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DETERMINATION OF EXPERIMENTAL EXCESS MOLAR PROPERTIES FOR MTBE+1-PROPANOL+OCTANE
Analysis and comparison with different theoretical methods

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Experimental excess molar enthalpies and densities have been measured for the ternary mixture x_1MTBE+$x_2$1-propanol+(1–x_1–x_2)octane and the involved binary mixtures at 298.15 K and atmospheric pressure. In addition, excess molar volumes were determined from the densities of the pure liquids and mixtures. A standard Calvet microcalorimeter was employed to determine the excess molar enthalpies. Densities were measured using a DMA 4500 Anton Paar densimeter. The UNIFAC group contribution model (in the versions of Larsen *et al.*, and Gmehling *et al.*) has been used to estimate excess enthalpies values. Experimental data were also used to test several empirical expressions for estimating ternary properties from experimental binary results.

Keywords: *empirical expressions, excess molar enthalpies, excess molar volumes, octane, 1-propanol, ternary mixture, tert-butyl methyl ether (MTBE), UNIFAC group contribution model*

Introduction

The thermodynamic properties of mixtures containing ethers, alkanes, and alkanols are of great industrial interest in view of the use of ethers as octane blending agents for gasolines. On the other hand, 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 experimental data of the thermodynamic properties of these mixtures provides information about intermolecular interactions between component molecules as well as essential knowledge from an ecological point of view. The purpose of this work is to report excess molar enthalpies, densities and excess molar volumes for the ternary system x_1MTBE +$x_2$1-propanol+$x_3$octane and the involved binary mixtures at 298.15 K and atmospheric pressure, with the aim of providing data for the characterization of the molecular interactions of these mixtures.

The excess molar enthalpies for the binary mixture xMTBE+(1–x)1-propanol and the excess molar volumes for the binary mixture xMTBE+(1–x)octane were reported in earlier works [1, 2]. The results were fitted by means of different variable degree polynomials, in order to correlate adequately the experimental data.

The group of literature referring to the excess molar enthalpies and excess molar volumes of binary liquid mixtures MTBE+1-propanol, MTBE+octane and 1-propanol+octane is considerable, but only one set of $H^{E}_{m,123}$data have been published in the literature for the ternary mixture MTBE+1-propanol+octane [3] and no previous measurement of $V^{E}_{m,123}$ data are available.

The UNIFAC group contribution model (in the versions of Larsen *et al.* [4], and Gmehling *et al.* [5]) has been employed to estimate excess molar enthalpies. The results obtained for the ternary mixture were used to test the predicting capability of several empirical methods. These equations offer reliable estimations of excess properties for a multicomponent mixture using the involved binary experimental data.

Experimental

Materials

MTBE and 1-propanol were obtained from Aldrich and octane was supplied by Fluka. The Chemical substances employed were degassed by ultrasound and stored over molecular sieves (Sigma, type 0.4 nm) to remove traces of water. The mole fraction purities stated by the manufacturers were better than 0.998, 0.995 and 0.995 for MTBE, 1-propanol and octane, respectively, as shown in Table 1. It can be observed that the measured densities of the pure liquids displayed good agreement with previously published values [6–8]. The handling and disposal of the chemicals used

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has been done according to the recommendation of the CRC Handbook of Chemistry and Physics [6].

Apparatus and procedure

The mixtures were prepared by mass using a Mettler AT201 balance (precision $\pm 1 \cdot 10^{-5}$ g), ensuring a probable error in the mole fraction less than 10^{-4}. All molar quantities are based on the IUPAC relative atomic mass table [9].

The experimental excess molar enthalpies were measured using a Calvet microcalorimeter equipped with a device allowing operation in the absence of vapour phase. A Philips PM2535 voltmeter and a data acquisition system were linked to the microcalorimeter. Calibration was performed electrically using a Setaram EJP30 stabilised current source. Further details about the experimental method of operation have been published [10, 11]. 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 [12] and Gmehling [13].

