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Excess Molar Enthalpies of Ternary and Binary Mixtures Containing 2-Methoxy-2-Methylpropane, Ethanol, and Nonane

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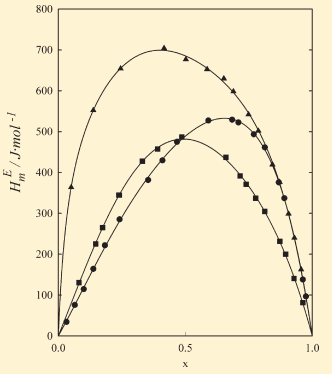
ABSTRACT: Forming part of the scientific project entitled "Study on Physical Properties of Mixtures Hydrocarbon + Alcohol + Ether Like Alternative Fuels", the present article reports experimental data of excess molar enthalpies for the ternary system $\{x_1$ 2-methoxy-2-methylpropane (MTBE) + x_2 ethanol + $(1 - x_1 - x_2)$ nonane$\}$ and the involved binary mixture $\{x$ ethanol + $(1 - x)$ nonane$\}$ 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 available literature for the ternary mixture under study. 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 excess molar enthalpies for the binary and ternary system are positive over the whole range of composition. The binary mixture $\{x$ ethanol + $(1 - x)$ nonane$\}$ is asymmetric, with its maximum displaced toward a high mole fraction of nonane. The ternary contribution is also positive, and the representation is asymmetric.



INTRODUCTION

This paper contributes to the series of ternary mixtures reported in earlier works,[1−12] where excess molar enthalpies of binary and ternary mixtures containing as components 2-methoxy-2-methylpropane (MTBE), alkanols, and alkanes, used as oxygenating agents in gasoline technology, were studied. All of them are part of the scientific project entitled "Study on Physical Properties of Mixtures Hydrocarbon + Alcohol + Ether Like Alternative Fuels", whose main objective has been the characterization of nonelectrolyte liquids and their mixtures, through experimental determination of thermophysical properties on mixing.

In this framework, the excess molar enthalpy determination is considered of primary interest from a thermodynamic point of view, as this property is essential in characterizing 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, which is essential when studying new theoretical approaches to the liquid state of matter and its mixtures. From a theoretical point of view, mixtures of alkanols and ethers are of interest due to their complexity, consequently 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. The complexity is increased when the mixture also contains one or more alkanes.

Following the above considerations, it is desirable to know the thermodynamic properties of binary and ternary mixtures formed by MTBE, hydrocarbons, and alkanols. Our group has reported thermodynamic properties of various similar mixtures;[1−12] the study is now continued considering ethanol as second component and nonane as the third component in the present work. This should help to study the effect of alkane chain length in the binary mixtures involved and subsequent effects on the ternary mixture.

So, the aim of this investigation was to measure, using a Calvet microcalorimeter, experimental excess molar enthalpies, over the whole composition range, for the ternary system $\{x_1$ MTBE + x_2 ethanol + $(1 - x_1 - x_2)$ nonane$\}$ and the involved binary mixture $\{x$ ethanol + $(1 - x)$ nonane$\}$ at the temperature of 298.15 K and atmospheric pressure. The binary experimental data for the mixtures $\{x$ MTBE + $(1 - x)$ ethanol$\}$ and $\{x$ MTBE + $(1 - x)$ nonane$\}$ were reported in previous works.[12,10] The results were fitted by means of polynomials of different variable degrees.

The literature referring to the binary systems $\{x$ 1-alkanol + $(1 - x)$ alkane$\}$ is very large. Christensen et al.[13] conducted measurements of H_m^E of $\{x$ ethanol + $(1 - x)$ nonane$\}$ at 298.15 K and 170 kPa. Savini et al.[14] report experimental data for this mixture at 303.15 K and 318.15 K, and Kwon et al.[15] published experimental data at 313.15 K.

The only experimental data of excess molar enthalpy, related to ternary mixtures MTBE + alkanol + *n*-alkane, available in the literature were published by Zhu et al.[16−18] They report data for MTBE + ethanol + *n*-alkane (hexane[16] and octane[17]) and MTBE + 1-propanol + *n*-alkane (hexane[18] and octane[17]) at 298.15 K.

