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EXPERIMENTAL AND THEORETICALLY ESTIMATED EXCESS MOLAR ENTHALPIES FOR *tert*-BUTYL METHYL ETHER+ 1-PENTANOL+OCTANE AT 298.15 K

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Forming part of the scientific project entitled 'Study on physical properties of mixtures hydrocarbon+alcohol+ether like alternative fuels', the present article reports experimental data of excess molar enthalpies for the ternary mixture {x_1*tert*-butyl methyl ether (MTBE)+$x_2$1-pentanol+(1–x_1–x_2)octane} and the involved binary mixture {x_1-pentanol+(1–x) octane} at the temperature of 298.15 K and atmospheric pressure. No experimental excess enthalpy values were found in the currently available literature for the ternary mixture under study. The group contribution model of the UNIFAC (in the versions of Larsen, and Gmehling) were used to estimate excess enthalpy values. Several empirical expressions for estimating ternary properties from binary results were also tested.

Keywords: *excess molar enthalpies, group contribution model, octane, 1-pentanol, ternary mixture, tert-butyl methyl ether (MTBE)*

Introduction

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.

In this case, earlier works [1–13] have been published reporting experimental excess molar properties of mixtures containing ethers, alkanes and alkanols. The series including the ternary systems MTBE+ 1-pentanol+nonane [11] and MTBE+1-pentanol+decane [12], is now continued, considering octane as the third component in this case. This should help to study the effect of alkane chain length in the binary mixtures involved, and subsequent effects on the ternary mixture.

The excess molar enthalpies for the involved binary mixtures {x*tert*-butyl methyl ether (MTBE)+ (1–x)octane} and {x*tert*-butyl methyl ether (MTBE)+ (1–x)1-pentanol} were reported in previous studies [3, 13]. Enthalpy of mixing was determined in every case by means of a Calvet microcalorimeter. The binary experimental data for {x1-pentanol+ (1–x)octane} were fitted with a variable degree polynomial due to Myers–Scott [14]. The ternary contribution to the excess enthalpy was correlated on the basis of an equation proposed in an earlier study [12].

Experimental values were compared with the estimates obtained by applying the group contribution model of UNIFAC, the latter in the versions introduced by Larsen [15] and Gmehling *et al.* [16]. Deviations of the ternary enthalpies calculated on the basis of several empirical methods were also listed. The symmetric equations used were those introduced by Kohler [17], Jacob and Fitzner [18], Colinet [19], Knobeloch and Schwartz [20], and the asymmetric ones due to Tsao and Smith [21], Toop [22], Scatchard *et al.* [23], Hillert [24], and Mathieson and Tynne [25]. These methods allow excess properties of generalised multicomponent mixtures to be estimated from the experimental correlated values of the binaries formed with its components.

Experimental

Materials and methods

The chemical substances employed were commercial products of the best quality grade (≥0.995 mole fraction). MTBE and 1-pentanol were obtained from Aldrich and octane was supplied by Fluka. These sub-

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Table 1 Experimental binary excess molar enthalpies, H_m^E, at 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}
			x1-pentanol+(1–x) octane				
0.0168	259	0.2023	610	0.6539	484	0.8970	138
0.0183	254	0.2650	638	0.6862	448	0.9321	83
0.0439	364	0.3344	657	0.7230	399	0.9578	42
0.0806	451	0.4993	626	0.7672	338		
0.0966	482	0.5569	591	0.8110	269		
0.1130	504	0.6232	529	0.8529	212		

stances were used as supplied, no further purification being applied. In order to avoid hydration and eliminate residual traces of water, chemicals were dried over Union Carbide 0.4 nm molecular sieves. In addition, they were degassed by an ultrasound technique.

The handling and disposal of the chemicals used has been done according to the recommendation of the CRC Handbook of Chemistry and Physics [26].

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 [27].

The experimental excess molar enthalpies were measured using a Calvet microcalorimeter equipped with a device allowing operation in the absence of vapour phase, and 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. Further details about the experimental method of operation have been published [28, 29]. The apparatus and procedures were tested by determining excess enthalpies for the standard system hexane+cyclohexane at 298.15 K, and the results were found to differ by less than 1% from those of Marsh [30] and Gmehling [31]. The uncertainty in excess molar enthalpy measurements is estimated to be better than 1%.

