

# APPLICATION OF DIFFERENT GROUP CONTRIBUTION MODELS AND EMPIRICAL METHODS TO EXCESS ENTHALPIES OF TERNARY MIXTURES

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## Abstract

Studies were previously made of the excess molar enthalpies,  $H_m^E$ , at 298.15 K and normal atmospheric pressure of the ternary mixtures (ethyl propanoate or 3-pentanone) + (*n*-hexane) + (*n*-decane, *n*-dodecane or *n*-tetradecane) and (1-propanol) + (3-pentanone) + (*n*-hexane, *n*-heptane, *n*-octane, 1-hexanol or 1-heptanol). In the present work, experimental values of  $H_m^E$  were correlated through use of the Cibulka and Nagata equations, and a new correlation equation is proposed. Experimental data were compared with the predictions of the UNIFAC I (version of Tassios), UNIFAC II (version of Larsen) and Nitta-Chao group contribution models.  $H_m^E$  values were used to test several empirical predictive methods, both symmetric (Kohler, Jacob-Fitzner, Colinet and Knobloch-Schwartz), and asymmetric (Tsao-Smith, Toop, Scatchard, Hillert and Mathieson-Tynne).

**Keywords:** empirical equations, excess enthalpy, group contribution, ternary mixtures

## Introduction

In previous works [1-7] we reported the excess molar enthalpies,  $H_m^E$ , at 298.15 K and normal atmospheric pressure of the ternary mixtures (ethyl propanoate or 3-pentanone)+(*n*-hexane)+(*n*-decane, *n*-dodecane or *n*-tetradecane) and (1-propanol)+(3-pentanone)+(*n*-hexane, *n*-heptane, *n*-octane, 1-hexanol or 1-heptanol).

In the present work, these experimental data were used to test several empirical predictive methods, in order to obtain information about the best way to improve predictions of thermodynamic properties of ternary mixtures. Group contribution models furnish their predictions through use of a set of parameters that

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have been previously adjusted to experimental data on mixtures including the same functional groups, and empirical methods involve use of the measured values of the thermodynamic magnitude for the binary mixtures to calculate the ternary values.

Three equations are also suggested to correlate the ternary experimental values of the magnitude. These equations exhibit deviations similar to the correlation with the Cibulka and Nagata Tamura equations, with use of a more reduced set of parameters.

**Table 1** Coefficients  $A_i$  calculated for the correlation of  $H_m^E$  ( $J mol^{-1}$ ) for the binary mixtures according to the Redlich-Kister equation (Eq. (2))

	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$s$
$xCH_3CH_2COOCH_2CH_3 +$							
$(1-x)CH_3(CH_2)_4CH_3$	4129	-220.3	550.8	-131.3	-672.6		1.7
$(1-x)CH_3(CH_2)_8CH_3$	5229	224.6	643.3	225.3			3.9
$(1-x)CH_3(CH_2)_{10}CH_3$	5729	486.5	683.3	507.5	357.1		4.0
$(1-x)CH_3(CH_2)_{12}CH_3$	6161	848.5	-18.48	779.5	1689		2.4
$xCH_3(CH_2)_4CH_3 +$							
$(1-x)CH_3(CH_2)_8CH_3$	60.61	-9.187	-1.180	-1.620			0.1
$(1-x)CH_3(CH_2)_{10}CH_3$	161.0	-18.48					1.9
$(1-x)CH_3(CH_2)_{12}CH_3$	275.3	-6.821	-147.9				1.1
$xCH_3CH_2COCH_2CH_3 +$							
$(1-x)CH_3(CH_2)_4CH_3$	4094	-779.1	635.3	-283.2			4.6
$(1-x)CH_3(CH_2)_5CH_3$	4422	-424.5	599.5	-232.3			2.2
$(1-x)CH_3(CH_2)_6CH_3$	4662	-437.0	728.9	-98.48			2.4
$(1-x)CH_3(CH_2)_8CH_3$	5163	-179.5	1180	125.1	-162.2		3.5
$(1-x)CH_3(CH_2)_{10}CH_3$	5606	-92.11	706.4	168.9	691.3		2.7
$(1-x)CH_3(CH_2)_{12}CH_3$	6022	-67.40	473.8	-137.1	808.7		3.3
$(1-x)CH_3(CH_2)_5OH$	5740	1011	1111				3.5
$(1-x)CH_3(CH_2)_6OH$	6041	1139	1454	3491			3.9
$xCH_3(CH_2)_2OH +$							
$(1-x)CH_3CH_2COCH_2CH_3$	4928	-450.6	65.51	14.17	683.2		3.6
$(1-x)CH_3(CH_2)_4CH_3$	2255	-1393	50.19	2223	2997	-5775	18.4
$(1-x)CH_3(CH_2)_5CH_3$	2477	-1260	302.6	1373	2587	-4717	10.5
$(1-x)CH_3(CH_2)_6CH_3$	2710	1214	167.2	1593	2850	-5261	11.7
$(1-x)CH_3(CH_2)_5OH$	255.3	45.15	30.00	21.97			0.16
$(1-x)CH_3(CH_2)_6OH$	413.5	54.15	2.58	7.29			0.27

