

EXCESS MOLAR ENTHALPIES OF THE TERNARY SYSTEM MTBE+ETHANOL+HEXANE

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Excess molar enthalpies of the ternary mixture $\{x_1 \text{ tert-butyl methyl ether (MTBE)} + x_2 \text{ ethanol} + (1-x_1-x_2) \text{ hexane}\}$ and, the involved binary mixtures $\{x \text{ tert-butyl methyl ether (MTBE)} + (1-x) \text{ ethanol}\}$, $\{x \text{ tert-butyl methyl ether (MTBE)} + (1-x) \text{ hexane}\}$ and $\{x \text{ ethanol} + (1-x) \text{ hexane}\}$ have been measured at 298.15 K and atmospheric pressure, over the whole composition range, using a Calvet microcalorimeter. The results were fitted by means of different variable degree polynomials.

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

Introduction

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. The properties studied have proved to be meaningful from the thermodynamic point of view, as they provide 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.

Forming 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 [1–11].

Several H_m^E data have been published in the literature for MTBE+n-alkane at 298.15 K and atmospheric pressure [12–14]. Wang *et al.* [13] have measured H_m^E of MTBE+hexane.

The group of literature referring to the binary system ethanol+(1-x) hexane is very large. The obtained experimental values are compared with the most recent literature values measured by Wang *et al.* [15]. Data from the binary system MTBE+ethanol are also presented in the literature [11, 14, 16, 17]. Zhu *et al.* [18] have published $H_{m,123}^E$ data from the ternary system x_1 MTBE+ x_2 ethanol+ x_3 hexane at 298.15 K.

Experimental

The sources and purities of the chemicals substances employed were: MTBE (Aldrich >99.8%), ethanol (Scharlau >99.8%), hexane (Fluka >99.5%). Before measurements, all liquids 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.

The experimental excess molar enthalpies were measured using a Calvet microcalorimeter equipped with a device allowing operation in the absence of vapor phase, and having a calorimeter-cell volume of approximately 10 cm³. A Philips PM2535 multimeter and a data acquisition system were linked to the microcalorimeter. Calibration was performed electrically using a Setaram EJP30 stabilised current source. Further details about the experimental method of operation have been published [19, 20]. The apparatus and procedures were tested by determining excess enthalpies for the standard system hexane+cyclohexane at 298.15 K. The uncertainty in excess molar enthalpy measurements is estimated to be better than 1%.

Several experimental series of measurements were carried out for the ternary compositions resulting from adding hexane to a binary mixture composed of $\{x'_1 \text{ MTBE} + x'_2 \text{ ethanol}\}$. The ternary composition point is then a pseudo-binary mixture composed by addition of hexane and the mentioned binary mixture. 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

$$H_{m,123}^E = H_{m,\phi}^E + (x_1 + x_2)H_{m,12}^E \quad (1)$$

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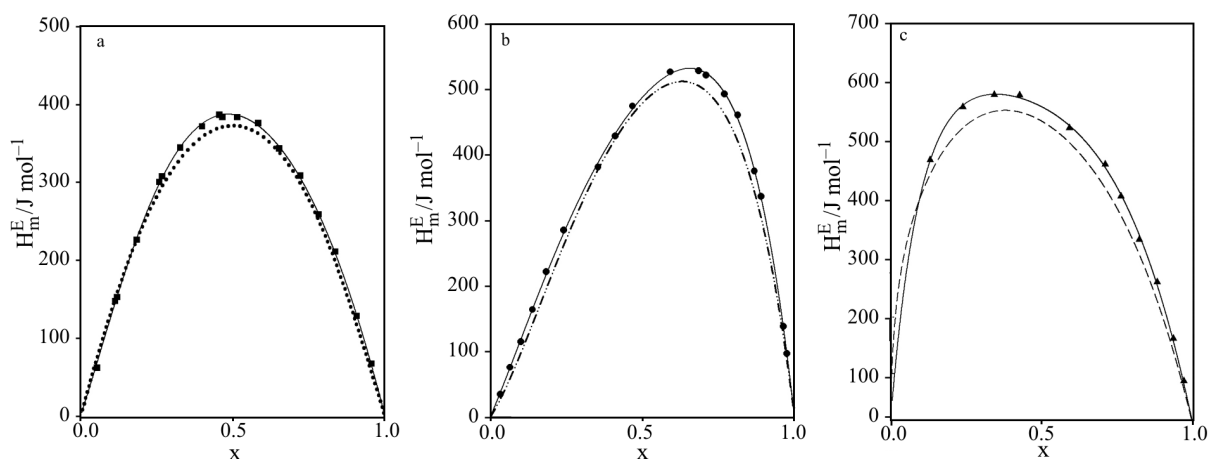


