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Experimental and Predicted Excess Molar Enthalpies of the Ternary System *tert*-Butyl Methyl Ether + 1-Pentanol + Decane at 298.15 K

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Excess molar enthalpies of {x_1 *tert*-butyl methyl ether (MTBE) + x_2 1-pentanol+ $(1 - x_1 - x_2)$decane} and the involved binary mixtures {x *tert*-butyl methyl ether (MTBE) + $(1 - x)$decane} and {x 1-pentanol+ $(1 - x)$decane} have been determined at 298.15 K and atmospheric pressure over the whole composition range using a Calvet microcalorimeter. The results were fit by means of different variable-degree polynomials. In the present work, we propose a new expression to fit the ternary excess molar enthalpy, which takes into account the asymmetric shape of the involved binary systems. 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.

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1. Introduction

Branched ethers, such as the *tert*-butyl methyl ether (MTBE), either pure or mixed with alkanols or alkanes have been recommended as oxygenate additives in unleaded gasoline. However, the most recent concern about health risks caused by the pollution of drinking water from MTBE into the ground makes it appear to be a somewhat controversial gasoline additive. The properties studied have proved to be meaningful from a thermodynamic point of view because they provide direct information about the energetic effects arising between the molecules present in the mixture, so they can help to explain the intermolecular interactions in solution.

The thermodynamic properties of binary and ternary mixtures formed by hydrocarbons, ethers, and lower alcohols are essential in the design of chemical processes involving these oxygenating agents.

The present work reports experimental excess molar enthalpies of {x_1 *tert*-butyl methyl ether (MTBE) + x_2 1-pentanol + $(1 - x_1 - x_2)$decane}, {x *tert*-butyl methyl ether (MTBE) + $(1 - x)$decane}, and {x 1-pentanol+ $(1 - x)$-decane} at 298.15 K and atmospheric pressure. The excess molar enthalpies for the binary mixture {x *tert*-butyl methyl ether (MTBE) + $(1 - x)$1-pentanol} were reported in earlier work.[1] The measurement of excess molar enthalpies was carried out using a Calvet microcalorimeter. The results were fit by means of different variable-degree polynomials.

Several H_m^E data have been published in the literature for MTBE + alkane[2−5] at 298.15 K and atmospheric pressure. Wang et al.[3] have measured the H_m^E of MTBE + decane[3].

The group of literature referring to the binary systems {x 1-alkanol + $(1 - x)$alkane} is very large. Christensen et al.[6] have published H_m^E data for binary system {x 1-pentanol+ $(1 - x)$decane} at 298.15 K and 170 kPa. No excess enthalpy values were found in the currently available literature for the binary mixture {x 1-pentanol+ $(1 - x)$decane} at atmospheric pressure.

Excess molar enthalpies of the ternary mixtures MTBE + 1-alkanol + alkane[7−9] are available in the literature at 298.15 K. Nevertheless, we are not aware of any previous measurement of $H_\mathrm{m,123}^\mathrm{E}$ of the ternary mixture to which this study is directed.

2. Experimental Section

Materials. The chemical substances employed were commercial products of the best quality grade (>0.99 mole fraction). All products were supplied by Aldrich and were subjected to no further purification other than drying with Union Carbide 0.4-nm molecular sieves to eliminate residual traces of water and degassing 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*.[10]

Apparatus and Procedure. The mixtures were prepared by mass using a Mettler H51 balance (precision ±1 × 10^{-5} g), ensuring a probable error in the mole fraction of less than 10^{-4}. All molar quantities are based on the IUPAC relative atomic mass table.[11]

The experimental excess molar enthalpies were measured using a Calvet microcalorimeter equipped with a device allowing operation in the absence of a vapor 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.[12,13] 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

