Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 333–337

EXCESS MOLAR VOLUMES FOR METHYL *TERT*-BUTYL ETHER+ 1-PENTANOL+HEPTANE AT 298.15 K

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

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

Densities at 298.15 K have been measured for the ternary mixture methyl *tert*-butyl ether (MTBE)+1-pentanol+heptane and for the involved binary mixtures. Excess molar volumes were calculated from densities. Attending to the symmetry of experimental excess molar volumes, suitable fitting equations have been used in order to correlate adequately the experimental data. Several empirical expressions for estimating ternary properties from experimental binary results.

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

Introduction

Densities and volumes of liquid mixtures are important from both practical and theoretical points of view. In the practical aspect, densities are necessary in a lot of chemical engineering calculations (i.e. dimension of storage deposits, design of condensers and boilers, etc.). From the theoretical point of view, excess volume can be used to study the interactions present in mixtures, such as dispersion forces, hydrogen bonding interactions, etc. The purpose of this work is to report excess molar volumes of $x_1$methyl *tert*-butyl ether (MTBE)+$x_2$1-pentanol+(1–x_1–x_2) heptane, and the involved binary mixtures with the aim of providing data for the characterization of the molecular interactions of these mixtures. This system has been chosen because in the past few years, mixtures of ethers, alkanes, and alkanols have been the object of several investigations [1–4], as these mixtures are of technological importance, since the compounds involved, tertiary-alkyl ethers, either pure or mixed with alkanols, have been recommended as octane blending agents for petrol.

The excess molar volumes at 298.15 K were calculated from density measurements made by using an Anton Paar DMA 4500 densimeter. Attending to the symmetry of the studied mixtures, suitable fitting equations have been used 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. Therefore, the applicability of predictive methods is of great interest for estimating ternary properties from the experimental data of the binaries involved.

Experimental

Materials

MTBE and 1-pentanol were obtained from Aldrich and heptane was supplied by Fluka. The mole fraction purities stated by the manufacturers were better than 0.998, 0.99 and 0.995 for MTBE, 1-pentanol and heptane, respectively. The chemical substances employed were degassed by ultrasound and stored over molecular sieves (Sigma, type 0.4 nm) to remove traces of water.

Apparatus and procedure

The excess molar volumes at 298.15 K and atmospheric pressure were calculated from density measurements, made with an DMA 4500 Anton Paar densimeter. The precision of the densities was $\pm 5 \cdot 10^{-2}$ kg m^{-3}. The temperature inside the vibrating tube was regulated to better than ±0.01 K.

Before each series of measurements the instrument was calibrated at atmospheric pressure with double-distilled and degassed water and heptane. Liquid mixtures were prepared by mass using a precision digital Mettler AT201 balance, with an accuracy of $\pm 1 \cdot 10^{-8}$ kg which leads to an estimated uncertainty in

* Author for correspondence: fapazand@usc.es

1388–6150/$20.00

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

mole fraction of 10^{-4}. 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 molar fractions calculations. The uncertainty in the determination of the excess molar volumes was estimated to better than 1%. All molar quantities are based on the IUPAC relative atomic mass table [5].

Results and discussion

Experimental densities of the pure MTBE, 1-pentanol and heptane are in agreement with the literature values [6–9], as can be seen in Table 1. The results for the excess molar volumes and densities at 298.15 K for the binary mixtures MTBE+1-pentanol, MTBE+heptane and 1-pentanol+heptane are listed in Table 2.

A Redlich–Kister equation [10] was fitted to the excess volume values for the binary systems *x* MTBE+(1–*x*)1-pentanol and *x*MTBE+(1–*x*) heptane:

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

while lower deviations for the mixture *x*1-pentanol+(1–*x*)heptane were obtained by fitting experimental data to the equation suggested by Treszczanowicz–Benson equation [11]:

