



Measurement and prediction of excess molar enthalpies of ternary mixtures involving ether with 1-alkanol and n-alkane

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ABSTRACT

This work aims to experimentally determine the excess molar enthalpies at 298.15 K and atmospheric pressure for the ternary mixture $\{x_1$ methyl *tert*-butyl ether (MTBE) + x_2 1-pentanol + $(1 - x_1 - x_2)$ heptane} and the corresponding binary system $\{x$ 1-pentanol + $(1 - x)$ heptane}, across the whole composition range. The excess molar enthalpy of the ternary system is positive throughout the composition range. Except for a region around compositions rich in 1-pentanol, the ternary contribution to the excess molar enthalpy is also positive and its representation is asymmetric.

A systematic review of the currently accessible literature on excess molar enthalpy for the ternary mixtures containing ethers with 1-alkanol and 1-alkane was conducted. According to our searches, no previous experimental measurements of excess enthalpy for the ternary combination under study have been reported.

The ternary excess enthalpy values and the involved binary mixtures were estimated using the UNIFAC group contribution model. Furthermore, several empirical equations for estimating ternary properties from binary results were tested against the experimental data to evaluate their predictive accuracy for ternary properties.

1. Introduction

The efficient design of industrial processes relies on a firm understanding of the phase behaviour and thermophysical properties of the mixtures involved [1]. Therefore, it is crucial to obtain experimental data by testing numerous different combinations to build adequate experimental databases. Analysing these databases allows us to gain a general understanding of the types of interactions that occur in mixtures and to apply theoretical models to predict their behaviour and verify their validity. In this context, the importance of a reliable, freely accessible benchmark database is pivotal and becomes absolutely necessary [2].

Biomass processing routes involve mixtures of organo-oxygenated compounds of almost all the organic families. Typically, these mixtures are highly non-ideal, and models to describe their phase behaviour should take into account specific association interactions. Ethers are involved as byproducts, intermediates, and/or products in several biomass conversion routes, highlighting the importance of developing a predictive thermodynamic model for the design and optimization of processes and products [3].

Alkanol-ether mixtures have a complex structure due to the partial replacement of alcohol-alcohol interactions by alcohol-ether OH-O bonds. The complexity increases when one or more alkanes are present in the mixture. A comprehensive investigation of the involved interactions is essential, and the data provided here will be relevant to industry and research.

It should be noted that some works report excess molar enthalpies of binary systems containing ethers with alcohols or alkanes, as well as many binary mixtures of alcohols plus alkanes. Marsh *et al.* [4] reported a detailed review of the thermophysical properties of mixtures containing ethers (MTBE, ETBE, DPE, DIPE and TAME) with non-polar solvents. Thanusha *et al.* [5] published a review on the thermophysical properties (excess molar enthalpies, excess molar volumes and viscosity) of binary mixtures composed of ethers with low alcohols. However, ternary mixtures containing ether, alcohol, and alkane are the subject of very few published investigations [6–34]. Table SI-1 (see the [Supporting Information](#)) summarizes the ternary mixtures found, with one of the following ethers as a component: methyl *tert*-butyl ether (MTBE) [6–25], diisopropyl ether (DIPE) [26], dibutyl ether (DBE) [26–31], ethyl *tert*-butyl ether (ETBE) [32], *tert*-amyl methyl ether (TAME) [33,34].

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¹ In memory of Prof. María Inmaculada Paz Andrade, who passed away on November 24, 2022. Thank you, Ada.

Table 1

Sources, Purities, Densities and Refractive Indices of the chemical substances employed in this work.

Chemical name	Source	Mass Fraction Purity	$\rho/\text{kg}\cdot\text{m}^{-3}$		n_d	
			Exp	Lit	exp	Lit
MTBE ^a	Aldrich	>0.998	735.61 ^b	735.58 ^c 735.66 ^d	1.36631	1.3663 ^c
1-Pentanol	Aldrich	>0.990	810.95 ^b	810.968 ^e	1.40790	1.40796 ^e 1.40787 ^f
Heptane	Fluka	>0.995	679.61 ^b	679.78 ^g	1.38530	1.385204 ^g

^a MTBE = Methyl *tert*- butyl ether.^b Ref. [46].^c Ref. [47].^d Ref. [48].^e Ref. [49].^f Ref. [50].^g Ref. [51].**Table 2**Experimental Binary Excess molar Enthalpies, H_m^E , at 298.15 K for the Binary Mixture $\{x$ 1-Pentanol + $(1 - x)$ Heptane $\}$.^a

x	$H_m^E / \text{J}\cdot\text{mol}^{-1}$	x	$H_m^E / \text{J}\cdot\text{mol}^{-1}$
0.0497	364	0.5420	533
0.1018	460	0.6021	477
0.1524	519	0.6436	433
0.2056	562	0.6940	363
0.2404	578	0.7460	290
0.2820	589	0.7990	218
0.3518	599	0.8437	160
0.4028	596	0.9022	85
0.5015	554	0.9262	55

^a x is the mole fraction of 1-pentanol in the binary mixture 1-pentanol + heptane. Standard uncertainties u are: $u(T) = 0.01$ K, $u(x) = 0.0001$, $u_r(H_m^E) = 0.01$.

On the other hand, no experimental data have been found on the enthalpies of the ternary systems studied, which contain the following ethers as a component: isopropyl methyl ether (IPME), diisobutyl ether (DIBE), 1,2-dimethoxyethane, dimethoxymethane (DMM), dimethyl ether (DME), diethyl ether (DEE), dipropyl ether (DPE), *tert*-amyl ethyl ether (TAEE), dipentyl ether, methyl ethyl ether (MEE), methyl propyl ether (MPE), ethyl propyl ether (EPE), methyl butyl ether (MBE), ethyl butyl ether (EBE), 1,2-diethoxyethane.

The experimental data of this work come to complete those already existing in the bibliography. To further with earlier investigations, we now report excess molar enthalpies at 298.15 K of the ternary mixture $\{x_1$ MTBE + x_2 1-pentanol + $(1 - x_1 - x_2)$ heptane $\}$ over the entire composition range. By considering 1-pentanol as a component, the series that includes the ternary mixtures MTBE + 1-alkanol (ethanol [8], 1-propanol [15]) + heptane, are continued; and similarly, we complete the series of mixtures MTBE + 1-pentanol + alkane (decane [25], nonane [24], octane [23], hexane [22]) by taking into account heptane as the chosen alkane.