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Table 1. Experimental Binary Excess Molar Enthalpies, H^{E}_{m}, at 298.15 K

x	H^E_m / J·mol^{-1}	x	H^E_m / J·mol^{-1}	x	H^E_m / J·mol^{-1}	x	H^E_m / J·mol^{-1}
xMTBE + (1 − x)decane							
0.1155	194.1	0.4233	514.3	0.6921	429.2	0.8461	288.3
0.1862	301.5	0.4962	531.4	0.7140	415.3	0.8795	238.5
0.1927	303.5	0.4966	532.0	0.7339	403.9	0.9235	172.6
0.2714	404.6	0.6491	459.0	0.7473	391.1	0.9459	125.9
0.3516	480.4	0.6832	437.6	0.8334	302.0	0.9573	104.2
x1-pentanol + (1 − x)decane							
0.0543	427.6	0.2871	726.6	0.5334	695.1	0.7860	382.7
0.0877	537.8	0.3411	741.2	0.5981	649.9	0.8531	270.9
0.1438	622.5	0.4074	748.5	0.6431	601.8	0.8886	204.4
0.2023	674.5	0.4312	737.5	0.7033	517.0	0.9214	142.1
0.2528	709.5	0.5096	715.5	0.7480	454.4		

differ by less than 1% from those of Marsh[14] and Gmehling.[15] The uncertainty in excess molar enthalpy measurements is estimated to be better than 1%.

Several experimental series of measurements were carried out for the ternary compositions resulting from adding decane to a binary mixture composed of {x'_1 MTBE + x'_2 1-pentanol}. The ternary composition point is then a pseudobinary mixture formed by the addition of decane and the mentioned 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

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

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 {x'_1 MTBE + x'_2 1-pentanol}. Values of $H^{E}_{m,12}$ at three mole fractions were interpolated by using a spline-fit method. Equation 1 does not involve any approximation.

3. Data Correlation

Experimental values of H^{E}_{m} for {x *tert*-butyl methyl ether (MTBE) + (1 − x)decane} and {x 1-pentanol+ (1 − x)decane} are listed in Table 1. The experimental data of excess molar enthalpies for the binary mixture {x *tert*-butyl methyl ether (MTBE) + (1 − x)1-pentanol} were reported in an early paper.[1] The experimental data of H^{E}_{m} corresponding to the binary mixtures {x *tert*-butyl methyl ether (MTBE) + (1 − x)1-pentanol} and {x *tert*-butyl methyl ether (MTBE) + (1 − x)decane} were fit to the variable-degree polynomials suggested by Redlich−Kister[16] of the form

$$H^{E}_{m}/\text{J·mol}^{-1} = x(1-x)\sum_{i=1}^{n} A_i(2x-1)^{i-1} \qquad (2)$$

and lower deviations for the mixture {x 1-pentanol+ (1 − x)decane} were obtained by fitting experimental data to the equation suggested by Myers−Scott:[17]

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

Equation 3 provides a more accurate representation of the experimental set of data by using a more reduced set of parameters in cases where the representation of data is clearly asymmetric.

The parameters k and A_i shown in eqs 2 and 3 have been obtained by a fitting computer program that uses the least-squares procedure and a Marquardt algorithm.[18] The number of parameters used was determined by applying the optimitazation F test.[19] These parameters and the standard deviations for H^{E}_{m} of the three binary mixtures involved in this ternary system are presented in Table 2.

A plot of the obtained experimental values together with the smoothing curves for H^{E}_{m} of the three involved binaries are shown in Figure 1.

