

# STUDY ON VOLUMETRIC MEASUREMENT AND CORRELATIONS FOR MTBE+1-PROPANOL+DECANE AT 298.15 K AND ATMOSPHERIC PRESSURE

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Experimental densities for the ternary mixture  $x_1$ MTBE+ $x_2$ 1-propanol+(1- $x_1$ - $x_2$ )decane and the binary mixtures  $x$ MTBE+(1- $x$ )1-propanol and  $x$ 1-propanol+(1- $x$ )decane have been measured at 298.15 K and atmospheric pressure, using a DMA 4500 Anton Paar densimeter. Excess molar volumes were determined from the densities of the pure liquids and mixtures. Attending to the symmetry of the studied mixtures, suitable fitting equations have been used in order to correlate adequately the experimental data. For the ternary mixture, experimental data were also used to test several empirical expressions for estimating ternary properties from experimental binary results.

**Keywords:** binary mixtures, decane, empirical expressions, excess molar volumes, 1-propanol, ternary mixture, tert-butyl methyl ether (MTBE)

## Introduction

The thermodynamic properties of mixtures containing ethers, alkanes and alkanols are of great industrial interest in view of the use of ethers as octane blending agents for gasolines. On the other hand, the most recent concern about health risks caused by the pollution of drinking water from MTBE into the ground makes it appear to be a somewhat controversial gasoline additive. The experimental data of the thermodynamic properties of these mixtures provides information about intermolecular interactions between component molecules as well as essential knowledge from an ecological point of view.

The purpose of this paper is to report experimental excess molar volumes of  $x_1$ MTBE+ $x_2$ 1-propanol+(1- $x_1$ - $x_2$ )decane,  $x$ MTBE+(1- $x$ )1-propanol and  $x$ 1-propanol+(1- $x$ )decane at the temperature of 298.15 K and atmospheric pressure.

Attending to the symmetry of the studied binary excess volumes, suitable fitting equations have been used. Redlich–Kister equation [1] were employed to correlate excess molar volumes for  $x$ MTBE+(1- $x$ )1-propanol, whereas the experimental data of binary system  $x$ 1-propanol+(1- $x$ )decane have been fitted with the Brandreth *et al.* equation [2]. For the ternary mixture, the Nagata and Tamura equation [3] has been used in order to correlate adequately the experimental data.

As the number of components in the mixture increases, the determination of thermodynamic properties becomes more arduous. Therefore, the applicability of predictive methods is of great interest for estimating ternary properties from the experimental data of the binaries involved. 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. In this work several empirical equations [4–12] were used to predict the ternary excess molar volumes studied.

## Experimental

The chemical substances employed, MTBE (purity >99.8%), 1-propanol (purity >99.5%) and decane (purity >99%) were supplied by Aldrich and were degassed by ultrasound and dried over molecular sieves (Sigma, type 0.4 nm) to remove traces of water. Mixtures were prepared by mass using a Mettler AT201 balance, with an accuracy of  $\pm 1 \cdot 10^{-5}$  g, which leads to an estimated uncertainty in mole fraction of  $10^{-4}$ .

Experimental values of density for the pure liquids at 298.15 K were compared with those found in [13–16], being in a fairly good agreement, as shown in Table 1.

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

Substances	Density/g mL <sup>-1</sup>	
	exp.	references
MTBE	0.7356	0.7353 <sup>a</sup> 0.7359 <sup>b</sup>
1-propanol	0.7997	0.7997 <sup>a</sup> 0.7995 <sup>c</sup>
decane	0.6550	0.7266 <sup>a</sup> 0.7263 <sup>d</sup>

<sup>a</sup>[13], <sup>b</sup>[14], <sup>c</sup>[15], <sup>d</sup>[16].