We are not aware of any previous experimental measurements of excess enthalpy in the literature for the ternary and binary

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Table 1. Sources and Purities of the Chemical Substances Employed in This Work

chemical name	source	mass fraction purity
MTBE[a]	Aldrich	>0.998
ethanol	Scharlau	>0.999
nonane	Aldrich	>0.998

[a] MTBE = 2-methoxy-2-methylpropane.

systems presented in this study at 298.15 K and atmospheric pressure.

MATERIALS AND METHODS

The chemical substances employed were commercial products of the best quality grade. Their sources and purities (stated by supplier) are listed in Table 1. All products were kept in argon (N-55) atmosphere, degassed by an ultrasound technique and used without further purification other than drying with Union Carbide 0.4 nm molecular sieves to remove residual traces of water. The handling and disposal of the chemicals used has been done according to the recommendation of the *CRC Handbook of Chemistry and Physics*.[19]

The experimental excess molar enthalpies were measured at 298.15 K 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 temperature was controlled using a digital thermometer and was regulated to better than ± 0.01 K. The mixtures were prepared by mass using a Mettler H51 balance (precision ± $1 \cdot 10^{-5}$ g), ensuring a uncertainty in the mole fraction less than 10^{-4}. All molar quantities are based on the International Union of Pure and Applied Chemistry (IUPAC) relative atomic mass table.[20] 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 microcalorimeter description and the experimental method have been published earlier.[21,22] 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[23] and Gmehling.[24] 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 ethanol$\}$, where $x'_2 = 1 - x'_1$. The ternary mixture is then a pseudobinary mixture composed of nonane and a mixture of MTBE and ethanol with constant x'_2. 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

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

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 ethanol$\}$. 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.

Table 2. Experimental Excess Molar Enthalpies, H^E_m, at the Temperatature T = 298.15 K for the Binary Mixture x Ethanol + $(1 - x)$ Nonane[a]

x	H^E_m / J·mol^{-1}	x	H^E_m / J·mol^{-1}
0.0507	364	0.7490	542
0.1378	552	0.7877	502
0.2453	654	0.8433	419
0.4164	704	0.8715	376
0.5022	677	0.9065	299
0.5860	652	0.9296	240
0.6518	630	0.9562	162
0.6895	598		

[a] x is the mole fraction of ethanol in the binary mixture ethanol + nonane. Standard uncertainties u are: $u(T)$ = 0.01 K, $u(x)$ = 0.0001, $u_r(H^E_m)$ = 0.01.

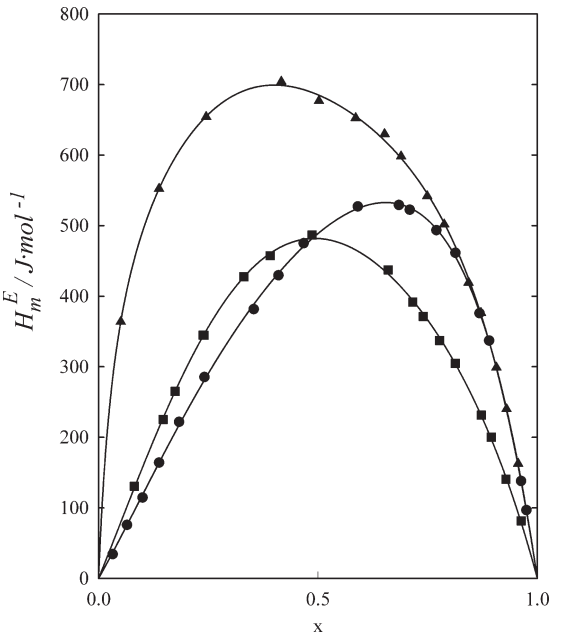

Figure 1. Excess molar enthalpies $H^E_m/(J \cdot mol^{-1})$ at 298.15 K of the three involved binary systems: Experimental values of: ●, $\{x$ MTBE + $(1 - x)$ ethanol$\}$ taken from ref 12; ■, $\{x$ MTBE + $(1 - x)$ nonane$\}$ taken from ref 10; ▲, $\{x$ ethanol + $(1 - x)$ nonane$\}$; —, fitting curve by eqs 2 and 3.

