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Excess Molar Enthalpies of Ternary and Binary Mixtures Containing 2-Methoxy-2-methylpropane, 1-Propanol, and Nonane[†]

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Excess molar enthalpies for the ternary system {x_1 2-methoxy-2-methylpropane (MTBE) + x_2 1-propanol + $(1 - x_1 - x_2)$ nonane} and the involved binary mixture {x 1-propanol + $(1 - x)$ nonane} have been measured at the temperature of 298.15 K and atmospheric pressure, over the whole composition range. No experimental excess enthalpy values were found in the currently avaliable literature for the ternary and binary mixtures under study in similar conditions. Values of excess molar enthalpies were measured using a Calvet microcalorimeter. The results were fitted by means of different variable degree polynomials. Smooth representations of the results are presented and used to construct constant excess molar enthalpy contours on Roozeboom diagrams. The group contribution model of the UNIFAC model (in the versions of Larsen et al. and Gmehling et al.) was used to estimate ternary excess enthalpy values. Several empirical expressions for estimating ternary properties from binary results were also tested.

Introduction

This paper is part of our systematic program of research concerning the experimental study of several thermodynamic and transport properties of binary and ternary liquid mixtures containing 2-methoxy-2-methylpropane, alkan-1-ol, and alkane used as oxygenating agents in gasoline technology. It is the continuation of previous works,[1−11] which form part of the scientific project entitled "Study on physical properties of mixtures Hydrocarbon + Alcohol + Ether like alternative fuels", where the main objective has been the characterization of nonelectrolyte liquids, and their mixtures, through experimental determination of thermophysical properties on mixing.

Tertiary alkyl ethers have become important additives for gasoline because their influence to increase the octane number and to decrease the emission of carbon monoxide is combined with a similarity of properties compared to hydrocarbons. So the use of 2-methoxy-2-methylpropane, pure or mixed with alkanols or alkanes, has been recommended as a high octane blending agent for motor gasoline. The most recent concern about health risks caused by the contamination of drinking water from MTBE into the ground makes it appear to be a somewhat controversial gasoline additive. These ethers are also increasingly used as solvents or chemical reactants. From a theoretical point of view, mixtures of alkanols and ethers are of interest due to the complex structure, consequent on the self-association of the alcohols, which is partially destroyed by the active ether molecules, and on the new intermolecular OH−O bonds created. Complexity is increased when the mixture also contains one or more alkanes.

The aim of this work is to provide a set of values for the characterization of the molecular interactions of these mixtures and to examine the effect of the enlargement of the CH_2 unit in the alkan-1-ol or *n*-alkane.

In this framework, excess molar enthalpy determination is considered of primary interest, as this property is essential in characterizing the mixing process. It provides direct information about the energetic effects arising between the molecules present in the mixture. 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, which is essential when studying new theoretical approaches to the liquid state matter and its mixtures.

Following the above, in this communication we report the measured values of excess molar enthalpies for a ternary mixture of 2-methoxy-2-methylpropane (MTBE) + 1-propanol + nonane and the involved binary mixture 1-propanol + nonane, over the whole mole fraction range at 298.15 K and atmospheric pressure. We are not aware of any excess enthalpy data in the literature for the ternary system presented in this study. For the binary mixture 1-propanol + nonane, only Christensen et al.[13] report experimental excess molar enthalpy at 298.15K and 170 kPa.

Experimental values were compared with the predictions obtained by applying the UNIFAC group contribution model in the versions of Larsen et al.[12] and Gmehling et al.[13] The predicting capability of several empirical methods[14−22] was also tested.

Materials and Methods

The chemicals were supplied by Aldrich. The mole fraction purities were all greater than 0.99. All products 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 handling and

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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 1-propanol + (1 − x) nonane
0.0794	494
0.1401	604
0.2595	711
0.3588	727
0.4410	723
0.5192	690
0.5829	646
0.7046	539
0.7517	488
0.7992	419
0.8361	360
0.8780	282
0.9110	218
0.9469	139
0.9689	86

disposal of the chemicals used has been done according to the recommendation of the *CRC Handbook of Chemistry and Physics*.[23]

The 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. The mixtures were prepared by mass using a Mettler H51 balance (precision $\pm 1 \cdot 10^{-5}$ g), ensuring a probable uncertainty in the mole fraction less than 10^{-4}. All molar quantities are based on the IUPAC relative atomic mass table.[24] A Philips PM2535 voltmeter 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 have been published.[25,26] 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[27] and Gmehling.[28] The uncertainty in excess molar enthalpy measurements is estimated to be better than 1 %.