## Correlation equations

The excess molar enthalpies of the ternary mixtures were correlated by using the equation

$$H_{m,1+2+3}^E = H_{m,1+2}^E + H_{m,1+3}^E + H_{m,2+3}^E + x_1x_2x_3\Delta_{123} \quad (1)$$

where  $H_{m,i+j}^E$  is the excess molar enthalpy of the binary  $i+j$  mixture, fitted to a variable degree polynomial, in the form suggested by Redlich and Kister [8].

$$H_{m,i+j}^E = x_ix_j \sum_{m=0}^M A_m(x_i - x_j)^m \quad (2)$$

The least-squares method was employed to calculate the parameters  $A_i$ , and in each case the number of parameters  $M$  was determined by using an  $F$ -test [9]. The parameters  $A_i$  calculated for this expression are listed in Table 1, together with the standard deviations.

**Table 2** Coefficients  $B_i$  calculated for the correlation of the ternary contribution  $\Delta_{123}$  to the excess enthalpy according to the Cibulka equation (Eq. (3))

	$B_0$	$B_1$	$B_2$	$s$
	$x_1\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 +$			
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	1002	-1493	-1460	4.3
$x_3\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	1344	-1715	-2048	3.1
$x_3\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	1552	-1802	-2385	3.8
	$x_1\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 +$			
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	2042	-2176	-615.9	14.7
$x_3\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	1211	1247	-1081	17.0
$x_3\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	855	3564	-1811	18.1
	$x_1\text{CH}_3(\text{CH}_2)_2\text{OH} + x_2\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 +$			
$x_3\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	17629	-17324	-8171.6	43
$x_3\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	18424	-16802	-10391	42
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	19069	-17187	-10623	44
	$x_1\text{CH}_3(\text{CH}_2)_2\text{OH} + x_2\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 +$			
$x_3\text{CH}_3(\text{CH}_2)_5\text{OH}$	3374	-2086	-9586	14
$x_3\text{CH}_3(\text{CH}_2)_6\text{OH}$	5506	-4225	-13573	14

In Eq. (1), the ternary contribution  $\Delta_{123}$  was correlated by using the expression suggested by Cibulka [10]:

$$\Delta_{123} - B_0 + B_1x_1 + B_2x_2 \quad (3)$$

and the expression due to Nagata and Tamura [11]:

$$\frac{\Delta_{123}}{RT} = B_0 - B_1x_1 - B_2x_2 - B_3x_1^2 - B_4x_2^2 - B_5x_1x_2 - B_6x_1^3 - B_7x_2^3 \quad (4)$$

In both cases, the parameters  $B_i$  were calculated by the unweighted least-squares method, using the non-linear optimization parameter due to Marquardt [12] parameters  $B_i$  for Eqs (3) and (4) are listed in Tables 2 and 3, respectively.

