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Experimental and theoretical study of excess molar volumes and enthalpies for the ternary mixture butyl butyrate + 1-octanol + decane at 308.15 K

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Abstract

This paper reports measurements on excess thermodynamic properties for the ternary system: butyl butyrate + 1-octanol + decane at the temperature 308.15 K and atmospheric pressure.

The binary and ternary experimental data were correlated using the Redlich–Kister and Cibulka equation, respectively. Experimental values were compared with the predictions obtained by several contribution models and several empirical equations.

Keywords: Excess enthalpies; Excess volumes; Butyl butyrate; 1-Octanol; Decane

1. Introduction

In previous papers [1–4] we reported experimental excess thermodynamic properties for ternary mixtures containing ester, 1-alkanol and alkane as components. The present article continues this work, exploring excess molar volumes and excess molar enthalpies at 308.15 K and normal atmospheric pressure of butyl butyrate+1-octanol+decane and of the constituent binary mixtures butyl butyrate+decane, and 1-octanol+decane. The butyl butyrate + 1-octanol mixture was published elsewhere [1] at the same temperature.

The binary experimental data were fitted using a variable-degree polynomial due to Redlich–Kister [5].

Table 1
Experimental excess molar enthalpies for binary mixtures at 308.15 K

x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})
x1-Octanol + (1 − x)decane					
0.1164	644	0.4546	715	0.8048	365
0.1603	685	0.5004	701	0.8530	277
0.2204	723	0.6153	618	0.8754	236
0.2762	748	0.6580	577	0.9149	163
0.3233	748	0.7125	502		
0.3818	746	0.7502	450		
xButyl butyrate + (1 − x)decane					
0.0922	303	0.4234	798	0.7426	615
0.1475	456	0.4564	810	0.7962	535
0.2044	575	0.5168	804	0.8341	449
0.2599	661	0.6040	776	0.8866	322
0.3081	719	0.6386	733	0.9351	210
0.3879	785	0.6986	676		

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The Cibulka equation [6] has been used to correlate the experimental values of ternary mixtures. Experimental values were compared with the predictions obtained by applying the group contribution model of Nitta–Chao [7]. In addition, the excess molar enthalpies were compared with the predictions of the UNIFAC group contribution model in the versions of Larsen et al. [8], Dang and Tassios [9], and by Weidlich and Gmehling [10].

The experimental values obtained were used to test several empirical expressions. These equations offer reliable estimation of excess properties for a ternary mixture using the involved binary experimental data. The symmetric equations used were those introduced by Kohler [11], Jacob–Fitzner, [12] and Colinet [13], while the asymmetric ones were those of Tsao–Smith [14], Toop [15], Scatchard et al. [16], and Hillert [17].

2. Experimental

Fluka and Aldrich supplied the chemical substances employed. The liquids were degassed by

Table 2
Experimental excess molar volumes for binary mixtures at 308.15 K

x	V_m^E (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})
x1-Octanol + (1 − x)decane					
0.0579	0.0865	0.3761	0.1570	0.7495	0.0539
0.1516	0.1601	0.4079	0.1515	0.7920	0.0357
0.2069	0.1698	0.4536	0.1375	0.7967	0.0282
0.2069	0.1692	0.6110	0.0950	0.8760	0.0114
0.2092	0.1707	0.6914	0.0642	0.9176	0.0012
0.3249	0.1659	0.7350	0.0564	0.9508	−0.0092
xButyl butyrate + (1 − x)decane					
0.0552	0.1411	0.3813	0.5351	0.6716	0.4742
0.1129	0.2511	0.4083	0.5454	0.7302	0.4276
0.1779	0.3546	0.4734	0.5596	0.7786	0.3765
0.2053	0.3926	0.5455	0.5403	0.8298	0.3053
0.2634	0.4509	0.5915	0.5325	0.8892	0.2108
0.2989	0.4914	0.6384	0.5077	0.9479	0.0976

