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

M. M. Mato[2]*, M. Illobre*[1]*, P. V. Verdes*[1]*, J. L. Legido*[2]*, E. Jiménez*[3] *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 del Mar, Campus As Lagoas- Marcosende, Universidad de Vigo
36310 Vigo, Spain
[3]Departamento de Física, Facultade de Ciencias, Universidade de A Coruña, 15071 A Coruña, Spain

Excess molar enthalpies of the ternary mixture {x_1 tert-butyl methyl ether (MTBE)+x_2 ethanol+(1–x_1–x_2) octane} and the involved binary mixture {x ethanol+(1–x) octane} 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, octane, ternary mixture, tert-butyl methyl ether (MTBE)*

Introduction

From a theoretical point of view, 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.

The present paper is the continuation of previous studies, where the main objective has been the characterisation of nonelectrolyte liquids, and their mixtures, through experimental determination of thermophysical properties on mixing. In this framework, excess molar enthalpy determination is considered of primary interest, as this property is essential in characterising the mixing process. The sign, magnitude, and symmetry of this quantity is a direct result of bond breaking and rearranging during the mixing process, and any effect arising from energetic interactions between both like and unlike molecules will be directly reflected in the enthalpy data and their representations.

As an extension of previous work on the excess thermodynamic properties of binary and ternary mixtures of MTBE, alkanols and alkanes [1–13], in this paper we report experimental data of excess molar enthalpies at 298.15 K and atmospheric pressure, for the ternary system {x_1 MTBE+x_2 ethanol+x_3 octane} and the involved binary mixture {x ethanol+(1–x) octane}, measured over the whole composition range using a Calvet microcalorimeter. For the other two involved binary systems, {x MTBE+(1–x) ethanol} and {x MTBE+(1–x) octane}, we have reported excess molar enthalpies measured using the same technique in previous papers [2, 3].

Excess molar enthalpies at 298.15 K have been published for {MTBE+ethanol+octane} and its binary mixtures by Zhu *et al.* [14], who used a flow microcalorimeter. Experimental data from the binary system ethanol+octane were also published by Ramalhoand Ruel [15]. We have decided to measure experimental excess molar enthalpies for the system {x ethanol+(1–x) octane} in order to use experimental values from the same microcalorimeter for all the binary systems involved in the ternary system.

Experimental

The sources and purities of the chemicals substances employed were: MTBE (Aldrich >99.8%), ethanol (Scharlau >99.8%), octane (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 cm^3. A Philips PM2535 multimeter and a data

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* Author for correspondence: fapazand@usc.es

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

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 [16, 17]. 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 octane to a binary mixture composed of $\{x_1'$ MTBE$+x_2'$ethanol$\}$. The ternary composition point is then a pseudo-binary mixture composed by

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

x	H_m^E/ J mol^{-1}	x	H_m^E/ J mol^{-1}	x	H_m^E/ J mol^{-1}	x	H_m^E/ J mol^{-1}
			x 1-ethanol+(1–x) octane				
0.0828	401	0.4191	683	0.7391	519	0.8976	286
0.1618	561	0.4769	671	0.8101	433	0.9277	223
0.2130	626	0.5497	634	0.8250	414	0.9556	147
0.2816	666	0.6489	593	0.8589	354	0.9788	73

Table 2 Fitting parameters, k, A_i and standard deviations, s

A_1	A_2	A_3	A_4	A_5	k	s
			x MTBE+(1–x) ethanol[1][a]			
1955	1034	698	510	0	–	4
			x MTBE+(1–x) octane[1][b]			
1867	–179	–277	415	326	–	3
			x ethanol+(1–x) octane[2]			
2639	1808	1096	1339	0	0.9455	5

[1] Redlich–Kister equation [21] was employed. [2] Fitting parameters for Eq. (2). [a] Fitting parameters were taken from [2], [b] Fitting parameters were taken from [3]

Fig. 1 Excess molar enthalpies H_m^E/J mol^{-1} at 298.15 K of the three involved binary systems. ● – {x MTBE+(1–x) ethanol}[a], ■ – {x MTBE+(1–x) octane}[b], ▲ – {x 1-ethanol+(1–x) octane} —— –fitting curves. [a] experimental data and fitting curve were taken from [2], [b] experimental data and fitting curve were taken from [3]