In the present work, we propose three new expressions to fit the ternary excess values of the magnitude, which do not take into account the experimental values of the magnitude of the binary mixture, a reduced set of coefficients being used. The first involves six coefficients and can be expressed as follows:

$$H_{m,1+2+3}^E = C_1x_1x_2 + C_2x_1x_3 + C_3x_2x_3 + C_4x_1^2x_2 + C_5x_1x_3^2 + C_6x_2^2x_3 \quad (5)$$

The other suggested equations involve nine coefficients:

$$H_{m,1+2+3}^E = C_1x_1x_2 + C_2x_1x_3 + C_3x_2x_3 + C_4x_1^2x_2 + C_5x_1x_3^2 + C_6x_2^2x_3 + C_7x_1^2x_2^2 + C_8x_1^2x_3^2 + C_9x_2^2x_3^2 \quad (6)$$

and

$$H_{m,1+2+3}^E = C_1x_1x_2 + C_2x_1x_3 + C_3x_2x_3 + C_4x_1^2x_2 + C_5x_1x_3^2 + C_6x_2^2x_3 + C_7x_1^3x_2 + C_8x_1x_3^3 + C_9x_2^3x_3 \quad (7)$$

Coefficients  $C_i$  for Eqs (5), (6) and (7) are listed in Tables 4, 5 and 6, respectively, together with the corresponding standard deviations  $s$ . Table 7 presents a comparison between the standard deviations obtained with the correlation equations applied.

## Theoretical models

The UNIFAC model was proposed by Fredenslund *et al.* [13], who added the functional group contribution solution to the UNIQUAC equation (Abrams and Prausnitz [14]), to calculate activity coefficients for pure liquids and liquid mixtures.

In 1984, Tassios *et al.* [15] made an exhaustive study of the existing group contribution models to predict mixing enthalpies, and concluded that the best results were achieved with the UNIFAC model modified by Skjold-Jorgensen *et al.* [16].

Table 3 Coefficients  $B_i$  calculated for the correlation of the ternary contribution  $\Delta_{123}$  to the excess enthalpy according to the Nagata (Ec. (4))

	$B_0$	$B_1$	$E_2$	$B_3$	$B_4$	$B_5$	$B_6$	$B_7$	$s$
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	0.704	0.067	2.869	5.577	-4.263	-2.737	-6.443	3.416	3.6
$x_3\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	0.630	-0.010	1.862	3.737	-1.226	-2.238	-3.187	1.007	2.4
$x_3\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	0.617	-0.070	1.383	3.698	-0.414	-1.762	-3.226	0.882	3.3
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	-1.480	-21.46	1.478	56.28	-5.260	2.114	-42.46	4.981	3.9
$x_3\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	-1.720	-25.52	3.073	70.22	-6.900	-1.949	-56.14	7.081	3.0
$x_3\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	-2.443	-29.55	0.520	79.11	3.411	-2.852	-53.69	-2.808	4.0
$x_3\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	14.27	50.92	14.37	-81.08	5.449	-31.09	29.83	-16.82	28
$x_3\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	14.93	52.51	17.51	-85.78	-2.309	-31.44	53.01	-9.398	22
$x_3\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	16.18	56.88	23.47	-95.07	-16.56	-34.76	60.87	1.981	23
$x_3\text{CH}_3(\text{CH}_2)_5\text{OH}$	1.206	10.27	-8.890	-18.44	39.85	-8.243	13.87	-31.31	5.7
$x_3\text{CH}_3(\text{CH}_2)_6\text{OH}$	2.503	12.23	-4.167	-19.93	30.60	-9.580	14.52	-22.18	2.5

Table 4 Coefficients  $C_i$  and standard deviations  $s$  calculated for the correlation of  $H_n^E$  ( $\text{J mol}^{-1}$ ), according to Eq. (5)

	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$	$C_6$	$s$
$x_1\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 +$							
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	4281	5074	97.66	-61.95	278.8	-64.13	8.5
$x_3\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	4172	5785	2.6.6	141.0	-156.9	-104.2	6.9
$x_3\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	4041	6730	233.2	206.6	-1239	77.26	6.3
$x_1\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 +$							
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	4986	4746	-78.15	-1458	259	426.0	13
$x_3\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	5143	5280	95.71	-1539	997.2	-14.7	14
$x_3\text{CH}_3(\text{C}_2\text{H}_5)_{12}\text{CH}_3$	5010	6203	165.1	-1437	124.3	-193.9	16
$x_1\text{CH}_3(\text{CH}_2)_2\text{OH} + x_2\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 +$							
$x_3\text{CH}_3(\text{C}_2\text{H}_5)_4\text{CH}_3$	6306	1200	7513	-1789	2939	-4640	44
$x_3\text{CH}_3(\text{C}_2\text{H}_5)_5\text{CH}_3$	6052	1261	7226	-1071	3696	-3179	45
$x_3\text{CH}_3(\text{C}_2\text{H}_5)_6\text{CH}_3$	6427	1566	7642	-1660	3481	-3756	45
$x_1\text{CH}_3(\text{CH}_2)_2\text{OH} + x_2\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 +$							
$x_3\text{CH}_3(\text{C}_2\text{H}_5)_5\text{OH}$	5539	222.0	5894	-1145	-131.1	-888.1	7.9
$x_3\text{CH}_3(\text{C}_2\text{H}_5)_6\text{OH}$	5479	364.5	6188	-1037	90.03	-838.8	7.2

