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EXPERIMENTAL AND PREDICTED EXCESS MOLAR VOLUMES OF THE TERNARY SYSTEM *Tert*-butylmethylether+1-propanol+heptane at 298.15 K

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Experimental excess molar volumes for the ternary system x_1MTBE+$x_2$1-propanol+(1–x_1–x_2) heptane and the three involved binary mixtures have been determined at 298.15 K and atmospheric pressure. Excess molar volumes were determined from the densities of the pure liquids and mixtures, using a DMA 4500 Anton Paar densimeter.

The ternary mixture shows maximum values around the binary mixture MTBE+heptane and minimum values for the mixture MTBE+propanol. The ternary contribution to the excess molar volume is negative, with the exception of a range located around the rich compositions of 1-propanol.

Several empirical equations predicting ternary mixture properties from experimental binary mixtures have been applied.

Keywords: *binary mixtures, empirical expressions, excess molar volumes, heptane, 1-propanol, ternary mixture, tert-butylmethylether (MTBE)*

Introduction

Branched ethers, such as the *tert*-butylmethylether (MTBE), either pure or mixed with alkanols or alkanes have been recommended as oxygenate additives in unleaded gasoline. These branched ethers are also increasingly used as solvents and chemical reactants. The thermodynamic properties of binary and ternary mixtures formed by hydrocarbons, ethers and lower alcohols are essential in the design of chemical processes involving in these oxygenating agents.

Forming part of the scientific project entitled 'Study on physical properties of mixtures hydrocarbon+alcohol+ether like alternative fuels', the present work reports experimental excess molar volumes of x_1MTBE+$x_2$1-propanol+(1–x_1–x_2)heptane, xMTBE+(1–x)heptane, xMTBE+(1–x) 1-propanol and x1-propanol+(1–x)heptane at the temperature of 298.15 K and atmospheric pressure.

A review paper of this kind of mixtures has been recently published [1], where the lack of thermophysical properties of ternary mixtures is pointed out. A survey of the literature shows previously reported excess molar volume data at 298.15 K for MTBE+1-propanol [2–4], MTBE+heptane [5] and 1-propanol+ heptane [6–13]. We have decided to measure experimental excess molar volumes for the three binary mixtures in order to use experimental values from the same procedure for all the binary systems involved in the ternary system. We are not aware of any previous measurement of $V^{E}_{m,123}$ in the literature for the ternary mixture to which this study is directed.

Attending to the symmetry of the studied mixtures, the experimental data were fitted by means of different variable degree polynomials. The experimental data corresponding to the binary mixtures xMTBE+(1–x) 1-propanol, xMTBE+(1–x)heptane were fitted to the variable-degree polynomials suggested by Redlich-Kister [14], while lower deviations were obtained by fitting experimental data for the mixture x1-propanol+(1–x) heptane to the equation suggested by Brandreth *et al.* [15]. The ternary excess molar volumes was correlated using the Nagata and Tamura equation [16].

The experimental data of this work were used to test several empirical equations [17–25], whose have been suggested for parametrizing and predicting excess properties of ternary mixtures from the experimental data of the involved binary systems and require the binary coefficients which appear in the predictive multicomponent expression. These equations offer reliable estimations of excess properties for a multicomponent mixture using the involved binary experimental data.

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Experimental

The chemical substances employed, MTBE (Aldrich, purity >99.8%), 1-propanol (Aldrich, purity >99.5%), heptane (Fluka, purity >99.5%) were degassed by ultrasound and dried over molecular sieves (Sigma, type 0.4 nm). The measured densities of the pure liquids present good agreement with the literature values [3, 26, 27], as it can be seen in Table 1. The handling and disposal of the chemicals used has been done according to the recommendation of the CRC Handbook of Chemistry and Physics [26].