The UNIFAC group contribution model, in the versions introduced by Larsen [35] and Gmehling *et al.* [36], was applied to the experimental data of the binary and ternary mixtures related to this work.

For the prediction of a multicomponent mixture property, nine empirical prediction equations that only require binary correlation parameters, without the need for higher order coefficients, were tested [37–45]. These equations can be classified as either symmetric or asymmetric. The symmetric equations treat the contribution of each of the binary mixtures equally, while the asymmetric ones give greater weight to the contribution of one component.

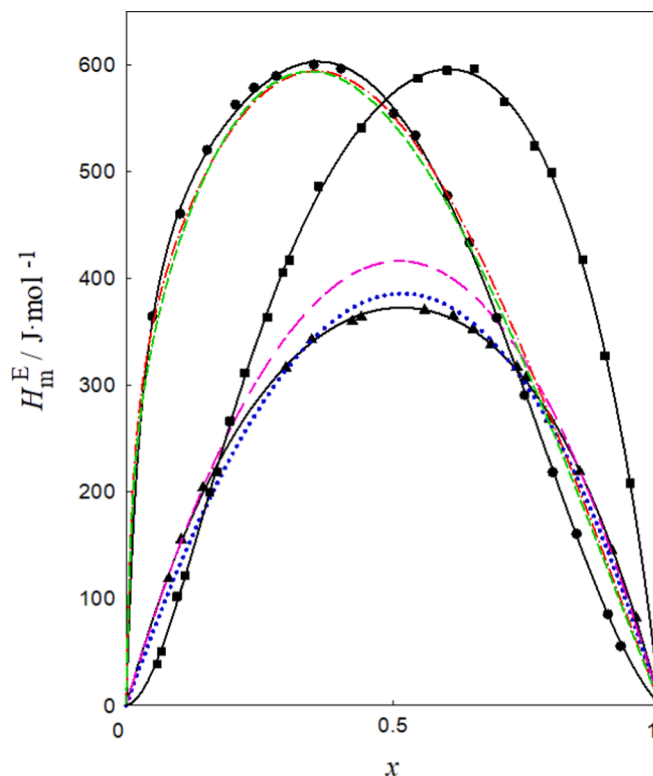


Fig. 1. Excess molar enthalpies, $H_m^E/(\text{J}\cdot\text{mol}^{-1})$, at 298.15 K of the three involved binary systems. Experimental values of: (■) $\{x$ MTBE + $(1 - x)$ 1-pentanol $\}$ from Ref. [57]; (▲) $\{x$ MTBE + $(1 - x)$ heptane $\}$ from Ref. [15]; (●) $\{x$ 1-pentanol + $(1 - x)$ heptane $\}$; (—) fitted curve used in this work. Fitted curve of: 1-pentanol + heptane (—) from Ref. [64] and (—) from Ref. [65]; MTBE + heptane (---) from Ref. [66] and (· · · ·) from Ref. [67].

2. Experimental

2.1. Samples

The chemicals used were premium quality commercially available compounds and were all handled just as they were supplied. They were only dried on Union Carbide 0.4 nm molecular sieves to prevent hydration and remove any lingering water residue. Table 1 lists the suppliers and the purities (as claimed by the provider), densities (previously published [46]) and refractive indices. The refractive indices were measured with the automatic refractometer ABBEMAT-HP Dr Kemchen with a precision of ± 0.00001 .

Table 3Excess molar Enthalpies, $H_{m,123}^E$, at 298.15 K for the Ternary Mixture $\{x_1$ MTBE + x_2 1-Pentanol + $(1 - x_1 - x_2)$ Heptane $\}^a$, calculated with Eq. (1).

x_1	x_2	$H_{m,q}^E/J\cdot mol^{-1}$	$H_{m,123}^E/J\cdot mol^{-1}$	x_1	x_2	$H_{m,q}^E/J\cdot mol^{-1}$	$H_{m,123}^E/J\cdot mol^{-1}$
$x_1' = 0.2469, H_{m,12}^E = 344 J\cdot mol^{-1}$							
0.2359	0.7195	84	413	0.1339	0.4084	517	703
0.2285	0.6968	124	443	0.1158	0.3534	532	694
0.2194	0.6693	179	485	0.1006	0.3067	542	683
0.2130	0.6495	216	513	0.0906	0.2763	549	675
0.2042	0.6230	480	545	0.0752	0.2293	536	641
0.1864	0.5685	353	613	0.0566	0.1728	509	588
0.1762	0.5376	388	634	0.0462	0.1411	480	545
0.1649	0.5029	437	667	0.0179	0.0546	374	399
0.1591	0.4852	455	677				
$x_1' = 0.4999, H_{m,12}^E = 573 J\cdot mol^{-1}$							
0.4834	0.4836	63	618	0.2890	0.2892	500	831
0.4584	0.4585	150	676	0.2545	0.2547	527	819
0.4422	0.4423	199	706	0.2325	0.2325	533	799
0.4294	0.4296	238	731	0.2032	0.2033	316	768
0.3941	0.3942	535	768	0.1835	0.1835	535	746
0.3699	0.3701	373	797	0.1530	0.1530	523	699
0.3554	0.3556	409	817	0.1191	0.1191	500	637
0.3334	0.3336	447	830	0.0894	0.0894	453	556
0.3108	0.3110	479	835	0.0649	0.0649	412	486
$x_1' = 0.7500, H_{m,12}^E = 540 J\cdot mol^{-1}$							
0.7332	0.2444	44	573	0.4202	0.1401	507	810
0.6866	0.2289	157	652	0.3799	0.1267	531	805
0.6647	0.2216	208	687	0.3388	0.1129	541	785
0.6408	0.2136	268	730	0.3047	0.1015	539	758
0.6043	0.2014	318	754	0.2558	0.0853	514	698
0.5678	0.1893	371	781	0.2294	0.0765	508	673
0.5336	0.1779	413	798	0.1621	0.0540	456	573
0.5035	0.1678	439	802	0.1252	0.0417	401	491
0.4631	0.1544	477	811	0.0448	0.0149	229	261

^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' 1-pentanol $\}$, where $x_2' = 1 - x_1'$. x_1' is the mole fraction of MTBE, x_2' is the mole fraction of 1-pentanol and $H_{m,12}^E$ is the excess molar enthalpy in the initial binary mixture. x_1 is the mole fraction of MTBE and x_2 is the mole fraction of 1-pentanol in the ternary mixture MTBE + 1-pentanol + heptane. Standard uncertainties u are: $u(T) = 0.01$ K, $u(x_1) = 0.0001$, $u(x_2) = 0.0001$, $u(x_1') = 0.0001$, $u_r(H_{m,12}^E) = 0.01$, $u_r(H_{m,q}^E) = 0.01$, $u_r(H_{m,123}^E) = 0.01$.