Table 5 Coefficients  $C_i$  and standard deviations  $s$  calculated for the correlation of  $H_n^h$  ( $\text{J mol}^{-1}$ ) according to Eq. (6)

	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$	$C_6$	$C_7$	$C_8$	$C_9$	$s$
$x_1\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 +$										
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	4888	4989	-111.9	-159.8	541.3	-389.0	-2694	-646.7	1180	7.2
$x_3\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	4822	5518	176.4	87.1	156.4	-471.9	-2949	-46.01	436.35	5.6
$x_3\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	4655	6450	140.2	21.80	-952.5	-389.8	-2231	286.9	998.9	5.4
$x_1\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 +$										
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	5938	4754	-103.1	-1602	1644	100.2	-4716	-2198	-572.1	6.7
$x_3\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	5394	5144	60.27	-1586	1451	-519.6	-6545	-1889	-429.1	8.0
$x_3\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	5948	6278	104.82	-1554	530.6	-519.7	-4554	-2617	-507.6	8.9
$x_1\text{CH}_3(\text{CH}_2)_2\text{OH} + x_2\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 +$										
$x_3\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	5367	2196	8925	-441.6	2670	-2657	-1391	-6783	-12717	16
$x_3\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	5132	3768	8149	-643.4	2454	-1566	-6.729	-11473	-10707	17
$x_3\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	4648	4040	8545	-451.2	2378	-913.3	1791	-11103	-12240	18
$x_1\text{CH}_3(\text{CH}_2)_2\text{OH} + x_2\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 +$										
$x_3\text{CH}_3(\text{CH}_2)_5\text{OH}$	5032	-378.5	6136	-737.6	336.7	-953.7	-3257	987.4	-1322	5.4
$x_3\text{CH}_3(\text{CH}_2)_6\text{OH}$	5357	-96.93	6071	-1164	548.0	-1447	-3586	541.6	1315	5.3

Table 6 Coefficients  $C_i$  and standard deviations  $s$  calculated for the correlation of  $H_m^E$  ( $\text{J mol}^{-1}$ ) according to Eq. (7)

	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$	$C_6$	$C_7$	$C_8$	$C_9$	$s$
$x_1\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	4959	5587	65.09	-3271	-1392	56.75	3072	1321	-707.2	5.9
$x_2\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	4909	6257	248.2	-3172	-1676	-346.1	3102	1141	-331.0	3.7
$x_3\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	4605	6916	282.3	-2111	-1847	-229.5	2154	426.8	-147.1	4.7
$x_1\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 +$										
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	5950	5404	-238.2	-5680	-998.5	1215	3846	1916	-1867	11
$x_2\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	5777	6178	-213.4	-8219	-1992	1493	5862	2461	-3702	12
$x_3\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	5170	6931	-181.7	-6269	-2466	1611	4359	2326	-3422	14
$x_1\text{CH}_3(\text{CH}_2)_2\text{OH} + x_2\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 +$										
$x_3\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	5491	3130	8734	-47.29	-4725	-11185	-1523	6631	9341	28
$x_2\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	5144	4717	7773	-2658	-9115	-3751	474.9	10964	2768	28
$x_3\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	5173	4582	7911	-2085	-8104	-5547	-243.0	10435	2895	27
$x_1\text{CH}_3(\text{CH}_2)_2\text{OH} + x_2\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 +$										
$x_3\text{CH}_3(\text{CH}_2)_5\text{OH}$	5969	445.8	6118	-3272	-797.6	-2225	2209	373.4	1469	4.5
$x_2\text{CH}_3(\text{CH}_2)_6\text{OH}$	5320	501.0	6148	-4604	-206.9	-699.4	3469	107.7	-919.6	4.8



