A_p (2x-1)^p$$ (4)

where A_p are the fitting parameters (Table 2), and p is the degree of the polynomial which was optimized by applying the F-test [8].

Table 1 Densities ρ, speed of sound u, and isoentropic compressibilities κ_s, for MTBE(1)+1-butanol(2) at different temperatures

x_1	ρ/g cm^{-3}	u/m s^{-1}	κ_s/TPa^{-1}	ρ/g cm^{-3}	u/m s^{-1}	κ/TPa^{-1}	ρ/g cm^{-3}	u/m s^{-1}	κ_s/TPa^{-1}
		288.15 K			293.15 K			298.15 K	
0	0.81324	1273.7	758.0	0.80948	1257.0	781.9	0.80567	1239.8	808.0
0.05976	0.80932	1262.3	775.4	0.80550	1245.1	800.9	0.80162	1227.4	828.1
0.11266	0.80585	1251.9	791.8	0.80196	1234.1	818.7	0.79802	1216.2	847.3
0.17550	0.80173	1240.0	811.3	0.79776	1221.9	839.5	0.79371	1203.4	869.9
0.22438	0.79840	1230.4	827.3	0.79436	1212.0	857.0	0.79025	1193.4	888.6
0.29881	0.79346	1216.0	852.3	0.78930	1197.1	884.1	0.78509	1178.0	917.9
0.39812	0.78687	1196.8	887.3	0.78258	1177.3	921.9	0.77821	1157.5	959.1
0.44006	0.78399	1188.8	902.5	0.77965	1169.1	938.4	0.77522	1148.9	977.3
0.50322	0.77981	1176.5	926.4	0.77536	1156.4	964.5	0.77085	1136.0	1005.3
0.59803	0.77354	1158.9	962.6	0.76896	1138.2	1003.8	0.76430	1117.2	1048.2
0.64123	0.77056	1150.9	979.8	0.76592	1129.9	1022.7	0.76121	1108.7	1068.7
0.69852	0.76671	1140.2	1003.3	0.76198	1118.8	1048.4	0.75718	1097.3	1096.8
0.80311	0.75965	1121.7	1046.2	0.75478	1099.7	1095.5	0.74982	1077.5	1148.7
0.90325	0.75269	1102.5	1093.1	0.74766	1079.8	1147.0	0.74255	1057.0	1205.3
0.94811	0.74945	1093.3	1116.4	0.74437	1070.3	1172.7	0.73921	1047.3	1233.4
1	0.74579	1082.4	1144.5	0.74060	1059.5	1203.0	0.73535	1036.1	1266.8

Table 1 Continued

x_1	ρ/g cm^{-3}	u/m s^{-1}	κ_s/TPa^{-1}	ρ/g cm^{-3}	u/m s^{-1}	κ_s/TPa^{-1}
		303.15 K			308.15 K	
0	0.80185	1222.7	834.2	0.79799	1205.9	861.8
0.05976	0.79768	1209.9	856.4	0.79371	1192.4	886.2
0.11266	0.79399	1198.2	877.2	0.78994	1180.3	908.8
0.17550	0.78961	1185.2	901.6	0.78546	1166.8	935.1
0.22438	0.78607	1174.7	921.8	0.78187	1156.1	956.9
0.29881	0.78079	1158.8	953.7	0.77647	1139.8	991.3
0.39812	0.77378	1137.8	998.3	0.76931	1118.1	1039.8
0.44006	0.77073	1129.0	1017.9	0.76619	1109.1	1061.0
0.50322	0.76626	1115.6	1048.5	0.76163	1095.3	1094.5
0.59803	0.75958	1096.4	1095.2	0.75481	1075.4	1145.5
0.64123	0.75641	1087.5	1117.8	0.75157	1066.3	1170.2
0.69852	0.75231	1075.9	1148.4	0.74738	1054.3	1203.6
0.80311	0.74479	1055.5	1205.2	0.73971	1033.4	1266.0
0.90325	0.73738	1034.4	1267.6	0.73214	1011.6	1334.7
0.94811	0.73396	1024.4	1298.4	0.72867	1001.6	1368.5
1	0.73006	1013.0	1334.8	0.72473	990.1	1407.5

Table 2 Parameters B_{ij} and A_p of Eqs (3) and (4) respectively and corresponding standard deviation s

	$i=1$	$i=2$	$i=3$	$i=4$	$i=5$
			B_{ij}		
$j=1$	−2.615	−0.3431	−0.3546	0.0199	0.1721
$j=2$	−0.2559	−0.0308	−0.0052	−0.0282	−0.2197
$j=3$	0.0197	0.0079	−0.0037	0.0224	0.1386
s	0.005				
			A_p		
T/K	288.15	293.15	298.15	303.15	308.15
A_0	−280.4	−311.4	−347.0	−385.7	−426.4
A_1	−3.1	−3.4	−5.2	−6.3	−5.7
A_2	−40.9	−38.5	−41.5	−42.3	−36.7
s	0.6	0.6	0.6	0.7	0.8