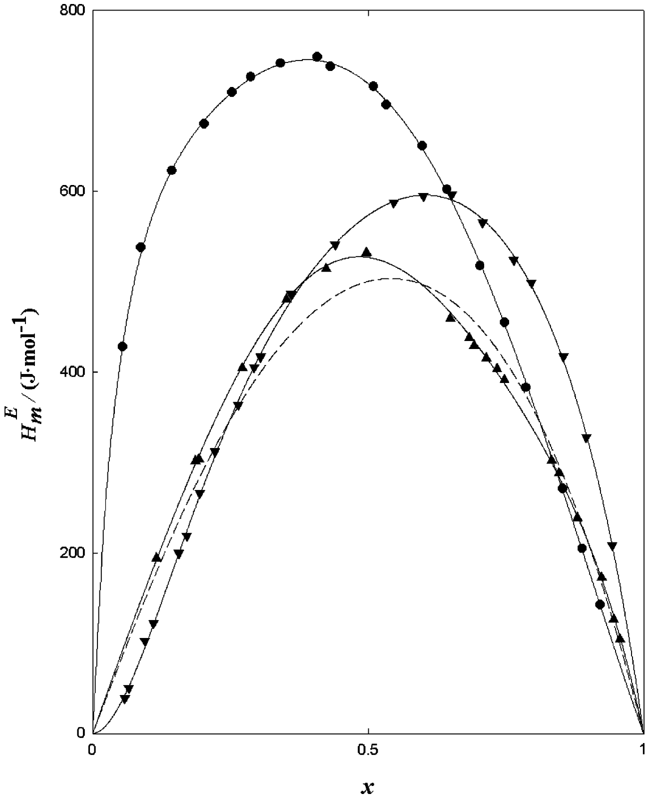

Figure 1. Excess molar enthalpies H^{E}_{m}/(J mol^{-1}) at 298.15 K of the three involved binary systems. Experimental values of ▼, {x MTBE + (1 − x)1-pentanol}; ▲, {x MTBE + (1 − x)decane}; and ●, {x 1-pentanol + (1 − x)decane}; —, fit by eqs 3 and eq 4; and − − −, ref 3.

Table 2. Fitting Parameters k and A_i for Equations 2 and 3 and Standard Deviations s

A_1	A_2	A_3	A_4	A_5	A_6	k	s
xMTBE + (1 − x)1-pentanol[a]							
2294	831	442	576	−514	762		4
xMTBE + (1 − x)decane							
2106	−167	−402	728	619			3
x1-pentanol + (1 − x)decane							
2875	1553	−384	−847			0.8832	4

[a] Reference 1.

Table 3. Excess Molar Enthalpies, $H^{E}_{m,123}$, at 298.15 K for the Ternary Mixture x_1MTBE + $x_2$1-Pentanol+ (1 − x_1 − x_2)Decane[a]

x_1	x_2	$\frac{H^{E}_{m,\phi}}{J\cdot mol^{-1}}$	$\frac{H^{E}_{m,123}}{J\cdot mol^{-1}}$	x_1	x_2	$\frac{H^{E}_{m,\phi}}{J\cdot mol^{-1}}$	$\frac{H^{E}_{m,123}}{J\cdot mol^{-1}}$
$x'_1 = 0.2452$, $H^{E}_{m,12} = 342$ J·mol^{-1}							
0.2378	0.7322	75	407	0.1599	0.4922	590	813
0.2322	0.7146	131	454	0.1421	0.4376	655	853
0.2232	0.6869	210	521	0.1338	0.4119	658	845
0.2166	0.6666	266	568	0.1184	0.3646	686	851
0.2073	0.6382	327	616	0.1077	0.3314	698	849
0.1983	0.6103	396	672	0.0961	0.2960	686	821
0.1892	0.5823	450	714	0.0710	0.2187	670	769
0.1791	0.5512	513	763	0.0541	0.1667	629	704
0.1668	0.5136	560	793	0.0387	0.1192	577	631
$x'_1 = 0.4974$, $H^{E}_{m,12} = 572$ J·mol^{-1}							
0.4828	0.4878	80	636	0.2879	0.2909	625	957
0.4510	0.4558	230	749	0.2634	0.2662	647	950
0.4374	0.4420	287	791	0.2391	0.2415	660	935
0.4230	0.4274	345	831	0.2112	0.2135	674	917
0.3966	0.4007	431	888	0.1821	0.1841	651	860
0.3798	0.3838	493	930	0.1464	0.1479	633	802
0.3624	0.3662	530	947	0.1127	0.1138	594	723
0.3381	0.3417	564	953	0.0804	0.0812	539	632
0.3149	0.3182	606	969	0.0411	0.0415	422	470
$x'_1 = 0.7391$, $H^{E}_{m,12} = 549$ J·mol^{-1}							
0.7169	0.2531	80	613	0.3855	0.1361	665	951
0.6938	0.2449	177	693	0.3126	0.1103	663	895
0.6418	0.2266	310	787	0.2654	0.0937	623	820
0.6120	0.2161	383	838	0.2198	0.0776	593	756
0.5899	0.2082	429	867	0.1483	0.0524	521	631
0.5497	0.1941	498	906	0.0986	0.0348	423	496
0.5206	0.1838	542	929	0.0678	0.0240	346	396
0.4996	0.1764	563	934	0.0441	0.0155	268	301
0.4438	0.1567	612	941				