**Table 7** Comparison of the standard deviations  $s$  obtained with correlation equations (Eqs (3) to (8))

	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)
$x_1\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 +$					
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	4.3	3.6	8.5	7.2	5.9
$x_3\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	3.1	2.4	6.9	5.6	3.7
$x_3\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	3.8	3.3	6.3	5.4	4.7
$x_1\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 +$					
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	14	3.9	13	6.7	11
$x_3\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	17	3.0	14	8.0	12
$x_3\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	18	4.0	16	8.9	14
$x_1\text{CH}_3(\text{CH}_2)_2\text{OH} + x_2\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 +$					
$x_3\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	43	28	44	16	28
$x_3\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	42	22	45	17	28
$x_3\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	44	23	45	18	27
$x_1\text{CH}_3(\text{CH}_2)_2\text{OH} + x_2\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 +$					
$x_3\text{CH}_3(\text{CH}_2)_5\text{OH}$	14	5.7	7.9	5.4	4.5
$x_3\text{CH}_3(\text{CH}_2)_6\text{OH}$	14	2.5	7.2	5.3	4.8

This version of the model includes an association term in calculations of the excess enthalpy. This term takes into consideration the presence of chemical association effects, such as the formation of hydrogen bonds.

In 1987, Larsen *et al.* [17] modified the UNIFAC model so that it could predict simultaneously vapour-liquid equilibrium, liquid-liquid equilibrium and excess enthalpies, using the same set of parameters.

The parameters used in the present work to calculate the ternary excess enthalpy values were those provided by the authors in their original articles.

In 1977, Nitta *et al.* [18] developed a group contribution model to describe the thermodynamic properties of polar and non-polar liquids and their solutions, including the enthalpy of vaporization, PVT relations, excess properties and activity coefficients. The model adopts the cell theory of Lee *et al.* [19] for the liquid state. Formally, this is done by dividing the molecular partition function into cell partition functions, and then expressing them in terms of the contributions due to the different constituent groups. The model uses the Carnahan-Starling [20] hard sphere partition function. The advantages of this model with respect to other group contribution models are its greater theoretical rigour, because of the physical significance of its parameters, its ability to predict a larger number of thermodynamic properties, and the inclusion of a chemical association term.

The parameters used in the calculations were those provided by Nitta *et al.* in the original work, except those corresponding to the ester-alkane interaction, which were obtained from Ortega *et al.* [21].

## Empirical equations

Several empirical methods have been proposed for estimation of the ternary excess properties from experimental results on the constituent binaries. These methods are asymmetric when the predictions depend on the arbitrary designation of the numbering, and symmetric otherwise.

The symmetric equations tested were those of Kohler [22], Jacob and Fitzner [23], Colinet [24] and Knobloch and Schwartz [25].

The asymmetric expressions were those of Tsao and Smith [26], Toop [27], Scatchard *et al.* [28], Hillert [29] and Mathieson and Tynne [30]. For these equations, different numberings of the components were considered, in order to check the differences in the predicted values, and also to seek a rule to decide which ordering should be used in each case.

**Table 8** Average percentage deviations of the ternary excess enthalpy values  $H_m^E$  ( $\text{J mol}^{-1}$ ) predicted by the theoretical models from the experimental data

	UNIFAC		Nitta-Chao
	Tassios	Larsen	
	$x_1\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 +$		
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	25.3	18.2	5.05
$x_3\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	29.3	22.4	8.08
$x_3\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	29.1	22.4	6.21
	$x_1\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 +$		
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	28.7	8.06	9.26
$x_3\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	32.9	6.13	7.63
$x_3\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	32.0	4.94	7.14
	$x_1\text{CH}_3(\text{CH}_2)_2\text{OH} + x_2\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 +$		
$x_3\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	21.6	7.65	11.3
$x_3\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	20.7	7.05	11.4
$x_3\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	20.7	7.57	12.0
	$x_1\text{CH}_3(\text{CH}_2)_2\text{OH} + x_2\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 +$		
$x_3\text{CH}_3(\text{CH}_2)_5\text{OH}$	43.3	14.2	3.54
$x_3\text{CH}_3(\text{CH}_2)_6\text{OH}$	44.0	16.4	6.37