The experimental excess molar volumes were determined from the densities of the pure liquids and mixtures. The measurements of densities were carried out with a DMA 4500 Anton Paar densimeter. The temperature inside the vibrating-tube cell was controlled using digital thermometer and was regulated to better than ±0.01 K. The experimental technique has been described previously [28, 29]. The uncertainty in density measurements was $\pm 5 \cdot 10^{-5}$ g cm^{-3}. Before each series of measurements, the apparatus was calibrated at atmospheric pressure using double-distilled and degassed water and heptane (Fluka, purity >99.5%), density data were taken from literature: [30] for heptane and [31] for water. The mixtures were prepared by mass using a Mettler AT201 (precision $\pm 1 \cdot 10^{-5}$g) balance, ensuring an accuracy in the mole fraction less than 10^{-4}. All molar quantities are based on the IUPAC relative atomic mass table [32].

The excess molar volumes were calculated from the densities of the pure liquids and their mixtures using following equation

$$V^{E}_{m,123} = \sum_{i=1}^{n} x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (1)$$

with x, M and ρ being mole fraction, molar mass, and density, respectively; n is the number of the components in the mixture and the subscript i indicates values for the pure components.

The uncertainty in the determination of the excess molar volumes was estimated to better than 1%.

Table 1 Comparison of experimental densities with literature values at 298.15 K

Substances	Density/g cm^{-3}	
	exp.	References
MTBE	0.7356	0.73528[a] 0.7359[b]
1-propanol	0.7997	0.79975[a] 0.7995[c]
heptane	0.6796	0.67946[a] 0.6794[c]

[a][26], [b][3], [c][27]

Results and discussion

The experimental data corresponding to the binary mixtures xMTBE+(1–x)1-propanol, xMTBE+(1–x)heptane were fitted by the following variable-degree polynomials of the form:

$$V^{E}_{m}\,(\mathrm{cm}^3\ \mathrm{mol}^{-1}) = x(1-x)\sum_{i=1}^{n} A_i (2x-1)^{i-1} \quad (2)$$

suggested by Redlich-Kister [14], while lower deviations for the mixture x1-propanol+(1–x) heptane were

Table 2 Experimental binary excess molar volumes, V^{E}_{m}, at 298.15 K.

x	ρ/g cm^{-3}	V^{E}_{m}/cm^3 mol^{-1}	x	ρ/g cm^{-3}	V^{E}_{m}/cm^3 mol^{-1}	x	ρ/g cm^{-3}	V^{E}_{m}/cm^3 mol^{-1}
				xMTBE+(1–x)1-propanol				
0.0543	0.79576	–0.1433	0.3987	0.77199	–0.6318	0.7856	0.74816	–0.4701
0.1065	0.79198	–0.2560	0.4914	0.76591	–0.6454	0.8957	0.74174	–0.2754
0.1912	0.78604	–0.4156	0.5967	0.75957	–0.6409	0.9446	0.73888	–0.1593
0.2932	0.77896	–0.5425	0.6916	0.75375	–0.5831			
				xMTBE+(1–x)heptane				
0.0529	0.68169	0.0744	0.3951	0.69693	0.4102	0.7997	0.72063	0.3107
0.1069	0.68385	0.1527	0.4954	0.70213	0.4439	0.8960	0.72748	0.1902
0.2055	0.68805	0.2645	0.5920	0.70752	0.4434	0.9500	0.73159	0.1011
0.3007	0.69239	0.3452	0.7001	0.71406	0.3983			
				x1-propanol+(1–x)heptane				
0.0497	0.68206	0.1403	0.3922	0.70748	0.3099	0.7946	0.75809	0.1392
0.0996	0.68499	0.2103	0.4940	0.71766	0.2869	0.8993	0.77732	0.0768
0.1945	0.69131	0.2806	0.5953	0.72935	0.2431	0.9485	0.78768	0.0417
0.2927	0.69881	0.3087	0.6946	0.74263	0.1884			