Table 4Fitting Parameters, k , A_i , 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	
x MTBE + $(1 - x)$ 1-pentanol ^a								
2294	831	442	576	-514	762	-	4	
x MTBE + $(1 - x)$ heptane ^b								
1489	72	354	-	-	-	-	3	
x 1-pentanol + $(1 - x)$ heptane								
2238	835	-1149	-953	-	-	0.9291	4	
B_0	B_1	B_2	B_3	B_4	B_5	B_6	B_7	s
x ₁ MTBE + x ₂ 1-pentanol + $(1 - x_1 - x_2)$ heptane								
2.1116	9.7875	-14.7082	-20.4210	29.2292	1.9541	16.5061	-16.0135	6

^a Ref. [57].

^b Ref. [15].

2.2. Equipment and procedure

The microcalorimeter used to determine the excess molar enthalpies in this work was built in the Department of Applied Physics of the University of Santiago de Compostela by Prof. Paz-Andrade [52] with thermopiles designed and made by Prof. E. Calvet [53]. The Calvet-type microcalorimeter allows recording very small heat flows, on the order of one microwatt. It consists of two parts: a thermostatic system and a detector system, formed by two twin calorimetric elements

(thermopiles). A detailed illustration of the structure and arrangement of the two thermopiles is provided in references [54,55]. Using a Mettler H51 balance with a precision of $\pm 1 \cdot 10^{-5}$ g, the mixtures were prepared by mass, assuring a likely error in the mole fraction of less than 10^{-4} . The IUPAC relative atomic mass table [56] provides the basis for all molar amounts. The equipment, the mixing device, and the measuring technique employed in this work have been described in detail in earlier articles [22,54].

The calorimeter was calibrated electrically introducing a calibration

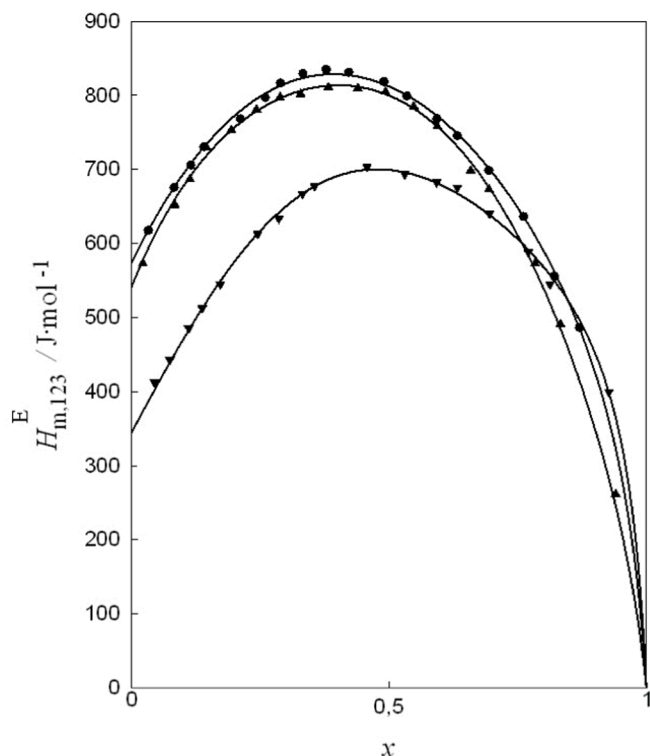


Fig. 2. Pseudobinary representation of the ternary excess molar enthalpies $H_{m,123}^E/(\text{J}\cdot\text{mol}^{-1})$ for $\{(1-x)(x'_1 \text{ MTBE} + x'_2 \text{ 1-pentanol}) + x \text{ heptane}\}$ at 298.15 K: (▼) $x'_1 = 0.2469$, $x'_2 = 0.7531$; (●) $x'_1 = 0.4999$, $x'_2 = 0.5001$; (▲) $x'_1 = 0.7500$, $x'_2 = 0.2500$; (—) correlated using Eqs. (2) and (5).

cell in the laboratory thermopile, connected to an EJP30 stabilized current source (SETARAM, Lyon, France). By measuring the excess enthalpies for the reference system $\{x \text{ cyclohexane} + (1-x) \text{ hexane}\}$ at 298.15 K, the equipment and methods were put to the test. Experimental values for excess molar enthalpies obtained for this standard system were previously published in Ref. [22].

To determine the excess molar enthalpy of the ternary mixture, we

prepared three pseudobinary mixtures, that is, mixtures with two of the three components at a known mole fraction to which we add the third component. Specifically, three binary mixtures of $\{x'_1 \text{ MTBE} + x'_2 \text{ 1-pentanol}\}$ were prepared at concentrations, x'_i , of around 0.25, 0.5, and 0.75 mol fractions of MTBE each. So, the ternary excess molar enthalpy at composition x_1 , x_2 , and $x_3 = 1 - x_1 - x_2$ was obtained by adding heptane to the initial binary mixture of $\{x'_1 \text{ MTBE} + x'_2 \text{ 1-pentanol}\}$ and can be expressed as

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

where $H_{m,op}^E$ 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 $\{x'_1 \text{ MTBE} + x'_2 \text{ 1-pentanol}\}$. Values of $H_{m,12}^E$ at three mole fractions were interpolated by using a spline-fit method.

The ternary excess enthalpy, $H_{m,123}^E$, was correlated by the equation:

$$H_{m,123}^E(\text{J}\cdot\text{mol}^{-1}) = H_{m,bin}^E + x_1x_2(1-x_1-x_2)\Delta_{123} \quad (2)$$

where $H_{m,bin}^E$ represents the binary contribution and $x_1x_2(1-x_1-x_2)\Delta_{123}$ corresponds to the ternary contribution to the excess enthalpy.

The binary contribution is the sum of the excess molar enthalpies of the corresponding binary systems, which were calculated from the fitting equations previously obtained for each of the involved binary systems. Experimental data of excess molar enthalpies for the binary mixtures $\{x \text{ MTBE} + (1-x) \text{ 1-pentanol}\}$ and $\{x \text{ MTBE} + (1-x) \text{ heptane}\}$ were previously published [57,15] and correlated with the Redlich-Kister equation [58].