Fig. 2 Pseudo-binary representation of ternary excess molar enthalpies $H_{m,123}^E$/J mol^{-1} for {(1–x) (x_1' MTBE+x_2' ethanol)+x octane} at 298.15 K: ● – x_1'=0.2496, x_2'=0.7504; ▲ – x_1'=0.5054, x_2'=0.4946, ▼ – x_1'=0.7493, x_2'=0.2507, —— – correlated using Eq. (3)

Table 3 Experimental excess molar enthalpies, $H^E_{m,123}$, at the temperature 298.15 K for the ternary mixture: x_1 MTBE+x_2 ethanol+$(1–x_1–x_2)$ octane[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=0.2496, $H^E_{m,12}$=290 J mol^{-1}				
0.0315	0.0946	462	499	0.1997	0.6004	458	690
0.0620	0.1863	616	688	0.2226	0.6691	303	561
0.0834	0.2506	635	732	0.2308	0.6938	332	500
0.1251	0.3761	633	778	0.2371	0.7127	158	433
0.1452	0.4366	620	789	0.2417	0.7267	105	386
0.1584	0.4763	596	780				
			x'_1=0.5054, $H^E_{m,12}$=491 J mol^{-1}				
0.1042	0.102	533	635	0.3597	0.352	539	889
0.1425	0.1395	602	741	0.3855	0.3773	483	858
0.1805	0.1767	631	807	0.4073	0.3986	423	819
0.2138	0.2092	667	875	0.4232	0.4142	372	784
0.2588	0.2532	656	907	0.4686	0.4586	195	650
0.3304	0.3233	578	899	0.4875	0.4771	105	579
			x'_1=0.7493, $H^E_{m,12}$=508 J mol^{-1}				
0.1361	0.0455	433	525	0.5047	0.1689	505	848
0.1859	0.0622	500	626	0.5545	0.1855	454	830
0.2422	0.081	556	720	0.589	0.1971	401	801
0.2994	0.1002	597	800	0.6223	0.2082	338	760
0.3422	0.1145	620	853	0.6494	0.2173	287	728
0.3888	0.1301	615	878	0.7107	0.2378	133	615
0.4687	0.1568	539	858				

[a] Three experimental series of measurements were carried out for the ternary compositions resulting from adding octane to a binary mixture composed of {x'_1 MTBE+x'_2 ethanol}, where $x'_2=1-x'_1$

addition of octane 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

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

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'_2ethanol}. Values of $H^E_{m,12}$ 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^E_m, listed in Table 1, corresponding to the binary mixture {x ethanol+$(1–x)$ octane} were fitted to the variable-degree polynomial suggested by Myers-Scott [18] of the form:

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

The parameters k, A_i, shown in Eq. (2), have been obtained by a fitting computer program which uses the least squares procedure and a Marquardt algorithm [19]. The number of parameters used was determined by applying the optimization F test [20].

Experimental data for the binary mixtures {x tert-butyl methyl ether (MTBE)+$(1–x)$ 1-ethanol}, taken from [2], and {x tert-butyl methyl ether (MTBE)+$(1–x)$ octane}, taken from [3], were fitted to the variable-degree polynomials suggested by Redlich-Kister [21]. The fitting parameters and the standard deviations for the three binary mixtures involved in this ternary system are summarized in Table 2. A graphical representation of all these experimental values together with the smoothing curves are shown in Fig. 1.

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

$$H^{\mathrm{E}}_{\mathrm{m},123}/\mathrm{J\ mol^{-1}}=H^{\mathrm{E}}_{\mathrm{m,bin}}+x_1x_2(1-x_1-x_2)\Delta_{123} \quad (3)$$

where

$$H^{\mathrm{E}}_{\mathrm{m,bin}}=H^{\mathrm{E}}_{\mathrm{m},12}+H^{\mathrm{E}}_{\mathrm{m},13}+H^{\mathrm{E}}_{\mathrm{m},23} \quad (4)$$

is known as the binary contribution to the excess ternary enthalpy.