RESULTS AND DISCUSSION

Experimental values of H^E_m for the binary mixture $\{x$ ethanol + $(1 - x)$ nonane$\}$ are listed in Table 2. The experimental data, the fitting parameters, and the standard deviations of excess molar enthalpies, corresponding to the binary mixtures $\{x$ MTBE + $(1 - x)$ ethanol$\}$ and $\{x$ MTBE + $(1 - x)$ nonane$\}$, were reported in previous papers.[12,10] These experimental data were fitted to the variable-degree polynomials suggested by Redlich−Kister.[25]

$$H^E_m/J \cdot mol^{-1} = x(1-x)\sum_{i=1}^{n} A_i(2x-1)^{i-1} \quad (2)$$

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Table 3. Excess Molar Enthalpies, $H^E_{m,123}$, at the Temperature T = 298.15 K for the Ternary Mixture: x_1 MTBE + x_2 Ethanol + $(1 - x_1 - x_2)$ Nonane[a]

		$H^E_{m,\phi}$	$H^E_{m,123}$			$H^E_{m,\phi}$	$H^E_{m,123}$
x_1	x_2	J·mol^{-1}	J·mol^{-1}	x_1	x_2	J·mol^{-1}	J·mol^{-1}
			$x'_1 = 0.2687$, $H^E_{m,12} = 309$ J·mol^{-1}				
0.2538	0.6910	186	478	0.1543	0.4200	679	857
0.2433	0.6624	290	570	0.1395	0.3798	717	878
0.2255	0.6139	427	687	0.1180	0.3212	722	858
0.2145	0.5840	492	739	0.0924	0.2514	674	780
0.2008	0.5466	558	789	0.0649	0.1765	606	681
0.1879	0.5116	606	823	0.0399	0.1087	514	560
0.1734	0.4719	649	849				
			$x'_1 = 0.4933$, $H^E_{m,12} = 485$ J·mol^{-1}				
0.4755	0.4883	117	585	0.3007	0.3088	679	975
0.4579	0.4703	215	665	0.2611	0.2681	708	964
0.4423	0.4543	287	722	0.2283	0.2344	717	942
0.4203	0.4316	382	795	0.1945	0.1997	687	878
0.3924	0.4029	474	860	0.1500	0.1540	652	800
0.3683	0.3782	535	897	0.1144	0.1175	586	699
0.3260	0.3348	620	940	0.0817	0.0839	502	582
			$x'_1 = 0.7431$, $H^E_{m,12} = 512$ J·mol^{-1}				
0.7118	0.2460	129	620	0.4328	0.1496	633	931
0.6825	0.2359	210	680	0.3666	0.1267	666	918
0.6520	0.2254	294	743	0.3184	0.1101	658	878
0.6244	0.2158	367	797	0.2434	0.0841	607	774
0.5746	0.1986	460	856	0.1870	0.0646	547	676
0.5360	0.1853	514	883	0.1364	0.0472	460	554
0.4695	0.1623	582	905				

[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 ethanol$\}$, where $x'_2 = 1 - x'_1$. x'_1 is the mole fraction of MTBE, x'_2 is the mole fraction of ethanol, and $H^E_{m,12}$ 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 ethanol in the ternary mixture MTBE + ethanol + nonane. Standard uncertainties u are: $u(T) = 0.01$ K, $u(x_1) = 0.0001$, $u(x_2) = 0.0001$, $u(x'_1) = 0.0001$, $u_r(H^E_{m,12}) = 0.01$, $u_r(H^E_{m,\phi}) = 0.01$, $u_r(H^E_{m,123}) = 0.01$.

However the set of data measured in this work for the binary mixture $\{x$ ethanol + $(1 - x)$ nonane$\}$ was fitted to a variable-degree polynomial suggested by Myers–Scott.[26]

$$H^E_m/\text{J·mol}^{-1} = \frac{x(1-x)}{1 + k(1-x)} \sum_{i=1}^{n} A_i(2x-1)^{i-1} \qquad (3)$$

The experimental values of H^E_m measured in this work are compared in Figure 1 with those measured in the early works[12,10] for the other two involved binary mixtures. We decided to measure experimental excess molar enthalpies for the system $\{x$ ethanol + $(1 - x)$ nonane$\}$ to use experimental values measured with the same microcalorimeter and under similar conditions of pressure and temperature, for all of the binary systems involved in the ternary system.