Fig. 1 Excess molar enthalpies $H_m^E/\text{J mol}^{-1}$ at 298.15 K of the three involved binary systems. a – ■ $\{x \text{ MTBE}+(1-x) \text{ hexane}\}$ — fitted by Eq. (2), ... from [13], b – ● $\{x \text{ MTBE}+(1-x) \text{ ethanol}\}$ — fitted by Eq. (2), --- from [14], c – ▲ $\{x \text{ 1-ethanol}+(1-x) \text{ hexane}\}$ — fitted by Eq. (3), --- from [15]

where $H_{m,\phi}^E$ is the measured excess molar enthalpy for the pseudo-binary mixture, and $H_{m,12}^E$ is the excess molar enthalpy of the initial binary $\{x'_1 \text{ MTBE}+x'_2 \text{ ethanol}\}$. Values of $H_{m,12}^E$ at three mole fractions were interpolated by using a spline-fit method. Equation (1) does not involve any approximation.

Results and discussion

The experimental values of H_m^E , listed in Table 1, corresponding to the binary mixtures $\{x \text{ tert-butyl methyl ether (MTBE)}+(1-x) \text{ 1-ethanol}\}$, $\{x \text{ tert-butyl methyl ether (MTBE)}+(1-x) \text{ hexane}\}$ were fitted to the variable-degree polynomials suggested by Redlich-Kister [21],

$$H_m^E / \text{J mol}^{-1} = x(1-x) \sum_{i=1}^n A_i (2x-1)^{i-1} \quad (2)$$

while lower deviations for the mixture $\{x \text{ 1-ethanol}+(1-x) \text{ hexane}\}$ were obtained by fitting experimental data to the equation suggested by Myers-Scott [22]

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

The parameters k, A_i , shown in Eqs (2) and (3), have been obtained by a fitting computer program which uses the least squares procedure and a Marquardt algorithm [23]. The number of parameters used was determined by applying the optimization F test [24]. These parameters and the standard devia-

Table 1 Excess molar enthalpies, H_m^E , of the binary systems at the temperature 298.15 K

x	$H_m^E/\text{J mol}^{-1}$	x	$H_m^E/\text{J mol}^{-1}$	x	$H_m^E/\text{J mol}^{-1}$	x	$H_m^E/\text{J mol}^{-1}$
$x \text{ MBTE}+(1-x) \text{ ethanol}$							
0.0323	34	0.2411	285	0.6843	529	0.8902	337
0.0647	76	0.3538	382	0.7090	522	0.9628	138
0.1002	115	0.4098	429	0.7699	494	0.9748	97
0.1382	164	0.4671	475	0.8130	461		
0.1837	222	0.5910	527	0.8680	376		
$x \text{ MBTE}+(1-x) \text{ hexane}$							
0.0527	61	0.2668	305	0.5142	380	0.8361	209
0.1125	146	0.3262	341	0.5827	373	0.9066	127
0.1191	151	0.3985	369	0.6520	341	0.9551	67
0.1837	224	0.4549	383	0.7215	306		
0.2577	298	0.4648	381	0.7818	257		
$x \text{ 1-ethanol}+(1-x) \text{ hexane}$							
0.1325	481	0.4266	597	0.7595	416	0.9323	163
0.2401	575	0.5897	538	0.8198	339	0.9665	87
0.3432	597	0.7077	473	0.8782	263		

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
			x MTBE+(1-x) ethanol				
1955	1034	698	510	0	0		4
			x MTBE+(1-x) hexane				
1534	-97	0	257	-166			3
			x ethanol+(1-x) hexane				
2301	927	1054	0			0.6471	6

tions for H_m^E of the three binary mixtures involved in this ternary system are presented in Table 2.