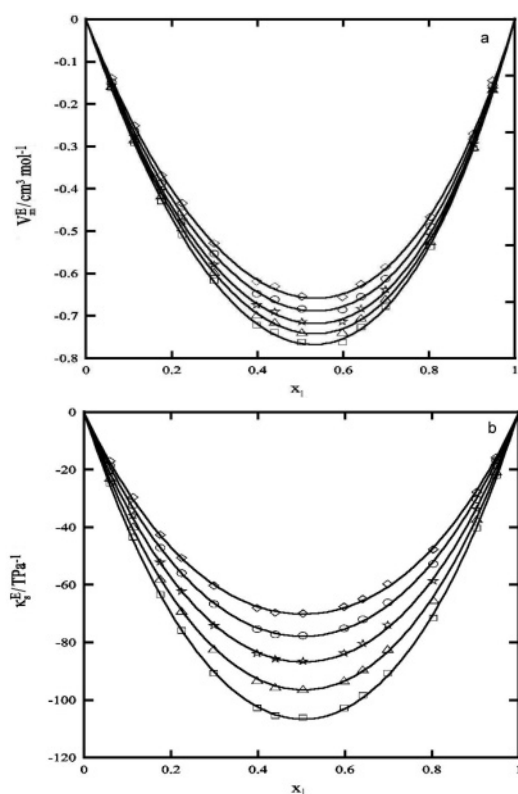**Fig. 1** a – Excess molar volumes V_m^E/cm^3 mol^{-1}; b – excess isoentropic compressibilities κ_S^E/TPa^{-1} for MTBE(1)+1-butanol(2) at ◊ – 288.15 K; o – 293.15 K; ☆ – 298.15 K; Δ – 303.15 K; □ – 308.15 K
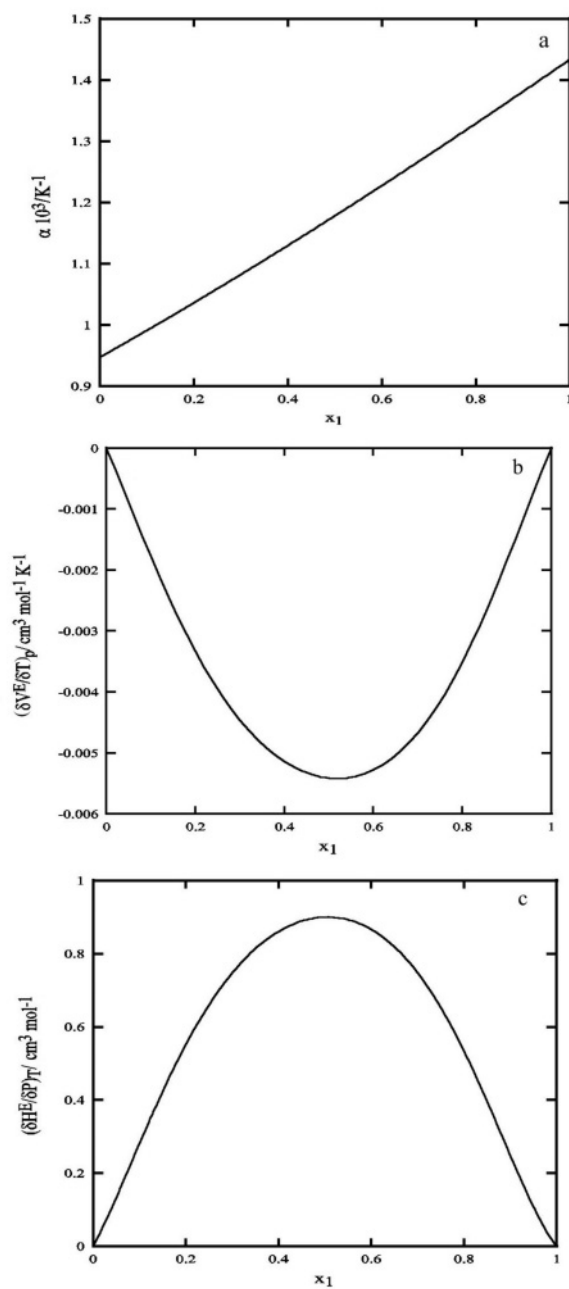
Fig. 2 a – Isobaric expansibility α; b – $(\delta V^E/\delta T)_p$; c – $(\delta H^E/\delta P)_T$, at 298.15 K for MTBE(1)+1-butanol(2)

V_m^E, κ_S^E are plotted in Fig. 1. Experimental V_m^E at 288.15, 293.15 and 298.15 K agree within 5, 8, 5%, respectively, with the data obtained by Rodríguez *et al*. [4]. At a temperature of 298.15 K agree within 8% with the values of Arce *et al*. [9]. Isobaric expansibility $\alpha = -1/\rho(\delta\rho/\delta T)_p$, $(\delta V_m^E/\delta T)_{p,x}$ and $(\delta H_m^E/\delta P)_{T,x} = V_m^E - T(\delta V_m^E/\delta T)_p$ were computed by analytical differentiation of the fitting equation of density and excess molar volume and are plotted in Fig. 2. The volumetric behaviour of this mixture and its trend with temperature can be considered as a result of complex formation through crossed association between ether and alcohol functional groups. Soave–Redlich–Kwong [1] equation of state has been applied to the prediction of excess volumes. Three different mixing rules were used to calculate the values of copressure (*a*) and covolume (*b*) in the mixture. These rules can be expressed in a general way as follows:

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j [1 - k_{ij} - l_{ij}(x_i - x_j)](a_i a_j)^{1/2} \tag{5}$$

$$b = \sum_{i=1}^{n}\sum_{j=1}^{n} \frac{x_i x_j (1 - m_{ij})(b_i - b_j)}{2} \tag{6}$$

being $l_{ij} = m_{ij} = 0$ for the first mixing rule (R1); $l_{ij} = 0$ for the second one (R2) and l_{ij}, m_{ij} and $k_{ij} \neq 0$ for the last one (R3).

The results obtained in cm^3 mol^{-1} are: (R1) $k_{ij} = 0.0330$, $\sigma = 0.04$; (R2) $k_{ij} = 0.0131$, $m_{ij} = -0.0035$, $\sigma = 0.02$; (R3) $k_{ij} = 0.0499$, $m_{ij} = -0.0166$, $l_{ij} = 0.0027$, $\sigma = 0.006$. The obtained deviations depend only on the selected mixing rule.

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