Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 1, 179–183

TERNARY MIXTURE MTBE+1-PENTANOL+NONANE AT 298.15 K AND ATMOSPHERIC PRESSURE
Measurements and analysis of densities and excess molar volumes

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

[1]Departamento de Física Aplicada, Facultad de Física, 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

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+nonane and for the involved binary mixture 1-pentanol+nonane. 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.

Experimental data were also used to test several empirical expressions for estimating ternary properties from experimental binary results.

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

Introduction

As part of the scientific project entitled 'Study on physical properties of mixtures hydrocarbon+alcohol+ether like alternative fuels', the present work continues our previous studies on excess thermodynamic properties of the binary and ternary mixtures containing MTBE, alkanols, alkanes, as components [1–15], where the main objective has been the characterisation of non-electrolyte liquids, and their mixtures, through experimental determination of thermophysical properties on mixing. In this paper, we report experimental densities and excess molar volumes at 298.15 K and atmospheric pressure, for the ternary system $\{x_1$MTBE+$x_2$1-pentanol+$x_3$nonane$\}$ and the involved binary mixture $\{x$1-pentanol+$(1-x)$nonane$\}$.

The excess molar volumes were calculated from density measurements made by using an Anton Paar DMA 4500 vibrating tube densimeter operating under static mode. The apparatus was calibrated at atmospheric pressure before each series of measurements using bidistilled and degassed water and *n*-heptane; density data were taken from literature for *n*-heptane [16] and for water [17]. The results were fitted by means of different variable degree polynomials, in order to correlate adequately the experimental data.

Furthermore, experimental values were also used to test different symmetric [18–21] and asymmetric [22–26] empirical equations, 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. As the number of components in the mixture increases, the determination of thermodynamic properties becomes more laborious. Therefore, the applicability of predictive methods is of great interest for estimating ternary properties from the experimental data of the binaries involved.

Experimental

The chemical substances employed, MTBE, 1-pentanol, nonane 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.

* Author for correspondence: fapazand@usc.es

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

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

	Source	Purity	Density (ρ/g cm^{-3})	
			exp.	reference
MTBE	Aldrich	>99.8%	0.7356	0.7353[a] 0.7359[b]
1-Pentanol	Aldrich	>99.5%	0.8110	0.8107[c] 0.8111[b]
Nonane	Aldrich	≥99%	0.7138	0.7137[d] 0.7139[e]

[a][29], [b][30], [c][31], [d][32], [e][33]

The handling and disposal of the chemicals used has been done according to the recommendation of the CRC Handbook of Chemistry and Physics [27].

The mixtures were prepared by mass using a Mettler H51 balance (precision $\pm 1 \cdot 10^{-5}$ 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 [28].

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 $\pm 5 \cdot 10^{-5}$ g cm^{-3}. The measured densities of the pure liquids, MTBE, 1-pentanol and nonane, displayed good agreement with previously published values [29–33], 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: [16] for heptane and [17] for water. The uncertainty in the determination of the excess molar volumes was estimated to better than 1%. Further details about the experimental method of operation have been published [34, 35].

Results and discussion

Table 2 summarizes the experimental values of excess molar volumes and densities for the binary mixtures at 298.15 K and atmospheric pressure. The experimental data for MTBE+nonane and MTBE+1-pentanol were taken from [3, 15].

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)nonane} were fitted to the variable-degree polynomials suggested by Redlich–Kister [36], 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 {x1-pentanol+(1–x)nonane} were obtained by fitting experimental data to the equation suggested by Treszczanowicz-Benson *et al.* equation [37],

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

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:

$$V_{m,123}^E = V_{12}^E + V_{13}^E + V_{23}^E + x_1x_2x_3\Delta_{123} \qquad (3)$$

where V_{ij}^E is the binary contribution for each ij binary mixture, x_3=1–x_1–x_2, and $x_1x_2x_3\Delta_{123}$ is ternary contribution which was correlated using the expression suggested Nagata and Tamura [38].

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

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 [39]. The number of parameters used in Eqs (1), (2) and (4) 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 [40].

