Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 1, 185–189

EXCESS ENTHALPIES OF TERNARY MIXTURE CONSISTING OF *tert*-BUTYL METHYL ETHER, ETHANOL AND HEPTANE

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

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

Excess molar enthalpies, measured at 298.15 K in a Calvet microcalorimeter, are reported for {x_1*tert*-butyl methyl ether (MTBE)+$x_2$ethanol (EtOH)+($1-x_1-x_2$)heptane}. Smooth representations of the results are presented and used to construct constant excess molar enthalpy contours on Roozeboom diagrams.

Keywords: *ethanol (EtOH), excess enthalpy, heptane, ternary mixture, tert-butyl methyl ether (MTBE)*

Introduction

Mixtures of alkanols and ethers are of interest due to the complex structure resulting from the partial replacement of alcohol-alcohol interactions by alcohol-ether OH–O bonds. Complexity is increased when the mixture also contains one or more alkanes. The thermophysical properties of such mixtures are important in the petrochemical industry because ethers, alkanes and alkanols can all be present in lead-free gasoline as oxygenating agents.

As an extension of our work on the excess thermodynamic properties of binary and ternary mixtures consisting of MTBE, alkanols and alkanes [1–14], we report experimental data of excess molar enthalpies at 298.15 K and atmospheric pressure for the ternary system {x_1MTBE+x_2EtOH+($1-x_1-x_2$)heptane}.

Experimental

MTBE and EtOH were the same as used in our previous works [1, 3]. Heptane, supplied by Fluka (purity >99.5%), was dried using Union Carbide 0.4 nm molecular sieves. Its density, measured at 298.15 K in an Anton Paar DMA 4500 densimeter, was 0.6796 g cm^{-3}, in reasonable agreement with the literature values.

Excess molar enthalpies were determined in a Calvet microcalorimeter having a calorimeter-cell volume of approximately 10 cm^3. A Philips PM2535 multimeter and a data acquisition system were linked to the microcalorimeter. Calibration was performed electrically using a Setaram EJP30 stabilized current source. Details of the equipment and the operation procedure have been described previously [15, 16].

Several measurements were carried out for the ternary compositions resulting from adding heptane to a binary mixture composed of {x_1'MTBE+ x_2'EtOH}. The excess molar enthalpy $H^E_{m,123}$ was determined for several pseudo-binary systems in which component 3 (heptane) was added to a binary mixture of component 1 (MTBE) and component 2 (EtOH), having a fixed mole ratio x_1/x_2. Thus, the ternary excess molar enthalpy at the pseudo-binary composition x_1, x_2, ($x_3=1-x_1-x_2$) can be expressed as

$$H^E_{m,123}=H^E_{m,\varphi}+(x_1+x_2)H^E_{m,12} \qquad (1)$$

where $H^E_{m,\varphi}$ is the measured excess molar enthalpy for the pseudo-binary mixture and $H^E_{m,12}$ is the excess molar enthalpy of the initial binary {x_1'MTBE+x_2'EtOH}. Values of $H^E_{m,12}$ at three mole fractions were interpolated by using a spline-fit method.

Results and discussion

Experimental excess molar enthalpies H^E_m for the two binary mixtures {xEtOH+($1-x$)heptane} and {xMTBE+($1-x$)heptane} are summarized in Table 1. {xMTBE+($1-x$)heptane} data were fitted to the variable-degree polynomials suggested by Redlich–Kister [17]

$$H^E_m/\text{J mol}^{-1}=x(1-x)\sum_{i=1}^{n}A_i(2x-1)^{i-1} \qquad (2)$$

while lower deviations for the mixture {xEtOH+($1-x$)heptane} were obtained by fitting ex-

