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## Physics and Chemistry of Liquids

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### Excess Molar Enthalpies of the Ternary System $\{x_1\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$ , $x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3$ , $(1-x_1-x_2)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}\}$ at 298.15 K, and Prediction Using Different Theoric Methods

M. López<sup>a</sup>; M. M. Piñeiro<sup>b</sup>; J. Salgado<sup>a</sup>; B. E. De Cominges<sup>b</sup>; J. L. Legido<sup>b</sup>; M. I. Paz Andrade<sup>a</sup>

<sup>a</sup> Departamento de Física Aplicada, Facultade de Física, Universidade de Santiago de Compostela, Santiago de Compostela, Spain <sup>b</sup> Departamento de Física Aplicada, Facultade de Ciencias, Universidade de Vigo, Vigo, Spain

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**EXCESS MOLAR ENTHALPIES  
OF THE TERNARY SYSTEM  
{ $x_1\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 +$   
 $(1 - x_1 - x_2)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ }  
AT 298.15 K, AND PREDICTION  
USING DIFFERENT THEORIC METHODS**

M. LÓPEZ<sup>a</sup>, M. M. PIÑEIRO<sup>b</sup>, J. SALGADO<sup>a</sup>,  
B. E. DE COMINGES<sup>b</sup>, J. L. LEGIDO<sup>b,\*</sup>  
and M. I. PAZ ANDRADE<sup>a</sup>

<sup>a</sup> *Departamento de Física Aplicada, Facultad de Física,  
Universidade de Santiago de Compostela, E-15706 Santiago de Compostela,  
Spain;* <sup>b</sup> *Departamento de Física Aplicada, Facultad de Ciencias,  
Universidade de Vigo, E-36200, Vigo, Spain*

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Excess molar enthalpies at the temperature 298.15 K and atmospheric pressure of the ternary mixture  $\{x_1\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 + (1 - x_1 - x_2)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}\}$  and of the involved binary mixtures  $\{x\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + (1 - x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}\}$  and  $\{x\text{CH}_3(\text{CH}_2)_4\text{CH}_3 + (1 - x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}\}$  were measured using a Calvet microcalorimeter. Variable degree polynomials were fitted to the results. The group contribution models of Nitta-Chao and UNIFAC (versions of Tassios, Larsen and Gmehling) were used to estimate ternary excess enthalpy values, and the results were compared to the experimental data. Several empirical expressions for estimating ternary properties from binary results were also applied.

**Keywords:** Excess enthalpy; group contribution models; ethyl propanoate; hexane; 1-propanol

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\*Corresponding author.

## 1. INTRODUCTION

This paper continues our previous studies on calorimetric properties of non electrolyte ternary liquid mixtures [1–7]. In this work, excess molar enthalpies at 298.15 K, and normal atmospheric pressure, of the ternary mixture  $\{x_1\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 + (1 - x_1 - x_2)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}\}$  and of the involved binaries  $\{x\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + (1 - x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}\}$  and  $\{x\text{CH}_3(\text{CH}_2)_4\text{CH}_3 + (1 - x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}\}$  are presented. Excess enthalpy of the binary  $\{x\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + (1 - x)\text{CH}_3(\text{CH}_2)_4\text{CH}_3\}$  was reported in a previous work [3]. Enthalpy on mixing was determined in every case using a Calvet microcalorimeter. The binary experimental data were fitted using a variable degree polynomial, due to Redlich Kister [8]. Ternary contribution to the excess enthalpy was correlated using Cibulka [9] and Nagata [10] equations. Ternary magnitude was also fitted to three equations proposed in an earlier work [11].

Experimental values were compared with the predictions obtained applying the group contribution models of Nitta-Chao [12] and UNIFAC, the latter in the versions of Tassios [13], Larsen [14] and Gmehling [15]. Deviations of the ternary enthalpies calculated using several empirical methods are also listed. The symmetric equations used were those introduced by Kohler [16], Jacob-Fitzner [17], Colinet [18], Knobloch-Schwartz [19], and the asymmetric ones due to Tsao-Smith [20], Toop [21], Scatchard *et al.* [22], Hillert [23] and Mathieson-Tynne [24]. These methods predict excess properties of ternary mixtures from the values measured for the implicated binaries.

