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MEASUREMENTS AND ANALYSIS OF EXCESS MOLAR VOLUMES FOR THE TERNARY MIXTURE MTBE + 1-PENTANOL + DECANE

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Densities at 298.15 K and atmospheric pressure have been measured, using a DMA 4500 Anton Paar densimeter, for the ternary mixture methyl *tert*-butyl ether (MTBE)+1-pentanol+decane and for the involved binary mixtures MTBE+1-pentanol and 1-pentanol+decane. The excess molar volumes for the binary mixture MTBE+decane was reported in an earlier work [1]. In addition, excess molar volumes were determined from the densities of the pure liquids and mixtures. Suitable fitting equations have been used in order to correlate adequately the excess molar volumes.

The empirical expressions of Kohler [18], Jacob and Fitzner [19], Colinet [20], Knobeloch and Schwartz [21], Tsao and Smith [22], Toop [23], Scatchard *et al.* [24], Hillert [25], Mathieson and Thynne [26] were applied to estimate ternary properties from binary results.

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

Introduction

As part of the scientific project titled 'Study on physical properties of mixtures Hydrocarbon+Alcohol+Ether like alternative fuels', the present article reports experimental densities and excess molar volumes for the ternary system x_1 MTBE+$x_2$1-pentanol+$x_3$decane and the involved binary mixtures at 298.15 K and atmospheric pressure, with the aim of providing data for the characterization of the molecular interactions of these mixtures. This system has been chosen because branched ethers, such as the tert-butyl methyl ether (MTBE), either pure or mixed with alkanols or alkanes have been recommended as oxygenate additives in unleaded gasoline. 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.

Densities and volumes of liquid mixtures has proved to be meaningful from the thermodynamic point of view, as it provides direct information about the energetic effects arising between the molecules present in the mixture, so it can help to explain the intermolecular interactions in solution such as dispersion forces, hydrogen bonding interactions, etc. Besides, the densities are necessary in a lot of chemical engineering calculations (i.e. dimension of storage deposits, design of condensers and boilers, etc.).

The excess molar volumes at 298.15 K were calculated from density measurements made by using an Anton Paar DMA 4500 densimeter. The results were fitted by means of different variable degree polynomials, in order to correlate adequately the experimental data. Furthermore, several empirical expressions were applied to estimate ternary properties from binary results. As the number of components in the mixture increases, the determination of thermodynamic properties becomes more laborious.

Several V_m^E data have been published in the literature for MTBE+1-pentanol [2] and 1-pentanol+decane [3–5] at 298.15 K and atmospheric pressure.

Experimental

The chemical substances employed were commercial products of the best quality grade. The sources and purities of the chemicals used in this work are shown in Table 1. All products were subjected to no further purification other than drying with Union Carbide 0.4 nm molecular sieves to eliminate residual traces of water and degassed by ultrasound technique. Precautions were taken during samples preparation, such as weighing liquids in increasing order of volatility and reducing to a minimum the vapour space in the vessels, to avoid losses by evaporation during manipulation and possible errors in mole fractions calculations.

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Table 1 Source, purity and densities of chemicals used. Comparison of experimental densities with literature values at 298.15 K

Substances	Source	Purity	Density (ρ/ g cm^{-3})	
			exp.	References
MTBE	Aldrich	>99.8%	0.7356	0.73528[a] 0.7359[b]
1-pentanol	Aldrich	>99.5%	0.8110	0.8107[c] 0.8111[b]
Decane	Aldrich	≥99%	0.7262	0.7266[a] 0.7263[d]

[a]Ref. [6], [b]Ref. [8], [c]Ref. [9],[d]Ref. [10]

The handling and disposal of the chemicals used has been done according to the recommendation of the CRC Handbook of Chemistry and Physics [6].

The mixtures were prepared by mass using a Mettler H51 balance (precision ±1·10^{-5} g), ensuring a probable error in the mole fraction less than 10^{-4}. All molar quantities are based on the IUPAC relative atomic mass table [7].