---

[*] Author for correspondence: fapazand@usc.es

1388–6150/$20.00

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

Table 1 Excess molar enthalpies, H^E_m, of the binary systems at the temperature 298.15 K

x	H^E_m/J mol^{-1}	x	H^E_m/J mol^{-1}	x	H^E_m/J mol^{-1}	x	H^E_m/J mol^{-1}
				xEtOH+(1–x)heptane			
0.0741	400	0.4171	650	0.7749	452	0.9509	145
0.1184	474	0.4456	649	0.8211	394	0.9790	73
0.1685	544	0.5383	629	0.8652	326		
0.2700	623	0.5991	586	0.8908	278		
0.3685	654	0.7309	500	0.9208	220		
				xMTBE+(1–x)heptane			
0.0799	119	0.4234	360	0.6829	338	0.9086	145
0.1029	155	0.4400	363	0.7309	317	0.9537	82
0.1441	204	0.5585	370	0.7485	307		
0.2989	316	0.6117	364	0.7919	268		
0.3471	342	0.6491	352	0.8487	218		

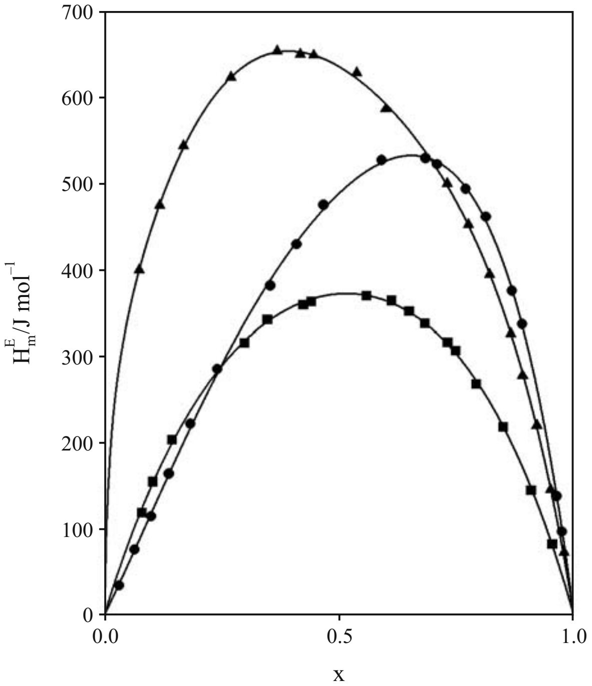

Fig. 1 Excess molar enthalpies H^E_m/J mol^{-1} at 298.15 K of the three involved binary systems.
● – {xMTBE+(1–x)EtOH} from [3];
■ – {xMTBE+(1–x)heptane} – fitted by Eq. (2);
▲ – {xEtOH+(1–x)heptane – fitted by Eq. (3)

perimental data to the equation suggested by Myers–Scott [18]

$$H^E_m/\text{J mol}^{-1}=\frac{x(1-x)}{1+k(1-x)}\sum_{i=1}^{n}A_i(2x-1)^{i-1} \qquad (3)$$

Values of the coefficients A_i and k are listed in Table 2, along with the standard deviation s for each representation. Previously, we report the excess molar enthalpy for the other constituent binary mixture {xMTBE+(1–x)EtOH} [3].

Table 2 Fitting parameters, k, A_i for Eqs (2) and (3) and standard deviations, s

A_1	A_2	A_3	A_4	A_5	A_6	k	s
			xMTBE+(1–x)EtOH[a]				
1955	1034	698	510	0	0		4
			xMTBE+(1–x)heptane				
1489	72	354					3
			xEtOH+(1–x)heptane				
2542	1848	657	1131	430		0.9778	4

[a] Fitting parameters were taken from [3]

The experimental results and their representations by Eqs (2) or (3) are plotted in Fig. 1.

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

$$H^E_{m,123}/\text{J mol}^{-1}=H^E_{m,bin}+x_1x_2(1-x_1-x_2)\Delta_{123} \qquad (4)$$

where

$$H^E_{m,bin}=H^E_{m,12}+H^E_{m,13}+H^E_{m,23} \qquad (5)$$

is known as the binary contribution to the excess ternary enthalpy, and $H^E_{m,ij}$ are given by Eq. (2) or Eq. (3).