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

$$H^E_{m,123}/\text{J·mol}^{-1} = H^E_{m,bin} + x_1x_2(1 - x_1 - x_2)\Delta_{123} \qquad (4)$$

where Δ_{123}, was fitted to the expression suggested by Morris et al.[27] of the form:

$$\frac{\Delta_{123}}{RT} = (B_0 + B_1x_1 + B_2x_2 + B_3x_1^2 + B_4x_2^2 + B_5x_1x_2 + B_6x_1^3 + B_7x_2^3 + \ldots) \qquad (5)$$

The fitting parameters k, A_i, and B_i were computed from the unweighed least-squares method using a nonlinear optimization algorithm due to Marquardt.[28] The number of parameters was determined by applying to every new parameter the F-test proposed by Bevington.[29] The fitting coefficients and the corresponding standard deviations from experimental values 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 5 was applied to fit the ternary contribution. The lines of constant ternary excess molar enthalpy, $H^E_{m,123}$, calculated using eq 4 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 5.

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Table 4. Fitting Parameters for Equations 2, 3, and 5 and Standard Deviations, *s*

A_1	A_2	A_3	A_4	A_5	A_6	k	s
x MTBE + $(1-x)$ Ethanol[a]							
1955	1034	698	510	0	0		4
x MTBE + $(1-x)$ Nonane[b]							
1927	−58		447				3
x Ethanol + $(1-x)$ Nonane							
2742	2015	1128	1383	673		0.6471	6
x_1 MTBE + x_2 Ethanol + x_3 Nonane							
B_0	B_1	B_2	B_3	B_4	B_5	B_6	B_7	s
1.8068	9.8323	−9.1546	−24.0226	21.7554	1.9749	22.5605	−13.0435	8

[a] Reference 12. [b] Reference 10.

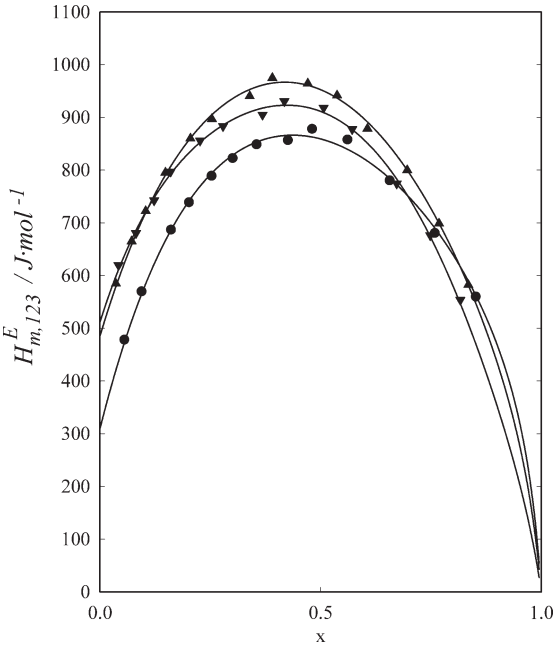

Figure 2. Pseudobinary representation of ternary excess molar enthalpies $H^E_{m,123}/(J\cdot mol^{-1})$ for $\{(1-x)\ (x'_1$ MTBE + x'_2 ethanol) + x nonane$\}$ at 298.15 K: ●, $x'_1 = 0.2687$, $x'_2 = 0.7313$; ▲, $x'_1 = 0.4933$, $x'_2 = 0.5067$; ▼, $x'_1 = 0.7431$, $x'_2 = 0.2569$; —, fitting curve correlated using eq 4.

The excess molar enthalpy for the ternary system is positive over the whole range of composition, showing a maximum value at $x_1 = 0.3280$, $x_2 = 0.2510$, $x_3 = 0.4210$, and $H^E_{m,123} = 974\ J\cdot mol^{-1}$.