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

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

$$H^{E}_{m,123}(\mathrm{J\cdot mol^{-1}}) = H^{E}_{m,bin} + x_1x_2(1 - x_1 - x_2)\Delta_{123} \quad (4)$$

where

$$H^{E}_{m,bin} = H^{E}_{m,12} + H^{E}_{m,13} + H^{E}_{m,23} \quad (5)$$

is known as the binary contribution to the excess ternary properties and $H^{E}_{m,ij}$ are given by eq 2 or 3.

The last term stands for the ternary contribution to the magnitude. Several equations have been tested to correlate Δ_{123}, the first of them suggested Cibulka,[20]

$$\Delta_{123} = (B_0 + B_1x_1 + B_2x_2) \quad (6)$$

the second one proposed by Nagata and Tamura,[21]

$$\frac{\Delta_{123}}{RT} = (B_0 + B_1x_1 + B_2x_2 + B_3{x_1}^2 + B_4{x_2}^2) \quad (7)$$

and the one suggested by Morris et al.,[22]

$$\frac{\Delta_{123}}{RT} = (B_0 + B_1x_1 + B_2x_2 + B_3{x_1}^2 + B_4{x_2}^2 + B_5x_1x_2 + B_6{x_1}^3 + B_7{x_2}^3 + ...) \quad (8)$$

which differs slightly from the number of adjustable parameters. Table 4 shows the standard deviations obtained when the different correlation expressions tested were applied. It can be observed that none of these expressions was capable of adequately correlating the experimental results. The deviations obtained are rather high, and this fact can be attributed to the fact that the obtained curves for experimental data present a marked asymmetry.

Table 4. Comparison of the Standard Deviations, *s*, Obtained with the Correlation Equations Applied

equation	*s*
Cibulka[20]	40
Nagata and Tamura[21]	33
Morris et al.[22]	22
eq 9	8

In view of these results, it seemed to be suitable to use an equation that considered this asymmetry. The following equation, having a polynomial expansion similar to that introduced by the Morris et al.[22] equation and a term of the type of the Padé approximation, was used to correlate the ternary excess enthalpies:

$$\frac{\Delta_{123}}{RT} = \frac{\left.\begin{array}{c} B_0 + B_1x_1 + B_2x_2 + B_3{x_1}^2 + B_4{x_2}^2 + \\ B_5x_1x_2 + B_6{x_1}^3 + B_7{x_2}^3 + B_8x_2{x_1}^2 + ... \end{array}\right)}{1 + (x_2 - x_3)} \quad (9)$$

The B_i parameters were calculated by an unweighted least-squares method using a nonlinear optimization algorithm due to Marquardt.[18] These parameters and the corresponding standard deviations are included in Table 5. As can be seen, the proposed equation remarkably improves the results obtained with the Cibulka,[20] Nagata and Tamura,[21] and Morris et al.[22] equations.

Figure 2 shows the pseudobinary representation of the measured experimental values of the $H^{E}_{m,123}$ together with