Table 3
Coefficients A_p and B_p of Eqs. (2) and (3) and standard deviations, s

	A_0	A_1	A_2	A_3	A_4	A_5	s
xButyl butyrate + (1 − x)1-octanol[a]							
V_m^E	1.0041	0	0.2381	−0.3200			0.0047
H_m^E	6433.8	904.6	1139.5	2075.9	0	−2088.1	8
x1-Octanol + (1 − x)decane							
V_m^E	0.5065	−0.5300	0.3430	−0.5269			0.0031
H_m^E	2817.4	−1236.2	725.3	0	2678.4	−4059.7	8
xButyl butyrate + (1 − x)decane							
V_m^E	2.2183	−0.2200	0.2008	0.3311	−0.0387	−0.6647	0.0038
H_m^E	3101.7	−131.8	184.1				2
	B_0	B_1	B_2	s			
x_1Butyl butyrate + $x_2$1-octanol + (1 − x_1 − x_2)decane							
V_m^E	2.9152	−2.6538	−4.9440	0.0149			
H_m^E	16310.6	−3954.2	−20202.2	29			

[a] From [1].

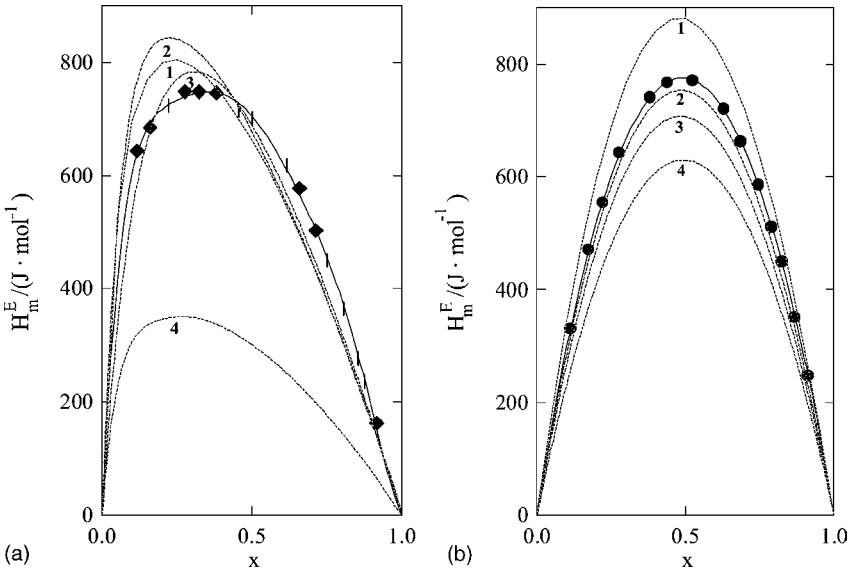

Fig. 1. Experimental values of H_m^E for: (a) x1-octanol + $(1-x)$decane, (b) $x$butyl butyrate + $(1-x)$decane where solid line (Eq. (2)) and symbols (experimental data); (1) Nitta–Chao; (2) UNIFAC (Gmehling); (3) UNIFAC (Larsen); (4) UNIFAC (Tassios).

ultrasound, and dried over 0.4 nm molecular sieves. The substances were butyl butyrate (Fluka, purity >99%), 1-octanol (Fluka, purity >99.5%), and decane (Aldrich, purity >99%).

Excess molar volumes were determined from the densities of the pure liquids and of their mixtures measured with an Anton Paar DMA 60/602 densimeter with a resolution of $\pm 2 \times 10^{-6}$ g cm^{-3}, thermostated