Three experimental runs of measurements were carried out for the ternary compositions resulting from adding octane to an initial binary mixture of $\{x'_1$MTBE$+x'_2$1-pentanol$\}$. The ternary composition point may be regarded as a pseudobinary mixture composed by the addition of octane to the mentioned binary mixture. Thus, the ternary excess molar enthalpy at the pseudobinary composition x_1, x_2 and $x_3=1-x_1-x_2$ can be expressed as

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

where $H_{m,\phi}^E$ is the measured excess molar enthalpy for the pseudobinary mixture and $H_{m,12}^E$ is the excess molar enthalpy of the initial binary mixture $\{x'_1$MTBE+$x'_2$1-pentanol$\}$. 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.

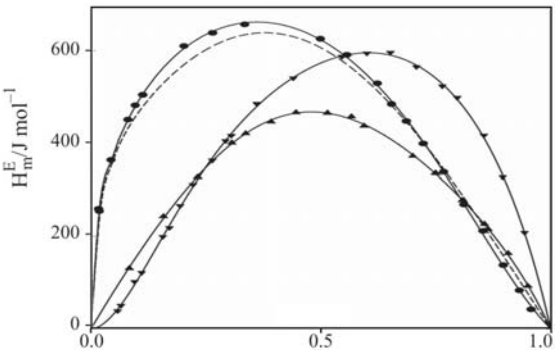

Fig. 1 Excess molar enthalpies H_m^E/J mol^{-1} at 298.15 K of the three involved binary systems. Experimental values of: ▼– $\{x$MTBE+(1–x)1-pentanol$\}$ from [13], ▲– $\{x$MTBE+(1–x) octane$\}$ from [3], ● – $\{x$1-pentanol+(1–x) octane$\}$; —— fitted curve, – – – – [32]

Data correlation

The experimental data of excess molar enthalpies for the binary mixtures $\{x$*tert*-butyl methyl ether (MTBE)+(1–x)octane$\}$ and $\{x$*tert*-butyl methyl ether (MTBE)+(1–x)1-pentanol$\}$ were reported in early papers [3, 13]. Experimental values of H_m^E for the $\{x$1-pentanol+(1–x)octane$\}$ are listed in Table 1. This set of data was fitted to a variable-degree polynomial suggested by Myers–Scott [14].

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

A plot of the obtained experimental values as well as the corresponding fitting curves for H_m^E of the three involved binary, are shown in Fig. 1.

The measured values of ternary excess enthalpy $H_{m,123}^E$, listed in Table 2, were correlated using the following equation:

$$H_{m,123}^E(\text{J mol}^{-1}) = H_{m,\text{bin}}^E + x_1 x_2(1-x_1-x_2)\Delta_{123} \qquad (2)$$

where Δ_{123}, were fitted to the expression suggested by Verdes *et al.* [12] of the form:

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

The fitting parameters *k*, A_i and B_i were computed from the unweighed least-squares method using a non-linear optimization algorithm due to Marquardt [33]. The number of parameters was determined by applying to every new parameter the F-test proposed by Bevington [34].

The fitting coefficients and the corresponding standard deviations from experimental values are presented in Table 3.

Figure 2 shows the pseudobinary representation of the measured experimental values of the $H^{\mathrm{E}}_{\mathrm{m},123}$, together with the correlated curves, where Eq. (3) was applied to fit the ternary contribution.

The lines of constant ternary excess molar enthalpy, $H^{\mathrm{E}}_{\mathrm{m},123}$ calculated using Eq. (2) 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. (3).

Table 2 Excess molar enthalpies, $H^{\mathrm{E}}_{\mathrm{m},123}$, at 298.15 K for the ternary mixture x_1 MTBE+x_2 1-pentanol+$(1-x_1-x_2)$ octane[a]