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

However, the Myers-Scott [59] equation was used to fit the binary mixture $\{x \text{ pentanol} + (1-x) \text{ heptane}\}$ because of the asymmetry in the experimental data.

$$H_m^E/\text{J}\cdot\text{mol}^{-1} = \frac{x(1-x)}{1+k(1-x)} \sum_{i=1}^n A_i(2x-1)^{i-1} \quad (4)$$

Finally, the ternary contribution, Δ_{123} , was fitted to the expression suggested by Verdes et al. [25] of the form:

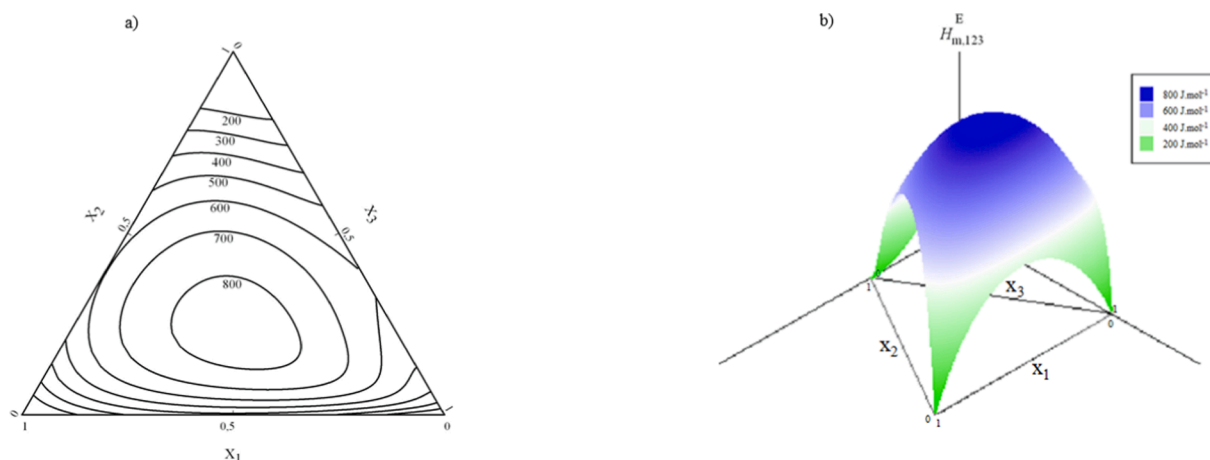


Fig. 3. Ternary excess molar enthalpy, $H_{m,123}^E/(\text{J}\cdot\text{mol}^{-1})$ for the mixture $\{x_1 \text{ MTBE} + x_2 \text{ 1-pentanol} + x_3 \text{ heptane}\}$ at 298.15 K (a) Lines of constant $H_{m,123}^E/(\text{J}\cdot\text{mol}^{-1})$, calculated with Eqs. (2) and (5). (b) Representation 3D. The maximum enthalpy is $846 \text{ J}\cdot\text{mol}^{-1}$ at $x_1 = 0.3720$, $x_2 = 0.2320$, $x_3 = 0.3960$.

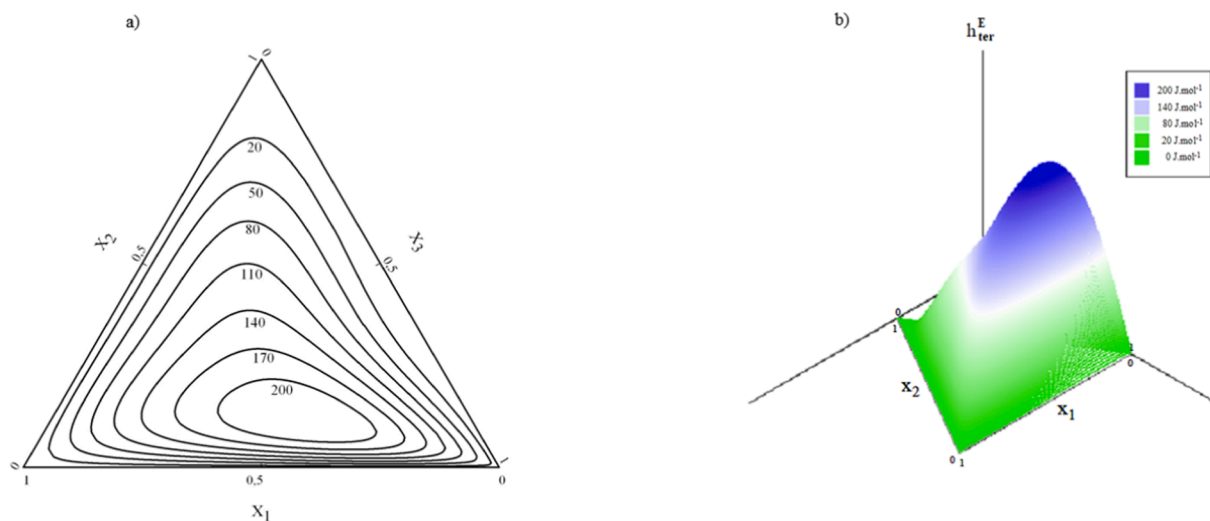


Fig. 4. (a) Lines of constant ternary contribution, $h_{ter}^E = x_1 x_2 (1 - x_1 - x_2) \Delta_{123} / (\text{J} \cdot \text{mol}^{-1})$ to the excess molar enthalpy for $\{x_1 \text{ MTBE} + x_2 \text{ 1-pentanol} + x_3 \text{ heptane}\}$ calculated with Eq. (5). (b) Representation 3D. $h_{ter,\min}^E = -0.4 \text{ J} \cdot \text{mol}^{-1}$ at $x_1 = 0.0070$, $x_2 = 0.3510$, $x_3 = 0.6420$; $h_{ter,\max}^E = 229 \text{ J} \cdot \text{mol}^{-1}$ at $x_1 = 0.3500$, $x_2 = 0.1190$, $x_3 = 0.5310$.