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_m^E, as well as the corresponding fit-

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}
x1-pentanol+(1–x)nonane								
0.0493	0.71636	0.1030	0.3911	0.73973	0.2620	0.7936	0.2064	0.1072
0.0967	0.71909	0.1538	0.4913	0.74837	0.2463	0.8976	0.1024	0.0467
0.1944	0.72525	0.2171	0.5904	0.75789	0.2131	0.9496	0.0504	0.0191
0.2974	0.73242	0.2604	0.6963	0.76930	0.1632			

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-pentanol+(1–x_1–x_2)nonane

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}
0.0530	0.0506	0.71714	0.1389	0.2947	0.3005	0.74190	–0.0118
0.0472	0.8994	0.79957	–0.0891	0.2921	0.5034	0.76351	–0.2708
0.1085	0.1963	0.72779	0.1810	0.2980	0.6032	0.77671	–0.4361
0.0989	0.2960	0.73515	0.1710	0.3968	0.0923	0.72641	0.1789
0.0975	0.4089	0.74468	0.1386	0.3987	0.1933	0.73537	0.0268
0.0959	0.5017	0.75341	0.0938	0.3948	0.2985	0.74556	–0.1324
0.1063	0.5917	0.76345	0.0096	0.3983	0.5010	0.76968	–0.5062
0.0991	0.6994	0.77590	–0.0789	0.5049	0.0943	0.72929	0.1445
0.1022	0.7988	0.78941	–0.1687	0.5006	0.1952	0.73903	–0.0775
0.2017	0.0980	0.72268	0.1917	0.4937	0.2965	0.74973	–0.2887
0.1975	0.1851	0.72906	0.1548	0.4866	0.4107	0.76330	–0.5238
0.1920	0.2945	0.73788	0.0918	0.5925	0.0953	0.73198	0.0777
0.2018	0.3923	0.74714	0.0159	0.6014	0.1936	0.74279	–0.2025
0.2013	0.5940	0.76917	–0.1921	0.5919	0.3049	0.75566	–0.4835
0.2020	0.6978	0.78286	–0.3268	0.6967	0.0939	0.73526	–0.0065
0.3005	0.1015	0.72496	0.1872	0.7993	0.0991	0.73988	–0.1615
0.3039	0.1945	0.73262	0.0967	0.8983	0.0502	0.73796	–0.1052

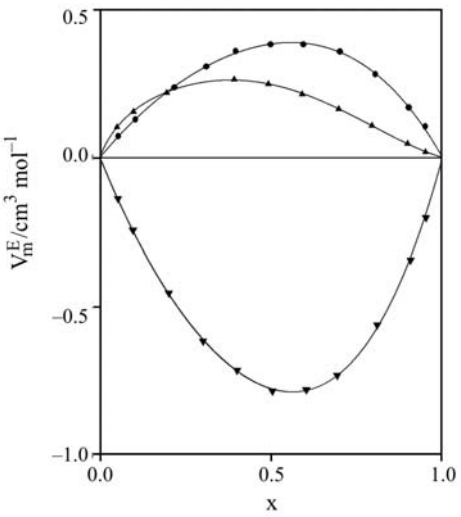

Fig. 1 Excess molar properties of the binary mixtures: ▲ – x1-pentanol+(1–x)nonane, ● – xMTBE+(1–x)nonane [3], ▼ – xMTBE+(1–x)1-pentanol [15]

ting curves. The isolines of $V^E_{m,123}$ and the corresponding ternary contribution have been plotted in Fig. 2.

The experimental volumes for the binary mixtures MTBE+nonane and 1-pentanol+nonane 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+nonane is shifted around the rich compositions in nonane.

The ternary mixture shows maximum values at x_1=0.5580, x_3=0.4420, $V^E_{m,123}$=0.385 cm^3 mol^{-1} and minimum values at x_1=0.5610, x_2=0.4390, $V^E_{m,123}$= –0.786 cm^3 mol^{-1}. The ternary contribution to the excess molar volume is negative over the whole range of composition, showing minimum values about –0.088 cm^3 mol^{-1} at x_1=0.3940, x_2=0.1610, x_3= 0.4450. Figure 2 shows ternary excess molar volume present an isoline of ideal behavior. In both cases, the representation is asymmetric. It means that the position of the minimum does not coincide with the centre of the Gibbs triangle.