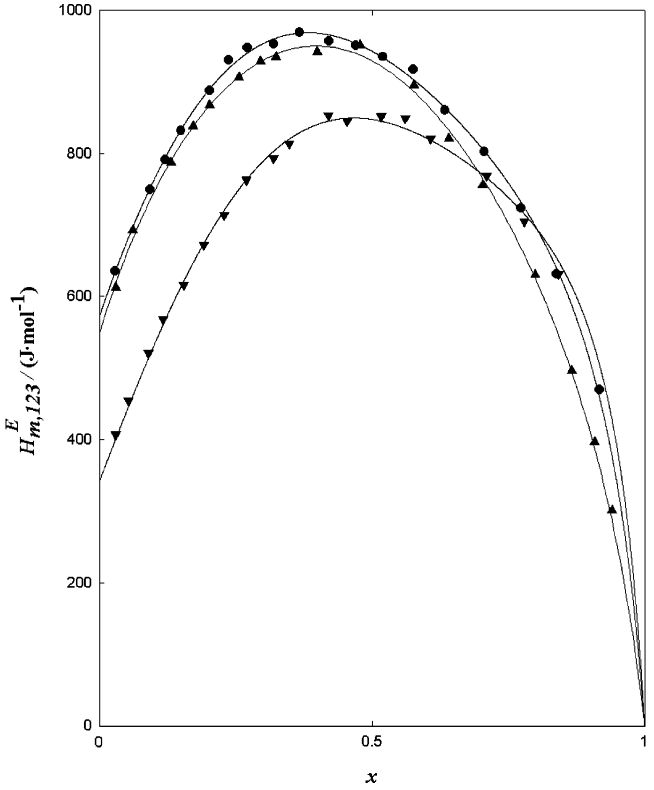

Figure 2. Pseudobinary representation of ternary excess molar enthalpies $H^{\mathrm{E}}_{\mathrm{m},123}$/(J mol^{-1}) for $\{(1 - x)(x'_1$ MTBE + x'_2 1-pentanol) + x decane} at 298.15 K: ▼, $x'_1 = 0.2452$, $x'_2 = 0.7548$; ●, $x'_1 = 0.4974$, $x'_2 = 0.5026$; ▲, $x'_1 = 0.7391$, $x'_2 = 0.2609$; —, correlated using eq 9.

the correlated curves, where eq 9 was applied to fit the ternary contribution.

The lines of constant ternary excess molar enthalpy $H^{\mathrm{E}}_{\mathrm{m},123}$ calculated using eq 9 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 9.

Table 5. Fitting Parameters B_i for Equation 9 and Standard Deviations s

	$H^{\mathrm{E}}_{\mathrm{m},123}$
B_0	3.5748
B_1	−3.6430
B_2	−20.0992
B_3	6.0692
B_4	39.5495
B_6	28.1816
B_7	5.3152
B_8	−28.6048
B_5	−35.2528
s	8

4. Theoretical Estimation Methods

The UNIFAC group contribution model was originally developed by Fredenslund et al.[23] from the UNIQUAC equation by Abrams and Prausnitz[24] 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 in the 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.[25] 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.[26] 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 that 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