Excess molar volumes were determined from the densities of the pure liquids and mixtures. The measurements of densities were carried out with a DMA 4500 Anton Paar densimeter. The temperature inside the vibrating-tube cell was controlled using digital thermometer and was regulated to better than ±0.01 K. The experimental technique has been described previously [14, 15]. The uncertainty in density measurements was $\pm 5 \cdot 10^{-5}$ g mL^{-1}. Before each series of measurements, the apparatus was calibrated at atmospheric pressure using double-distilled and degassed water and heptane (Fluka >0.995); density data were taken from literature: [16] for heptane and [17] for water.

Table 1 Purity and densities of chemicals used

Substances	Purity	Density/g mL^{-1}	
		exp.	references
MTBE	>99.8%	0.7356	0.73528[a] 0.73590[b]
1-propanol	>99.5%	0.7997	0.79970[a] 0.79950[c]
octane	≥99.5%	0.6986	0.69860[a] 0.69850[c]

[a][6], [b][7], [c][8]

Results

Experimental values for the binary mixtures measured in this work are listed in Table 2. The excess molar enthalpies for the binary mixture {xMTBE+(1–x)1-propanol} were reported in an earlier paper [1] and the excess molar volumes for {xMTBE+(1–x)octane} were taken from [2].

Table 2 Experimental binary excess molar enthalpies, H_m^E, excess molar volumes, V_m^E, and densities, ρ, at 298.15 K

x	H_m^E /J mol^{-1}	x	H_m^E /J mol^{-1}	x	H_m^E /J mol^{-1}	x	H_m^E /J mol^{-1}
			xMTBE+(1–x)octane				
0.0836	130.7	0.3919	446.4	0.7000	372.4	0.8641	215.1
0.1578	242.9	0.4457	466.3	0.7491	335.7	0.9075	163.1
0.2324	327.4	0.5145	465.2	0.7509	334.9	0.9502	92.4
0.3062	400.9	0.5664	457.2	0.8073	277.7		
0.3367	421.1	0.5942	437.3	0.8561	226.5		
			x1-propanol+(1–x)octane				
0.1292	536.2	0.5142	636.5	0.7385	456.2	0.9053	205.8
0.2464	643.0	0.5967	603.7	0.7909	388.8	0.9087	203.2
0.3440	675.4	0.6400	552.2	0.8247	344.0	0.9497	115.3
0.4186	666.1	0.6930	512.7	0.8657	280.2	0.9783	50.6

x	ρ/g mL^{-1}	V_m^E /mL mol^{-1}	x	ρ/g mL^{-1}	V_m^E /mL mol^{-1}	x	ρ/g mL^{-1}	V_m^E /mL mol^{-1}
				xMTBE+(1–x)1-propanol				
0.0543	0.79576	–0.1433	0.3987	0.77199	–0.6318	0.7856	0.74816	–0.4701
0.1065	0.79198	–0.2560	0.4914	0.76591	–0.6454	0.8957	0.74174	–0.2754
0.1912	0.78604	–0.4156	0.5967	0.75957	–0.6409	0.9446	0.73888	–0.1593
0.2932	0.77896	–0.5425	0.6916	0.75375	–0.5831			
				x1-propanol+(1–x)octane				
0.0523	0.70044	0.1497	0.4146	0.72130	0.3731	0.7936	0.76133	0.2230
0.0974	0.70238	0.2195	0.5021	0.72840	0.3606	0.8998	0.77873	0.1312
0.1950	0.70725	0.3054	0.5972	0.73734	0.3334	0.9503	0.78865	0.0695
0.2950	0.71310	0.3473	0.7051	0.74940	0.2853			

Experimental values of ternary excess molar enthalpies, $H^{E}_{m,123}$ and ternary excess molar volumes, $V^{E}_{m,123}$, for the ternary system x_1MTBE+$x_2$1-propanol +(1–x_1–x_2)octane are listed in Table 3.