The form

$$\frac{\Delta_{123}}{RT}=\frac{B_0+B_1x_1+B_2x_2+B_3x_1^2+B_4x_2^2+B_5x_1x_2+}{1+(x_2-x_3)}$$
$$\frac{+B_6x_1^3+B_7x_2^3+B_8x_2x_1^2+\dots}{1+(x_2-x_3)} \qquad (6)$$

Table 3 Experimental excess molar enthalpies, $H^E_{m,123}$, at the temperature 298.15 K for the ternary mixture: x_1MTBE+x_2EtOH+(1–x_1–x_2)heptane[a]

x_1	x_2	$H^E_{m,\varphi}$/J mol^{-1}	$H^E_{m,123}$/J mol^{-1}	x_1	x_2	$H^E_{m,\varphi}$/J mol^{-1}	$H^E_{m,123}$/J mol^{-1}
			x_1'=0.2391, $H^E_{m,12}$=279 J mol^{-1}				
0.2316	0.7370	95	365	0.1564	0.4976	576	758
0.2238	0.7121	174	435	0.1489	0.4739	592	766
0.2148	0.6835	254	505	0.1270	0.4040	645	793
0.2046	0.6510	327	565	0.1098	0.3493	659	787
0.1928	0.6134	408	633	0.0796	0.2532	617	710
0.1846	0.5873	465	680	0.0557	0.1773	571	636
0.1702	0.5415	521	719	0.0284	0.0905	468	501
			x_1'=0.4966, $H^E_{m,12}$=487 J mol^{-1}				
0.4775	0.4841	577	109	0.2881	0.2921	891	609
0.4603	0.4667	631	180	0.2389	0.2421	871	637
0.4381	0.4441	701	271	0.2016	0.2044	839	641
0.4134	0.4191	759	353	0.1852	0.1878	816	635
0.4005	0.4060	788	395	0.0975	0.0988	611	515
0.3751	0.3803	827	459	0.0601	0.0609	478	419
0.3482	0.3529	852	510				
			x_1'=0.7521, $H^E_{m,12}$=507 J mol^{-1}				
0.7185	0.2368	97	581	0.4404	0.1452	549	846
0.6855	0.2260	179	641	0.3931	0.1296	576	841
0.6461	0.2130	268	703	0.3444	0.1135	582	814
0.6034	0.1989	351	757	0.2844	0.0938	564	755
0.5693	0.1877	398	781	0.1788	0.0589	487	607
0.5357	0.1766	427	788	0.1278	0.0421	401	487
0.5035	0.1660	475	814				

[a]Three experimental series of measurements were carried out for the ternary compositions resulting from adding heptane to a binary mixture composed of {x_1'MTBE+x_2'EtOH}, where $x_2'=1-x_1'$

Table 4 Fitting parameters, B_i , for Eq. (6) and standard deviation, s

				x_1MTBE+x_2EtOH+$x_3$heptane				
B_0	B_1	B_2	B_3	B_4	B_5	B_6	B_7	s
2.5068	6.6051	–11.3088	–11.5739	27.3393	0	7.9913	–18.9989	8

was adopted for the ternary term $x_1x_2(1–x_1–x_2)\Delta_{123}$ [13].

B_i parameters were calculated by an unmass least-squares method using a non-linear optimization algorithm due to Marquardt [19]. These parameters and the corresponding standard deviation are included in Table 4.

Figure 2 shows the pseudo-binary representation of the experimental values measured of the $H^E_{m,123}$, together with the correlated curves, where Eq. (6) was applied to fit the ternary contribution.

The lines of constant ternary excess molar enthalpy, $H^E_{m,123}$ calculated using Eq. (4) are plotted in Fig. 3a. Figure 3b represents the ternary contribution, $x_1x_2(1–x_1–x_2)\Delta_{123}$, to the excess molar enthalpy correlated with Eq.(6).

The excess molar enthalpy of the ternary system is positive over the whole range of composition, reaching its maximum value, x_1=0.3270, x_2=0.2510, x_3=0.4220, $H^E_{m,123}$=894 J mol^{-1}.