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–Fitner [19], Colinet [20], Knobeloch–Schwartz [21], Tsao–Smith [22], Toop [23], Scatchard *et al*. [24], Hillert [25], Mathieson–Thynne [26], were applied to estimate ternary properties from binary results. 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 asymmetric equation suggested by Toop [23], choosing the nonane 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.

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[a]			
V_m^E/cm^3 mol^{-1}	–3.1007	–0.6851	–0.4388			0.007
			xMTBE+(1–x)nonane[b]			
V_m^E/cm^3 mol^{-1}	1.221	0.3239	0.1906			0.005
			x1-pentanol+(1–x)nonane			
V_m^E/cm^3 mol^{-1}	3.7583	–9.7578	12.8708	–6.5485		0.002
	B_0	B_1	B_2	B_3	B_4	s
			x_1MTBE+$x_2$1-pentanol+$x_3$nonane			
$V_{m,123}^E$/cm^3 mol^{-1}	–6.3019	3.2775	16.8976	–3.0161	–14.0023	0.005

[a][15], [b][3]

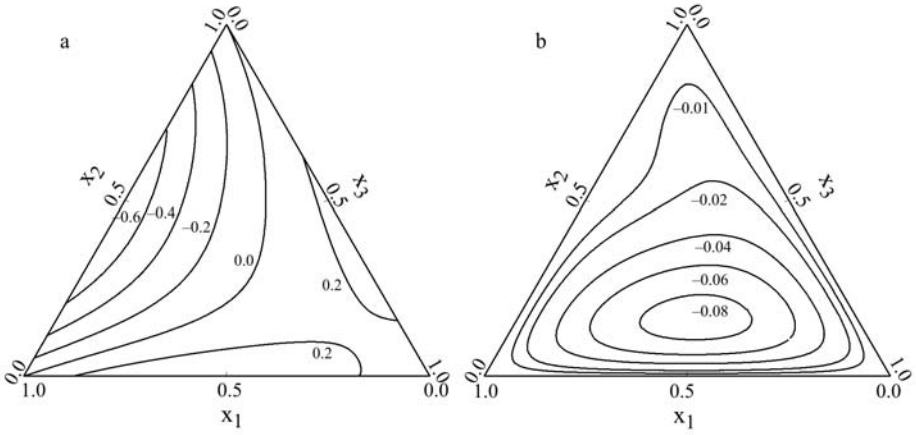

Fig. 2 a – Isolines of $V_{m,123}^E$ (cm^3 mol^{-1}), for the ternary system {x_1MTBE+$x_2$1-pentanol+$x_3$nonane} at 298.15 K, calculated with Eq. (3). b – Curves of constant ternary contribution, $x_1x_2x_3\Delta_{123}$, to the excess molar volume $V_{m,123}^E$ (cm^3 mol^{-1}), calculated with Eq.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

Table 5 Mean square 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		0.028	
Jacob–Fitner		0.027	
Colinet		0.027	
Knobeloch–Schwartz		0.029	
Tsao–Smith	0.068[a]	0.037[b]	0.088[c]
Toop	0.036[a]	0.026[b]	0.021[c]
Scatchard	0.048[a]	0.025[b]	0.024[c]
Hillert	0.035[a]	0.027[b]	0.021[c]
Mathieson–Thynne	0.045[a]	0.026[b]	0.025[c]

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

Acknowledgements

The authors wish to acknowledge financial support from the Spanish Ministerio de Educación y Ciencia and the European Union through the project reference REN2003-09796-C02 and by the Xunta de Galicia PGIDT99PXI30103B.

P. V. Verdes and M. M. Mato thank 'Xunta de Galicia' for their 'Isidro Parga Pondal' position.

References

1 P. V. Verdes, M. M. Mato, E. Jiménez, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 89 (2007) 73.
2 M. M. Mato, M. Illobre, P. V. Verdes and M. I. Paz Andrade, J. Therm. Anal. Cal., 88 (2007) 607.
3 M. M. Mato, S. M. Cebreiro, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 84 (2006) 279.
4 M. M. Mato, M. Illobre, P. V. Verdes and M. I. Paz Andrade, J. Therm. Anal. Cal, 84 (2006) 291.
5 M. M. Mato, S. M. Cebreiro, P. V. Verdes, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 80 (2005) 245.

