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APPLICATION OF SEVERAL EMPIRICAL METHODS TO MTBE+1-PENTANOL+OCTANE

P. V. Verdes[1], *M. M. Mato*[2], *J. Salgado*[1], *J. L. Legido*[2] *and M. I. Paz Andrade*[1*]

[1]Departamento de Física Aplicada, Facultad de Físicas, Campus Universitario Sur, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain
[2]Departamento de Física Aplicada, Facultad de Ciencias, Universidade de Vigo, 36200 Vigo, Spain

Excess molar volumes of methyl *tert*-butyl ether (MTBE)+1-pentanol+octane and the binary mixtures MTBE+1-pentanol and 1-pentanol+octane, were measured at 298.15 K and atmospheric pressure, using a DMA 4500 Anton Paar densimeter. All the experimental values were compared with the results obtained by empirical expressions for estimating ternary properties from binary results.

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

Introduction

Theoretical and experimental studies on thermophysical properties of mixtures formed by hydrocarbons, ethers and alkanols are interesting for the characterization of the interactions taking place in mixtures. Furthermore, thermophysical properties of these mixtures are useful in petrochemical industry as ethers and alkanols are used in lead-free gasoline as oxygenating agents.

In previous works [1–4] we have reported experimental excess molar enthalpies and volumes of ternary and binary mixtures containing, MTBE, alcohol and alkanes as components. In this paper, we continue our studies and we present the excess molar volumes of x_1MTBE+$x_2$1-pentanol+$x_3$octane and the binary systems MTBE+1-pentanol and 1-pentanol+octane at 298.15 K.

The excess molar volumes obtained were used to test the empirical methods of Kohler [5], Jacob and Fitzner [6], Colinet [7], and Knobeloch and Schwartz [8], Tsao and Smith [9], Toop [10], Scatchard *et al.* [11], Hillert [12], and Mathieson and Thynne [13]. These methods predict excess properties of the ternary mixtures from those of involved binary mixtures. The Nagata and Tamura equation [14] been used to correlate the experimental values of ternary mixtures.

Experimental

The experimental excess molar volumes were determined from densities of the pure liquids and mixtures, measured with an Anton Paar DMA 4500 vibrating tube densimeter with estimated uncertainty of $\pm 5 \cdot 10^{-5}$ g cm^{-3}. The measuring cell is thermostated with a temperature uncertainty of ±0.01 K. The substances employed were supplied by Fluka and Aldrich. Their mole-fraction purities were: MTBE (Aldrich) >99.8%; 1-pentanol (Aldrich) >99.5% and octane (Fluka) ≥99.5%. All chemical products were degassed by ultrasound and dried over Union Carbide 0.4 nm molecular sieves. Desities of pure liquids agrees with the literature values as Table 1 shows.

Results and discussion

Experimental values of densities, ρ, and excess molar volumes for binary mixtures are reported in Table 2. The experimental data for MTBE+octane were taken from [1].

The experimental data of V_m^E corresponding to the binary mixtures *xtert*-butyl methyl ether (MTBE) +(1–*x*)1-pentanol, *xtert*-butyl methyl ether (MTBE) +(1–*x*)octane were fitted to the variable-degree polynomials suggested by Redlich–Kister [19], of the form

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

while lower deviations for the mixture *x*1-pentanol +(1–*x*)octane were obtained by fitting experimental data to the equation suggested by Treszczanowicz–Benson equation [20].

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

* Author for correspondence: fapazand@usc.es

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Table 1 Densities of pure liquids at 298.15 K

Substance	Density (ρ/g cm^{-3})		
	experimental	literature	
MTBE	0.73561	0.73528[a]	0.7359[b]
1-pentanol	0.81095	0.8107[c]	0.8111[b]
octane	0.69860	0.6986[a]	0.6985[d]

[a]from [15], [b]from [16], [c]from [17], [d]from [18]

The experimental values of densities and excess molar volumes of the ternary system, $V^{E}_{m,123}$, are shown in Table 3. Data were correlated using the following equation:

$$V^{E}_{m,123} = V^{E}_{12} + V^{E}_{13} + V^{E}_{23} + x_1 x_2 x_3 \Delta_{123} \quad (3)$$

where V^{E}_{ij} 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 expression suggested Nagata and Tamura [14].

$$\Delta_{123} = (B_0 + B_1 x_1 + B_2 x_2 + B_3 x_1^2 + B_4 x_2^2) \quad (4)$$

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 [21]. The number of parameters used in Eqs (1), (2) and (4) for each mixture were calculated using a least-squares method, with the degree of the polynomial previously optimized through the application of the F-test [22]. Paramenters and standard deviations are listed in Table 4.