## 2. EXPERIMENTAL

The chemicals employed were supplied by Fluka,  $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$  (puriss. > 99 mass%),  $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$  (puriss. > 99.5 mass%),  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  (puriss. > 99.5 mass%) and were used with no further purification than being dried over Union Carbide 0.4 nm molecular sieves to eliminate residual traces of water and avoid moisturising, and degassed by ultrasound technique.

The experimental measurements were carried out using a Calvet microcalorimeter equipped with a device allowing operation in the

absence of vapour phase. Calibration was performed electrically using a Setaram EJP 30 stabilised current source. Details of the experimental procedure have been previously published [2, 25].

Three experimental series of measurements were carried out for ternary compositions formed by adding  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  to a binary mixture composed by  $\{x'_1\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + x'_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3\}$ , where  $x'_2 = 1 - x'_1$ . The ternary composition point may be regarded as a pseudobinary mixture composed by the addition of 1-propanol to the described binary mixture. Thus, the ternary excess molar enthalpy at ternary composition  $x_1$ ,  $x_2$  and  $x_3 = 1 - x_1 - x_2$  can be expressed as:

$$H_{m,1+2+3}^E = H_{m,(1+2)+3}^E + (x_1 + x_2)H_{m,1+2}^E \quad (1)$$

where  $H_{m,(1+2)+3}^E$  is the measured excess molar enthalpy for the pseudobinary mixture and  $H_{m,1+2}^E$  is the excess enthalpy of the initial binary mixture  $\{x'_1\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + x'_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3\}$ .

Values of  $H_{m,1+2}^E$ , at three mole fractions were interpolated by using a spline-fit method. Equation (1) does not involve any approximation.

### 3. DATA CORRELATION

Excess molar enthalpies of the binary mixtures, listed in Table I, were fitted to a variable-degree polynomial suggested by Redlich-Kister [8]:

$$H_{m,i+j}^E/(\text{J} \cdot \text{mol}^{-1}) = x_i x_j \sum_{m=0}^M A_m (x_i - x_j)^m \quad (2)$$

except those corresponding to the binary mixture  $x\text{CH}_3(\text{CH}_2)_4\text{CH}_3 + (1-x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ , where due to the asymmetry of the data, the equation used was the following:

$$H_{m,ij}^E/(\text{J} \cdot \text{mol}^{-1}) = x_i x_j \sum_{m=0}^M A_m (1 - x_i)^{-m/2} \quad (3)$$

Equation (3) provides a more accurate representation of the experimental set of data using a more reduced set of parameters. In Eqs.

TABLE I Experimental binary excess molar enthalpies  $H_{m,i+j}^E$  ( $J \cdot mol^{-1}$ ) at 298.15 K

$x$	$H_{m,i+j}^E/(J \cdot mol^{-1})$	$x$	$H_{m,i+j}^E/(J \cdot mol^{-1})$
$xCH_3CH_2COOCH_2CH_3 + (1-x)CH_3CH_2CH_2OH$			
0.0724	399	0.5652	1492
0.1408	705	0.5812	1487
0.2748	1132	0.6180	1459
0.3117	1217	0.6726	1403
0.3748	1341	0.7250	1299
0.4251	1414	0.8071	1078
0.4638	1462	0.8963	676
0.4879	1486	0.9340	457
0.5312	1500		
$xCH_3(CH_2)_4CH_3 + (1-x)CH_3CH_2CH_2OH$			
0.1187	177	0.5714	588
0.1947	278	0.6129	588
0.2749	380	0.6576	617
0.3065	402	0.7071	601
0.3562	450	0.7358	593
0.4148	497	0.7803	584
0.4736	546	0.8337	531
0.5149	555	0.9258	407

(2 and 3), the fitting parameters,  $A_m$ , were computed using the unweighed least-squares method. The number of parameters,  $M$ , was determined using the F-test proposed by Bevington [26]. The coefficients  $A_m$  and the corresponding standard deviations  $s$  are shown in Table II. Figure 1 shows experimental values of  $H_{m,i+j}^E$  plotted against the curves calculated from the fitting Eqs. (2) and (3). The measured data for the binary mixture  $xCH_3(CH_2)_4CH_3 + (1-x)CH_3CH_2CH_2OH$  were compared with those found in literature [27], and the difference was  $\approx 0.03 |H_{m,i+j}^E|$ . No data of excess enthalpy were found in currently available literature for the ternary mixture.