Different polynomial equations have been employed in order to minimize the set of the parameters needed to correlate adequately the magnitude. The experimental data corresponding to the binary mixtures xMTBE+(1–x)1-propanol, xMTBE+(1–x)octane were fitted to the variable-degree polynomials suggested by Redlich–Kister [18],

$$Q^{E}_{m} = x(1-x)\sum_{i=1}^{n} A_i\,(2x-1)^{i-1} \qquad (1)$$

Table 3 Excess molar enthalpies[a], $H^{E}_{m,123}$, densities, ρ, and excess molar volumes, $V^{E}_{m,123}$, at 298.15 K for the ternary mixture x_1MTBE+$x_2$1-propanol+(1–x_1–x_2)octane

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}
$x_1' = 0.2516$, $H^{E}_{m,123}$ =361.3 J mol^{-1}							
0.0517	0.1539	606.4	680.7	0.1791	0.5326	527.3	784.4
0.0769	0.2287	667.1	777.5	0.1921	0.5713	462.8	738.5
0.0938	0.2791	690.9	825.6	0.2029	0.6036	405.7	697.1
0.1154	0.3431	701.1	866.8	0.2161	0.6427	322.3	632.5
0.1345	0.4000	669.6	862.7	0.2254	0.6703	250.1	573.7
0.1487	0.4423	637.6	851.1	0.2351	0.6994	173.5	511.1
0.1636	0.4865	583.2	818.0	0.2438	0.7250	87.9	437.9
$x_1' = 0.4979$, $H^{E}_{m,123}$ =556.0 J mol^{-1}							
0.0488	0.0492	414.3	468.7	0.3431	0.3442	556.9	938.1
0.0982	0.0990	552.0	661.6	0.3693	0.3724	489.4	901.7
0.1406	0.1418	614.5	771.5	0.3937	0.3970	428.9	868.4
0.1787	0.1802	669.8	869.4	0.4189	0.4224	352.3	820.0
0.2146	0.2164	675.8	915.5	0.4394	0.4430	275.4	766.0
0.2536	0.2557	677.1	960.2	0.4605	0.4644	183.1	697.4
0.2803	0.2826	658.0	971.0	0.4785	0.4825	100.9	635.2
0.3127	0.3153	616.5	965.7				
$x_1' = 0.7548$, $H^{E}_{m,123}$ =5 6.0 J mol^{-1}							
0.0724	0.0235	257.4	306.0	0.4840	0.1572	545.5	869.9
0.1318	0.0428	394.7	483.0	0.5383	0.1748	483.4	844.3
0.1978	0.0642	519.9	652.5	0.5880	0.1910	412.6	806.7
0.2528	0.0821	585.4	754.9	0.6261	0.2034	336.1	755.9
0.3039	0.0987	617.1	820.8	0.6666	0.2165	262.4	709.3
0.3599	0.1169	621.6	862.9	0.6906	0.2243	203.5	666.5
0.4083	0.1326	618.4	892.1	0.7213	0.2343	117.1	600.6
0.4514	0.1466	597.3	899.9				