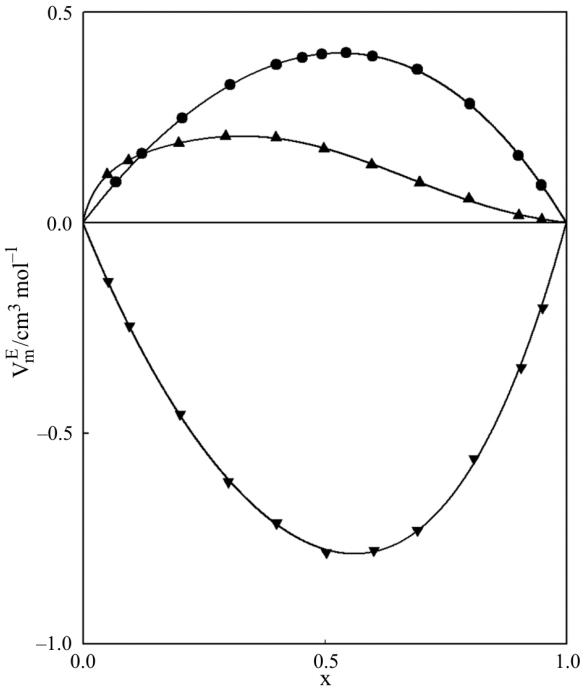

Fig. 1 Excess molar properties of the binary mixtures: ▲ – x1-pentanol+(1–x)octane, ● –xMTBE+(1–x)octane [1], ▼ – xMTBE+(1–x)1-pentanol [1]

Figure 1 shows the experimental values of V^{E}_{m}, as well as the corresponding fitting curves. The lines of constant ternary excess molar volume, $V^{E}_{m,123}$, and the corresponding ternary contribution have been plotted in Fig. 2.

The ternary mixture shows a maximum at x_1=0.5320, x_3=0.4680, $V^{E}_{m,123}$ =0.403 cm^3 mol^{-1} and a minimum at x_1=0.5610, x_2=0.4390, $V^{E}_{m,123}$ = –0.7858 cm^3 mol^{-1}. The ternary contribution to the excess molar volume is negative over the whole range of composition, showing a minimum value about –0.095 cm^3 mol^{-1} at x_1=0.3100, x_2=0.1960, x_3=0.4940.

Several methods have been proposed to estimate ternary excess properties from experimental results on constituent binaries [5–13]. These methods have been described previously [23]. For asymmetrical equations