Three experimental measurements were carried out for the ternary compositions resulting from adding nonane to a binary mixture composed of $\{x_1'$ MTBE + x_2' 1-propanol$\}$, where $x_2' = 1 - x_1'$. The ternary composition point is then a pseudobinary mixture composed by addition of nonane to the binary mixture. Thus, the ternary excess molar enthalpy at the pseudobinary composition x_1, x_2, $(x_3 = 1 - x_1 - x_2)$ can be expressed as

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

where $H^E_{m,\phi}$ is the measured excess molar enthalpy for the pseudobinary mixture and $H^E_{m,12}$ is the excess molar enthalpy of the initial binary mixture $\{x_1'$ MTBE + x_2' 1-propanol$\}$. Values of $H^E_{m,12}$ at different mole fractions were interpolated by using a spline-fit method. Equation 1 does not involve any approximation.

Data Correlation and Experimental Results

The experimental data, fitting parameters, and the standard deviations of excess molar enthalpies for the binary mixtures $\{x$ 2-methoxy-2-methylpropane (MTBE) + $(1 - x)$ 1-propanol$\}$ and $\{x$ 2-methoxy-2-methylpropane (MTBE) + $(1 - x)$ nonane$\}$ were reported in early papers.[10,8]

Experimental values of H_m^E for the $\{x$ 1-propanol + $(1 - x)$ nonane$\}$ are listed in Table 1. This set of data was fitted to a variable-degree polynomial suggested by Myers−Scott.[29]

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

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 Figure 1. Table 2 shows fitting coefficients and the corresponding standard deviations of all three involved systems.

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

$$H^E_{m,123}/(\text{J·mol}^{-1}) = H^E_{m,\text{bin}} + x_1 x_2 (1 - x_1 - x_2)\Delta_{123} \tag{3}$$

where Δ_{123} were fitted to the expression suggested by Morris et al.[30] of the form

$$\frac{\Delta_{123}}{RT} = (B_0 + B_1 x_1 + B_2 x_2 + B_3 x_1^2 + B_4 x_2^2 + B_5 x_1 x_2 + B_6 x_1^3 + B_7 x_2^3 + \ldots) \tag{4}$$

The fitting parameters k, A_i, and B_i were computed from the unweighed least-squares method using a nonlinear optimization

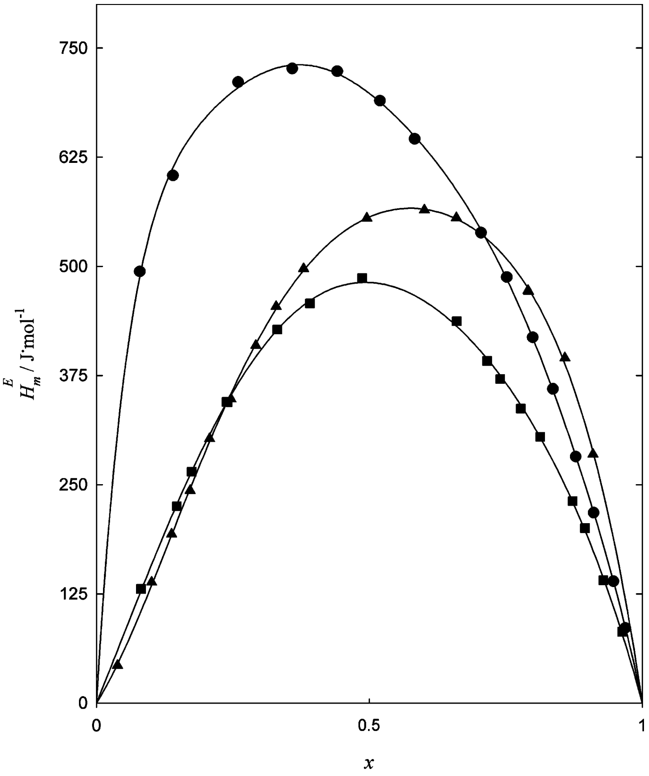

Figure 1. Excess molar enthalpies H_m^E/(J·mol^{-1}) at 298.15 K of the three involved binary systems measured in this work. Experimental values of: ▲, $\{x$ MTBE + $(1 - x)$ 1-propanol$\}$ taken from ref 10; ■, $\{x$ MTBE + $(1 - x)$ nonane$\}$ taken from ref 8; ●, $\{x$ 1-propanol + $(1 - x)$ nonane$\}$ from this work; —, fitting curve.