x_1	x_2	$H^{\mathrm{E}}_{\mathrm{m},\phi}$/J mol^{-1}	$H^{\mathrm{E}}_{\mathrm{m},123}$/J mol^{-1}	x_1	x_2	$H^{\mathrm{E}}_{\mathrm{m},\phi}$/J mol^{-1}	$H^{\mathrm{E}}_{\mathrm{m},123}$/J mol^{-1}
			x_1'=0.2642, $H^{\mathrm{E}}_{\mathrm{m},12}$=369 J mol^{-1}				
0.2562	0.7134	58	416	0.1424	0.3966	576	774
0.2468	0.6874	114	458	0.1316	0.3665	597	781
0.2373	0.6607	182	513	0.1164	0.3242	605	767
0.2268	0.6316	254	570	0.1011	0.2817	619	760
0.2046	0.5700	372	658	0.0821	0.2287	588	702
0.2001	0.5571	391	670	0.0673	0.1876	578	672
0.2036	0.5672	376	660	0.0517	0.1441	534	607
0.1698	0.4728	512	749	0.0374	0.1042	494	546
0.1586	0.4417	533	754				
			x_1'=0.4972, $H^{\mathrm{E}}_{\mathrm{m},12}$=572 J mol^{-1}				
0.4691	0.4744	128	668	0.2657	0.2686	589	895
0.4494	0.4544	184	701	0.2407	0.2434	597	874
0.4161	0.4208	297	776	0.2175	0.2199	603	854
0.3932	0.3976	355	808	0.1961	0.1984	602	828
03606	0.3647	442	857	0.1585	0.1602	572	755
0.3462	0.3501	467	866	0.1164	0.1177	558	692
0.3201	0.3238	503	872	0.0995	0.1006	507	621
0.2989	0.3022	538	882	0.0356	0.0360	336	377
0.2980	0.3013	535	878				
			x_1'=0.7497, $H^{\mathrm{E}}_{\mathrm{m},12}$=541 J mol^{-1}				
0.7115	0.2376	135	648	0.3946	0.1318	583	868
0.6786	0.2266	199	688	0.3190	0.1065	577	808
0.6461	0.2157	275	741	0.2905	0.0970	580	789
0.6247	0.2086	336	787	0.2541	0.0849	558	742
0.5829	0.1946	380	800	0.1901	0.0635	517	654
0.5564	0.1857	422	824	0.1393	0.0465	447	548
0.5199	0.1736	465	840	0.1066	0.0356	386	462
0.4991	0.1666	488	848	0.0586	0.0196	285	327
0.4796	0.1601	511	857				

[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_2'1-pentanol$\}$, where $x_2'=1-x_1'$

Table 3 Fitting parameters, k, A_i and B_i and standard deviations, s, for the **ternary** and the three involved binary mixtures

A_1	A_2	A_3	A_4	A_5	A_6	k		s
xMBTE+(1–x) 1-pentanol[a]								
2294	831	442	576	–514	762			4
xMBTE+(1–x) octane[b]								
1867	–179	–277	415	326				3
x1-pentanol+(1–x) octane								
2494	1345	–601	–688	–576		0.9839		5
B_0	B_1	B_2	B_3	B_4	B_5	B_6	B_7	s
x_1 MTBE+x_2 1-pentanol+(1–x_1–x_2) octane								
2.42	6.00	–14.16	–19.61	28.07	6.53	21.64	–19.12	9

[a][13], [b][3]

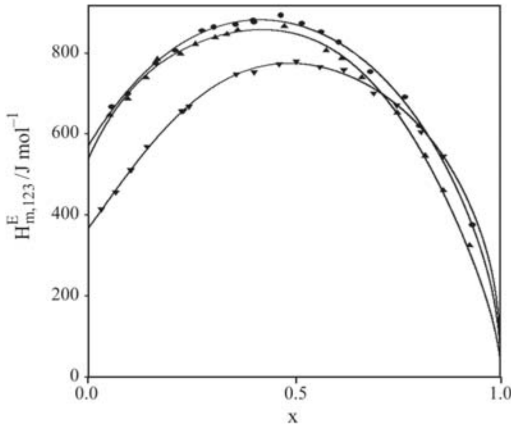

Fig. 2 Pseudobinary representation of ternary excess molar enthalpies $H^E_{m,123}$/(J mol^{-1}) for {(1–x)(x_1'MTBE+x_2'1-pentanol)+x octane} at 298.15 K: ▼ – x_1'=0.2642, x_2'=0.7358; ● – x_1'=0.4972, x_2'=0.5028, ▲ – x_1'=0.7797, x_2'=0.250, —– correlated using Eq. (2)