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

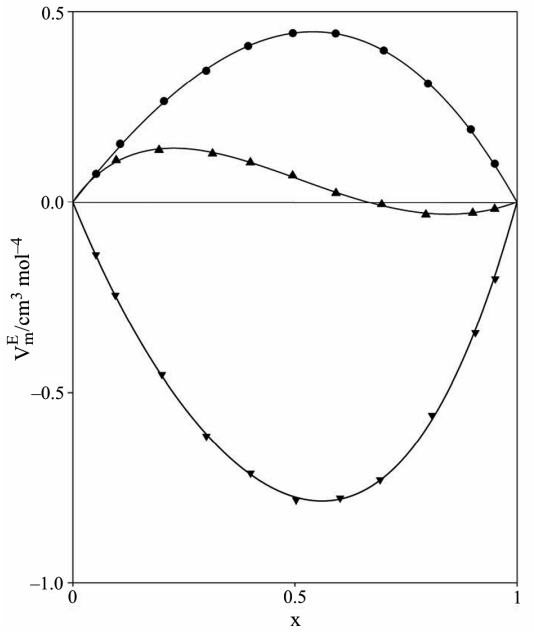

Fig. 1 Excess molar properties of the binary mixtures: ▲ – *x*1-pentanol+(1–*x*)heptane, ● – *x*MTBE+(1–*x*) heptane, ▼ – *x*MTBE+(1–*x*) 1-pentanol

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

Substances	ρ/kg m^{-3}		
	exp.	References	
MTBE	735.61	735.28[a]	735.9[b]
1-pentanol	810.95	810.7[c]	811.1[b]
heptane	679.61	679.46[a]	679.4[d]

[a][6], [b][7], [c][8], [d][9]

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

x	ρ/kg m^{-3}	V_m^E/10^{-6}m^3 mol^{-1}	*x*	ρ/kg m^{-3}	V_m^E/10^{-6} m^3 mol^{-1}	*x*	ρ/kg m^{-3}	V_m^E/10^{-6}m^3 mol^{-1}
				*x*MTBE+(1–*x*)1-pentanol				
0.0522	807.66	–0.1386	0.4000	791.05	–0.7124	0.8087	752.50	–0.5599
0.0960	804.85	–0.2444	0.5028	783.97	–0.7827	0.9063	744.22	–0.3435
0.2007	797.88	–0.4534	0.6018	776.55	–0.7780	0.9510	740.22	–0.2013
0.3008	791.05	–0.6148	0.6920	769.05	–0.7301			
				*x*MTBE+(1–*x*)heptane				
0.0529	681.69	0.0744	0.3951	696.93	0.4102	0.7997	720.63	0.3107
0.1069	683.85	0.1527	0.4954	702.13	0.4439	0.8960	727.48	0.1902
0.2055	688.05	0.2645	0.5920	707.52	0.4433	0.9500	731.59	0.1011
0.3006	692.39	0.3451	0.7001	714.06	0.3982			
				*x*1-pentanol+(1–*x*)heptane				
0.0977	688.79	0.1105	0.4949	734.29	0.0704	0.9001	793.97	–0.0287
0.1943	698.75	0.1371	0.5924	747.40	0.0243	0.9498	802.30	–0.0186
0.3145	712.13	0.1282	0.6954	762.04	–0.0057			
0.3997	722.28	0.1047	0.7948	777.11	–0.0335			

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) heptane

x_1	x_2	ρ/kg m^{-3}	$V^E_{m,123}/10^{-6}$m^3 mol^{-1}	x_1	x_2	ρ/kg m^{-3}	$V^E_{m,123}/10^{-6}$ m^3 mol^{-1}
0.0524	0.0499	686.43	0.1188	0.2914	0.4015	743.15	–0.2440
0.1054	0.0982	693.84	0.1537	0.2859	0.6132	775.18	–0.5073
0.1145	0.1731	702.59	0.1102	0.3903	0.0890	707.80	0.1895
0.1024	0.3022	717.04	0.0368	0.3913	0.1976	721.96	–0.0220
0.1033	0.3801	726.80	–0.0118	0.3987	0.2925	735.59	–0.2074
0.1100	0.4927	742.22	–0.0989	0.3910	0.3976	750.36	–0.3711
0.0922	0.6857	768.93	–0.2094	0.4015	0.4968	766.89	–0.5663
0.1011	0.8011	788.01	–0.2556	0.4938	0.0993	715.26	0.1376
0.1974	0.1041	699.15	0.1648	0.5202	0.1803	728.25	–0.0943
0.1954	0.1935	709.48	0.0757	0.4998	0.2887	742.68	–0.3347
0.2015	0.2910	721.89	–0.0206	0.4909	0.4044	759.91	–0.5592
0.1967	0.3912	734.73	–0.1194	0.5907	0.0980	721.27	–0.0796
0.2003	0.4970	749.84	–0.2334	0.6018	0.1951	736.38	–0.2358
0.2007	0.5997	765.30	–0.3393	0.5904	0.3083	753.10	–0.5274
0.1989	0.6993	780.93	–0.4084	0.6914	0.1008	728.67	–0.0374
0.2934	0.1002	703.79	0.1746	0.6910	0.2087	745.50	–0.4143
0.2966	0.1891	714.93	0.0409	0.8093	0.0930	736.21	–0.1610
0.2959	0.2946	728.57	–0.0954	0.9005	0.0489	736.03	–0.0932