x_1	x_2	ρ/g mL^{-1}	$V^{E}_{m,123}$ /mL mol^{-1}	x_1	x_2	ρ/g mL^{-1}	$V^{E}_{m,123}$ /mL mol^{-1}
0.0500	0.8999	0.78538	–0.0548	0.3018	0.3950	0.73608	0.0165
0.0964	0.0922	0.70488	0.2531	0.2918	0.4831	0.74520	–0.0986
0.0925	0.1947	0.71044	0.2873	0.2965	0.6051	0.76206	–0.3291
0.0896	0.3085	0.71772	0.2928	0.3903	0.1067	0.71575	0.2663
0.1063	0.3930	0.72494	0.2573	0.3905	0.2019	0.72317	0.1448
0.0961	0.5012	0.73402	0.2163	0.3905	0.3031	0.73225	0.0095
0.1012	0.5956	0.74435	0.1369	0.3928	0.4043	0.74314	–0.1551
0.1062	0.6918	0.75693	0.0317	0.3986	0.5023	0.75628	–0.3767
0.1068	0.7954	0.77303	–0.0998	0.5017	0.0965	0.71953	0.2395
0.1996	0.0932	0.70810	0.2832	0.4977	0.1936	0.72769	0.0696
0.1993	0.1913	0.71423	0.2540	0.5033	0.2917	0.73780	–0.1226
0.2035	0.3027	0.72251	0.1994	0.4989	0.4020	0.75086	–0.3781
0.2034	0.3937	0.73017	0.1489	0.6046	0.0953	0.72405	0.1794
0.2002	0.4980	0.74040	0.0536	0.5931	0.1997	0.73350	–0.0540
0.1965	0.6007	0.75245	–0.0670	0.5995	0.2993	0.74527	–0.3269
0.2066	0.6926	0.76684	–0.2476	0.6969	0.2035	0.74046	–0.2450
0.2973	0.0892	0.71115	0.2893	0.7958	0.1038	0.73523	–0.0847
0.2951	0.1982	0.71858	0.2145	0.8971	0.0505	0.73530	–0.0505
0.2918	0.2990	0.72655	0.1233	0.0502	0.8993	0.79524	–0.0506

where Q_m^E is H_m^E/J mol^{-1} or V_m^E/mL mol^{-1}, while lower deviations for the mixture x1-propanol+(1–x)octane were obtained by fitting experimental data of excess molar enthalpies to the equation introduced by Myers and Scott [19],

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

and excess molar volumes to the equation suggested by Brandreth *et al.* [20].

$$V_m^E\,(\mathrm{mL\,mol^{-1}}) = x(1-x)\sum_{i=1}^{n} A_i\,(1-x)^{\frac{i-1}{2}} \quad (3)$$

Equations (2) and (3) provide 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.

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

The measured values of ternary excess properties $Q_{m,123}^E$, were correlated using an equation of the form:

$$Q_{m,123}^E = Q_{m,bin}^E + x_i x_j (1 - x_i - x_j)\Delta_{123} \quad (4)$$

where Δ_{123} was correlated using Morris *et al.* equation [21] for excess molar enthalpies.

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

and the Nagata and Tamura equation [22] has been used in order to correlate adequately the experimental excess molar volumes:

$$\Delta_{123} = (B_0 + B_1x_1 + B_2x_2 + B_3x_1^2 + B_4x_2^2) \quad (6)$$

The parameters A_i and B_i were calculated using the unweighed least-squares method, with the degree of the polynomial previously optimized through the application of the F-test [23]. The values of the A_i and B_i parameters and their corresponding standard deviations are listed in Table 4 for each system. The uncertainty of the excess molar properties is estimated to better than 1%. Experimental results for the ternary system are plotted in Figs 2 and 3.

The UNIFAC group contribution model (in the versions of Larsen *et al.* [4], and Gmehling *et al.* [5]) has been employed to estimate excess molar enthalpies. Table 5 list the mean deviations of the values predicted by the mentioned models. The experimental results show concordance with those predicted by both versions of the UNIFAC model, that predicts the endothermicity of the mixtures as well as the shape of the curves, as shown in Fig. 4.