The ternary contribution to $H^E_{m,123}$ is likewise positive, with a maximum value of 260 J mol^{-1} x_1=0.3390, x_2=0.1460, x_3=0.2510. Thus about a 29% of the value of the total ternary excess molar enthalpy is attributable to three-way interactions among the self-associating alkanol, MTBE and the non-polar alkane.

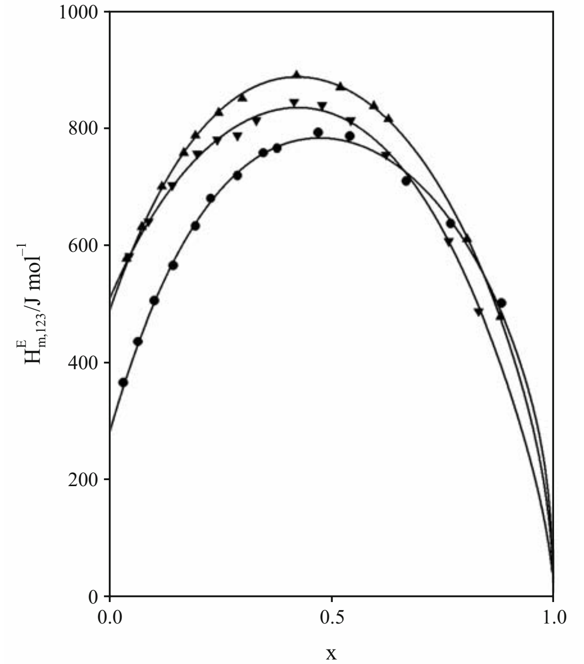

Fig. 2 Pseudo-binary representation of ternary excess molar enthalpies $H^{E}_{m,123}$/J mol^{-1} for {(1–x)(x'_1MTBE+x'_2EtOH)+$x$heptane} at 298.15 K: ● – x'_1=0.2391, x'_2=0.7609; ▲ – x'_1=0.4966, x'_2=0.5034, ▼ – x'_1=0.7521, x'_2=0.2479 – correlated using Eq. (4)

Experimental excess molar enthalpies are positive for all binary systems studied over the whole composition range. It can be qualitatively explained with a net destruction, in the mixing process, of the structural order present in the pure liquids (hydrogen bonding, dipolar interaction, and orientational order).

In previous papers, we have measured the excess molar enthalpies of mixtures MTBE+ethanol+*n*-alkane (*n*-hexane [3], *n*-octane [1]) and now, we report experimental data of MTBE+ethanol+*n*-heptane. In MTBE+ethanol+*n*-alkane systems, H^{E}_{m} increases as the chain length of the alkane increases. During the mixing process, the existing order in the *n*-alkanes disrupts, and contributes positively to H^{E}. This contribution is more important for longer *n*-alkanes (Patterson's effect).

The curve for {xMTBE+(1–x) heptane} is symmetrical, while those of the other two binaries are asymmetrical, that of {xMTBE+(1–x)ethanol} peaking at MTBE-rich compositions and that of {x ethanol+(1–x)heptane} at heptane-rich compositions. Both these asymmetries can be interpreted as reflecting the strength of ethanol–ethanol hydrogen bonds in comparison with other interactions in the mixture.

Recent works from our laboratory have reported measurements of excess molar enthalpies of the ternary mixtures: MTBE+alkanol (ethanol [1], propanol [6], pentanol [12])+octane. In these cases, $H^{E}_{m,123}$ increases when passing from ethanol to propanol, and then decreases for 1-pentanol. In MTBE+alkanols systems, similar behavior is observed. H^{E}_{m} increases as the alkyl chain length of the 1-alkanol increases, from methanol to 1-propanol, and then it is slowly decreased. This may be because the decrease in alcohol-alcohol interactions is balanced by weaker interactions between the OH groups and O atoms.