The experimental results, their representations by Eqs (2) or (3) and bibliography data [13–15] are plotted in Fig. 1.

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

$$H_{m,123}^E / \text{J mol}^{-1} = H_{m,\text{bin}}^E + x_1 x_2 (1 - x_1 - x_2) \Delta_{123} \quad (4)$$

where

$$H_{m,\text{bin}}^E = H_{m,12}^E + H_{m,13}^E + H_{m,23}^E \quad (5)$$

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

The form,

$$\frac{\Delta_{123}}{RT} = \frac{B_0 + B_1 x_1 + B_2 x_2 + B_3 x_1^2 + B_4 x_2^2 + B_5 x_1 x_2 + B_6 x_1^3 + B_7 x_2^3 + B_8 x_2 x_1^2 + \dots}{1 + (x_2 - x_3)} \quad (6)$$

was adopted for the ternary term $x_1 x_2 (1 - x_1 - x_2) \Delta_{123}$ [10].

The B_i parameters were calculated by an unweight least-squares method using a non-linear optimization algorithm due to Marquardt [23]. These

Table 3 Experimental excess molar enthalpies, $H_{m,123}^E$, at the temperature 298.15 K for the ternary mixture: x_1 MTBE+ x_2 ethanol+(1- x_1 - x_2) hexane^a

x_1	x_2	$H_{m,q}^E / \text{J mol}^{-1}$	$H_{m,123}^E / \text{J mol}^{-1}$	x_1	x_2	$H_{m,q}^E / \text{J mol}^{-1}$	$H_{m,123}^E / \text{J mol}^{-1}$
$x_1^t = 0.2451, H_{m,12}^E = 285 \text{ J mol}^{-1}$							
0.2352	0.7243	105	379	0.1458	0.4491	573	743
0.2260	0.6959	182	445	0.1580	0.4864	535	718
0.2179	0.6709	253	507	0.1037	0.3194	604	725
0.2088	0.6431	312	555	0.0887	0.2733	601	704
0.1976	0.6086	373	603	0.0269	0.0827	420	452
$x_1^t = 0.4966, H_{m,12}^E = 487 \text{ J mol}^{-1}$							
0.4742	0.4806	112	577	0.3394	0.3440	466	799
0.4574	0.4636	176	625	0.2579	0.2614	531	784
0.4374	0.4433	244	673	0.2128	0.2157	544	753
0.4039	0.4094	348	744	0.1647	0.1669	540	701
0.3746	0.3796	415	783	0.0934	0.0947	483	574
0.3519	0.3567	433	778	0.0572	0.0580	383	439
$x_1^t = 0.7558, H_{m,12}^E = 505 \text{ J mol}^{-1}$							
0.7205	0.2328	92	573	0.3618	0.1169	518	759
0.6859	0.2216	176	633	0.3222	0.1041	517	732
0.6329	0.2045	269	692	0.2739	0.0885	513	696
0.5885	0.1901	346	739	0.2193	0.0708	489	635
0.5630	0.1819	386	762	0.1590	0.0514	421	527
0.5201	0.1680	420	767	0.1111	0.0359	367	441
0.4722	0.1525	464	780	0.0873	0.0282	313	371

^aThree experimental series of measurements were carried out for the ternary compositions resulting from adding hexane to a binary mixture composed of $\{x_1^t \text{ MTBE} + x_2^t \text{ ethanol}\}$, where $x_2^t = 1 - x_1^t$

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

x_1 MTBE+ x_2 ethanol+ x_3 hexane								
B_0	B_1	B_2	B_3	B_4	B_5	B_6	B_7	s
4.1241	-7.1755	-19.5740	22.0987	54.1322	0.3925	-14.6181	-41.3734	7

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 $H_{m,123}^E$, together with the correlated curves, where Eq. (6) was applied to fit the ternary contribution.