The excess molar volumes at 298.15 K and atmospheric pressure were calculated from density measurements, made with a DMA 4500 Anton Paar densimeter . The temperature inside the vibrating tube was regulated to better than ±0.01 K. The precision of the densities was ±5·10^{-5} g·cm^{-3}. Experimental densities of the pure MTBE, 1-pentanol and decane are in agreement with the literature values [6], [8–10], as can be seen in Table 1. Before each series of measurements the instrument was calibrated at atmospheric pressure with double-distilled and degassed water and heptane (Fluka >0.995); density data were taken from literature: [11] for heptane and [12] for water. The uncertainty in the determination of the excess molar volumes was estimated to better than 1 %.

Results and discussion

Table 2 summarizes the experimental values of excess molar volumes and densities for the binary mixtures MTBE+1-pentanol and 1-pentanol+decane at 298.15 K and atmospheric pressure. The experimental data for MTBE+decane were taken from. [1].

The experimental data of V_m^E corresponding to the binary mixtures *x tert*-butyl methyl ether (MTBE)+(1–*x*) 1-pentanol, *x tert*-butyl methyl ether (MTBE)+(1–*x*) decane were fitted to the variable-degree polynomials suggested by Redlich- Kister [13], of the form

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

while lower deviations for the mixture *x*1-propanol+(1–*x*) decane were obtained by fitting experimental data to the equation suggested by Treszczanowicz-Benson equation [14],

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

Equation 2 provides a more accurate representation of the experimental set of data by using a more reduced set of parameters in cases where the representation of data is clearly asymmetric.

The measured values of the ternary excess molar volumes $V_{m,123}^E$ listed in Table 3, were correlated using the following equation:

$$V_{m,123}^E = V_{12}^E + V_{23}^E + x_1x_2x_3\cdot\Delta_{123} \qquad (3)$$

where V_{ij}^E is the binary contribution for each ij binary mixture, x_3=1–x_1–x_2, and $x_1x_2x_3\cdot\Delta_{123}$ is ternary contribution which was correlated using the expression suggested Nagatay, Tamura [15].

$$\Delta_{123} = (B_0 + B_1x_1 + B_2x_2 + B_3x_1^2 + B_4x_2^2) \qquad (4)$$

Table 2 Experimental binary excess molar volumes, V_m^E, and densities, ρ, at 298.15 K

x	ρ / g cm^{-3}	V_m^E/cm^3 mol^{-1}	*x*	ρ / g cm^{-3}	V_m^E/cm^3 mol^{-1}	x	ρ / g cm^{-3}	V_m^E/ cm^3 mol^{-1}
				x MTBE+(1–*x*) 1-pentanol				
0.0522	0.80766	–0.1386	0.4000	0.79105	–0.7124	0.8087	0.75250	–0.5599
0.0960	0.80485	–0.2444	0.5028	0.78397	–0.7827	0.9063	0.74422	–0.3435
0.2007	0.79788	–0.4534	0.6018	0.77655	–0.7780	0.9510	0.74022	–0.2013
0.3008	0.79105	–0.6148	0.6920	0.76905	–0.7301			
				x 1-pentanol+(1–*x*) decane				
0.0500	0.72807	0.1328	0.4078	0.74815	0.3116	0.7971	0.78342	0.1400
0.1015	0.73044	0.1868	0.4963	0.75464	0.3024	0.9004	0.79641	0.0659
0.2006	0.73546	0.2592	0.5952	0.76287	0.2619	0.9501	0.80341	0.0298
0.2995	0.74112	0.2980	0.6985	0.77269	0.2025			

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 [16]. The number of parameters used in Eqs (2), (3) and (5) for each mixture were calculated using the unweighted least-squares method, with the degree of the polynomial previously optimized through the application of the F-test [17].

Table 4 presents the parameters A_i and B_i of Eqs (1), (2) and (4) and the corresponding standard deviations for all mixtures. Figure 1 shows the experimental values of $V^E_{m,123}$, as well as the corresponding fitting curves. The isolines of V^E_m and the corresponding ternary contribution have been plotted in Fig. 2.

The experimental volumes for the binary mixtures MTBE+decane and 1-pentanol+decane are positive over the whole range of composition nevertheless the curve for the system MTBE+1-pentanol is negative all through the composition range. The maximum of the V^E_m curve for the binary system 1-pentanol+decane is shifted around the rich compositions in decane.