Table 3 Excess molar volumes, $V^E_{m,123}$, and densities, ρ, at 298.15 K for the ternary mixture x_1MTBE+ x_2 1-propanol+(1–x_1–x_2)heptane

x_1	x_2	ρ/g cm^{-3}	$V^E_{m,123}$/cm^3 mol^{-1}	x_1	x_2	ρ/g cm^{-3}	$V^E_{m,123}$/cm^3 mol^{-1}
0.0524	0.0481	0.68423	0.1843	0.3022	0.2979	0.71915	0.0934
0.0549	0.8953	0.78448	–0.0891	0.3019	0.3975	0.73064	–0.0278
0.0880	0.0986	0.68913	0.2425	0.2988	0.4998	0.74401	–0.1664
0.1062	0.1952	0.69719	0.2600	0.2953	0.6082	0.76065	–0.3369
0.1008	0.2979	0.70560	0.2321	0.3952	0.1960	0.71486	0.1495
0.1080	0.3924	0.71519	0.1879	0.4039	0.2940	0.72629	–0.0109
0.0981	0.5019	0.72652	0.1355	0.3943	0.5082	0.75494	–0.3817
0.0947	0.5926	0.73768	0.0807	0.4944	0.1052	0.71204	0.2435
0.1078	0.6868	0.75280	–0.0271	0.5039	0.1910	0.72185	0.0652
0.1030	0.7959	0.77116	–0.1286	0.4964	0.2976	0.73416	–0.1452
0.1980	0.1978	0.70268	0.2380	0.5038	0.3953	0.74854	–0.3842
0.2055	0.2951	0.71212	0.1761	0.5976	0.0987	0.71811	0.1868
0.2028	0.3969	0.72265	0.0992	0.6051	0.1959	0.73008	–0.0759
0.1993	0.4971	0.73451	0.0040	0.5941	0.3054	0.74386	–0.3467
0.1981	0.5969	0.74839	–0.1102	0.6931	0.1000	0.72500	0.0795
0.2026	0.6992	0.76579	–0.2634	0.6925	0.2040	0.73836	–0.2508
0.2951	0.0981	0.69970	0.2989	0.7968	0.1002	0.73299	–0.0789
0.2994	0.1959	0.70859	0.2169	0.8969	0.0521	0.73448	–0.0502

Table 4 Fitting parameters, A_i, B_i, and standard deviations, s, for excess molar volumes

	A_1	A_2	A_3	A_4	A_5	s
			xMTBE+(1–x)1-propanol			
V^E_m/cm^3 mol^{-1}	–2.6182	–0.1305	–0.3518			0.0046
			xMTBE+(1–x)heptane			
V^E_m/cm^3 mol^{-1}	1.7791	0.2940	—			0.0027
			x1-propanol+(1–x)heptane			
V^E_m/cm^3 mol^{-1}	6.5078	–24.5124	49.4944	–49.6686	19.0709	0.0020
	B_0	B_1	B_2	B_3	B_4	s
			x_1MTBE+$x_2$1-propanol+$x_3$heptane			
V^E_m/cm^3 mol^{-1}	–6.7430	10.7284	10.6788	–10.8804	–3.0169	0.0039

Table 5 Mean deviations from the experimental values obtained with the empirical predictive methods. For the asymmetric equations three numberings of the components have been compared, in this order, 123, 231, 312

	s/cm^3 mol^{-1}		
Kohler	0.0217		
Jacob–Fitner	0.0186		
Colinet	0.0198		
Knobeloch–Schwartz	0.0296		
Tsao–Smith	0.0521[a]	0.0874[b]	0.0550[c]
Toop	0.0233[a]	0.0292[b]	0.0378[c]
Scatchard	0.0328[a]	0.0297[b]	0.0396[c]
Hillert	0.4881[a]	0.0297[b]	0.0373[c]
Mathieson–Thynne	0.0343[a]	0.0227[b]	0.0267[c]