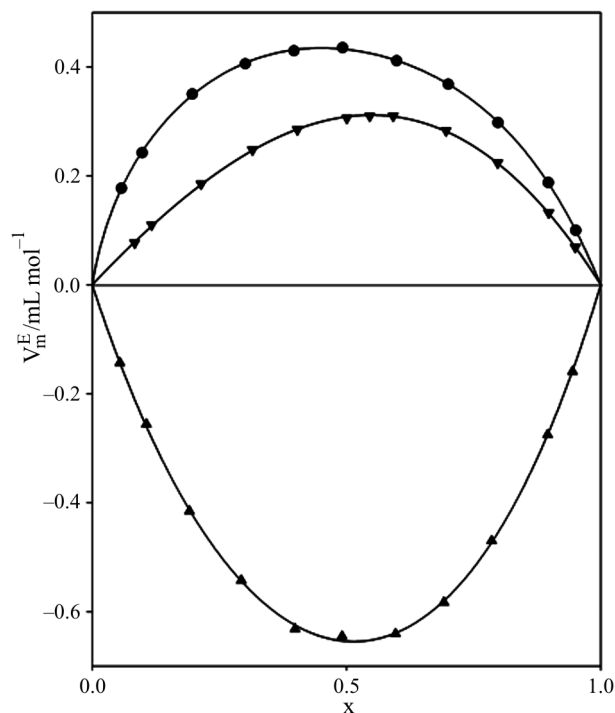
The experimental excess molar volumes were determined from the densities of the pure liquids and mixtures. The measurements of densities were carried out with a DMA 4500 Anton Paar densimeter with an estimated uncertainty of  $\pm 5 \cdot 10^{-5}$  g mL<sup>-1</sup>, the experimental technique has been described previously [17, 18]. The temperature inside the measuring cell was controlled using digital thermometer and was regulated to better than  $\pm 0.01$  K. Apparatus calibration was performed periodically using double-distilled and degassed water and heptane (Fluka, purity > 99.5%).

## Results and discussion

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

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

with  $x$ ,  $M$  and  $\rho$  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%.



**Fig. 1** Excess molar volumes of the binary mixtures:  $\nabla$  –  $x$ MTBE+(1– $x$ )1-propanol,  $\blacktriangle$  –  $x$ MTBE+(1– $x$ )decane<sup>a</sup>,  $\bullet$  –  $x$ 1-propanol+(1– $x$ )decane; <sup>a</sup>[21]

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

$$V_m^E \text{ (mL mol}^{-1}\text{)} = x(1-x) \sum_{i=1}^n A_i (2x-1)^{i-1} \quad (2)$$

suggested by Redlich–Kister [1], while lower deviations for the mixture  $x$ 1-propanol+(1– $x$ )decane were obtained by fitting experimental data to the equation suggested by Brandreth *et al.* [2]

$$V_m^E \text{ (mL mol}^{-1}\text{)} = x(1-x) \sum_1^n A_i x^{\frac{i-1}{2}} \quad (3)$$

**Table 2** Experimental binary excess molar volumes,  $V_m^E$ , and densities,  $\rho$ , at 298.15 K

$x$	$\rho$ /g mL <sup>-1</sup>	$V_m^E$ /mL mol <sup>-1</sup>	$x$	$\rho$ /g mL <sup>-1</sup>	$V_m^E$ /mL mol <sup>-1</sup>	$x$	$\rho$ /g mL <sup>-1</sup>	$V_m^E$ /mL mol <sup>-1</sup>
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			
x1-propanol+(1– $x$ )decane								
0.0572	0.72716	0.1774	0.3968	0.73883	0.4298	0.7977	0.76811	0.2980
0.0980	0.72815	0.2425	0.4923	0.74372	0.4354	0.8969	0.78104	0.1880
0.1966	0.73099	0.3503	0.5985	0.75041	0.4115	0.9508	0.78996	0.1001
0.3008	0.73471	0.4061	0.7001	0.75838	0.3684			

**Table 3** Excess molar volumes,  $V_{m,123}^E$ , and densities,  $\rho$ , at 298.15 K for the ternary mixture  $x_1$ MTBE+ $x_2$ 1-propanol+(1- $x_1-x_2$ ) decane