The ternary mixture shows maximum values at x_2=0.4020, x_3=0.5980, $V^E_{m,123}$=0.3130 cm^3 mol^{-1} and minimum values at x_1=0.5610, x_2=0.4390, $V^E_{m,123}$ = –0.7858 cm^3 mol^{-1}. The ternary contribution to the

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

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}
0.0513	0.0471	0.72821	0.1492	0.2934	0.4073	0.75632	–0.1029
0.0933	0.0961	0.73088	0.1931	0.2914	0.5065	0.76618	–0.2437
0.1099	0.1938	0.73642	0.2178	0.2991	0.6172	0.77961	–0.4494
0.0992	0.2897	0.74225	0.2140	0.3941	0.1009	0.73414	0.1682
0.0955	0.3943	0.74947	0.1962	0.3989	0.1951	0.74113	0.0358
0.0985	0.4998	0.75802	0.1370	0.3919	0.3045	0.75009	–0.1187
0.1041	0.6010	0.76758	0.0543	0.3931	0.4015	0.7594	–0.2750
0.1145	0.6867	0.77724	–0.0576	0.3937	0.5069	0.77128	–0.4877
0.1010	0.8015	0.79058	–0.1538	0.4960	0.0987	0.73535	0.1323
0.1847	0.1001	0.73187	0.1969	0.4938	0.1978	0.74332	–0.0527
0.2069	0.1877	0.73744	0.1593	0.4934	0.3093	0.75372	–0.2816
0.1966	0.2821	0.74362	0.1254	0.4905	0.4096	0.76454	–0.5040
0.1931	0.4988	0.76131	–0.0334	0.6004	0.3046	0.75732	–0.4830
0.1967	0.6005	0.7719	–0.1600	0.6908	0.0990	0.73884	–0.0179
0.1929	0.7068	0.78439	–0.2943	0.6899	0.2045	0.74946	–0.3481
0.2974	0.0961	0.73275	0.1867	0.7968	0.1000	0.7415	–0.1584
0.2930	0.2160	0.7407	0.0984	0.8962	0.0508	0.73875	–0.0946
0.2997	0.2877	0.74624	0.0257				

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
			x MTBE+(1–x) 1-pentanol			
V^E_m/cm^3 mol^{-1}	–3.1007	–0.6851	–0.4388	–	–	0.0070
			x MTBE+(1–x) decane[a]			
V^E_m/cm^3 mol^{-1}	1.2348	0.2456	–	–	–	0.0020
			x 1-pentanol+(1–x) decane			
V^E_m/cm^3 mol^{-1}	6.5300	–29.4964	53.1815	–48.6927	16.1133	0.0024
	B_0	B_1	B_2	B_3	B_4	s
			x_1 MTBE+x_2 1-pentanol+x_3 decane			
V^E_m/cm^3 mol^{-1}	–3.8427	–2.1290	12.5823	8.2397	–9.8271	0.0043

[a]Ref [1]

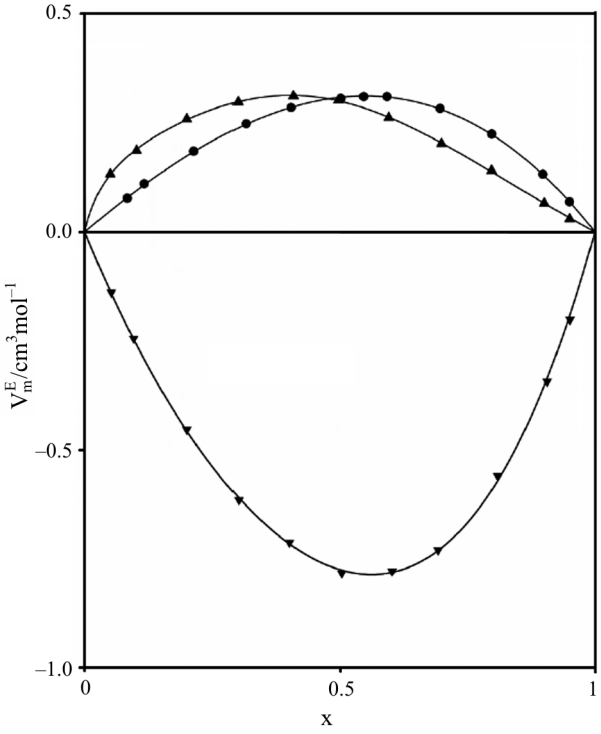

Fig. 1 Excess molar properties of the binary mixtures: ▲ – x 1-pentanol+(1–x) decane, ● – x MTBE+(1–x) decane [1], ▼ – x MTBE+(1–x) 1-pentanol