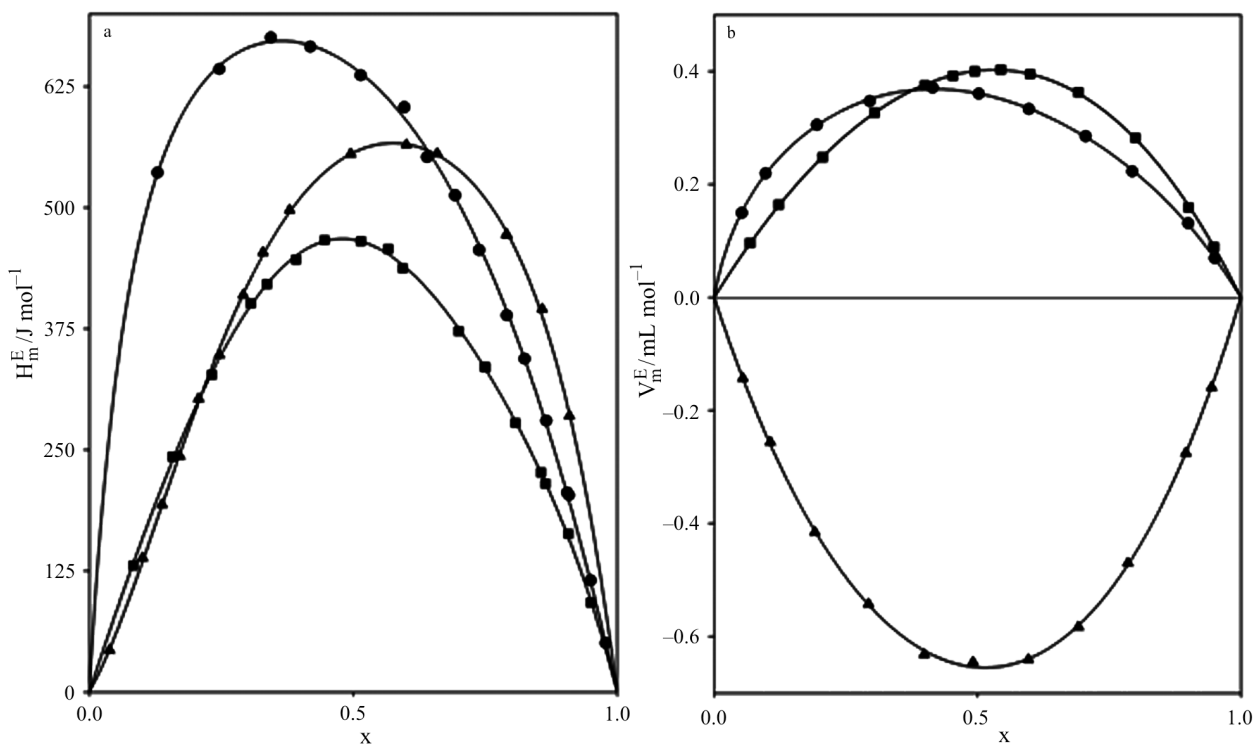

Fig. 1 Excess molar properties, a – H_m^E, b – V_m^E, of the binary mixtures: ■ – xMTBE+(1–x)octane[a], ▲ – xMTBE+(1–x)1-propanol[b], ● – x1-propanol+(1–x)octane; [a]experimental data of V_m^E were taken from [2], [b]experimental data of H_m^E were taken from [1]

Table 4 Fitting parameters, A_i, B_i and standard deviations, s, for the ternary system and the three involved mixtures

	A_1	A_2	A_3	A_4	A_5	k	s
			xMTBE+(1–x)1-propanol				
[a]H^E_m/J mol^{-1}	2226.2	533.9	361.3	1073.5	–	–	3.6
V^E_m/mL mol^{-1}	–2.6182	–0.1305	–0.3518	–	–	–	0.0046
			xMTBE+(1–x)octane				
H^E_m/J mol^{-1}	1867.4	–178.8	–276.6	414.5	325.8	–	3.0
[b]V^E_m/mL mol^{-1}	1.6039	0.1923	0.0923	–	–	–	0.0020
			x1-propanol+(1–x)octane				
H^E_m/J mol^{-1}	2578.9	1319.2	490.5	–	–	0.8184	5.0
V^E_m/mL mol^{-1}	6.2047	–20.9908	39.0062	–36.2022	13.5133	–	0.0021
	B_0	B_1	B_2	B_3	B_4		s
			x_1MTBE+$x_2$1-propanol+$x_3$octane				
$H^E_{m,123}$/J mol^{-1}	8.7459	–11.6025	–21.5035	7.3790	16.1391	17.0245	8.4
$V^E_{m,123}$/mL mol^{-1}	–5.8462	3.0483	16.2219	0.7819	–11.7468	–	0.0040