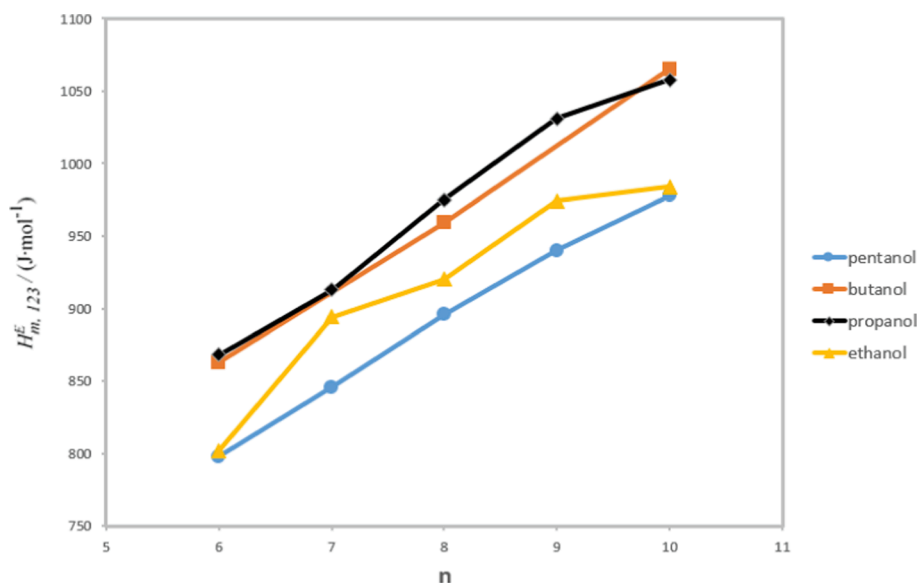


Fig. 5. Maximum values of ternary excess molar enthalpies against the number of carbons of the alkane (n) of mixtures $\{x_1 \text{ MTBE} + x_2 \text{ 1-alkanol} + (1 - x_1 - x_2) \text{ alkane}\}$ [11,12,14–21,22–25,7–9].

$$\frac{\Delta_{123}}{RT} = \frac{B_0 + B_1 x_1 + B_2 x_2 + B_3 x_1^2 + B_4 x_2^2 + B_5 x_1 x_2 + B_6 x_1^3 + B_7 x_2^3 + B_8 x_2 x_1^2 + \dots}{1 + (x_2 - x_3)} \quad (5)$$

The fitting parameters k , A_i and B_i were computed from the unweighted least-squares method using a non-linear optimization algorithm due to Marquardt [60]. The number of parameters was determined by applying to every new parameter the F-test proposed by Bevington [61].

3. Theoretical estimations

3.1. UNIFAC group contribution model

Group contribution models assume that the thermodynamic properties of the liquids in a mixture can be described by the sum of the contributions of each functional group, allowing a large number of compounds to be correlated and predicted using a much smaller set of parameters than if the molecular interactions were analyzed directly. The original UNIFAC model [62] combines the UNIQUAC quasichemical

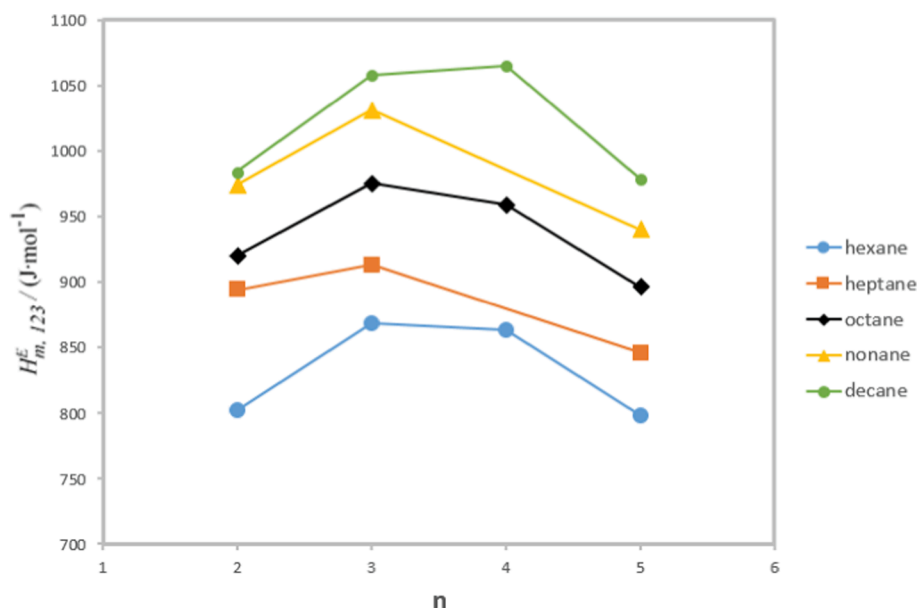


Fig. 6. Maximum values of ternary excess molar enthalpies against the number of carbons of the alkanol (n) of mixtures $\{x_1 \text{ MTBE} + x_2 \text{ 1-alkanol} + (1 - x_1 - x_2) \text{ alkane}\}$ [11,12,14–21,22–25,7–9].

Table 5

Mean deviations of the excess molar enthalpies ($\text{J}\cdot\text{mol}^{-1}$) predicted by theoretical models from the experimental data.

	LARSEN <i>et al.</i> [35]	GMEHLING <i>et al.</i> [36]
MTBE + 1-pentanol ^a	170	160
MTBE + heptane ^b	113	25
1-pentanol + heptane	30	54
MTBE + 1-pentanol + heptane	111	57

^a Ref. [25].

^b Ref. [15].

model [63] with the concept of functional groups.

Larsen *et al.* [35], modified the UNIFAC model as they considered that the temperature dependence was not appropriate for simultaneously predicting liquid–vapour equilibria, liquid–liquid equilibria and excess enthalpy using the same set of parameters. They modified the combinatorial term and made the interaction parameters temperature-dependent. Their modifications improved the results of the original UNIFAC model in all cases.

Gmehling *et al.* [36] changed the combinatorial term to apply the model to compounds with molecules of very different sizes, the residual interaction parameters were made temperature-dependent and the group structural parameters were fitted along with the interaction parameters.

Structural parameters and interaction parameters are shown in Table SI-2 and Table SI-3 (see Supporting Information).