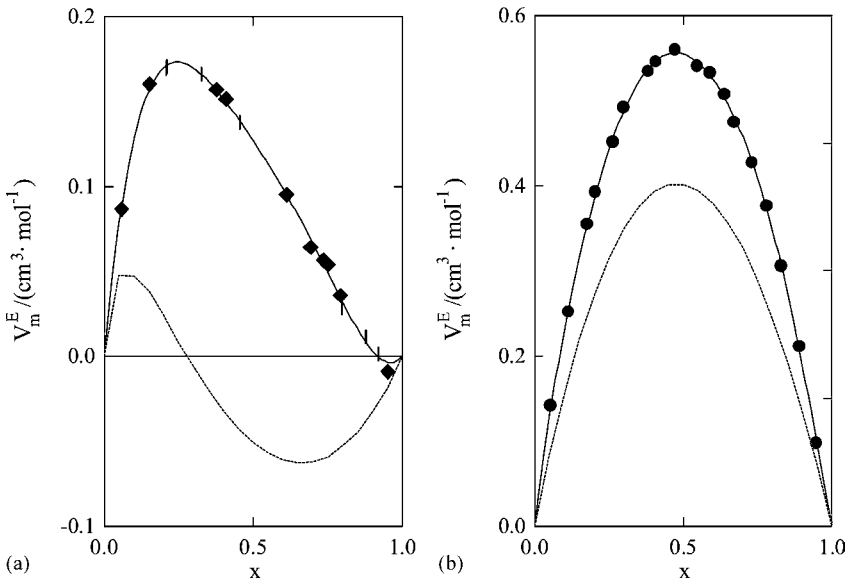

Fig. 2. Experimental values of V_m^E (a) x1-octanol + $(1-x)$decane, (b) $x$butyl butyrate + $(1-x)$decane where solid line (Eq. (2)) and symbols (experimental data); (1) Nitta–Chao model.

at (308.15 ± 0.01 K) in a Haake F3 circulating water-bath.

The excess molar enthalpies were measured using a Calvet microcalorimeter. Paz Andrade et al. [18,19] described the calibration and operating conditions. The inaccuracy of excess molar enthalpies is better than 1%.

In all cases, the samples were prepared covering the whole composition range of the mixtures using a Mettler AT 201 balance with a precision of 1×10^{-8} kg. The precision of the molar fraction is estimated to be better than 1×10^{-4} kg.

3. Results

Experimental excess molar volumes and excess molar enthalpies for binary mixtures are reported in Tables 1 and 2, respectively. A Redlich–Kister variable-degree polynomial were used to fit the results for each binary mixture by the unweighted least-square method. This expression has the following form:

$$Q^{\mathrm{E}}_{\mathrm{m}}(x_i, x_j) = x_i x_j \sum_{p=0}^{q} A_p (x_i - x_j)^p \quad (1)$$

where $Q^{\mathrm{E}}_{\mathrm{m}}$ represents $V^{\mathrm{E}}_{\mathrm{m}}$ or $H^{\mathrm{E}}_{\mathrm{m}}$ the degree of the polynomial, q, was optimised by applying the F-test [20]. The coefficients A_p and the standard deviations are given in Table 3. Figs. 1 and 2 present the experimental binary $V^{\mathrm{E}}_{\mathrm{m}}$ and $H^{\mathrm{E}}_{\mathrm{m}}$ values plotted against molar fraction of the first component of the binary mixture in each case, and the curves were calculated from the smoothing Eq. (1).

The excess molar enthalpies for the 1-octanol + decane mixture were also measured by Featherstone and Dickinson [21] and more recently by Amigo et al. [22], being the difference at the equimolar composition between our results and theirs less than 6 and 1.5%, respectively.

The experimental excess molar volumes and excess molar enthalpies for the ternary mixture, $V^{\mathrm{E}}_{\mathrm{m},123}$ and $H^{\mathrm{E}}_{\mathrm{m},123}$, are shown in Tables 4 and 5. The Cibulka equation has been employed to fit the experimental values of the ternary mixtures:

$$Q^{\mathrm{E}}_{\mathrm{m},123} = Q^{\mathrm{E}}_{\mathrm{m,bin}} + x_i x_j (1 - x_i - x_j) \times (B_0 + B_1 x_i + B_2 x_j) \quad (2)$$