Table 2. Fitting Parameters, A_i/J·mol^{-1}, and Standard Deviations, s/J·mol^{-1}

A_1	A_2	A_3	A_4	k	s
		x MTBE + (1 − x) 1-propanol[a]			
2226	534	361	1074	-	4
		x MTBE + (1 − x) nonane[b]			
1927	−58	—	447	-	3
		x 1-propanol + (1 − x) nonane			
2790	1757	425	544	0.9620	3

[a] Ref 10. [b] Ref 8.

Table 3. Excess Molar Enthalpies, $H^{E}_{m,123}$, at 298.15 K for the Ternary Mixture x_1 MTBE + x_2 1-Propanol + $(1 - x_1 - x_2)$ Nonane[a]

x_1	x_2	$H^{E}_{m,\phi}$ J·mol^{-1}	$H^{E}_{m,123}$ J·mol^{-1}	x_1	x_2	$H^{E}_{m,\phi}$ J·mol^{-1}	$H^{E}_{m,123}$ J·mol^{-1}
			$x_1' = 0.2429$, $H^{E}_{m,12} = 350$ J·mol^{-1}				
0.0270	0.0842	495	534	0.1772	0.5521	539	794
0.0547	0.1704	650	728	0.1892	0.5898	488	760
0.0756	0.2356	722	830	0.1999	0.6230	419	707
0.1007	0.3139	743	888	0.2089	0.6510	358	659
0.1158	0.3610	739	906	0.2200	0.6857	258	574
0.1291	0.4023	711	897	0.2283	0.7115	178	505
0.1506	0.4695	646	863	0.2358	0.7349	91	431
0.1596	0.4974	618	848				
			$x_1' = 0.5020$, $H^{E}_{m,12} = 557$ J·mol^{-1}				
0.0551	0.0547	401	462	0.3511	0.3484	591	980
0.1008	0.1001	575	687	0.3780	0.3751	525	944
0.1480	0.1469	680	844	0.4044	0.4012	446	895
0.1871	0.1856	730	937	0.4289	0.4255	366	842
0.2274	0.2256	740	992	0.4474	0.4439	285	782
0.2975	0.2952	697	1028	0.4678	0.4641	195	714
0.3234	0.3209	653	1012	0.4862	0.4824	97	636
			$x_1' = 0.7541$, $H^{E}_{m,12} = 507$ J·mol^{-1}				
0.0648	0.0211	250	293	0.5149	0.1679	563	909
0.1342	0.0437	420	510	0.5551	0.1810	495	868
0.2010	0.0655	548	683	0.5913	0.1928	438	835
0.2689	0.0877	647	828	0.6369	0.2076	354	782
0.3213	0.1048	671	887	0.6669	0.2174	279	727
0.3730	0.1216	680	930	0.6977	0.2275	193	661
0.4160	0.1356	659	938	0.7301	0.2380	96	586
0.4664	0.1520	616	929				

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

Table 4. Fitting Parameters, B_i, for Equation 4 and Standard Deviations, s

	$H^{E}_{m,123}$/ J·mol^{-1}
B_0	9
B_1	−9
B_2	−24
B_3	4
B_4	19
B_5	19
s	9

algorithm due to Marquardt.[31] The number of parameters was determined by applying to every new parameter the F-test proposed by Bevington.[32] The fitting coefficients and the corresponding standard deviations from experimental values of ternary mixture are presented in Table 4.

Figure 2 shows the pseudobinary representation of the measured experimental values of the $H^{E}_{m,123}$, together with the correlated curves, where eq 4 was applied to fit the ternary contribution.

The lines of constant ternary excess molar enthalpy, $H^{E}_{m,123}$, calculated using eq 3 are plotted in Figure 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 4.