[a]order 123, [b]order 231, [c]order 312

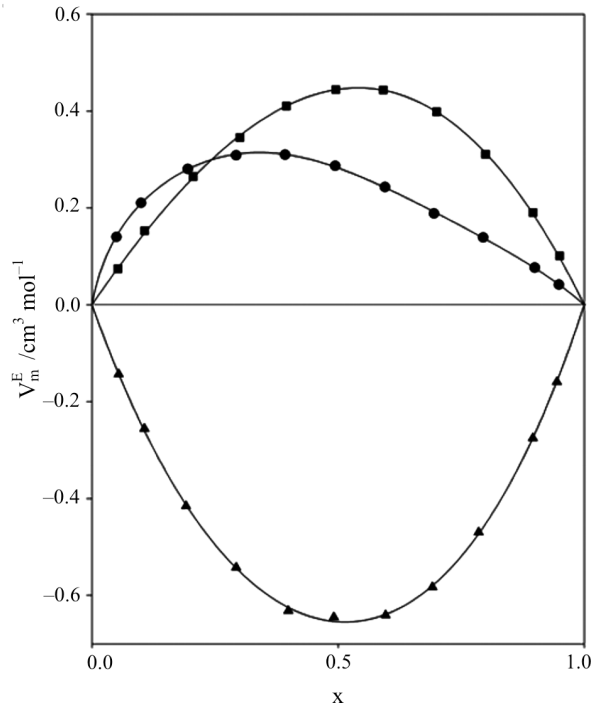

Fig. 1 Excess molar volumes of the binary mixtures:
▲ – *x* MTBE+(1–*x*)1-propanol, ■ –*x*MTBE+(1–*x*)heptane,
● – *x*1-propanol+(1–*x*) heptane

obtained by fitting experimental data to the equation suggested by Brandreth *et al.* [15],

$$V_m^E(\text{cm}^3\ \text{mol}^{-1}) = x(1-x)\sum_{i=1}^{n} A_i\,(1-x)^{\frac{i-1}{2}} \qquad (3)$$

The measured values of ternary excess molar volumes, $V_{m,123}^E$, were correlated using the Nagata and Tamura equation [3] of the form:

$$V_{m,123}^E = V_{m,bin}^E + x_1x_2x_3(B_0+B_1x_1+B_2x_2+B_3x_1^2+B_4x_2^2) \quad (4)$$

The parameters A_i and B_i have been obtained by a fitting computer program which uses the least squares procedure and a Marquard algorithm [33]. The number of parameters used in Eqs (2), (4) for each mixture were calculated using the unweighed least-squares method, with the degree of the polynomial previously optimized through the application of the *F*-test [34].

Experimental values of V_m^E for all the binary mixtures are listed in Table 2. Experimental data of ternary excess molar volumes, $V_{m,123}^E$, and densities, ρ, for the ternary system x_1MTBE+$x_2$1-propanol+(1–x_1–x_2)heptane are shown in Table 3. Table 4 presents the values of the A_i and B_i parameters and their corresponding standard deviations. Figures 1 and 2 show the experimental data obtained in this work.

The experimental volumes for the binary mixtures MTBE+heptane, and propanol+heptane are positive over the whole range of composition. A different situation is found for the binary mixture MTBE+propanol, the experimental values are negative over the whole range of composition. The curves for the binary systems *x*MTBE+(1–*x*)heptane and *x*MTBE+(1–*x*)1-propanol are symmetrical. Nevertheless, the obtained curve for the binary system *x*1-propanol+(1–*x*) heptane is asymmetric, with its maximum displace toward a high mole fraction of heptane. The ternary mixture shows maximum values for the MTBE+heptane at x_1=0.5405, x_3=0.4595, $V_{m,123}^E$=0.4477 cm^3 mol^{-1}and minimum values for the mixture MTBE+propanol at x_1=0.5225, x_2=0.4775, $V_{m,123}^E$= –0.6550 cm^3 mol^{-1}.