3.2. Empirical prediction equations

Many empirical methods have been proposed to estimate multi-component mixture properties from experimental data on constituent binaries. Depending on whether or not the premise that the three binaries contribute equally to the magnitude of the ternary mixture is adopted, these methods can be classified as symmetric or asymmetric. The presence of a strongly polar component or associative in the mixture is often thought to cause asymmetry. For the asymmetric equations, we tested three different mixing orders to determine which is the most appropriate. Depending on the type of mixture, the ordering of the components will significantly contribute to the goodness of the

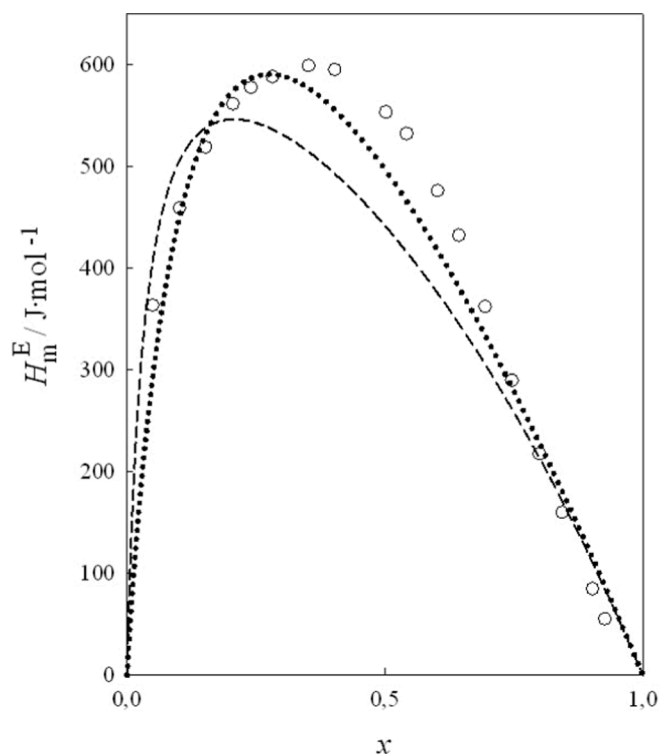


Fig. 7. Excess molar enthalpies, $H_m^E/(\text{J}\cdot\text{mol}^{-1})$, at 298.15 K of the binary mixture $\{x \text{ 1-pentanol} + (1 - x) \text{ heptane}\}$; (O) experimental values; (····) Larsen *et al.* model [35]; (---) Gmehling *et al.* model [36].

prediction obtained. The symmetric equations analyzed in this research were those proposed by Tsao and Smith [37], Toop [38], Scatchard *et al.* [39], Hillert [40], and Mathieson and Tynne [41], while the asymmetric equations were those published by Kohler [42], Jacob and Fitzner [43], Colinet [44], and Knobloch and Schwartz [45].

In the case of the asymmetric equations, three possible mixing orders were investigated to determine which provided the best prediction and to establish a rule for selecting the appropriate order for each situation.

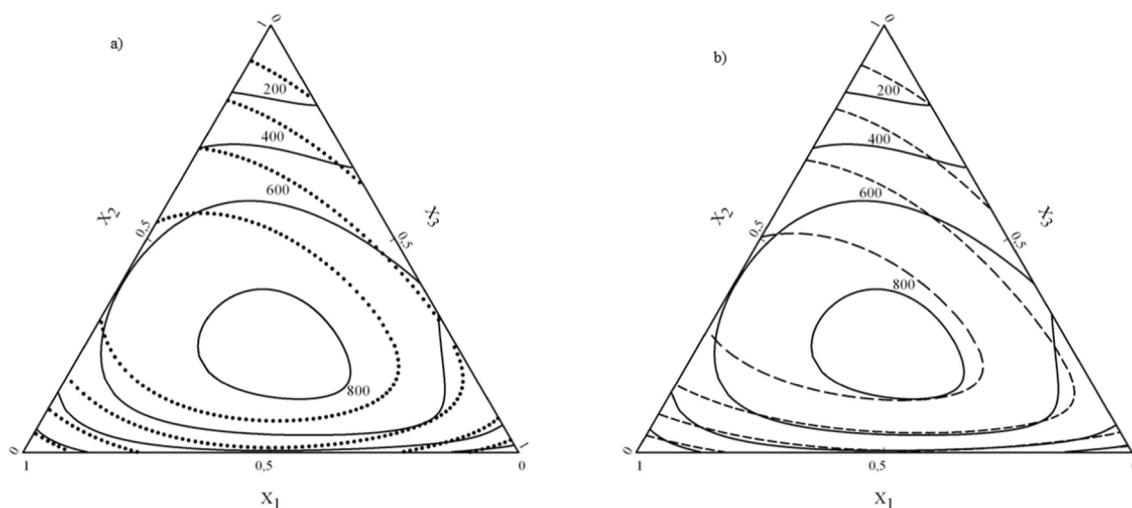


Fig. 8. Excess molar enthalpies, $H_{m,123}^E$ ($\text{J}\cdot\text{mol}^{-1}$), for the ternary mixture $\{x_1 \text{ MTBE} + x_2 \text{ 1-pentanol} + x_3 \text{ heptane}\}$ at $T = 298.15 \text{ K}$; (—) fitted by Eqs. (2) and (5); (a) (⋯) Larsen et al. model [35]; (b) (---) Gmehling et al. model [36].

Table 6

Mean deviations from the experimental values obtained with empirical predictive methods.

Empirical equations	$H_{m,123}^E/\text{J}\cdot\text{mol}^{-1}$		
Kohler		96	
Jacob Fitzner		116	
Colinet		102	
Knobloch-Schwartz		25	
Tsao-Smith	46 ^a	27 ^b	61 ^c
Toop	119 ^a	35 ^b	147 ^c
Scatchard et al	136 ^a	37 ^b	148 ^c
Hillert	125 ^a	35 ^b	147 ^c
Mathieson-Tynne	125 ^a	83 ^b	133 ^c

^a Order 123.

^b Order 231.

^c Order 312.

MTBE, 1-pentanol, and heptane were respectively designated as 1,2 and 3. The ternary system was arranged as 123, 231 and 312. Consequently, the three possible mixing orders evaluated were MTBE + 1-pentanol + heptane, 1-pentanol + heptane + MTBE or heptane + MTBE + 1-pentanol.

4. Results and discussion

Table 2 shows the experimental data of excess molar enthalpies, H_m^E , measured in this work for the binary mixture $\{x \text{ 1-pentanol} + (1-x) \text{ heptane}\}$. The excess molar enthalpies, fitting coefficients and the corresponding standard deviations for the binary mixtures $\{x \text{ MTBE} + (1-x) \text{ 1-pentanol}\}$ and $\{x \text{ MTBE} + (1-x) \text{ heptane}\}$, as measured by our team, were reported in early papers [57,15].