The measured values of the ternary excess enthalpies,  $H_{m,1+2+3}^E$ , listed in Table III, were correlated as follows:

$$H_{m,1+2+3}^E = H_{m,1+2}^E + H_{m,1+3}^E + H_{m,2+3}^E + x_1x_2(1-x_1-x_2)\Delta_{123} \quad (4)$$

where the ternary contribution to the magnitude,  $\Delta_{123}$ , was correlated using the equation proposed by Cibulka [9]:

$$\Delta_{123} = B_0 + B_1x_1 + B_2x_2 \quad (5)$$

TABLE II Fitting coefficients  $A_m$ ,  $B_i$  and  $C_j$  for Eqs. (2–9), and standard deviations  $s$  (J·mol<sup>-1</sup>)

	Equation 2						
	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$s$	
$x\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + (1-x)\text{CH}_3(\text{CH}_2)_4\text{CH}_3^a$	4129	-220.3	550.8	-131.3	-672.6	1.7	
$x\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + (1-x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	5926	943.6	994.4			6.7	
	Equation 3						
$x\text{CH}_3(\text{CH}_2)_4\text{CH}_3 + (1-x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	-12.37	1583				7.3	
	$x_1\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 + (1-x_1-x_2)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$						
Equation 5	$B_0$ 3713	$B_1$ 5703	$B_2$ 6997			$s$ 28	
Equation 6	$B_0$ 7.622	$B_1$ 26.24	$B_2$ 12.38	$B_3$ -43.91	$B_4$ -0.5758	$B_5$ -32.20	
Equation 7	$C_1$ 6304	$C_2$ 8065	$C_3$ 2602	$C_4$ 1754	$C_5$ -2904	$C_6$ 2068	
Equation 8	$C_1$ 6166	$C_2$ 9309	$C_3$ 2602	$C_4$ -1874	$C_5$ -3037	$C_6$ 2849	
Equation 9	$C_1$ 6627	$C_2$ 10549	$C_3$ 2113	$C_4$ -3924	$C_5$ -12975	$C_6$ 410.4	
				$C_7$ -1767	$C_8$ -8385	$C_9$ -8414	
				$C_7$ 792.5	$C_8$ 9182	$C_9$ 1496	

<sup>a</sup> Ref. 3.

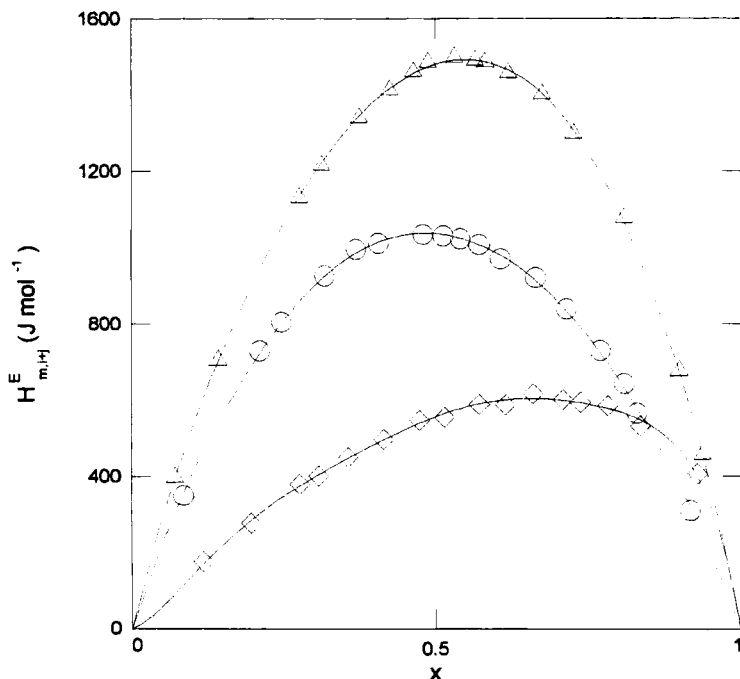


FIGURE 1 Excess molar enthalpies  $H_{m,i+j}^E$  at 298.15 K of the binary mixtures: ○  $x\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + (1-x)\text{CH}_3(\text{CH}_2)_4\text{CH}_3$  (Ref. 3); Δ,  $x\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + (1-x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ; ◇  $x\text{CH}_3(\text{CH}_2)_4\text{CH}_3 + (1-x)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ .

and that proposed by Nagata-Tamura [10]:

$$\begin{aligned} \Delta_{123}/RT = & B_0 - B_1x_1 - B_2x_2 - B_3x_1^2 - B_4x_2^2 \\ & - B_5x_1x_2 - B_6x_1^3 - B_7x_2^3. \end{aligned} \quad (6)$$

The following equations, introduced in an earlier work [11], were also used to correlate the ternary excess enthalpies. The first uses six adjustable coefficients  $C_i$ :

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

and the second and third include nine coefficients:

$$\begin{aligned} H_{1+2+3}^E = & C_1x_1x_2 + C_2x_1x_3 + C_3x_2x_3 + C_4x_1^2x_2 + C_5x_1x_3^2 \\ & + C_6x_2^2x_3 + C_7x_1^2x_2^2 + C_8x_1^2x_3^2 + C_9x_2^2x_3^2 \end{aligned} \quad (8)$$

TABLE III Excess molar enthalpies  $H_{m,1+2+3}^E$  for the ternary mixture  $x_1\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 + (1 - x_1 - x_2)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ 

$x_1$	$x_2$	$H_{m,(1+2)+3}^E/H_{m,1+2+3}^E/$ ( $J \cdot \text{mol}^{-1}$ )( $J \cdot \text{mol}^{-1}$ )		$x_1$	$x_2$	$H_{m,(1+2)+3}^E/H_{m,1+2+3}^E/$ ( $J \cdot \text{mol}^{-1}$ )( $J \cdot \text{mol}^{-1}$ )	
$x_1' = 0.2494 H_{m,1+2}^E = 815 J \cdot \text{mol}^{-1}$							
0.2420	0.7282	311	1099	0.1461	0.4396	771	1247
0.2370	0.713	417	1189	0.1327	0.3994	742	1175
0.2219	0.667	615	1338	0.1167	0.3512	700	1080
0.2132	0.6416	682	1377	0.1028	0.3093	657	992
0.2015	0.6064	740	1397	0.0868	0.2611	594	877
0.1870	0.562	779	1388	0.0643	0.1935	471	680
0.1762	0.5301	785	1359	0.0486	0.1462	372	530
0.1699	0.5111	790	1343	0.0171	0.0516	140	196
0.1599	0.4811	793	1314				
$x_1' = 0.4991 H_{m,1+2}^E = 1032 J \cdot \text{mol}^{-1}$							
0.4900	0.4917	194	1212	0.3045	0.3055	985	1617
0.4771	0.4787	390	1381	0.2851	0.2860	977	1569
0.4527	0.4542	649	1590	0.2501	0.2509	944	1464
0.4329	0.4344	764	1663	0.2124	0.2131	877	1318
0.4170	0.4184	833	1699	0.1841	0.1847	812	1194
0.3970	0.3984	901	1726	0.1523	0.1528	722	1038
0.3650	0.3662	960	1718	0.0787	0.0790	425	589
0.3465	0.3477	981	1701	0.0503	0.0504	282	387
0.3387	0.3399	988	1692				
$x_1' = 0.7494 H_{m,1+2}^E = 769 J \cdot \text{mol}^{-1}$							
0.7274	0.2430	264	1005	0.4337	0.1449	1220	1662
0.6847	0.2288	592	1290	0.4006	0.1338	1210	1619
0.6562	0.2193	771	1440	0.3521	0.1176	1170	1529
0.6322	0.2112	885	1529	0.3131	0.1046	1120	1439
0.5987	0.2000	1009	1619	0.2694	0.0900	1041	1315
0.5554	0.1856	1126	1691	0.2099	0.0701	891	1104
0.5280	0.1764	1172	1710	0.1691	0.0565	757	929
0.5105	0.1706	1195	1715	0.1244	0.0416	59	719
0.4763	0.1592	1216	1701	0.0775	0.0259	392	471

$$H_{1+2+3}^E = C_1 x_1 x_2 + C_2 x_1 x_3 + C_3 x_2 x_3 + C_4 x_1^2 x_2 + C_5 x_1 x_3^2 + C_6 x_2^2 x_3 + C_7 x_1^3 x_2 + C_8 x_1 x_3^3 + C_9 x_2^3 x_3 \quad (9)$$

The  $B_i$  and  $C_i$  parameters corresponding to Eqs. (7–9) were calculated with the unweighed least-squares method using a non-linear optimisation algorithm due to Marquardt [28]. These parameters and the corresponding standard deviations are also enclosed in Table II.