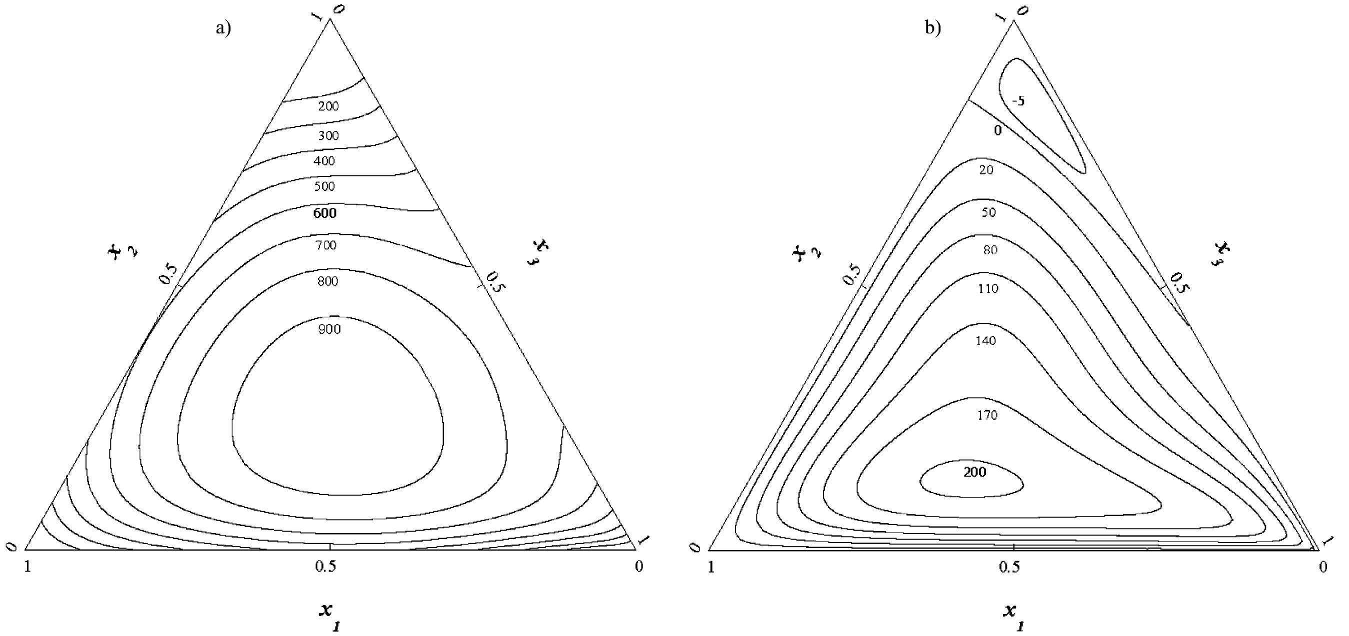

Figure 3. Representation for $\{x_1$MTBE + $x_2$1-pentanol + $(1 - x_1 - x_2)$decane} at 298.15 K of (a) curves of constant ternary excess molar enthalpy, $H^{\mathrm{E}}_{\mathrm{m},123}$/(J mol^{-1}) and (b) curves of constant ternary contribution, $x_1x_2(1 - x_1 - x_2)\Delta_{123}$, for the excess molar enthalpy $H^{\mathrm{E}}_{\mathrm{m},123}$/(J mol^{-1}) calculated with eq 9.

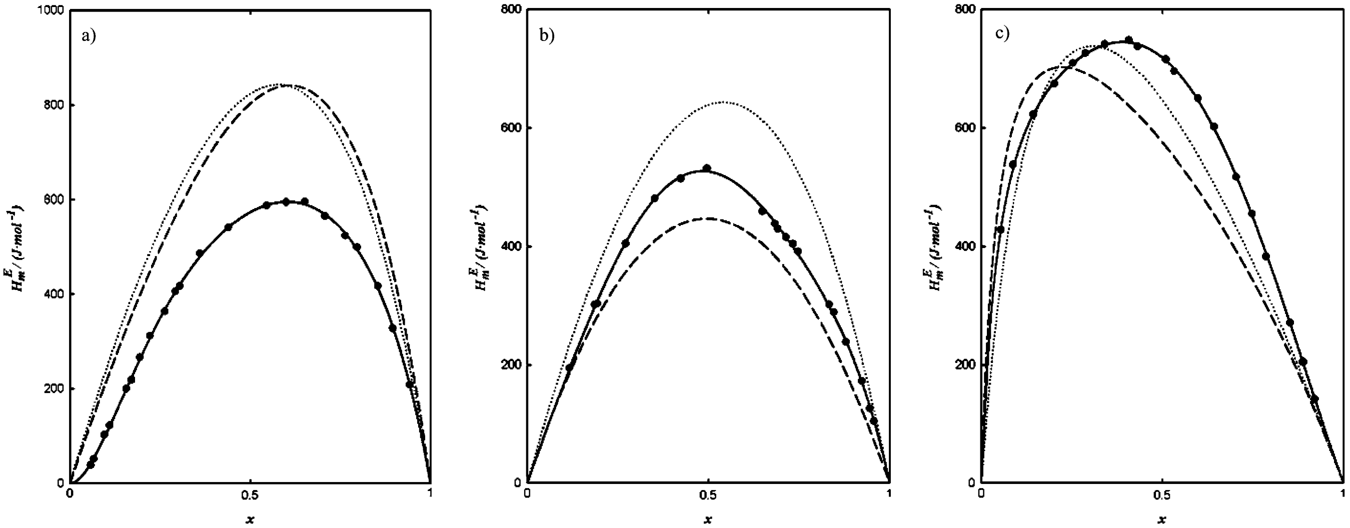

Figure 4. Excess molar enthalpies H_m^E/(J mol^{-1}) at 298.15 K of binary mixtures (a) {x MTBE + (1 − x)1-pentanol}, (b) {x MTBE + (1 − x)decane}, and (c) {x 1-pentanol + (1 − x)decane. ●, Experimental values; —, fit by eqs 3 and 4; ···, Larsen et al. model;[25] and − − −, Gmehling et al. model.[26]