The ternary contribution to the excess molar volume is negative, with the exception of a range located around the rich compositions of 1-propanol, showing maximum values at x_1=0.2645, x_2=0.6303, x_3=0.1051, and

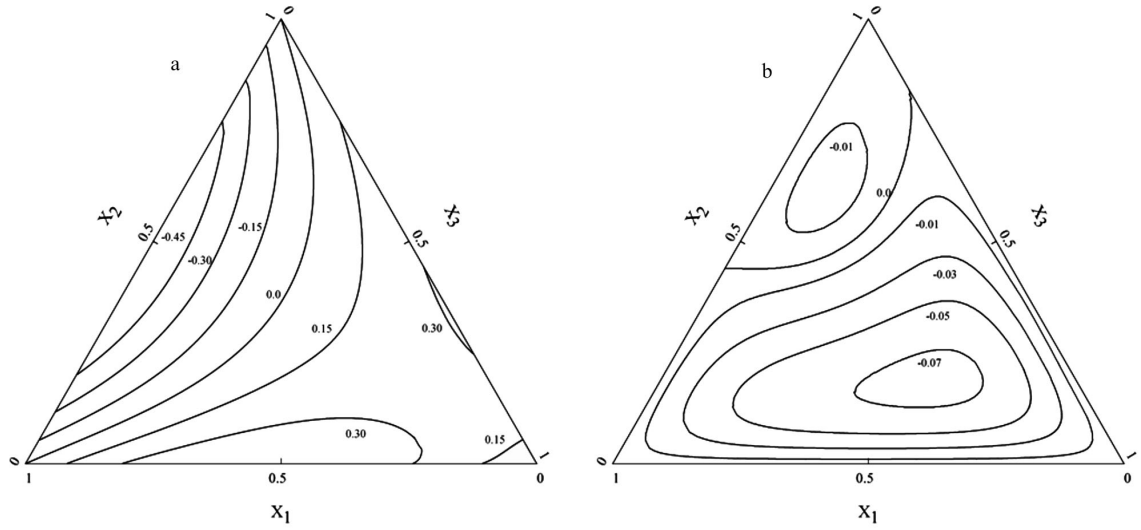

Fig. 2 a – Isolines of $V_{m,123}^E$/cm^3 mol^{-1}, for the ternary system x_1MTBE+$x_2$1-propanol+$x_3$heptane at 298.15 K, calculated with Eq. 4;
b – Curves of constant ternary contribution, $x_1x_2x_3\Delta_{123}$, to the excess molar volume $V_{m,123}^E$/cm^3 mol^{-1}

$V^{E}_{m,132}$=0.0152 cm^3 mol^{-1}and minimum values at x_1=0.2792, x_2=0.1856, x_3=0.5352, and $V^{E}_{m,132}$= –0.0754 cm^3 mol^{-1}. The representation is asymmetric, as can be seen in Fig. 2. It means that the position of the minimum does not coincide with the centre of the Gibbs triangle. The empirical expressions of Kohler [17], Jacob and Fitzner [18], Colinet [19], and Knobeloch and Schwartz [20], Tsao and Smith [21], Toop [22], Scatchard *et al.* [23], Hillert [24], and Mathieson and Thynne [25] were applied to estimate ternary properties from binary results. These methods can be divided into symmetric and asymmetric, depending on whether the assumption of the three binaries contributing equally to the ternary mixture magnitude is accepted or not. For the asymmetric equations [17–21], three different numberings of the components have been tested, in order to check the differences in the predicted values, and to find a rule to decide which ordering should be used in each case. MTBE, 1-propanol or heptane were respectively named as 1,2,3. Deviations between experimental data and estimated values are shown in Table 5. The deviations obtained are rather high, and this fact can be attributed to the comparatively important significance of the ternary contribution to the studied magnitude. The best agreement with the experimental data was achieved by the symmetric equation suggested by Jacob–Fitner [18]. Meanwhile, the best results were obtained using asymmetric equations are those predicted by Mathieson-Thynne [25], choosing the 1-propanol as the first component in the numbering. It can be observed that the dependence on the arrangement of the components varies in each asymmetric equation.

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