Figure 2 shows the pseudobinary representation of the measured experimental values of the ternary excess enthalpies together with the correlated curves, using Eq. (5) to correlate the ternary contribution.



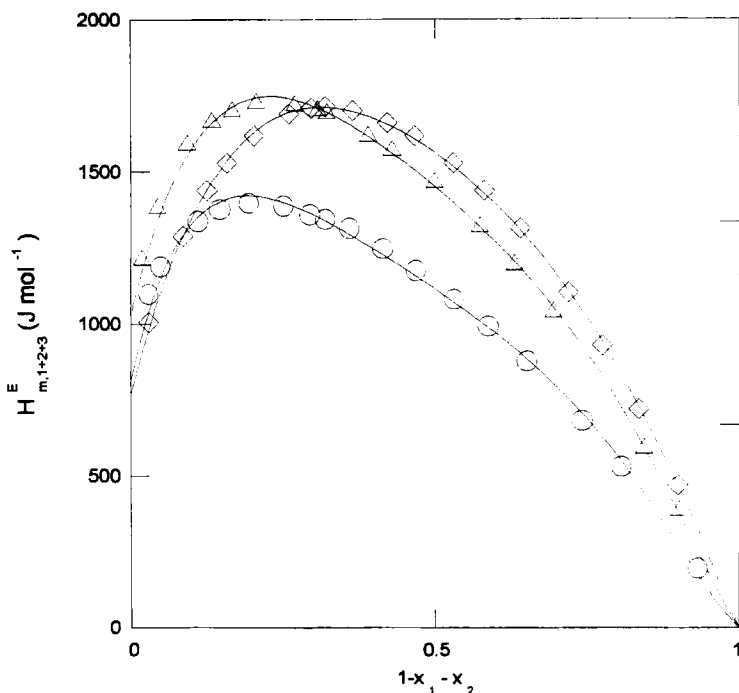


FIGURE 2 Pseudobinary representation of the excess molar enthalpies  $H_{m,1+2+3}^E$  ( $\text{J} \cdot \text{mol}^{-1}$ ) at 298.15 K, of:  $\{(x_1 + x_2)(x'_1 \text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + x'_2 \text{CH}_3(\text{CH}_2)_4\text{CH}_3) + (1 - x_1 - x_2)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}\}$ ;  $\circ$ ,  $x'_1 = 0.2494$ ,  $x'_2 = 0.7506$ ;  $\triangle$ ,  $x'_1 = 0.4991$ ,  $x'_2 = 0.5009$ ,  $\diamond$ ,  $x'_1 = 0.7494$ ,  $x'_2 = 0.2506$ ; —, correlated using Eqs. (4) and (6).

Figure 3 represents the lines of constant ternary excess molar enthalpy calculated using Eqs. (4) and (6). The excess molar enthalpy is positive over the whole range of concentration and shows a maximum of  $1783 \text{ J} \cdot \text{mol}^{-1}$  at  $x_1 = 0.450$  and  $x_2 = 0.298$ . Figure 4 shows the ternary contribution to the excess enthalpy  $\Delta_{123}$  correlated with Eq. (5). The ternary contribution is also positive and shows a maximum of  $291 \text{ J} \cdot \text{mol}^{-1}$  at  $x_1 = 0.418$  and  $x_2 = 0.298$ . The value of this maximum, coinciding closely with the maximum of the ternary magnitude, and representing about a 21% of the total ternary magnitude in that composition range, gives a good idea of the strong energetic interaction existing between the groups present in the mixture.