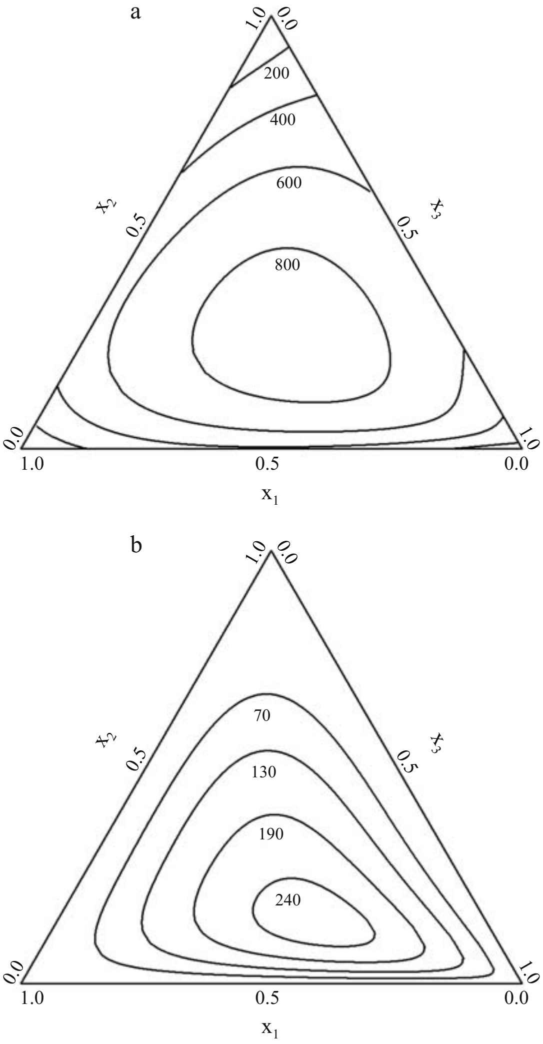

Fig. 3 Representation for {x_1MTBE+x_2 EtOH+(1–x_1–x_2) heptane} at 298.15 K. a – Curves of constant ternary excess molar enthalpy, $H^{E}_{m,123}$/J mol^{-1}, b – Curves of constant ternary contribution, $x_1x_2(1-x_1-x_2)\Delta_{123}$, to the excess molar enthalpy $H^{E}_{m,123}$/J mol^{-1}, calculated with Eq. (6)

Acknowledgements

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

References

1 M. M. Mato, M. Illobre, P. V. Verdes, J. L. Legido, E. Jimenez and M. I. Paz Andrade, J. Therm. Anal. Cal., 88 (2007) 607.

2 P. V. Verdes, M. M. Mato, E. Jimenez, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 89 (2007) 73.

3 M. M. Mato, M. Illobre, P. V. Verdes and M. I. Paz Andrade, J. Therm. Anal. Cal., 84 (2006) 291.

4 M. M. Mato, S. M. Cebreiro, P. V. Verdes, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 80 (2005) 245.

5 M. M. Mato, S. M. Cebreiro, P. V. Verdes, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 80 (2005) 303.

6 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.

7 P. V. Verdes, M. M. Mato, J. Salgado, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 80 (2005) 323.

8 P. V. Verdes, M. M. Mato, J. Salgado, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 80 (2005) 329.

9 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.

10 P. V. Verdes, M. M. Mato, X. Villaverde, J. L. Legido and M. I. Paz Andrade, J. Therm. Anal. Cal., 80 (2005) 339.

11 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.

12 P. V. Verdes, M. M. Mato, J. Salgado, J. L. Legido and M. I. Paz Andrade, Fluid Phase Equilib., 232 (2005) 16.

13 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.

14 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.

15 M. I. Paz Andrade, Les Développements Récents de la Microcalorimétrie et de la Thermogenèse, 1st Ed., CRNS, Paris 1967.

16 M. I Paz Andrade, S. Castromil and M. C. Baluja, J. Chem. Thermodyn., 2 (1970) 775.

17 O. Redlich and A. Kister, T. Ind. Eng. Chem., 40 (1948) 345.

18 D. B. Myers and R. L. Scott, Ind. Eng. Chem., 55 (1963) 43.

19 D. W. Marquardt, J. Soc. Ind. Appl. Math., 2 (1963) 431.

DOI: 10.1007/s10973-007-8760-x