The excess molar enthalpy $H^E_{m,123}$ of the ternary systems MTBE + ethanol + alkane (hexane,[7] heptane,[4] octane,[6] decane[1]) is also positive over the whole composition diagram, reaching its maximum values at $x_1 = 0.3960$, $x_2 = 0.2490$, $x_3 = 0.3550$, $H^E_{m,123}$ (hexane) = 802 J·mol^{-1}; $x_1 = 0.3270$, $x_2 = 0.2510$, $x_3 = 0.4220$, $H^E_{m,123}$ (heptane) = 894 J·mol^{-1}; at $x_1 = 0.3480$, $x_2 = 0.2410$, $x_3 = 0.4110$, $H^E_{m,123}$ (octane) = 920 J·mol^{-1}, $x_1 = 0.3530$, $x_2 = 0.2470$, $x_3 = 0.4000$, $H^E_{m,123}$ = 984 J·mol^{-1} (decane), respectively. Similar behavior is shown in the experimental data published by Zhu et al. for MTBE + ethanol + hexane[16] or octane.[17]

This trend is also observed in the published ternary systems MTBE + propanol + alkane (hexane,[9,18] octane,[8,17] nonane,[2] decane[3]) and MTBE + pentanol + alkane (octane,[5] nonane,[10] decane[11]).

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. The maximum values of the ternary contribution to excess molar enthalpy are reached at $x_1 = 0.3510$, $x_2 = 0.1690$, $x_3 = 0.4800$, and $H^E_{m,123} = 246\ J\cdot mol^{-1}$. The value of the maximum ternary contribution is about 25 % of the value of the ternary enthalpy itself. That means that the 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 endothermicity observed for all ternary mixtures MTBE + 1-alkanol + alkane suggests 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. So, the main contribution to this behavior may be attributed to the breaking of alcohol hydrogen bonding autoassociation, added to two other effects, as the breaking of dipole−dipole interactions of MTBE and the contribution due to the loss of orientation order between alkane linear molecules are more significant than the cross association between MTBE−ethanol, the crossed interactions dipole−induced dipole, and the weak ethanol−nonane interactions due to dispersive forces.

The excess molar enthalpy $H^E_{m,123}$ of the ternary systems MTBE + alkanol (propanol[2] or pentanol[10]) + nonane is also positive over the whole composition diagram, reaching its maximum values at $x_1 = 0.3087$, $x_2 = 0.2585$, $x_3 = 0.4428$, $H^E_{m,123}$ (propanol) = 1031 J·mol^{-1} and at $x_1 = 0.3710$, $x_2 = 0.2340$, $x_3 = 0.3950$, $H^E_{m,123}$ (pentanol) = 940 J·mol^{-1}, respectively.

Comparing the present experimental data with the excess molar enthalpy values obtained in previous works[2,10] for ternary mixtures of MTBE + alkanol + nonane, we conclude that the excess enthalpies increase from ethanol to propanol and decrease for the pentanol, like the trend obtained with the binary mixtures of alkanol + alkane.

Alkanols are polar liquids, strongly self-associated by hydrogen bonding that may differ depending on chain length and position of the hydroxyl group. In this case, the alkanol chain length is an important parameter that must be taken into account to explain the behavior interaction of the MTBE + alkanol + alkane mixtures. The diminution of $H^E_{m,123}$ observed is in agreement with the predominance of the breaking of the existing hydrogen bonds of the pure alkanol, and it can be interpreted as reflecting the decrease of the strength of alkanol−alkanol hydrogen bonds with the alkanol chain length.

In MTBE + alkanol systems H^E_m increase, from methanol to propan-1-ol, and then H^E_m is nearly constant for butanol[30] and pentanol.[12] This may be because the decrease in alcohol−alcohol is balanced by weaker interactions between the OH groups and O atoms.

Besides, both for binary systems MTBE + alkane (hexane,[31,9] heptane,[32,33,4] octane,[17,8] nonane,[10] decane[31,11]) as for the binary mixtures ethanol + alkane (hexane,[34,35,7] heptane,[36,4] octane,[37,17,6] nonane, decane[35,38,1]), excess molar enthalpy increases with the increasing chain length of the alkane.