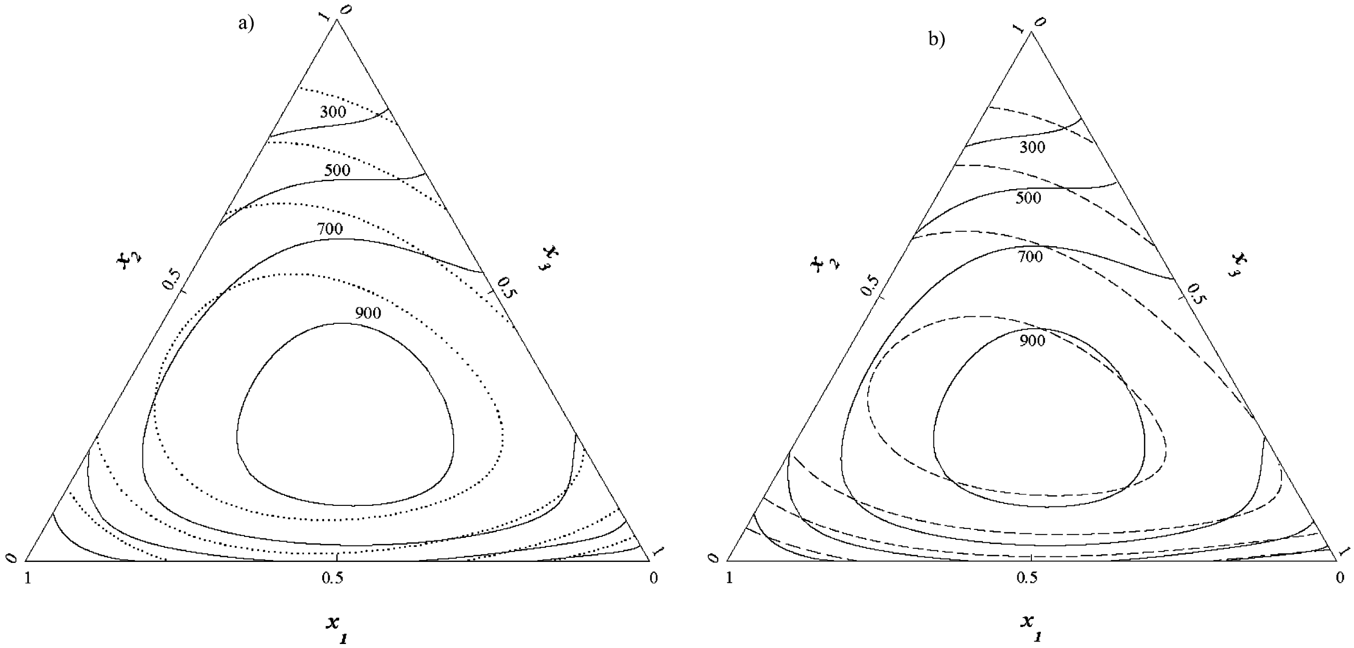

Figure 5. Excess molar enthalpies, $H_{m,123}^E$/(J mol^{-1}), for the ternary mixture {x_1MTBE + $x_2$1-pentanol + (1 − x_1 − x_2)decane} at 298.15 K. —, Fit by eq 9; ···, Larsen et al. model;[25] − − −, Gmehling et al. model.[26]

Table 6. 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 + decane	95	52
1-pentanol + decane	50	83
MTBE + 1-pentanol + decane	109	47

listed in Table 6. These results are displayed graphically in Figures 4 and 5.