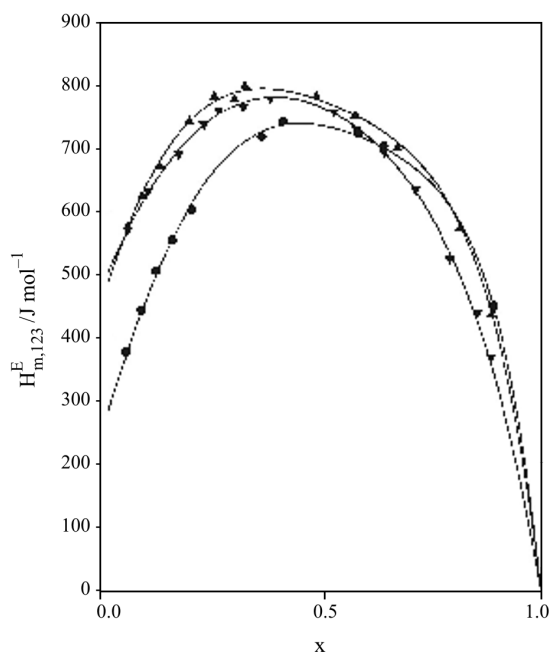


Fig. 2 Pseudo-binary representation of ternary excess molar enthalpies $H_{m,123}^E/\text{J mol}^{-1}$ for $\{(1-x)(x_1'$ MTBE+ x_2' ethanol)+ x hexane $\}$ at 298.15 K: ● - $x_1'=0.2451$, $x_2'=0.7549$, ▲ - $x_1'=0.4966$, $x_2'=0.5034$, ▼ - $x_1'=0.7558$, $x_2'=0.2442$, — correlated using Eq. (4)

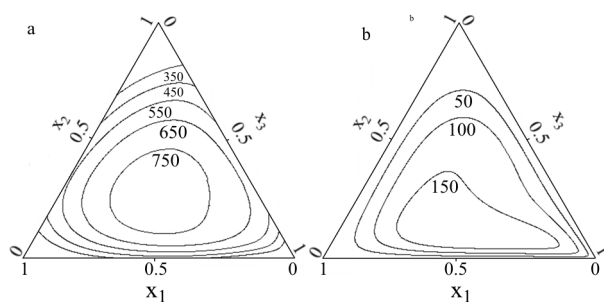


Fig. 3 Representation for $\{x_1$ MTBE+ x_2 ethanol+ $(1-x_1-x_2)$ hexane $\}$ at 298.15 K of a - curves of constant ternary excess molar enthalpy, $H_{m,123}^E/\text{J mol}^{-1}$, b - curves of constant ternary contribution, $x_1 x_2 (1-x_1-x_2) \Delta_{123}$, to the excess molar enthalpy $H_{m,123}^E/\text{J mol}^{-1}$, calculated with Eq. (6)

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

Conclusions

The experimental excess molar enthalpies H_m^E are positive for all binary systems studied over the whole composition range. This suggests the predominance of the breaking of previous interactions over the formation of new interactions during the mixing process.

The curve for the binary system $\{x$ *tert*-butyl methyl ether (MTBE)+ $(1-x)$ hexane $\}$ is symmetrical. Nevertheless, the obtained curve for $\{x$ *tert*-butyl methyl ether (MTBE)+ $(1-x)$ ethanol $\}$, is slightly asymmetric, with their maximum shifted around the rich compositions in MTBE. The binary system $\{x$ ethanol+ $(1-x)$ hexane $\}$ is asymmetric, with its maximum displaced toward a high mole fraction of hexane. This displacement can be interpreted on basis of the rupture of hydrogen bonds present on the pure alkanol. At those compositions, the rupture of hydrogen bonds reaches its maximum and it is not compensated by new possible interactions established during the mixing process.