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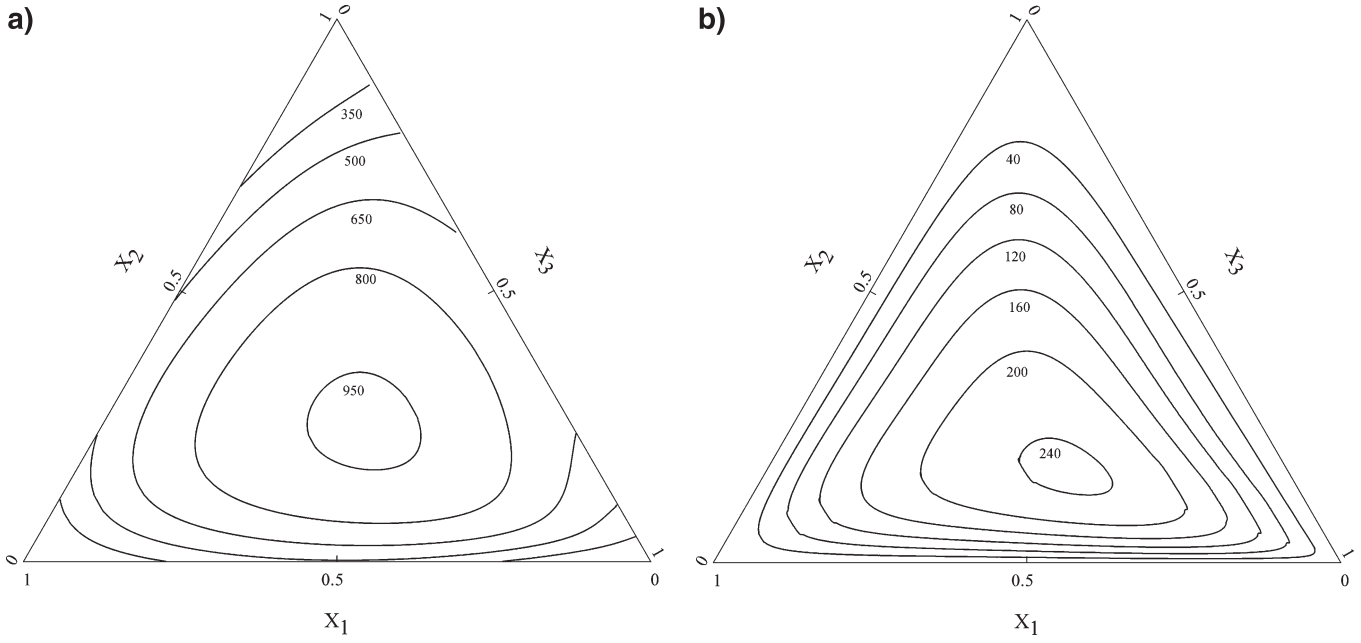

Figure 3. Representation for $\{x_1$ MTBE + x_2 ethanol + $(1 - x_1 - x_2)$ nonane$\}$ at 298.15 K of: (a) curves of constant ternary excess molar enthalpy, $H^E_{m,123}/(J \cdot mol^{-1})$; (b) curves of constant ternary contribution, $x_1x_2(1 - x_1 - x_2)\Delta_{123}$, to the excess molar enthalpy $H^E_{m,123}/(J \cdot mol^{-1})$, calculated with eq 5.

CONCLUSION

The excess enthalpies for the ternary system composed of MTBE, ethanol, and nonane and the involved binary mixture ethanol + nonane were measured and correlated by using a least-squares procedure. All excess enthalpies have positive values, and their graphical shapes are asymmetric.

After comparing our results with those found in the literature for the three involved binary mixtures (MTBE + *n*-alkane, MTBE + 1-alkanols, and 1-alkanol + alkane), we can conclude that the trend of these binary mixtures directly influences the behavior of the corresponding ternary mixture. So, excess molar enthalpy increases with increasing chain length of the alkane for binary systems MTBE + alkane and ethanol + alkane. Similar behavior occurs for the binary mixtures composed for propanol + alkane, butanol + alkane, or pentanol + alkane. However, for MTBE + 1-alkanol systems H^E_m increases, from methanol to propan-1-ol, and then H^E_m is nearly constant for butanol and pentanol; for alkanol + alkane excess enthalpies increase from ethanol to propanol and decrease for pentanol.

For the ternary mixtures MTBE + ethanol + alkane, the excess molar enthalpy increases with the increasing chain length of the alkane. A similar behavior is shown in the experimental published data for MTBE + propanol + alkane, MTBE + butanol + alkane, or MTBE + pentanol + alkane. Nevertheless, for ternary mixtures of MTBE + 1-alkanol + nonane, $H^E_{m,123}$ increases from ethanol to propanol and decreases for pentanol. A similar behavior occurs if we change the alkane, that is, for mixtures MTBE + 1-alkanol + hexane, MTBE + 1-alkanol + heptane, MTBE + 1-alkanol + octane, or MTBE + 1-alkanol + decane.

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