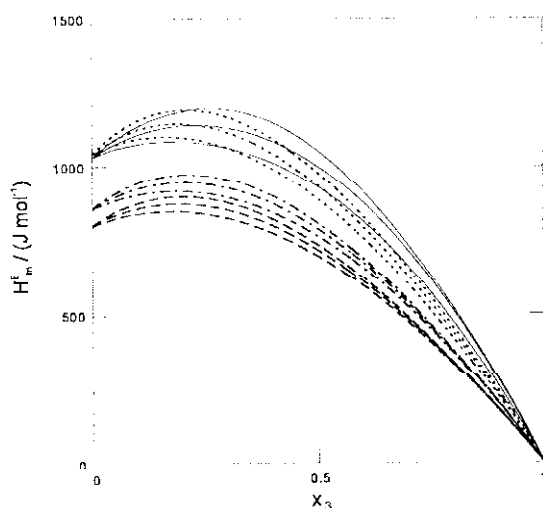
## Results and discussion

Table 7 shows the deviations obtained when the different correlation expressions tested were applied. It can be seen that the equations proposed afford results that improve the deviations obtained with the Redlich-Kister and Cibulka equations in almost every case, and although the Nagata equation uses a larger set of parameters, the results obtained with the new expressions are very similar, and are even improved for some mixtures. The new equations present the advantage that they do not need any binary coefficient to fit the ternary excess values of the magnitude, and achieve good accuracy by using a more reduced set of coefficients than when one equation is applied to correlate each binary mixture and another for the ternary contribution.

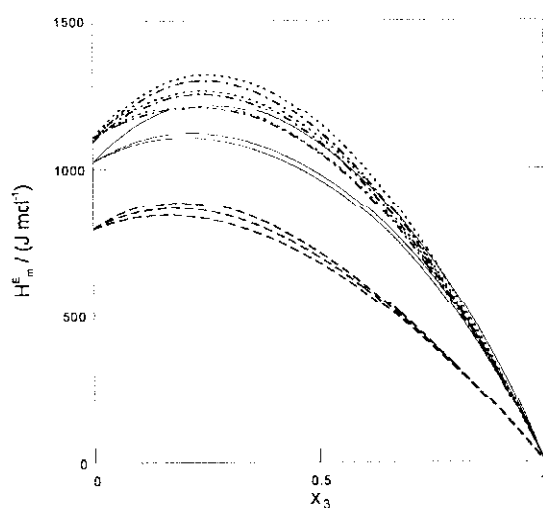
Table 8 lists the deviations as percentages of the excess molar enthalpies predicted by the theoretical models from the experimental values. These results are displayed graphically in Figs 1–4. As may be seen in Table 8, the accuracy achieved by the predictions of a theoretical model depends on the mixtures considered. In this case, the Nitta-Chao model offers the best results for the propylpropanoate+hexane+*n*-alkane and 1-propanol+3-pentanone+*n*-alkanol ternary mixtures, but the UNIFAC model in the version of Larsen gives the best prediction for 3-pentanone+hexane+*n*-alkane and 1-propanol+3-pentanone+*n*-alkane.

**Table 9** Average percentage deviations of the ternary excess enthalpy values  $H_m^E$  ( $J\ mol^{-1}$ ) predicted by the symmetric empirical equations from the corresponding experimental data

	Kohler	Jacob-Fitzner	Colinet	Knobloch-Schwartz
$x_1CH_3CH_2COCH_2CH_3 + x_2CH_3(CH_2)_4CH_3 +$				
$x_3CH_3(CH_2)_8CH_3$	1.10	0.89	1.09	28.6
$x_3CH_3(CH_2)_{10}CH_3$	1.16	1.01	1.16	29.1
$x_3CH_3(CH_2)_{12}CH_3$	1.68	0.96	1.01	26.0
$x_1CII_3CII_2COCH_2CII_3 + x_2CII_3(CII_2)_4CII_3 +$				
$x_3CH_3(CH_2)_8CH_3$	2.82	2.73	1.99	25.7
$x_3CH_3(CH_2)_{10}CH_3$	3.48	2.83	2.52	28.5
$x_3CH_3(CH_2)_{12}CH_3$	3.94	3.33	3.29	24.0
$x_1CH_3(CH_2)_2OH + x_2CH_3CH_2COCH_2CH_3 +$				
$x_3CH_3(CH_2)_4CH_3$	14.9	16.9	15.4	4.60
$x_3CH_3(CH_2)_5CH_3$	14.7	16.7	15.3	4.29
$x_3CH_3(CH_2)_6CH_3$	13.8	16.3	14.7	4.78
$x_1CH_3(CH_2)_2OH + x_2CH_3CH_2COCH_2CH_3 +$				
$x_3CH_3(CH_2)_5OH$	3.00	2.45	2.63	28.2
$x_3CH_3(CH_2)_6OH$	4.19	3.62	3.40	28.2