Theoretical Predictions

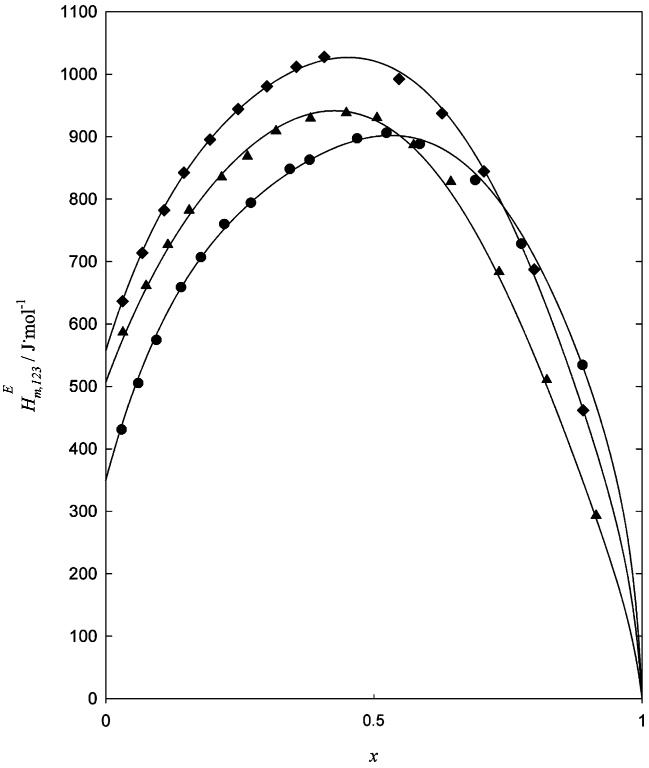

Figure 2. Pseudobinary representation of ternary excess molar enthalpies $H^{E}_{m,123}$/(J·mol^{-1}) for $\{(1 - x)(x_1'$ MTBE + x_2' 1-propanol) + x nonane$\}$ at 298.15 K: ●, $x_1' = 0.2429$, $x_2' = 0.7571$; ◆, $x_1' = 0.5020$, $x_2' = 0.4980$; ▲, $x_1' = 0.7541$, $x_2' = 0.2459$; —, correlated using eq 3.

The UNIFAC group contribution model was originally developed by Fredenslund et al.,[33] from the UNIQUAC equation by Abrams and Prausnitz[34] for a multicomponent mixture. The activity coefficient in this model was calculated as the sum of two terms. The first one was a combinatorial and takes into account the differences of shape and size of the molecules. The second one was 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.[12] modified the UNIFAC model to predict vapor−liquid and liquid−liquid equilibria as well as excess enthalpies. The interaction parameters became temperature dependent, and the combinatorial term was modified.

Gmehling et al.[13] proposed a new modified UNIFAC method whose main advantage was 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. 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 5.

Figure 4 illustrates the predictions for H^{E}_{m} of the binary mixtures obtained with the theoretical models. It is evident that there is not a good quantitative agreement between the estimation provided by the theory and the experimental curves; nevertheless, the shape of the H^{E}_{m} vs composition curves is well predicted for the three involved binary mixtures.

Experimental results for the ternary excess molar enthalpy and the ternary contribution, $x_1x_2(1 - x_1 - x_2)\,\Delta_{123}$, to the excess molar enthalpy were compared with the predictions of UNIFAC group contribution models considered by Larsen et al.[12] and Gmehling et al.,[13] in Figure 5.