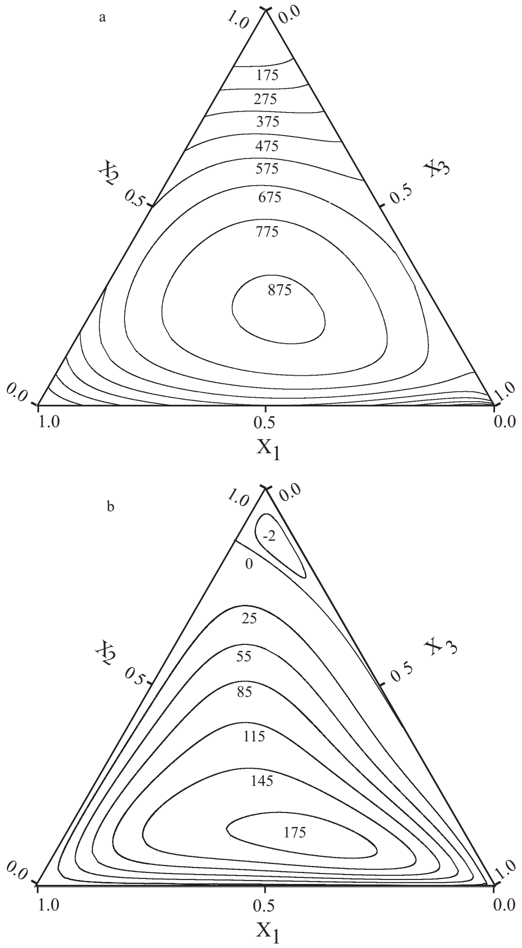

Fig. 3 Representation for {x_1MTBE+x_2 1-pentanol+(1–x_1–x_2)octane} at 298.15 K of: a – constant ternary excess molar enthalpy, $H^E_{m,123}$/J mol^{-1}; b – constant ternary contribution, $x_1x_2(1–x_1–x_2)\Delta_{123}$, to the excess molar enthalpy $H^E_{m,123}$/J mol^{-1}, calculated with Eq. (3)

Theoretical estimation methods

The UNIFAC group contribution model was originally developed by Fredenslund *et al.* [35], from the UNIQUAC equation by Abrams and Prausnitz [36] for a multicomponent mixture. The activity coefficient in this model is calculated as the sum of two terms. The first one is combinatorial and takes into account the differences of shape and size of the molecules. The second one is a residual term that includes the energetic interactions present in the mixture. The adjustable parameters in this model are the interaction parameters between groups.

Larsen *et al.* [15] modified the UNIFAC model in order to predict vapor–liquid and liquid–liquid equilibria besides excess enthalpies. The interaction parameters become temperature dependent, and the combinatorial term is modified.

Gmehling *et al.* [16] proposed a new modified UNIFAC method whose main advantages are a better description of the temperature dependence of G^E and of the activity coefficients in the dilute region. This modification can be applied more reliably for systems involving molecules which are very different in size.