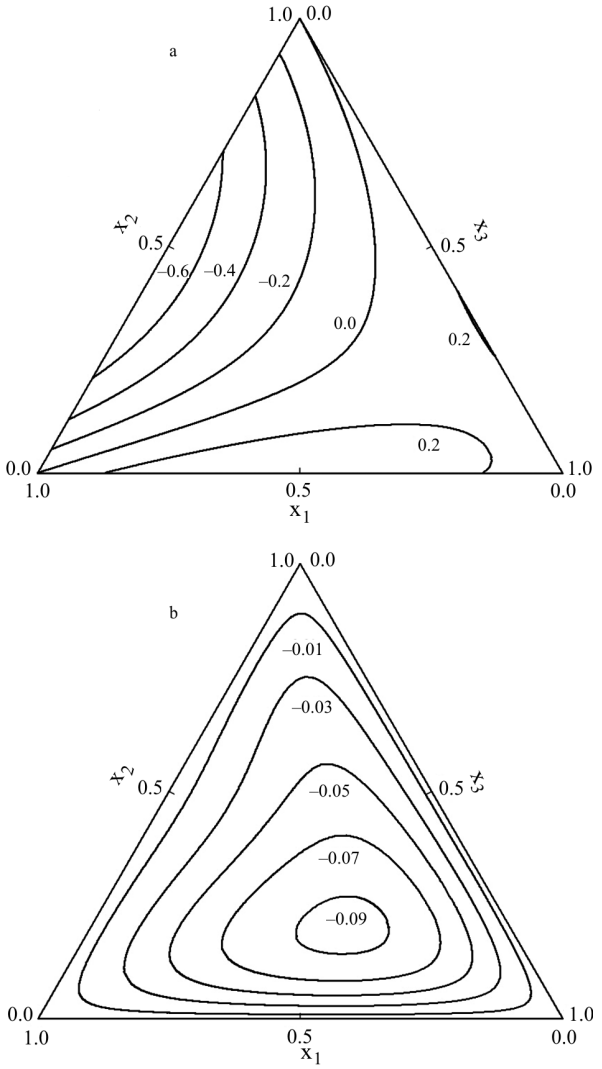

Fig. 2 a – Isolines of $V^{E}_{m,123}$ (cm^3 mol^{-1}), for the ternary system x_1MTBE+$x_2$1-pentanol+$x_3$octane at 298.15 K, calculated with Eq. (3), b – curves of constant ternary contribution, $x_1x_2x_3\Delta_{123}$, to the excess molar volume $V^{E}_{m,123}$ (cm^3 mol^{-1}), calculated with Eq. (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}
				xMTBE+(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			
				x1-pentanol+(1–x)octane				
0.0502	0.70191	0.1146	0.3992	0.73198	0.2013	0.7982	0.77963	0.0569
0.0938	0.70518	0.1470	0.4983	0.74232	0.1756	0.9008	0.79487	0.0165
0.1979	0.71355	0.1879	0.5969	0.75354	0.1376	0.9484	0.80240	0.0068
0.2949	0.72203	0.2055	0.6969	0.76593	0.0955			

Table 3 Excess molar volumes, $V_{m,123}^E$, and densities, ρ, at 298.15 K for the ternary mixture x_1MTBE+$x_2$1-pentanol+(1–x_1–x_2)octane

x_1	x_2	ρ/g cm^{-3}	$V_{m,123}^E$ /cm^3 mol^{-1}	x_1	x_2	ρ/g cm^{-3}	$V_{m,123}^E$ /cm^3 mol^{-1}
0.0516	0.0500	0.7032	0.1650	0.2916	0.4006	0.7609	–0.1740
0.0511	0.8996	0.7996	–0.1199	0.2917	0.5031	0.7756	–0.3154
0.1166	0.0883	0.7081	0.1905	0.2987	0.6019	0.7283	–0.4705
0.0922	0.1904	0.7162	0.1487	0.4003	0.1863	0.7409	0.0301
0.1099	0.2954	0.7267	0.1203	0.3945	0.2970	0.7538	–0.1588
0.1085	0.3894	0.7363	0.0722	0.4000	0.3957	0.7689	–0.3450
0.0967	0.4942	0.7474	0.0209	0.4052	0.5002	0.7345	–0.5422
0.1009	0.5950	0.7599	–0.0592	0.4905	0.2018	0.7472	–0.0825
0.1001	0.6990	0.7738	–0.1375	0.4913	0.3020	0.7615	–0.3044
0.0985	0.8003	0.7885	–0.2006	0.4967	0.4029	0.7267	–0.5412
0.1940	0.1890	0.7199	0.1300	0.5965	0.0934	0.7394	0.0962
0.2040	0.2974	0.7312	0.0321	0.5953	0.1953	0.7546	–0.1964
0.2128	0.3895	0.7418	–0.0540	0.5947	0.3063	0.7461	–0.5053
0.2039	0.4943	0.7539	–0.1528	0.6999	0.1977	0.7384	–0.3711
0.2003	0.5953	0.7670	–0.2516	0.7973	0.1012	0.7367	–0.1776
0.2024	0.7000	0.7823	–0.3718	0.9014	0.0461	0.7609	–0.0921
0.2970	0.0931	0.7145	0.2094				
0.3069	0.2967	0.7361	–0.0558				

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-pentanol			
V_m^E /cm^3 mol^{-1}	–3.1007	–0.6851	–0.4388	–	–	0.0066
			xMTBE+(1–x)octane			
V_m^E /cm^3 mol^{-1}	1.6039	0.1930	0.0923	–	–	0.0016
			x1-pentanol+(1–x)octane			
V_m^E /cm^3 mol^{-1}	6.2104	–27.0278	54.7733	–51.4193	17.5940	0.0027
	B_0	B_1	B_2	B_3	B_4	s
			x_1MTBE+$x_2$1-pentanol+$x_3$octane			
$V_{m,123}^E$ /cm^3 mol^{-1}	–6.9097	5.6757	14.2908	–3.4665	–12.4390	0.0052

Table 5 Standard deviations from the experimental values obtained with the empirical predictive methods

	s/cm^3 mol^{-1}		
Kohler		0.0312	
Jacob–Fitner		0.0323	
Colinet		0.0317	
Knobeloch–Schwartz		0.0309	
Tsao–Smith	0.0623[a]	0.0790[b]	0.0834[c]
Toop	0.0395[a]	0.0330[b]	0.0222[c]
Scatchard	0.0560[a]	0.0323[b]	0.0239[c]
Hillert	0.0411[a]	0.0330[b]	0.0212[c]
Mathieson–Thynne	0.0529[a]	0.0320[b]	0.0278[c]

[a]MTBE, [b]1-pentanol, [c]octane, is the asymmetric component in mixture respectively

the numerical predictions depend on the arbitrary designation of components-numbering. Table 5 shows the standard deviations between experimental and predicted values.

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