Table 4
Experimental excess molar enthalpies for ternary mixtures at 308.15 K

x_1	x_2	$H^{\mathrm{E}}_{\mathrm{m},\phi,\mathrm{exp}}$ (J mol^{-1})	$H^{\mathrm{E}}_{\mathrm{m},123}$ (J mol^{-1})
$x'_1 = 0.2245$		$H^{\mathrm{E}}_{\mathrm{m},12} = 1052$	
0.1074	0.3711	637	1140
0.0990	0.3420	641	1105
0.0957	0.3305	661	1109
0.0725	0.2502	680	1020
0.0615	0.2125	674	962
0.0515	0.1779	666	907
0.0421	0.1456	630	827
0.1428	0.4932	540	1209
0.1505	0.5198	517	1222
0.1597	0.5514	473	1221
0.1718	0.5934	401	1206
0.1763	0.6090	378	1204
0.1899	0.6559	278	1167
0.2033	0.7023	194	1146
0.1966	0.6791	236	1157
$x'_1 = 0.4917$		$H^{\mathrm{E}}_{\mathrm{m},12} = 1604$	
0.2305	0.2382	678	1430
0.1776	0.1836	704	1283
0.1696	0.1753	697	1250
0.1423	0.1471	680	1144
0.0857	0.0886	552	831
0.2978	0.3078	634	1605
0.3902	0.3317	576	1623
0.3520	0.3638	516	1664
0.3740	0.3866	455	1675
0.3979	0.4113	376	1674
0.4076	0.4214	647	1677
0.4515	0.5668	183	1656
$x'_1 = 0.7390$		$H^{\mathrm{E}}_{\mathrm{m},12} = 1408$	
0.4015	0.1418	741	1506
0.3518	0.1242	767	1437
0.4413	0.1559	716	1557
0.4781	0.1689	674	1585
0.5175	0.1827	608	1594
0.5545	0.1958	551	1607
0.5891	0.2080	470	1592
0.6223	0.2198	390	1576
0.6497	0.2295	303	1541

where

$$Q^{\mathrm{E}}_{\mathrm{m,bin}} = Q^{\mathrm{E}}_{\mathrm{m},12} + Q^{\mathrm{E}}_{\mathrm{m},13} + Q^{\mathrm{E}}_{\mathrm{m},23} \quad (3)$$

The symbol $Q^{\mathrm{E}}_{\mathrm{m},123}$ represents $V^{\mathrm{E}}_{\mathrm{m},123}$ or $H^{\mathrm{E}}_{\mathrm{m},123}$ and $Q^{\mathrm{E}}_{\mathrm{m},ij}$ is the excess molar enthalpy or volume for the binary mixtures. Table 3 also presents the parameters B_p and the standard deviation between experimental and fitted values.

Our results for binary and ternary mixtures were compared with those of the Nitta–Chao theory using the interaction parameters given in references [7, 23–25]. The curves obtained are presented in Figs. 1–4 by dashed lines. Table 6 shows standard deviations between the experimental and predicted properties.

Results for excess molar enthalpies were also compared with the predictions of the UNIFAC group contribution model considered by Larsen et al., Tassios et al., and Gmehling et al. Table 6 shows the mean deviation percentage obtained in each case. Fig. 1 shows, by dashed lines, the curves obtained by the application of these models.

Values of $V^{E}_{m,123}$ and $H^{E}_{m,123}$ have been also calculated using the empirical equations proposed by Kohler, Jacob and Fitzner, Colinet, Tsao and Smith,