The following form:

$$\frac{\Delta_{123}}{RT}=\frac{B_0+B_1x_1+B_2x_2+B_3x_1^2+B_4x_2^2+B_5x_1x_2+}{1+(x_2-x_3)} \quad (5)$$
$$\frac{+B_6x_1^3+B_7x_2^3+B_8x_2x_1^2+\ldots}{1+(x_2-x_3)}$$

suggested by Verdes *et al.* [12] was adopted for the ternary term $x_1x_2(1-x_1-x_2)\Delta_{123}$.

The B_i parameters were calculated by an unweight 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 $H^{\mathrm{E}}_{\mathrm{m},123}$, together with the correlated curves, where Eq. (5) was applied to fit the ternary contribution.

The lines of constant ternary excess molar enthalpy, $H^{\mathrm{E}}_{\mathrm{m},123}$ calculated using Eq. (3) 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. (5).

Conclusions

The experimental excess molar enthalpies $H^{\mathrm{E}}_{\mathrm{m}}$ are positive for all the binary systems studied over the whole composition range. This suggests, in all three cases, 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) octane} 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) octane} is asymmetric, with its maximum displaced toward a high mole fraction of octane. This displacement can be interpreted on basis of the rupture of hydrogen bonds present on the pure alkanol. Both these asymmetries reflect the strength and ready formation of ethanol-ethanol hydrogen bonds in comparison with other interactions in the mixture. 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=0.3480, x_2=0.2410, x_3=0.2970, $H^{\mathrm{E}}_{\mathrm{m},123}$=920 J mol^{-1}.

Table 4 Fitting parameters, B_i , for Eq. (5) and standard deviation, s

x_1 MTBE+x_2 ethanol+x_3 octane							
B_0	B_1	B_2	B_3	B_4	B_5	B_6	s
2.2138	3.9243	–9.6686	–11.1320	12.1034	10.2113	11.268	7

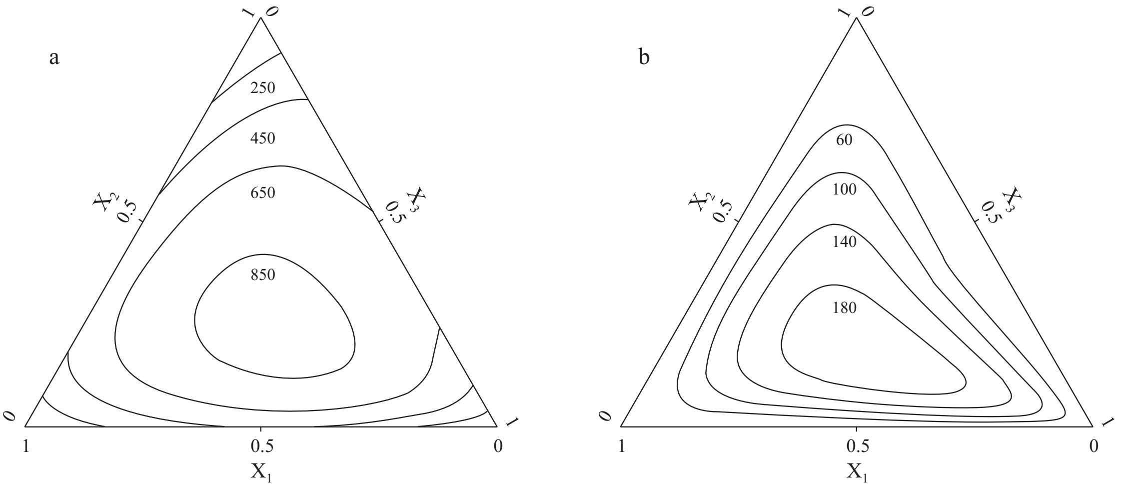

Fig. 3 Representation for {x_1 MTBE+x_2 ethanol+(1–x_1–x_2) octane} at 298,15 K of: a – Curves of constant ternary excess molar enthalpy, $H^{\mathrm{E}}_{\mathrm{m},123}$/J mol^{-1} correlated using Eq. (3), b – Curves of constant ternary contribution, $x_1x_2(1-x_1-x_2)\Delta_{123}$, to the excess molar enthalpy $H^{\mathrm{E}}_{\mathrm{m},123}$/J mol^{-1}, calculated with Eq. (5)

The ternary contribution is also positive, and has a maximum value at x_1=0.3850, x_2=0.1750, x_3=0.4400, $H^{E}_{m,123}$=208 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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