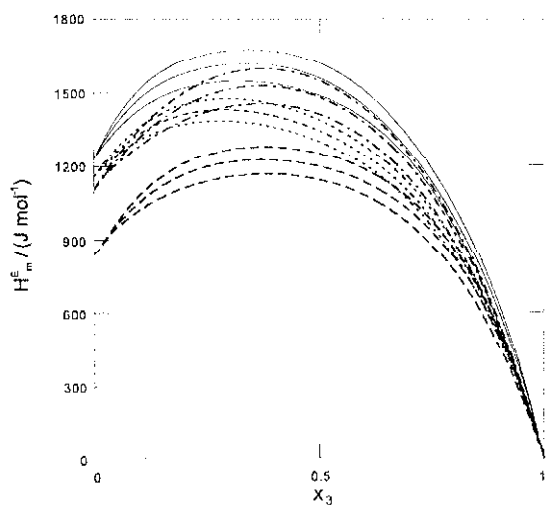
**Fig. 1** Excess molar enthalpies  $H_{m,1+2+3}^E$  at 298.15 K of the pseudobinary mixture  $\{x(0.50\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 + 0.50\text{CH}_3(\text{CH}_2)_4\text{CH}_3) + (1-x)\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_3\}$ ,  $n=10, 12, 14$ ; — Eq. (1); - - Tassios model; - · - Larsen model; ··· Nitta-Chao model



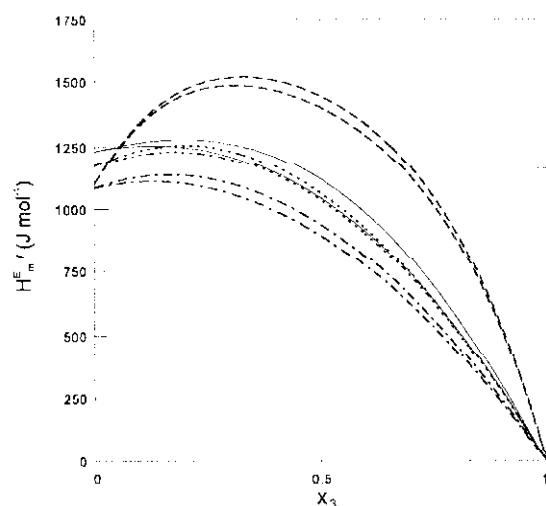
**Fig. 2** Excess molar enthalpies  $H_{m,1+2+3}^E$  at 298.15 K of the pseudobinary mixture  $\{x(0.50\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 + 0.50\text{CH}_3(\text{CH}_2)_4\text{CH}_3) + (1-x)\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_3\}$ ,  $n=10, 12, 14$ ; — Eq. (1); - - Tassios model; - · - Larsen model; ··· Nitta-Chao model

These variations are caused by the interaction parameters calculated for every pair of groups in each model. The accuracy of the predictions depends on how these parameters have been calculated. New calculated parameters will improve

the previous results when the experimental data base used has been extended, and more mixtures and thermodynamic properties have been included.



**Fig. 3** Excess molar enthalpies  $H_{m,1+2+3}^E$  at 298.15 K of the pseudobinary mixture  $\{x(0.50\text{CH}_3(\text{CH}_2)_2\text{OH} + 0.50\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3) + (1-x)\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_3\}$ ,  $n=4, 5, 6$ ;  
 — Eq. (1); - - - Tassios model; - · - · - Larsen model; · · · · Nitta-Chao model