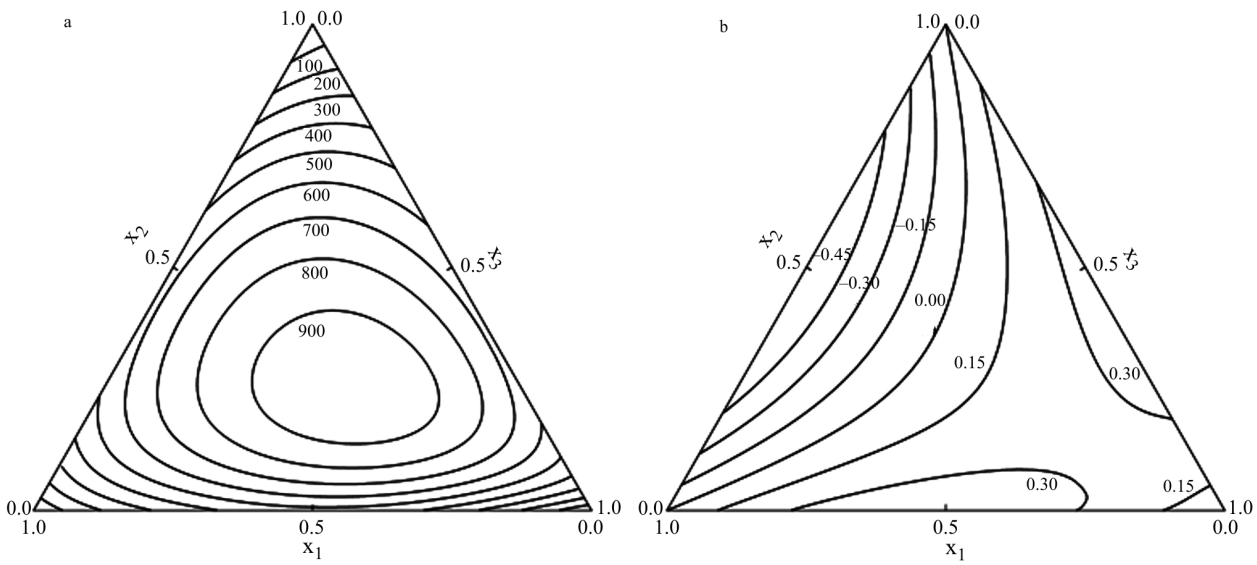

Fig. 2 Isolines for the ternary system x_1MTBE+$x_2$1-propanol+$x_3$octane at 298.15 K, a – $H^E_{m,123}$ (J mol^{-1}) calculated with Eq. (5), b – $V^E_{m,123}$ (mL mol^{-1}), calculated with Eq. (6)

The empirical expressions of Kohler [24], Jacob and Fitzner [25], Colinet [26] and Knobeloch and Schwartz [27], Tsao and Smith [28], Toop [29], Scatchard *et al.* [30], Hillert [31] and Mathieson and Thynne [32] were applied to estimate ternary properties from binary results. Deviations between experimental data and estimated values are shows in Table 6. The best agreement with the experimental data to excess molar enthalpies was achieved by the symmetric equation from Knobeloch and Schwartz [27], meanwhile to the ternary excess volumes the best predictions were obtained with Jacob and Fitzner [25].