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

	A_1	A_2	A_3	A_4	A_5	σ
			xMTBE+(1–x)1-pentanol			
$V^E_m/10^{-6}$ m^3 mol^{-1}	–3.1007	–0.6851	–0.4388	—	—	0.007
			xMTBE+(1–x)heptane			
$V^E_m/10^{-6}$ m^3 mol^{-1}	1.7791	0.2940	—	—	—	0.003
			x1-pentanol+(1–x)heptane			
$V^E_m/10^{-6}$ m^3 mol^{-1}	1.9474	–2.3892	—	—	—	0.003
	B_0	B_1	B_2	B_3	B_4	σ
			x_1MTBE+$x_2$1-pentanol+$x_3$heptane			
$V^E_{m,123}/10^{-6}$ m^3 mol^{-1}	–8.6428	7.2222	17.3998	–7.0637	–16.4185	0.005

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

$$V^E_{m,123} = V^E_{12} + V^E_{13} + V^E_{23} + x_1x_2x_3\Delta_{123} \quad (3)$$

where V^E_{ij} is the binary contribution for each *ij* binary mixture, x_3=1–x_1–x_2, and $x_1x_2x_3\cdot\Delta_{123}$ is ternary contribution which was correlated using the expression suggested Nagata and Tamura [12].

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

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 [13]. The number of parameters used in Eqs (1), (2) and (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 [14].

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

The ternary mixture shows maximum values at x_1=0.5405, x_3=0.4595, $V^E_{m,123}$= 0.4480 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}. Figure 2a shows that the magnitude present an isoline of ideal behavior. The

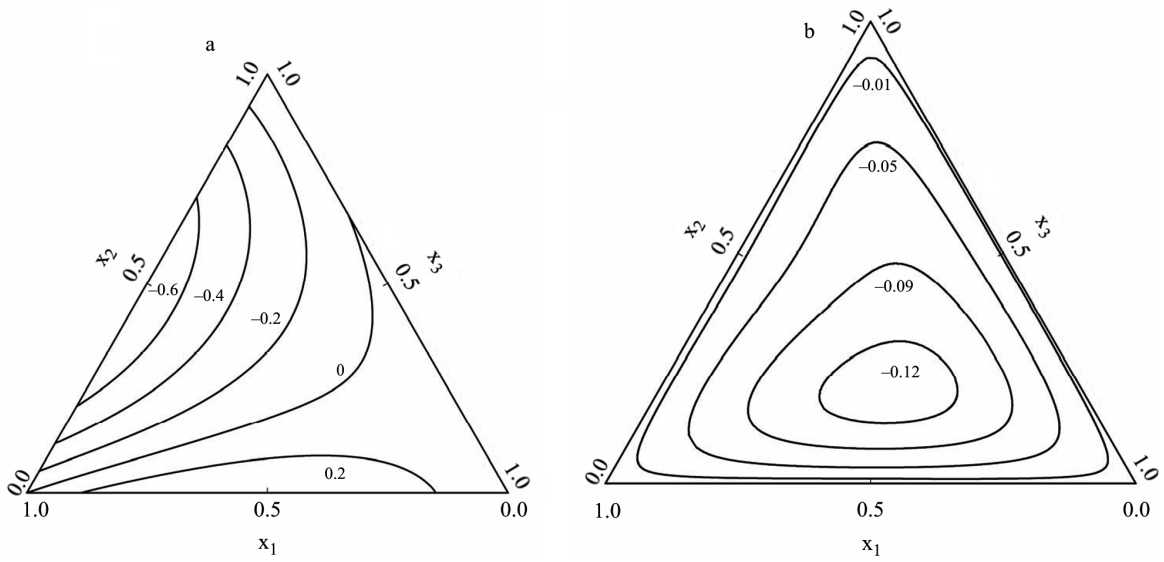

Fig. 2 a – Isolines of $V^{E}_{m,123}$/cm^3 mol^{-1}, for the ternary system x_1MTBE+$x_2$1-pentanol+$x_3$hexane at 298.15 K, calculated with Eq. (4), b – curves of constant ternary contribution, $x_1x_2x_3\Delta_{123}$, to the excess molar volume $V^{E}_{m,123}$/cm^3 mol^{-1}, calculated with Eq. (5)