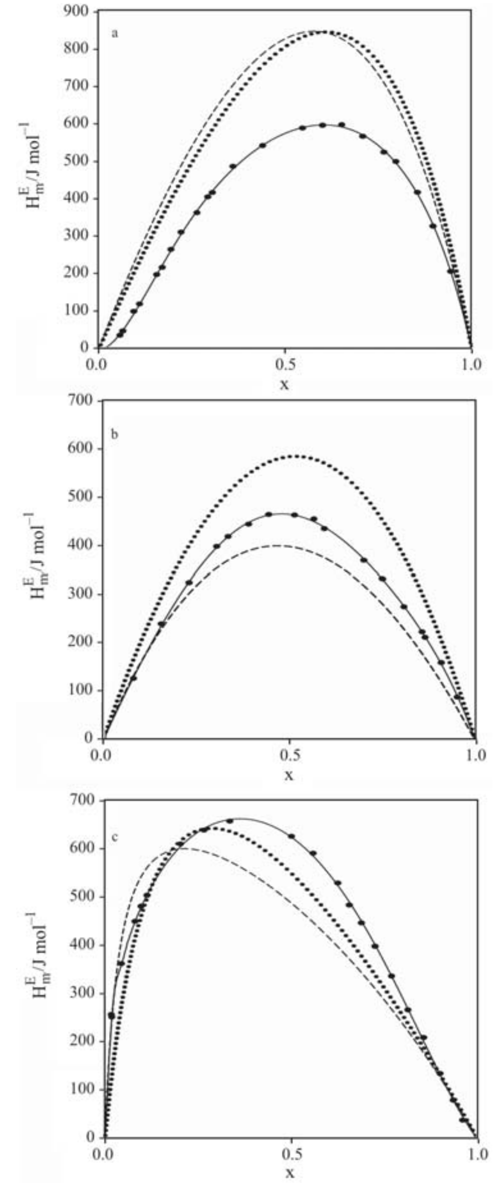

Fig. 4 Excess molar enthalpies H_m^E/J mol^{-1} at 298.15 K of binary mixtures: a – {xMTBE+(1–x)1-pentanol}, b – {xMTBE+(1–x)octane}, c – {x1-pentanol+(1–x)octane. O – experimental values, ····· – Larsen *et al.* model [15], – – – – Gmehling *et al.* model [16]

The parameters used in the present work to predict the ternary excess enthalpies were those provided by the authors in their original papers.

Deviations of the excess molar enthalpies predicted by the theoretical models from the experimental values are listed in Table 4. These results are displayed graphically in Figs 4 and 5.

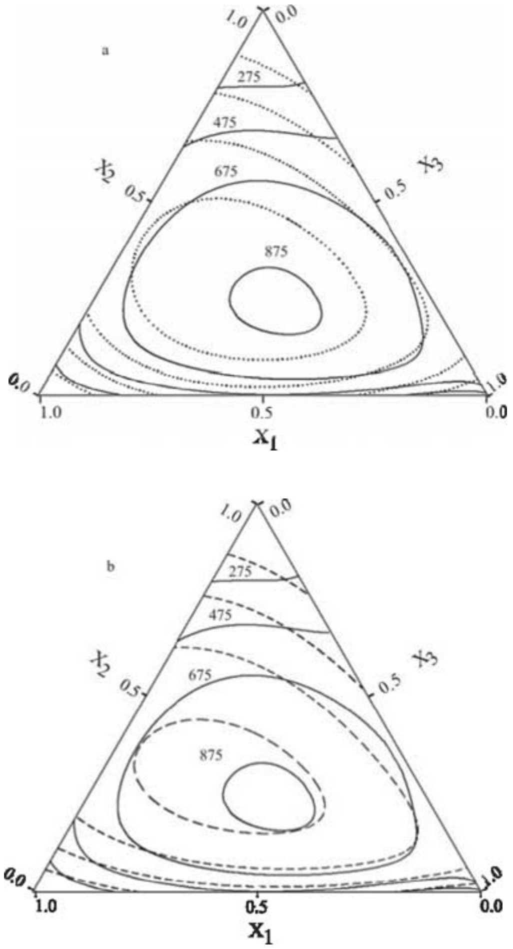

Fig. 5 Excess molar enthalpies, $H_{m,123}^E$/J mol^{-1}, for ternary mixture {x_1MTBE+x_2 1-pentanol+(1–x_1–x_2)octane} at 298.15 K. — – fitted by Eq. (2), ····· – Larsen *et al.* model [15], – – – – Gmehling *et al.* model [16]

Empirical equations

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. So, several empirical methods have been proposed to estimate ternary excess properties from experimental results on constituent binaries. These methods can be divided into symmetric and asymmetric, depending on whether the assumption of the three binaries contributing equally to the ternary mixture magnitude is accepted or not. Asymmetry is usually understood to be caused by the strongly polar or associative behavior of any of the compounds in the mixture. In these cases, different geometric criteria are applied to match each point of ternary composition with the contributing binary compositions.

The symmetric equations tested have been suggested by Kohler [17], Jacob and Fitzner [18], Colinet [19], Knobeloch and Schwartz [20], while the asymmetric ones have been introduced by Tsao and Smith [21], Toop [22], Scatchard *et al.* [23], Hillert [24] and Mathieson and Tynne [25]. Table 4 list

Table 4 Mean deviations of excess molar enthalpies (J mol^{-1}) predicted by theoretical models from the experimental data

	Larsen	Gmehling
MTBE+1-pentanol	170	160
MTBE+octane	91	44
1-pentane+octane	48	61
MTBE+1-pentanol+octane	100	48

the mean deviations of the excess molar enthalpies for ternary system predicted by empirical equations and the experimental values. For the asymmetric equations, three different numberings of the components have been tested, in order to check the differences in the predicted values, and to find a rule to decide which ordering should be used in each case. MTBE, 1-pentanol, octane were respectively named as 1,2,3. Then, the rows A, B, C of Table 4 fit to the *tert*-butyl methyl ether+1-pentanol+octane as 123, 231, 312 respectively ordered, being the first element considered in each case MTBE, 1-pentanol or octane in this order.