$x_1$	$x_2$	$\rho/\text{g mL}^{-1}$	$V_{m,123}^E/\text{mL mol}^{-1}$	$x_1$	$x_2$	$\rho/\text{g mL}^{-1}$	$V_{m,123}^E/\text{mL mol}^{-1}$
0.0512	0.8994	0.78667	-0.0265	0.3107	0.3924	0.74604	0.0494
0.1076	0.0976	0.72889	0.2496	0.2999	0.5007	0.75430	-0.0845
0.1099	0.1908	0.73197	0.3060	0.3015	0.5988	0.76454	-0.2807
0.0941	0.2851	0.73591	0.3324	0.3933	0.0992	0.73144	0.2477
0.1012	0.3897	0.74057	0.3161	0.3928	0.2003	0.73626	0.1624
0.1014	0.5012	0.74714	0.2747	0.3927	0.3009	0.74214	0.0466
0.0938	0.5970	0.75386	0.2286	0.3954	0.4002	0.74951	-0.1140
0.0963	0.6963	0.76309	0.1260	0.3952	0.5039	0.75934	-0.3324
0.1093	0.7941	0.77584	-0.0585	0.4963	0.0971	0.73261	0.2107
0.2122	0.1000	0.72975	0.2631	0.4977	0.1971	0.73811	0.0657
0.2030	0.2940	0.73773	0.2401	0.4932	0.3009	0.74504	-0.1120
0.2047	0.3918	0.74310	0.1929	0.4920	0.4071	0.75423	-0.3484
0.2009	0.5038	0.75066	0.1013	0.5958	0.1007	0.73430	0.1426
0.2009	0.5967	0.75569	-0.0102	0.5935	0.1983	0.74040	-0.0518
0.1993	0.7011	0.77029	-0.1833	0.5943	0.3047	0.74895	-0.3203
0.2957	0.1019	0.73059	0.2536	0.6914	0.1022	0.73616	0.0519
0.3025	0.1977	0.73473	0.2159	0.7024	0.1980	0.74352	-0.2275
0.3108	0.2912	0.73967	0.1471	0.8977	0.0506	0.73717	-0.0566

**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						
$V_m^E/\text{mL mol}^{-1}$	-2.6182	-0.1305	-0.3518	-	-	0.0046
xMTBE+(1-x)decane <sup>a</sup>						
$V_m^E/\text{mL mol}^{-1}$	1.2347	0.2456	-	-	-	0.0019
x1-propanol+(1-x)decane						
$V_m^E/\text{mL mol}^{-1}$	6.6330	-21.9703	41.9601	-41.1438	16.7943	0.0017
	$B_0$	$B_1$	$B_2$	$B_3$	$B_4$	$s$
$x_1$ MTBE+ $x_2$ 1-propanol+ $x_3$ decane						
$V_{m,123}^E/\text{mL mol}^{-1}$	-4.7022	5.2926	13.0855	-0.6834	-5.9639	0.0034

**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

	$s/\text{mL mol}^{-1}$		
Kohler	0.0249		
Jacob-Fitner	0.0254		
Colinet	0.0215		
Knobloch-Schwartz	0.0246		
Tsao-Smith	0.0409 <sup>a</sup>	0.0274 <sup>b</sup>	0.1014 <sup>c</sup>
Toop	0.0277 <sup>a</sup>	0.0243 <sup>b</sup>	0.0230 <sup>c</sup>
Scatchard	0.0272 <sup>a</sup>	0.0252 <sup>b</sup>	0.0230 <sup>c</sup>
Hillert	0.0240 <sup>a</sup>	0.0252 <sup>b</sup>	0.0228 <sup>c</sup>
Mathieson-Thynne	0.0258 <sup>a</sup>	0.0250 <sup>b</sup>	0.0200 <sup>c</sup>

<sup>a</sup>order 123, <sup>b</sup>order 231, <sup>c</sup>order 312

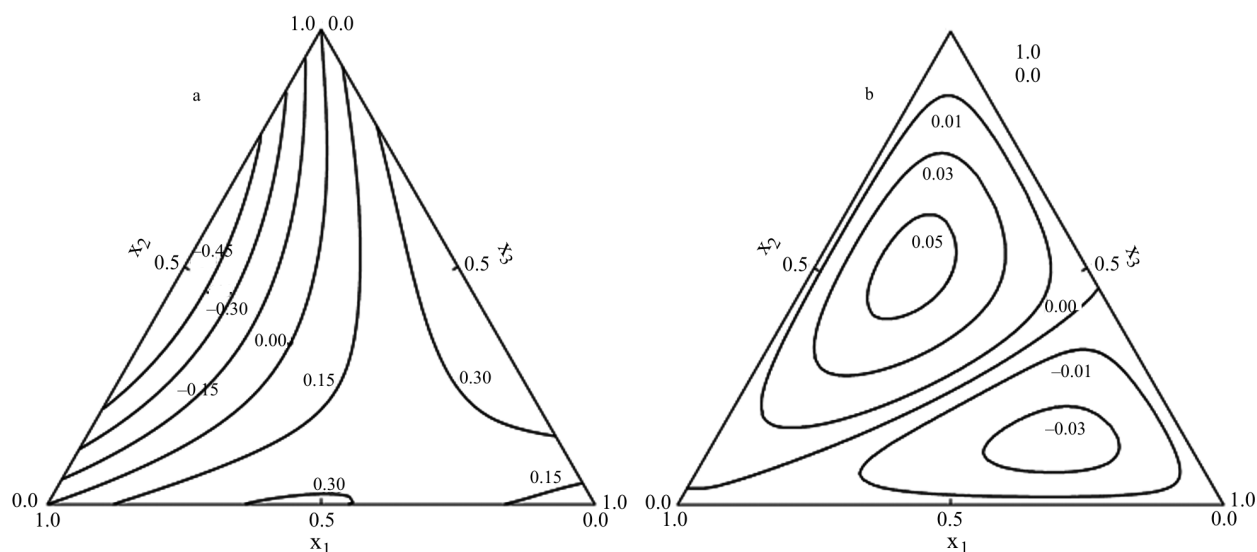
Experimental excess molar volumes for the ternary mixture were correlated using the equation