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

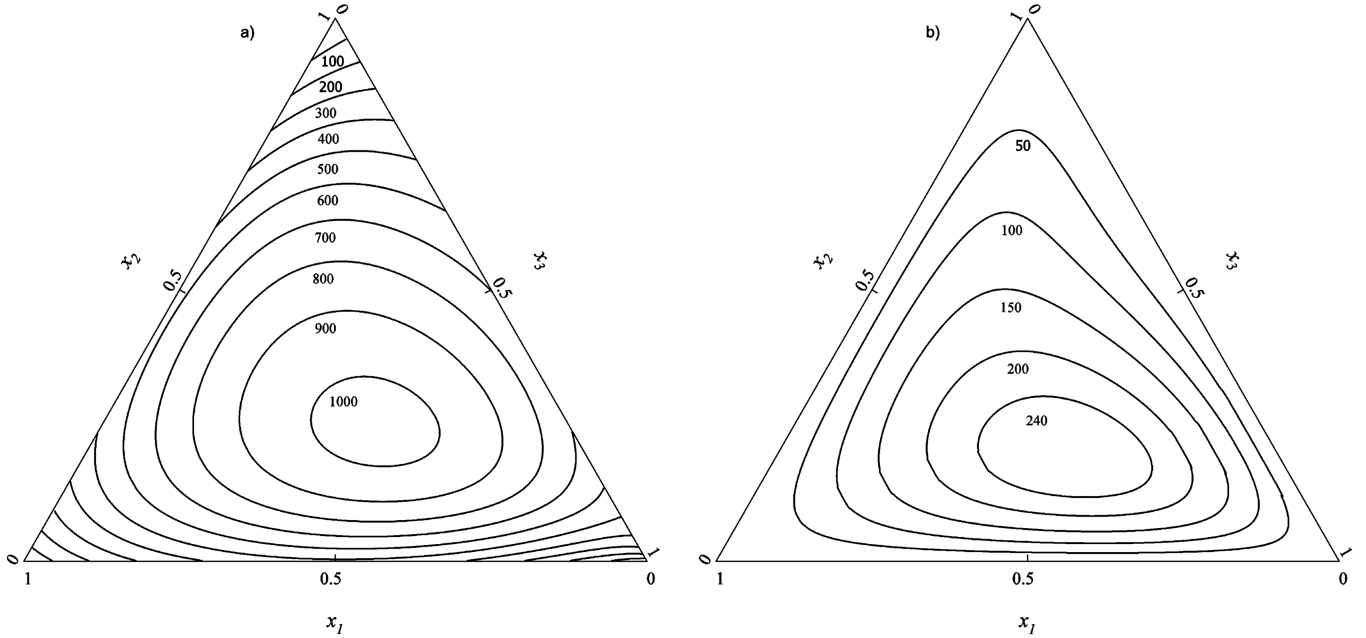

Figure 3. Representation for {x_1 MTBE + x_2 1-propanol + (1 − x_1 − x_2) nonane} at 298,15 K of: (a) —, Curves of constant ternary excess molar enthalpy, $H^{E}_{m,123}$/(J·mol^{-1}), calculated with eq 3. (b) —, Curves of constant ternary contribution, $x_1x_2(1 - x_1 - x_2)\Delta_{123}$, to the excess molar enthalpy $H^{E}_{m,123}$/(J·mol^{-1}), where Δ_{123} were fitted to eq 4.

Table 5. Mean Deviations of Excess Molar Enthalpies (J·mol^{-1}) Predicted by Theoretical Models from the Experimental Data

	Larsen	Gmehling
MTBE + 1-propanol	124	154
MTBE + nonane	85	39
1-propanol + nonane	52	54
MTBE + 1-propanol + nonane	67	56

Table 6. Mean Deviations from the Experimental Values Obtained with Empirical Predictive Methods[a]

empirical equations	$H^{E}_{m,123}$/J·mol^{-1}		
Kohler	122	—	—
Jacob Fitzner	141	—	—
Colinet	122	—	—
Knobeloch-Schwartz	24	—	—
Tsao-Smith	50[b]	26[c]	78[d]
Toop	142[b]	75[c]	156[d]
Scatchard et al.	159[b]	75[c]	158[d]
Hillert	143[b]	75[c]	156[d]
Mathieson-Tynne	149[b]	114[c]	152[d]

[a] For the asymmetric equations, three numberings of the components have been compared, in this order, 123, 231, 312. [b] Order 123. [c] Order 231. [d] Order 312.

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,[14] Jacob and Fitzner,[15] Colinet,[16] and Knobeloch and Schwartz,[17] while the asymmetric ones have been suggested by Tsao and Smith,[18] Toop,[19] Scatchard et al.,[20] Hillert,[21] and Mathieson and Thynne.[22] Table 6 lists the mean deviations of the excess molar enthalpies for the ternary system predicted by empirical equations and the experimental values. For the asymmetric equations, three different numberings of the components have been tested, 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-propanol, and nonane were, respectively, named as 1,2,3. Then, the rows A, B, C of Table 6 fit to the 2-methoxy-2-methylpropane + 1-propanol + nonane as 123, 231, 312, respectively, ordered, being the first element considered in each case MTBE, 1-propanol, or nonane in this order.