Excess molar enthalpy for the ternary system is positive over the whole range of composition, showing maximum values at $x_1=0.3960$, $x_2=0.2490$, $x_3=0.3550$, $H_{m,123}^E=802 \text{ J mol}^{-1}$. It is about 3% lower than the maximum value obtained by S. Zhu *et al.* [18] ($x_1=0.3407$, $x_2=0.2659$, $H_{m,123}^E=829 \text{ J mol}^{-1}$).

The ternary contribution is also positive, and has a maximum value at $x_1=0.43530$, $x_2=0.1150$, $x_3=0.4320$, $H_{m,123}^E=202 \text{ J mol}^{-1}$. This value is about 25% of the value of the ternary enthalpy itself. That means ternary contribution is very important and can be attributed to crossed energetic interactions between the associated compound (the hydroxyl group in the alkanol molecule), the molecule of MTBE and the non polar alkane.

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References

- 1 M. M. Mato, S. M. Cebreiro, P. V. Verdes, J. L. Legido and M. I. Paz Andrade, *J. Therm. Anal. Cal.*, 80 (2005) 245.
- 2 M. M. Mato, S. M. Cebreiro, P. V. Verdes, J. L. Legido and M. I. Paz Andrade, *J. Therm. Anal. Cal.*, 80 (2005) 303.
- 3 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.
- 4 P. V. Verdes, M. M. Mato, J. Salgado, J. L. Legido and M. I. Paz Andrade, *J. Therm. Anal. Cal.*, 80 (2005) 323.
- 5 P. V. Verdes, M. M. Mato, J. Salgado, J. L. Legido and M. I. Paz Andrade, *J. Therm. Anal. Cal.*, 80 (2005) 329.
- 6 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.
- 7 P. V. Verdes, M. M. Mato, X. Villaverde, J. L. Legido and M. I. Paz Andrade, *J. Therm. Anal. Cal.*, 80 (2005) 339.
- 8 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.
- 9 P. V. Verdes, M. M. Mato, J. Salgado, J. L. Legido and M. I. Paz Andrade, *Fluid Phase Equilib.*, 232 (2005) 16.
- 10 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.
- 11 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.
- 12 E. Tusel-Langer, J. M. García Alonso, M. A. Villamanan Olfos and R. N. Lichtenthaler, *J. Solution Chem.*, 20 (1991) 153.
- 13 L. Wang, G. C. Benson and B. C.-Y. Lu, *Thermochim. Acta*, 213 (1993) 83.
- 14 S. Zhu, S. Shen, G. C. Benson and B. C.-Y. Lu, *Fluid Phase Equilib.*, 94 (1994) 217.
- 15 L. Wang, G. C. Benson and B. C.-Y. Lu, *J. Chem. Thermodyn.*, 24 (1992) 1135.
- 16 I. Nagata, *J. Chem. Thermodyn.*, 26 (1994) 1137.
- 17 T. Letcher and P. U. Govender, *J. Chem. Eng. Data*, 40 (1995) 997.
- 18 S. Zhu, S. Shen, G. C. Benson and B. C.-Y. Lu, *J. Solution Chem.*, 22 (1993) 1073.
- 19 M. I. Paz Andrade, *Les Développements Récents de la Microcalorimétrie et de la Thermogénèse*, 1st ed.; CRNS: Paris 1967.
- 20 M. I. Paz Andrade, S. Castromil and M. C. Baluja, *J. Chem. Thermodyn.*, 2 (1970) 775.
- 21 O. Redlich and A. Kister, *T. Ind. Eng. Chem.*, 40 (1948) 345.
- 22 D. B. Myers and R. L. Scott, *Ind. Eng. Chem.*, 55 (1963) 43.
- 23 D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, 2 (1963) 431.
- 24 P. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill, New York 1969.

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