Table 5 Standard deviations from the experimental V_m^E 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		0.016	
Jacob-Fitner		0.012	
Colinet		0.013	
Knobeloch-Schwartz		0.028	
Tsao-Smith	0.045[a]	0.035[b]	0.124[c]
Toop	0.019[a]	0.014[b]	0.016[c]
Scatchard	0.021[a]	0.015[b]	0.015[c]
Hillert	0.014[a]	0.015[b]	0.016[c]
Mathieson-Thynne	0.019[a]	0.013[b]	0.013[c]

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

Experimental values were used to test several empirical equations [18–26] that 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. The empirical expressions of Kohler [18], Jacob and Fitzner [19], Colinet [20], Knobeloch and Schwartz [21], Tsao and Smith [22], Toop [23], Scatchard *et al.* [24], Hillert [25], Mathieson and Thynne [26] were applied to estimate ternary properties from binary results. Standard deviations between experimental and estimated values are shown in Table 5.

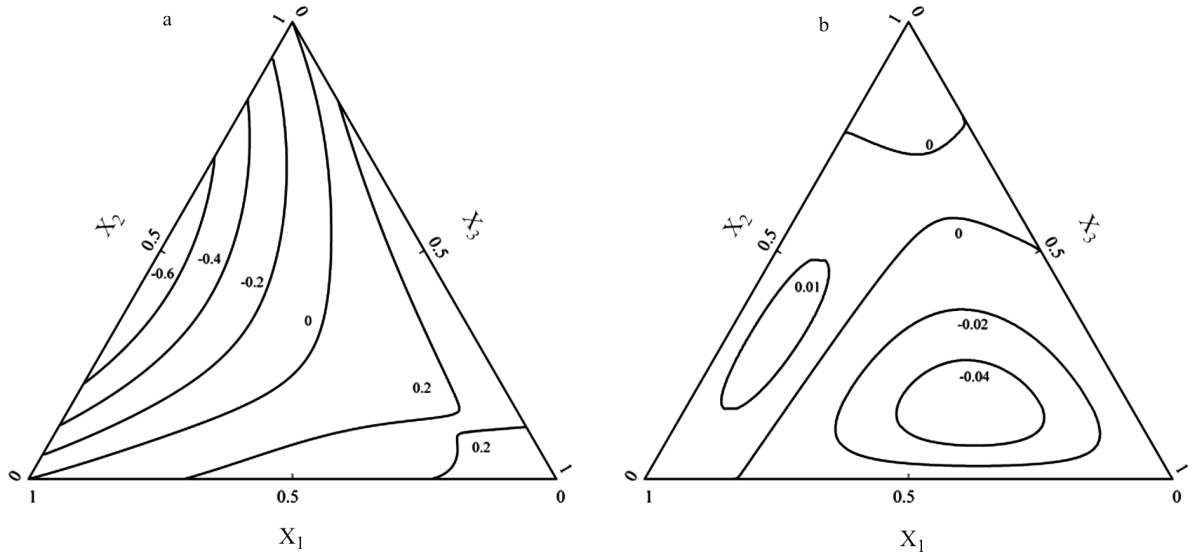

Fig. 2 a – Isolines of $V_{m,123}^E$/(cm^3 mol^{-1}), for the ternary system x_1 MTBE+x_2 1-pentanol+x_3 decane at 298.15 K, calculated with Eq .(3)
b – Curves of constant ternary contribution, $x_1x_2x_3\,\Delta_{123}$, to the excess molar volume $V_{m,123}^E$/(cm^3 mol^{-1}), calculated with Eq. (4)

excess molar volume is negative over the whole range of composition, showing minimum values about –0.051 cm^3 mol^{-1} at x_1=0.3060, x_2=0.1520, x_3=0.5420. Figure 2 shows both magnitudes present an isoline of ideal behavior.

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