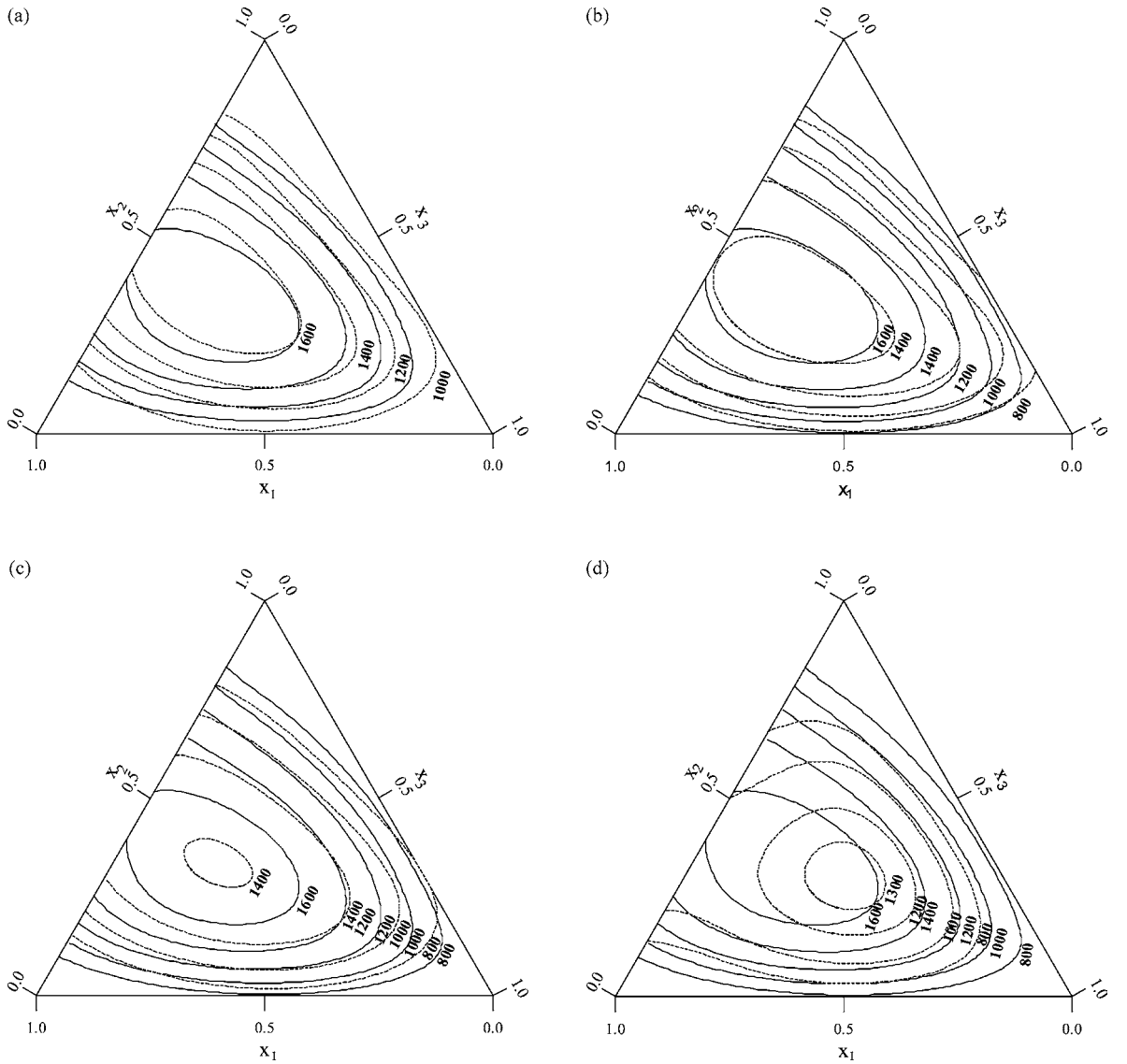

Fig. 3. Curves of constant $H^{E}_{m,123}$ in ($J\,mol^{-1}$) for $x_1$butyl butyrate + $x_2$1-octanol + $x_3$decane at 308.15 K obtained for theoric models (dashed lines): (a) Nitta–Chao, (b) Gmehling, (c) Larsen, (d) Tassios and solid line shows experimental data.

Table 5
Experimental excess molar volumes for ternary mixtures at 308.15 K

x_1	x_2	$V^E_{m,123}$ (cm^3 mol^{-1})	x_1	x_2	$V^E_{m,123}$ (cm^3 mol^{-1})
0.0155	0.0712	0.1714	0.4165	0.4660	0.3292
0.0267	0.1229	0.2134	0.0897	0.0542	0.2871
0.0515	0.2368	0.2611	0.1621	0.0980	0.3836
0.0756	0.3475	0.2706	0.2505	0.1515	0.4825
0.0981	0.4510	0.2611	0.3197	0.1933	0.4854
0.1068	0.4906	0.2513	0.3656	0.2211	0.4845
0.1191	0.5474	0.2371	0.4018	0.2430	0.4764
0.1403	0.6447	0.2052	0.4646	0.2810	0.4423
0.0508	0.1081	0.2450	0.0986	0.0325	0.2816
0.0922	0.1962	0.3131	0.1978	0.0652	0.4301
0.1354	0.2881	0.3385	0.3001	0.0988	0.5145
0.1730	0.3682	0.3542	0.4421	0.1456	0.5196
0.1910	0.4064	0.3399	0.4978	0.1639	0.5168
0.2142	0.4559	0.3295	0.5772	0.1901	0.4471
0.2498	0.5316	0.2996	0.0754	0.0095	0.1917
0.2853	0.6072	0.2413	0.4548	0.0574	0.5579
0.1293	0.1446	0.3600	0.5214	0.0658	0.5489
0.1913	0.2140	0.4145	0.6767	0.0854	0.4487
0.3079	0.3445	0.4136	0.7630	0.0963	0.3377
0.3537	0.3957	0.3872			