**Fig. 4** Excess molar enthalpies  $H_{m,1+2+3}^E$  at 298.15 K of the pseudobinary mixture  $\{x(0.50\text{CH}_3(\text{CH}_2)_2\text{OH} + 0.50\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3) + (1-x)\text{CH}_3(\text{CH}_2)_{n-1}\text{CH}_3\}$ ,  $n=6, 7$ ;  
 — Eq. (1); - - - Tassios model; - · - · - Larsen model; · · · · Nitta-Chao model

**Table 10** Average percentage deviations of the ternary excess enthalpy values  $H_m^E$  ( $\text{J mol}^{-1}$ ) predicted by the symmetric empirical equations from the corresponding experimental data. The orderings used for each mixture are 123, 231 and 312, respectively

	Tsao-Smith	Toop	Scatchard	Hillert	Mathieson-Tynne
$x_1\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 +$					
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	1.32	1.22	1.22	1.46	0.85
	20.0	1.12	1.10	1.01	0.96
	23.4	1.96	1.96	1.89	1.24
$x_3\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	0.84	0.87	0.87	1.05	0.89
	18.9	1.38	1.21	1.18	1.06
	22.8	3.24	3.27	3.20	1.36
$x_3\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	1.11	1.61	1.59	1.15	1.32
	20.0	1.98	1.28	1.29	1.08
	20.8	3.19	3.17	3.16	1.16
$x_1\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 +$					
$x_3\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	2.88	2.75	2.75	3.04	1.94
	17.4	3.68	3.98	3.29	3.40
	19.4	2.95	3.44	2.89	3.03
$x_3\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	4.17	4.15	4.15	4.57	2.82
	17.7	3.83	3.81	3.33	3.37
	20.6	3.38	3.76	3.10	2.81
$x_3\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	4.28	4.45	4.47	4.56	3.49
	18.1	4.29	4.30	3.92	3.78
	16.2	2.90	2.86	2.33	3.11
$x_1\text{CH}_3(\text{CH}_2)_2\text{OH} + x_2\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 +$					
$x_3\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	4.24	11.4	11.8	7.70	14.8
	7.99	14.1	15.4	14.6	16.3
	17.3	30.2	30.3	30.1	18.8
$x_3\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	3.44	11.3	11.8	7.58	14.7
	8.20	14.3	15.8	15.0	16.4
	17.0	29.8	30.0	29.7	18.4
$x_3\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	3.50	10.7	11.2	7.50	14.3
	7.20	13.5	15.5	14.5	16.1
	18.8	30.1	30.2	30.0	18.0

Table 10 Continued

	Tsao-Smith	Toop	Scatchard	Hillert	Mathieson-Tynne
	$x_1\text{CH}_3(\text{CH}_2)_2\text{OH} + x_2\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 +$				
$x_3\text{CH}_3(\text{CH}_2)_5\text{OH}$	20.9	2.93	2.46	37.8	2.41
	1.90	2.08	2.09	2.08	2.28
	26.9	33.0	33.1	32.8	2.92
$x_3\text{CH}_3(\text{CH}_2)_6\text{OH}$	19.4	3.70	3.30	40.3	3.50
	2.52	3.13	3.11	3.11	3.48
	28.2	36.4	36.4	36.2	4.09

If we calculate the mean deviation over the whole range of mixtures considered in this work, the best results are achieved with the Nitta-Chao model, with an 8.0% deviation from the measured values, followed by the Larsen version of UNIFAC with 12.2% and the Tassios version with 29.7%.

The results of application of the symmetric empirical equations are presented in Table 9. The deviations may be seen to increase with the ternary contribution to the magnitude (last term in Eq. (1)), except for the equation of Knobloch-Schwartz, which gives the opposite tendency. The ternary contribution can be calculated from the coefficients given for Eqs (3) and (4). For those systems whose ternary contribution has a reduced magnitude, i.e. all the present mixtures except 1-propanol+3-pentanone+n-alkane, the equations of Kohler, Jacob and Fitzner, and Colinet exhibit good agreement with the experimental results.

Table 10 presents the deviations of the predicted values of  $H_m^E$  when the above-mentioned asymmetric empirical equations are used. These equations were applied for three different numberings of the components, in order to check the differences arising from this factor. The results show the influence of the numbering in each case. For example, for the Tsao-Smith equation, the variation in the deviations with the numbering is very clear, while for the Mathieson-Tynne equation, these variations are very small. For those systems containing two similar substances, the best deviations from experimental data are achieved when these components are considered second and third in the numbering.

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