Table 5 Mean deviations of excess molar enthalpies predicted by the theoretical models from the experimental data

System	Larsen	Gmehling
MTBE+1-propanol	123.8	154.5
MTBE+octane	90.9	44.3
1-propanol+octane	52.3	48.8
MTBE+1-propanol+octane	72.6	54.6

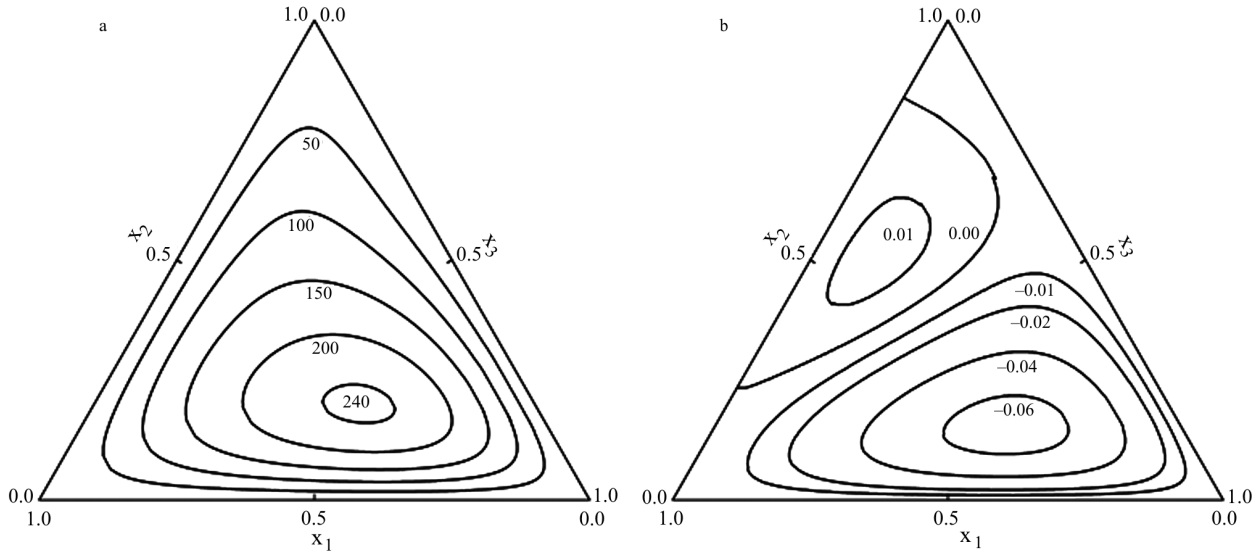

Fig. 3 Curves of constant ternary contribution, $x_1x_2x_3\Delta_{123}$, a – to the excess molar enthalpy $H^{E}_{m,123}$ (J mol^{-1}), b – to the excess molar volume $V^{E}_{m,123}$ (mL mol^{-1}), for x_1MTBE+$x_2$1-propanol+$x_3$octane at 298.15 K, correlated using Eqs (5) and (6), respectively