Table 5 Standard deviations between experimental and empirical predictive values. For the asymmetric equations three numberings of the components have been compared, in this order, 123, 231, 312

	σ/ 10^{-6} m^3 mol^{-1}		
Kohler		0.057	
Jacob–Fitner		0.058	
Colinet		0.057	
Knobeloch–Schwartz		0.041	
Tsao–Smith	0.077[a]	0.120[b]	0.069[c]
Toop	0.066[a]	0.061[b]	0.044[c]
Scatchard	0.085[a]	0.061[b]	0.045[c]
Hillert	0.065[a]	0.061[b]	0.041[c]
Mathieson–Thynne	0.083[a]	0.060[b]	0.051[c]

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

negative region in the ternary diagrams is probably ascribable to the intermolecular OH–O bonds created between 1-pentanol and MTBE molecules. The ternary contribution to the excess molar volume is relevant (Fig. 2b). It is negative over the whole range of composition, showing minimum values about –0.131 cm^3 mol^{-1} at x_1=0.3550, x_2=0.2050, x_3=0.4320.

Experimental values were used to test several empirical equations [15–23] 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 [15], Jacob and Fitzner [16], Colinet [17], Knobeloch and Schwartz [18], Tsao and Smith [19], Toop [20], Scatchard *et al*. [21], Hillert [22] and Mathieson and Thynne [23] were applied to estimate ternary properties from binary results. The standard deviations between experimental 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.

Acknowledgements

This work was supported by Xunta de Galicia (XUGA PGIDT99PXI30103B).

References

1 A.Rodriguez, J. Canosa and J. Tojo, J. Chem. Eng. Data, 44 (1999) 666.
2 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.

3 B. E. de Cominges, M. M. Piñeiro, E. Mascato, L. Mosteiro, T. P. Iglesias and J. L. Legido. J. Therm. Anal. Cal., 72 (2003) 129.
4 I. Gascón, V. Rodríguez, P. Cea, C. Lafuente and M. C. López, J. Therm. Anal. Cal., 76 (2004) 429.
5 IUPAC, Pure and Appl. Chem., 58 (1986) 1677.
6 CRC Handbook of Chemistry and Physics, 84th Ed., CRC Press, New York 2004.
7 A. Pal and G. Dass, J. Chem. Eng. Data, 44 (1999) 1325.
8 N. V. Sastry and M. K. Valand, J. Chem. Eng. Data, 43 (1998) 152.
9 B. Orge, M. Iglesias, A. Rodríguez, J. M. Canosa and J. Tojo, Fluid Phase Equilib., 133 (1997) 213.
10 O. Redlich and A. Kister, T. Ind. Eng. Chem., 40 (1948) 345.
11 A. J. Treszczanowicz and G. C. Benson, J. Chem. Thermodyn., 9 (1977) 1189.
12 I. Nagata and K. Tamura, J. Chem. Thermodyn., 22 (1990) 279.
13 D. W. Marquardt, J. Soc. Ind. Appl. Math., 2 (1963) 431.
14 P. Bevington, Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill, New York 1969.
15 F. Kohler, Monatsh. Chem., 91 (1960) 738.
16 K. T. Jacob and K. Fitzner, Thermochim. Acta, 18 (1977) 197.
17 C. Colinet, Thesis University of Grenoble, France 1967.
18 J. B. Knobeloch and C. E. Schwartz, J. Chem. Eng. Data, 7 (1962) 386.
19 C. C. Tsao and J. M. Smith, Chem. Eng. Prog. Symp. Series, 49 (1953) 107.
20 G. W. Toop, Trans. TMS-AIME, 223 (1965) 850.
21 G. Scatchard, L. B.Ticknor, J. R.Goates and E. R. McCartney, J. Am. Chem. Soc., 74 (1952) 3721.
22 M. Hillert, Calphad, 4 (1980) 1.
23 A. R. Mathieson and J. C. Thynne,. J. Chem. Soc., (1957) 3713.