Discussion of Results

The excess enthalpies for the three involved binary mixtures are positive over the whole range of composition. The endothermicity of these mixtures suggests then that the positive contributions to the excess enthalpy, namely, the breaking of interactions present in the pure liquids (hydrogen bonding, dipolar interaction, and orientational order), are energetically more important than the negative contribution, which is a specific interaction between unlike molecules.

The curve for {x MTBE + (1 − x) nonane} is symmetrical, while those of the other two binaries are asymmetrical, that of {x MTBE + (1 − x) propanol} peaking at MTBE-rich compositions and that of {x propanol + (1 − x) nonane} at nonane-rich compositions. Both these asymmetries can be interpreted as reflecting the strength of propanol−propanol 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.

In MTBE + propanol + *n*-alkane systems, $H^{E}_{m,123}$ increases as the chain length of the alkane increases. During the mixing process, the existing order in the *n*-alkanes disrupts, which contributes positively to $H^{E}_{m,123}$. This contribution is more important for longer *n*-alkanes

The excess molar enthalpy for the ternary system is positive over the whole range of composition, showing a maximum value at $x_1 = 0.3087$, $x_2 = 0.2585$, $x_3 = 0.4428$, $H^{E}_{m,123} = 1031$ J·mol^{-1}.

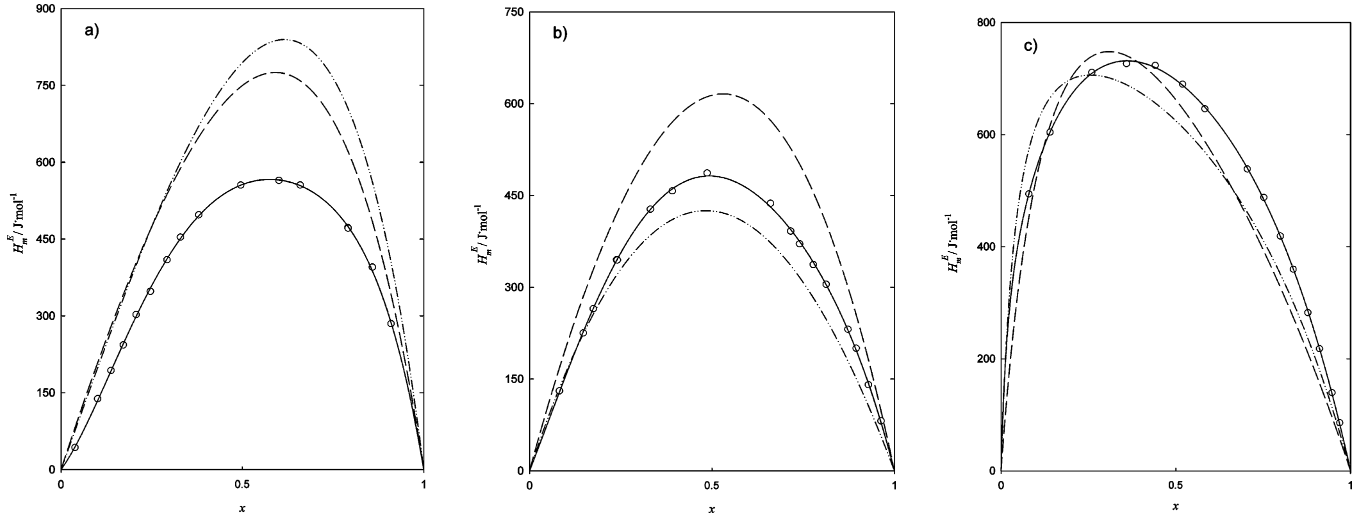

Figure 4. Excess molar enthalpies H_m^E/(J·mol^{-1}) at 298.15 K of binary mixtures: (a) {x MTBE + (1 − x) 1-propanol}, (b) {x MTBE + (1 − x) nonane}, (c) {x 1-propanol + (1 − x) nonane. ○, experimental values; —, fitting curve; - - -, Larsen et al. model;[12] -••-••-, Gmehling et al. model.[13]