The experimental data, H_m^E , for the three involved binary mixtures are plotted in Fig. 1 together with the fitting curves used to correlate our ternary mixture and those found in the literature [64–67]. As can be noted, the excess enthalpies for the three involved binary mixtures are positive over the entire composition range. While the binary system $\{x \text{ MTBE} + (1-x) \text{ heptane}\}$ is symmetric, the maximum of the binary system $\{x \text{ 1-pentanol} + (1-x) \text{ heptane}\}$ shifts towards compositions rich in 1-pentanol, and the maximum of the binary system $\{x \text{ MTBE} + (1-x) \text{ 1-pentanol}\}$ is slightly shifted towards MTBE-rich compositions. All three systems follow the same trend as the results found in the literature.

The measured values of ternary excess enthalpy, $H_{m,123}^E$, at 298.15 K are listed in Table 3. The fitting coefficients and the corresponding

standard deviations from the involved binary systems and ternary mixture are reported in Table 4. Fig. 2 illustrates the pseudobinary representation of the experimental $H_{m,123}^E$, where Eq. (5) was applied to fit the ternary contribution. The lines of the constant ternary excess molar enthalpy, $H_{m,123}^E$, calculated using Eqs. (2) and (5) are plotted in Fig. 3a, whereas Fig. 4a represents the ternary contribution, $x_1 x_2 (1-x_1-x_2) \Delta_{123}$, to the excess molar enthalpy, where Δ_{123} , was correlated with Eq. (5). Figs. 3b and 4b illustrate a 3D representation.

Excess molar enthalpy of the ternary system is positive throughout the composition range, reaching its maximum value, $H_{m,123}^E = 846 \text{ J}\cdot\text{mol}^{-1}$ at $x_1 = 0.3720$, $x_2 = 0.2320$, $x_3 = 0.3960$. Except for a region around compositions rich in 1-pentanol, the ternary contribution to the excess molar enthalpy is also positive and its representation is asymmetric. The maximum values of the ternary contribution to the excess ternary enthalpy are around $229 \text{ J}\cdot\text{mol}^{-1}$ at $x_1 = 0.3500$, $x_2 = 0.1190$, $x_3 = 0.5310$ and the minimum values are around $-0.4 \text{ J}\cdot\text{mol}^{-1}$ at $x_1 = 0.0070$, $x_2 = 0.3510$, $x_3 = 0.6420$. The maximum ternary contribution is around 27 % of the ternary enthalpy value. Therefore, the ternary contribution is quite significant and may be due to the crossed energetic interactions between the associated compound (the hydroxyl group in the alkanol molecule), the molecule of MTBE, and the non-polar alkane.

Table SI-4 (see the Supporting Information) allows us to visualize the trend of excess enthalpy changes when increasing the alkane or alkanol chain length. In addition, it can be seen that all mixtures analyzed are asymmetric with the molar fractions in which the maximums are reached, similar to ours (around 0.37 for MTBE and 0.23 for alcohol).

The maximum $H_{m,123}^E$, for our ternary system and the values obtained when the 1-alkanol (1-ethanol, 1-propanol, 1-butanol) or the n-alkane (hexane, heptane, nonane, decane) present in the mixture is another, were compared in Figs. 5 and 6.

It can be seen that regardless of the alcohol, the enthalpy increases with increasing chain length of the alkane. However, the maxima increases as the number, n, of alcohol carbons increases, from ethanol to propanol, and then decreases for 1-butanol and 1-pentanol, like the trend obtained with the binary mixtures of MTBE + alkanol [57]. Gonzalez et al. [68], justify the fact that the excess molar enthalpy remains practically constant for long-chain alcohols in ether + 1-alcohol mixtures, due to the decrease in alcohol-alcohol interactions being compensated by much weaker interactions, between the OH and O groups.

A similar behaviour of ether + alkanol + alkane ternary mixtures is observed, if instead of MTBE another branched ether is used, for example, diisopropyl ether (DIPE), *tert*-amyl methyl ether (TAME) or