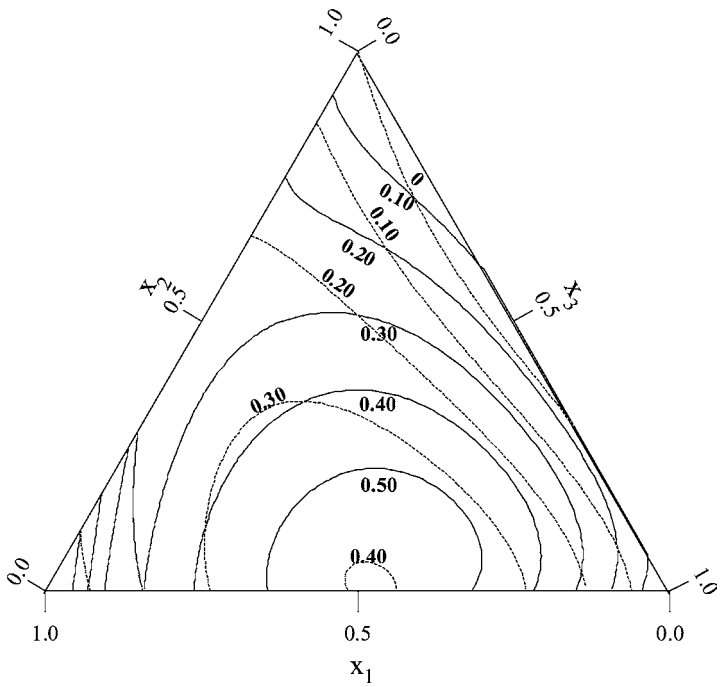

Fig. 4. Curves of constant $V^E_{m,123}$ in (cm^3 mol^{-1}) for $x_1$butyl butyrate + $x_2$1-octanol + $(1 - x_1 - x_2)$decane at 308.15 K obtained for theoric model Nitta–Chao (dashed lines) and solid line shows experimental data.

Table 6
Standard deviations achieved with the group contribution models used in this work

	s ($cm^3\,mol^{-1}$)	s ($J\,mol^{-1}$)			
		Nitta–Chao	Larsen	Tassios	Gmehling
Butyl butyrate + 1-octanol	0.03	84	253	437	201
1-Octanol + decane	0.13	61	41	114	76
Butyl butyrate + decane	0.12	74	57	114	23
Butyl butyrate +1-octanol + decane	0.13	55	209	332	144

Table 7
Standard deviations, s, of models for a, b, c[a]

	s ($cm^3\,mol^{-1}$)			s ($J\,mol^{-1}$)		
	a	b	c	a	b	c
Kohler	0.012			183		
Jacob–Fitzner	0.015			208		
Colinet	0.013			165		
Tsao–Smith	0.031	0.091	0.020	95	53	46
Toop	0.015	0.016	0.029	211	97	234
Scatchard	0.016	0.015	0.029	226	98	241
Hillert	0.015	0.017	0.028	201	96	223

[a] (a) x_1Butyl butyrate + $x_2$1-octanol + $(1 - x_1 - x_2)$decane, (b) $x_1$1-octanol + $x_2$decane + $(1 - x_1 - x_2)$butyl butyrate, (c) $x_1$decane + $x_2$butyl butyrate + $(1 - x_1 - x_2)$1-octanol.

Toop, Scatchard, and Hillert, which take into account only the binary contribution. For the asymmetric methods (Toop, Scatchard, Tsao–Smith and Hillert), we must indicate the order of components in the mixtures. Table 7 shows the standard deviation between experimental and predicted values.

4. Conclusions

The excess molar properties for binary and ternary mixtures studied are positive in all cases.

In general from the results obtained we can conclude that the best predictions for both magnitudes are due to the Nitta–Chao model. As exception we can to indicate that the UNIFAC model offers better accuracy for the enthalpies of 1-octanol + decane and butyl butyrate + decane in the versions of Larsen and Gmehling, respectively.

By applying the empirical expressions studied, we observe that the symmetric ones show a correlation slightly better for the excess molar volumes. In the case of the excess molar enthalpies the best prediction are due to the Tsao–Smith equation.

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