$$V_{m,123}^E = V_{12}^E + V_{13}^E + V_{23}^E + x_1x_2x_3\Delta_{123} \quad (4)$$

where  $V_{ij}^E$  is the binary contribution for each  $ij$  binary mixture,  $x_3=1-x_1-x_2$ , and  $x_1x_2x_3\Delta_{123}$  is ternary contribution which was correlated using the Nagata and Tamura equation [3].

$$\Delta_{123} = (B_0 + B_1x_1 + B_2x_2 + B_3x_1^2 + B_4x_2^2) \quad (5)$$

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 [19]. The number of parameters used in Eqs (2), (3) and (5) for each mixture were calculated using the unweighed least-squares



**Fig. 2** a – Isolines of  $V_{m,123}^E$  ( $\text{mL mol}^{-1}$ ), for the ternary system  $x_1\text{MTBE}+x_2\text{1-propanol}+x_3\text{decane}$  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  $V_{m,123}^E$  ( $\text{mL mol}^{-1}$ ), calculated with Eq. (5)

method, with the degree of the polynomial previously optimized through the application of the F-test [20].

Experimental values of densities,  $\rho$ , and excess molar volumes for the binary and ternary mixtures, are listed in Tables 2 and 3, respectively. Table 4 presents the parameters  $A_i$  and  $B_i$  of Eqs (2), (3) and (5) and the corresponding standard deviations for all mixtures. Figure 1 shows the experimental values of  $V_m^E$ , as well as the corresponding fitting curves. The isolines of  $V_{m,123}^E$  and the corresponding ternary contribution have been plotted in Fig. 2.

The experimental volumes for the binary mixture 1-propanol+decane are symmetrical and positive over the whole range of composition. The binary mixture MTBE+1-propanol are symmetrical too but the experimental values are negative over the whole range of composition. The ternary mixture shows maximum value at  $x_2=0.4510$ ,  $x_3=0.5490$ ,  $V_{m,123}^E = 0.435 \text{ mL mol}^{-1}$  and minimum value at  $x_1=0.5225$ ,  $x_2=0.4775$ ,  $V_{m,123}^E = -0.655 \text{ mL mol}^{-1}$ . The ternary contribution to the excess molar volume shows maximum value at  $x_1=0.3194$ ,  $x_2=0.5014$ ,  $x_3=0.1792$ ,  $V_{m,123}^E = 0.057 \text{ mL mol}^{-1}$  and minimum value at  $x_1=0.2372$ ,  $x_2=0.1298$ ,  $x_3=0.6329$ ,  $V_{m,123}^E = -0.037 \text{ mL mol}^{-1}$ .

Several empirical equations were used to predict the ternary excess molar volumes studied. The symmetrical equations tested have been suggested by Kohler [4], Jacob–Fitzner [5], Colinet [6], and Knobloch–Schwartz [7], while the asymmetric ones have been proposed by Tsao–Smith [8], Toop [9], Scatchard *et al.* [10], Hillert [11], and Mathieson–Thynne [12]. For the asymmetric equations [8–12], 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 order-

ing should be used in each case. MTBE, 1-propanol or decane were respectively named as 123. Table 5 shows deviations between experimental data and estimated values. 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 Colinet [6]. Meanwhile, the best results were obtained using asymmetric equations are those predicted by Hillert [11], for the order 123, and Mathieson–Thynne [12], for the 213 and 312.

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