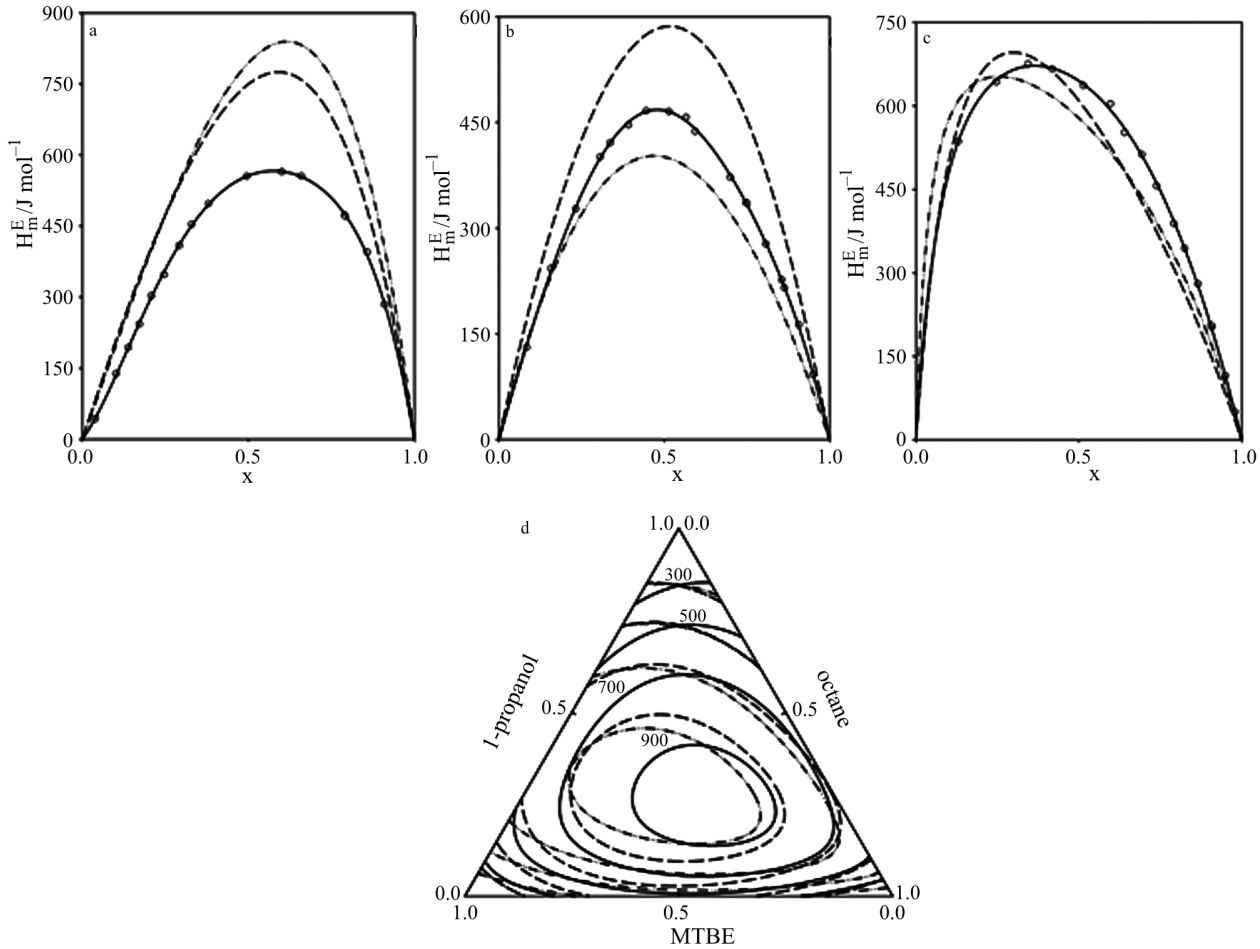

Fig. 4 Excess molar enthalpies for a – MTBE+(1–x)1-propanol, b – MTBE+(1–x)octane, c – x1-propanol+(1–x)octane d – x_1MTBE+$x_2$1-propanol+$x_3$octane at 298.15 K, — – fit of experimental data, — — – Larsen *et al*. model, —··— – Gmehling *et al*. model

Table 6 Mean deviations from the experimental values obtained with the empirical predictive methods. For the asymmetric equations three numberings of the components have been compared, in this order, 123, 231, 312

	s/J mol^{-1}			s/mL mol^{-1}		
Kohler	121.1			0.0142		
Jacob–Fitner	138.8			0.0109		
Colinet	123.4			0.0123		
Knobeloch–Schwartz	21.2			0.0287		
Tsao–Smith	47.9[a]	23.0[b]	74.3[c]	0.0572[a]	0.0718[b]	0.0687[c]
Toop	138.9[a]	72.4[b]	156.5[c]	0.0165[a]	0.0182[b]	0.0236[c]
Scatchard	155.4[a]	71.8[b]	158.4[c]	0.0229[a]	0.0187[b]	0.0252[c]
Hillert	142.1[a]	72.3[b]	155.8[c]	0.0147[a]	0.0188[b]	0.0229[c]
Mathieson–Thynne	145.9[a]	112.9[b]	150.8[c]	0.0229[a]	0.0137[b]	0.0153[c]

[a]order 123, [b]order 231, [c]Order 312

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