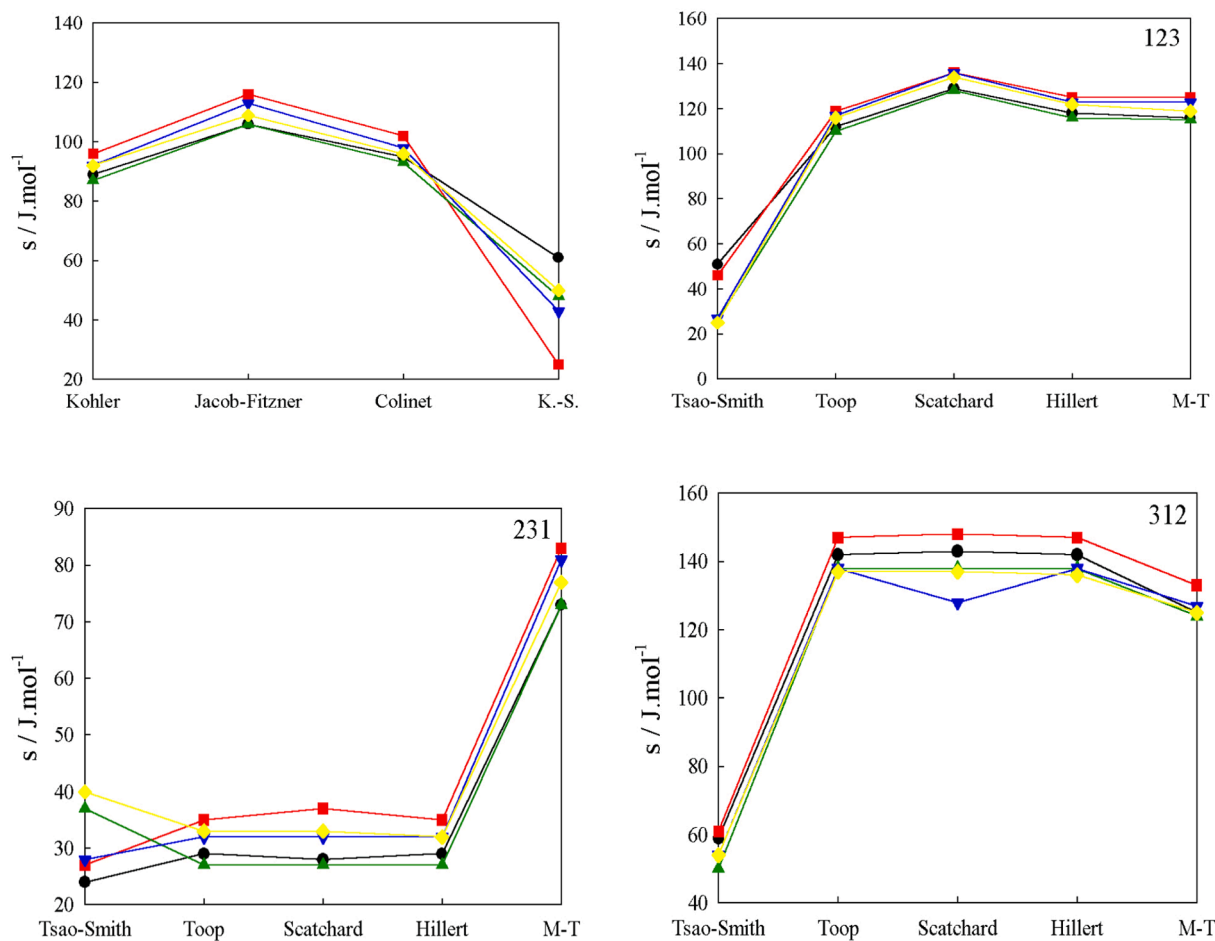


Fig. 9. Mean deviations calculated with results achieved with the empirical prediction equations applied to the ternary systems MTBE + pentanol + alkane (● hexane, ■ heptane, ▲ octane, ▼ nonane, ◆ decane).

ethyl *tert*-butyl ether (ETBE). The molar excess enthalpy is positive and increases with the length of the alcohol chain. [26,69,70]. In monoether + 1-alcohol systems, the excess enthalpy increases from methanol to 1-propanol and then slowly decreases [71,72].

The minimum value of the excess molar volume of all ternary mixtures MTBE + 1-alcohol + n-alkane, previously published by our group [14,16,19,20,46,73–79], is independent of the length of the alkane chain and is reached at the minimum value corresponding to the binary mixture MTBE + alcohol.

The excess molar volumes of MTBE + alcohol mixtures are symmetrical and negative throughout the concentration range [73,79–82]. The negative value is a consequence of better packing of the 1-alcohol molecules in the interstices of the ether molecules. The excess volume of the mixture would be expected to increase with the length of the alcohol chain, due to the greater difficulty in coupling. However, for alcohols with more than two carbon atoms, the volume decreases as the alcohol chain increases. This may be due to conformational changes in the alcohol molecules that produce better packing between the components of the mixture. Absolute mean deviations of the excess molar enthalpies predicted by the theoretical model of UNIFAC, in the versions of Larsen [35] and Gmehling [36], against the experimental values are listed in Table 5. The best results for the binary mixture 1-pentanol + heptane were achieved with the Larsen version. However, for the binary mixtures MTBE + 1-pentanol and MTBE + heptane, and for the ternary system MTBE + 1-pentanol + heptane, the results obtained with the Gmehling version are in better agreement with the experimental data

than the Larsen ones. Fig. 7, illustrates the predictions for H_m^E of the binary mixture {1-pentanol + heptane}. The graphical representation of the predictions for the other two involved binary mixtures, {MTBE + pentanol} and {MTBE + heptane} were previously published [25,15]. Fig. 8a and b, display graphically the predictions for $H_{m,123}^E$.

Table 6 list the absolute mean deviations calculated by comparing the experimental results of the excess molar enthalpy for the ternary system MTBE + 1-pentanol + heptane, with the estimated values provided by the tested symmetric and asymmetric empirical equations. For the asymmetric equations, three possible mixing orders have been compared: MTBE + 1-pentanol + heptane, named as 123; 1-pentanol + heptane + MTBE, named as 231 or heptane + MTBE + 1-pentanol, named as 312. It can be said that it is very difficult to anticipate a priori which of the equations would provide better predictions for a certain system. Fig. 9 illustrates the mean deviations calculated with the results achieved with the empirical prediction equations applied to the ternary systems MTBE + pentanol + alkane (hexane [22], heptane [this work], octane [23], nonane [24], decane [25]). For all these mixtures tested, the symmetric expression that provides the best result is the Knobloch-Schwartz equation, whereas the Jacob-Fitzner equation gives the worst results. The predictions obtained using the Colinet and the Kohler expressions show no discernible differences. Regarding the asymmetric equations, the dependence with the mixing order is very pronounced, obtaining the best deviations, in most cases, taking 1-pentanol as the first component in the mixing order 213. The Tsao-Smith is the one that provides the best results, for all systems and mixing orders tested except

for systems containing octane and decane, in which the deviation for the order of mixing 231, is slightly higher than that obtained with other asymmetric equations. The fact that the deviations achieved with these expressions are so high can be attributed to the relevance of ternary contribution term. Lower deviations are often found using this type of formulation for qualities when the ternary contribution is not significant.

5. Conclusions

Experimental data of excess molar enthalpy of the ternary mixture MTBE + 1-pentanol + heptane were measured and compared with those of other, previously reported, that contain ether + 1-alkanol + n-alkane. Excess molar enthalpy of our ternary system is positive throughout the composition range. The ternary contribution to the excess molar enthalpy is also positive, except for a region around compositions rich in 1-pentanol, and its representation is asymmetric. Regardless of the alcohol, the maxima enthalpy increases with increasing chain length of the alkane. However, the maxima increases as the number, *n*, of alcohol carbons increases, from ethanol to propanol, and then decreases for 1-butanol and 1-pentanol. A similar behaviour is observed, for other ternary mixtures of ether + alkanol + alkane, if instead of MTBE another branched ether is used.

Two versions of the UNIFAC group contribution model were applied to the experimental data of the binary and ternary mixtures related to this investigation. The best results for the ternary mixture were achieved with the Gmehling version. Furthermore, nine empirical equations for estimating ternary properties from binary results were put to the test using the experimental data to see how well they could predict ternary qualities.

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CRediT authorship contribution statement

Pedro V. Verdes: Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing – original draft. **Javier Vijande:** Writing – review & editing, Writing – original draft, Formal analysis. **Marta M. Mato:** Conceptualization, Methodology, Formal analysis, Visualization, Supervision, Writing – original draft, Writing – review & editing. **José Luis Legido:** Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **M.I. Paz Andrade:** Conceptualization, Methodology, Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Jose L. Legido reports financial support was provided by XUNTA DE GALICIA. Marta M. Mato reports article publishing charges was provided by University of Vigo. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2024.125323>.

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