5. 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. Therefore, 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,[27] Jacob and Fitzner,[28] Colinet,[29] and Knobeloch and Schwartz,[30] and the asymmetric ones have been suggested by Tsao and Smith,[31] Toop,[32] Scatchard et al.,[33] Hillert,[34] and Mathieson and Thynne.[35] Table 7 list 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 dif-

Table 7. Mean Deviations from the Experimental Values Obtained with Empirical Predictive Methods[a]

empirical equations	$H^{E}_{m,123}$/J·mol^{-1}		
Kohler	92		
Jacob Fitzner	109		
Colinet	96		
Knobeloch−Schwartz	50		
Tsao−Smith	25[b]	40[c]	54[d]
Toop	116[b]	33[c]	137[d]
Scatchard et al.	134[b]	33[c]	137[d]
Hillert	122[b]	32[c]	136[d]
Mathieson−Tynne	119[b]	77[c]	125[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.

ferent 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-pentanol, and decane were respectively named as 1, 2, and 3. Then, rows A, B, and C of Table 7 were fit to *tert*-butyl methyl ether + 1-pentanol+ decane as 123, 231, and 312, respectively ordered; the first element considered in each case was MTBE, 1-pentanol, or decane in this order.

6. Results and Discussion

The experimental excess molar enthalpies H^{E}_{m} 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 {x *tert*-butyl methyl ether (MTBE) + $(1 - x)$decane} is symmetrical. Nevertheless, the obtained curve for {x *tert*-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 + $(1 - x)$decane} is asymmetric, with its maximum displaced toward a high mole fraction of decane. This displacement can be interpreted on the basis of the rupture of hydrogen bonds present in the pure alkanol. At those compositions, the rupture of hydrogen bonds reaches its maximum and is not compensated by new possible interactions established during the mixing process.

Wang et al.[3] determined the H^{E}_{m} values for the system {x MTBE + $(1 - x)$1-decane} at 298.15 K, and they obtained $H^{E}_{m}(x = 0.5) = 500$ J·mol^{-1}, which is somewhat lower than our $H^{E}_{m}(x = 0.5) = 526.5$ J·mol^{-1}. The dotted curve shown in Figure 1 was calculated from the smoothing equation reported by those authors.

The excess molar enthalpy for the ternary system is positive over the whole range of composition, showing maximum values at $x_1 = 0.3630$, $x_2 = 0.2520$, $x_3 = 0.3850$, $H^{E}_{m,123} = 978$ J·mol^{-1}.

The ternary contribution is also positive, and the representation is asymmetric. That 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 $x_1 = 0.5120$, $x_2 = 0.1310$, $x_3 = 0.3570$, $H^{E}_{m,123} = 205$ J·mol^{-1}. The value of the maximum ternary contribution is about 21% 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 group contribution model of UNIFAC, in the versions of Larsen[25] and Gmehling,[26] was used to estimate ternary excess enthalpy values. In Table 6, we can be seen that for the binary mixture 1-pentanol + decane the best results are achieved with the Larsen version. For the systems MTBE + 1-pentanol, MTBE + decane, and MTBE + 1-pentanol + decane, the results obtained with the Gmehling version are in better agreement with the experimental data than the Larsen results.

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

The empirical expressions of Kohler,[27] Knobeloch-Schwartz,[30] Colinet,[29] Jacob-Fitner,[28] Scatchard,[33] Tsao−Smith,[31] Mathieson−Thynne,[35] Toop,[32] and Hillert[34] were also applied to estimate ternary properties from binary results. The best results were obtained with the Tsao−Smith equation with 1-pentanol as the asymmetric component.

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 expression, smaller deviations are usually obtained for those properties where the ternary contribution is not important. The best agreement with the experimental data of excess molar enthalpies was achieved by the asymmetric equation from Tsao and Smith,[31] choosing MTBE as the first component in the numbering. It can observed that the dependence on the arrangement of the components varies in each asymmetric equation. For all cases, except for the Tsao and Smith equation,[31] the best results are obtained using arrangement B (231).

The best results for the ternary excess enthalpies obtained using symmetric equations are those predicted by Knobeloch and Schwartz.[30]

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