6 M. M. Mato, S. M. Cebreiro, P. V. Verdes, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 80 (2005) 303.
7 M. M. Mato, S. M. Cebreiro, P. V. Verdes, A. V. Pallas, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 80 (2005) 317.
8 P. V. Verdes, M. M. Mato, J. Salgado, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 80 (2005) 323.
9 P. V. Verdes, M. M. Mato, J. Salgado, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 80 (2005) 329.
10 P. V. Verdes, M. M. Mato, J. Salgado, X. Villaverde, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 80 (2005) 333.
11 P. V. Verdes, M. M. Mato, X. Villaverde, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 80 (2005) 339.
12 M. M. Mato, S. M. Cebreiro, P. V. Verdes, A.V. Pallas, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 80 (2005) 345.
13 P. V. Verdes, M. M. Mato, J. Salgado, J. L. Legido and M. I. Paz Andrade, Fluid Phase Equilib., 232 (2005) 16.
14 P. V. Verdes, M. M. Mato, M. Illobre, S. M. Cebreiro, J. L. Legido and M. I. Paz Andrade, J. Chem. Eng. Data, 49 (2004) 1703.
15 S. M. Cebreiro, M. Illobre, M. M. Mato, P. V. Verdes, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 70 (2002) 251.
16 J. P. E. Grolier, G. C. Benson, Can. J. Chem., 62 (1984) 949.
17 J. A. Riddick, W. B. Bunger and T. K. Sakano, Organic Solvents, Physical Properties and Methods of Purification, 4th Ed., Wiley & Sons, New York 1986, Vol. II.
18 F. Kohler, Monatsh. Chem., 91 (1960) 738.
19 K. T. Jacob and K. Fitzner, Thermochim. Acta, 18 (1977) 197.
20 C. Colinet, Doctoral Thesis, University of Grenoble, France 1967.
21 J. B. Knobeloch and C. E Schwartz, J. Chem. Eng. Data, 7 (1962) 386.
22 C. C. Tsao and J. M. Smith, Chem. Eng. Prog. Symp. Series, 49 (1953) 107.
23 G. W. Toop, Trans. TMS-AIME., 223 (1965) 850.
24 G. Scatchard, L. B. Ticknor, J. R. Goates and E. R. McCartney, J. Am. Chem. Soc., 74 (1952) 3721.
25 M. Hillert, Calphad, 4 (1980) 1.
26 A. R. Mathieson and J. C. Thynne, J. Chem. Soc., (1957) 3713.
27 CRC Handbook of Chemistry and Physics, CRC Press, 84th Ed., (2003–2004).
28 IUPAC, Pure Appl. Chem., 58 (1986) 1677.
29 CRC Handbook of Chemistry and Physics 84th Ed., CRC Press, New York 2004.
30 A. Pal and G. Dass, J. Chem. Eng. Data, 44 (1999) 1325.
31 N. V. Sastry and M. K. Valand, J. Chem. Eng. Data, 43 (1998) 152.
32 TRC Thermodynamic Tables, Thermodynamic Research Center, A&M University, College Station, Texas 1994.
33 A. Rodríguez, J. Canosa and J. Tojo, J. Chem. Eng. Data, 44 (1999) 666.
34 M. T. Lorenzana, J. L. Legido, E. Jiménez, J. Fernández, L. Pías, J. Ortega and M. I. Paz Andrade, J. Chem. Thermodyn., 21 (1989) 1017.
35 J. L. Legido, M. T. Lorenzana, E. Jiménez, J. Fernández, A. Amigo and M. I. Paz Andrade, J. Sol. Chem., 19 (1990) 1095.
36 O. Redlich and A. T. Kister, Ind. End. Chem., 40 (1948) 341.
37 A. J. Treszczanowicz and G. C. Benson, J. Chem. Thermodyn., 9 (1977) 1189.
38 I. Nagata and K. Tamura, J. Chem. Thermodyn., 22 (1990) 279.
39 D. W. Marquardt, J. Soc. Ind. Appl. Math., 2 (1963) 431.
40 P. Bevington, Data Reduction and Error Analysis for the Physical Sciences; McGraw-Hill, New York 1969.

DOI: 10.1007/s10973-007-8759-3