Results and discussion

Figure 1 shows that 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 {*xtert*-butyl methyl ether (MTBE)+(1–*x*)octane} is symmetrical. Nevertheless, the obtained curve for {*xtert*-butyl methyl ether (MTBE)+(1–*x*) 1-pentanol}, is slightly asymmetric, with their maximum shifted around the rich compositions in MTBE. The binary system {*x*1-pentanol+(1–*x*)octane} is asymmetric, with its maximum displace 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. 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.

Ragaini *et al.* [36] determined the H_m^E values for the system {*x*1-pentanol+(1–*x*)octane} at 298.15 K and they obtained $H_m^E(x=0.5)=606$ J mol^{-1} somewhat lower than our $H_m^E(x=0.5)=623$ J mol^{-1}. The dotted curve shown in Fig. 1 was calculated from the smoothing equation reported by those authors.

Excess molar enthalpy for the ternary system is positive over the whole range of composition, showing maximum values at $x_1=0.3500$, $x_2=0.2360$, $x_3=0.4140$, $H_{m,123}^E=896$ J mol^{-1}.

The ternary contribution is also positive, and the representation is asymmetric. That means that, as can be seen in Fig. 3b, the position of the maximum does not coincide with the centre of the Gibbs triangle. There exists a maximum at $x_1=0.3170$, $x_2=0.1160$, $x_3=0.5670$, $H_{m,123}^E=187$ J mol^{-1}. The value of maximum ternary contribution is about 20% of the value of the ternary enthalpy itself. That means that ternary contribution in this case 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.

The group contribution model of UNIFAC, in the versions of Larsen [15] and Gmehling [16], was used to estimate ternary excess enthalpy values. In Table 4 can be seen that for the binary mixture 1-pentanol+octane the best results are achieved with the Larsen version. For the systems MTBE+octane and MTBE+1-pentanol+octane, the results obtained with the Gmehling version are in better agreement with the experimental data than the Larsen ones.

Table 5 Mean deviations from the experimental values obtained with empirical predictive methods. For the asymmetric equations three numberings of the components have been compared, in this order, 123, 231, 312

Empirical equations		$H_{m,123}^E/(\text{J mol}^{-1})$	
Kohler		87	
Jacob Fitzner		106	
Colinet		93	
Knobeloch–Schwartz		48	
Tsao–Smith	26^a	37^b	50^c
Toop	110^a	27^b	138^c
Scatchard *et al.*	128^a	27^b	138^c
Hillert	116^a	27^b	138^c
Mathieson–Tynne	115^a	73^b	124^c

^{a}Order 123, ^{b}Order 231, ^{c}Order 312

Figure 4 illustrates the predictions for H_m^E of the binary mixtures obtained with the theoretical models. It is possible to observe that there is no good quantitative agreement between the estimation provided by the theory and the experimental curves, nevertheless the shape of the H_m^E *vs.* compositions curves are well predicted for the three involved binary mixtures.

The empirical expressions of Kohler [17], Jacob and Fitzner [18], Colinet [19], Knobeloch and Schwartz [20], Tsao and Smith [21], Toop [22], Scatchard *et al.* [23], Hillert [24] and Mathieson and Tynne [25] were also applied to estimate ternary properties from binary results. The best agreement with the experimental data to excess molar enthalpies was achieved by the asymmetric equation from Tsao-Smith equation [21], with the MTBE as the first component in the numbering.

Deviations obtained with these expressions are rather high, and this fact can be attributed to the importance of the ternary contribution term to the studied magnitude. Using this kind of expressions, lower deviations are usually obtained for those properties where the ternary contribution is not important. It can be observed that the dependence on the arrangement of the components varies in each asymmetric equation. For all cases, except for Tsao–Smith equation [21], the best results are obtained using arrangement B (231) (Table 5).

The best results to the ternary excess enthalpies obtained using symmetric equations are those predicted by Knobeloch and Schwartz equation [20].

Acknowledgements

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