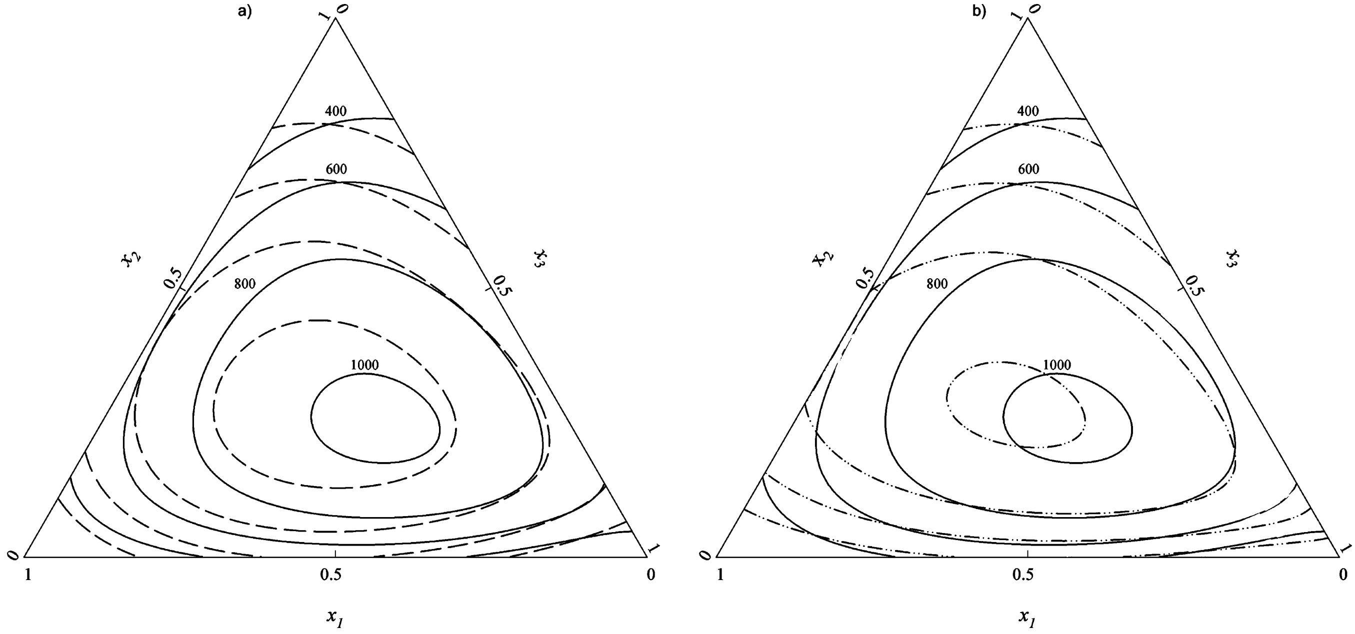

Figure 5. Comparison between experimental and predicted curves of the ternary excess molar enthalpy $H_{m,123}^E$/(J·mol^{-1}) for {x_1 MTBE + x_2 1-propanol + (1 − x_1 − x_2) nonane} at 298.15 K: —, fitted by eq 3; - - -, Larsen et al. model;[12] -••-••-, Gmehling et al. model.[13]

The ternary contribution is also positive, and the representation is asymmetric. This means that, as can be seen in Figure 3b, the position of the maximum does not coincide with the center of the Gibbs triangle. There exists a maximum at $x_1 = 0.3340$, $x_2 = 0.1961$, $x_3 = 0.4698$, and $H_{m,123}^E = 270$ J·mol^{-1}. The value of the maximum ternary contribution is about 26 % 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 nonpolar alkane.

The theoretical predictions using the Larsen and Gmeling models are shown in Table 5 and Figures 4 and 5. It can be seen that for the binary mixtures 1-propanol + nonane and MTBE + 1-propanol the best results are achieved with the Larsen version. For the systems MTBE + nonane and MTBE + 1-propanol + nonane, the results obtained with the Gmehling version are in better agreement with the experimental data than the Larsen ones.

Deviations obtained using empirical methods[14−22] are rather high, and this fact can be attributed to the importance of the ternary contribution term. Using this kind of expression, lower deviations are usually obtained for those properties where the ternary contribution is not important. The best agreement with the experimental data was achieved by the symmetric equation from Knobeloch and Schwartz.[17] The dependence on the arrangement of the components in each asymmetric equation can be observed. For all cases, the best results are obtained using arrangement B (231).

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