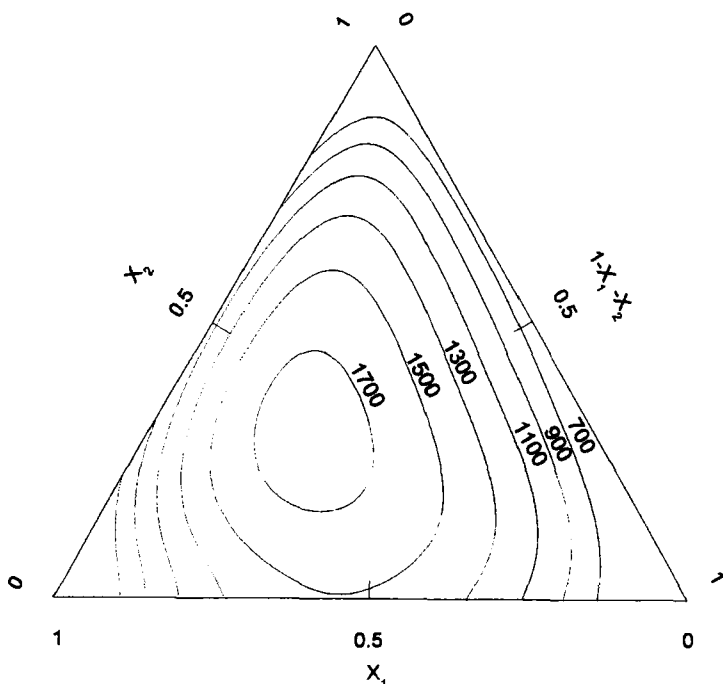


FIGURE 3 Curves of constant  $H_{m,1+2+3}^E/(J \cdot \text{mol}^{-1})$  for the ternary mixture  $x_1\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 + (1 - x_1 - x_2)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ , calculated with Eqs. (4) and (6), at 298.15 K.

#### 4. EXCESS ENTHALPY THEORIC PREDICTION

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 is accepted or not. Asymmetry is usually understood to be caused by the strongly polar or associative behaviour 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 were the suggested by Kohler [16], Jacob-Fitzner [17], Colinet [18] and Knobloch Schwartz [19], while

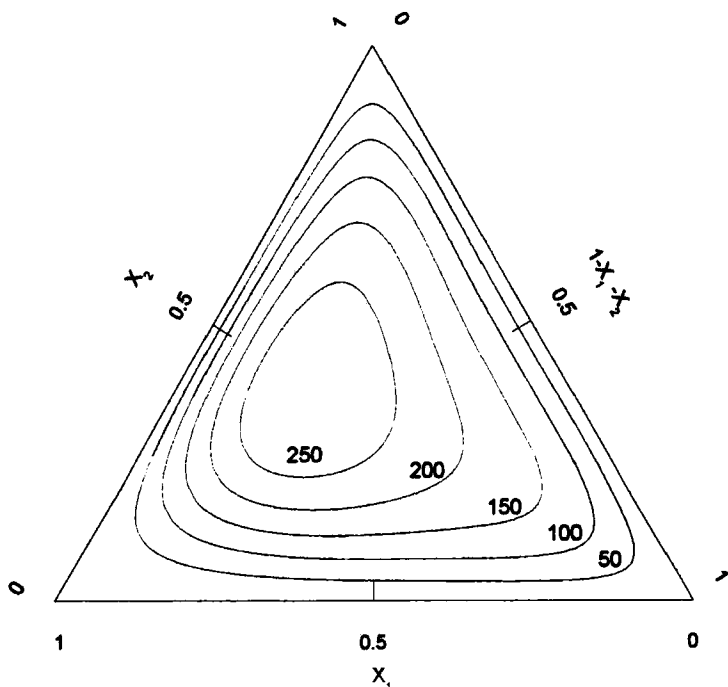


FIGURE 4 Curves of constant ternary contribution  $\Delta_{123}/(\text{J} \cdot \text{mol}^{-1})$  to the excess molar enthalpy  $H_{m,1+2+3}^E$  for the ternary  $x_1\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + x_2\text{CH}_3(\text{CH}_2)_4\text{CH}_3 + (1 - x_1 - x_2)\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ , at 298.15 K, correlated using Eq. (6).

the asymmetric ones were those of Tsao-Smith [20], Toop [21], Scatchard [22], Hillert [23] and Mathieson-Tynne [24]. The average percent deviations from the experimental data are listed in Table IV. For the asymmetric equations, three different numberings of the compounds have been tested, being the first element considered in each case  $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$ ,  $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$  or  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ , in this order. The deviations obtained are rather high, and this fact can be attributed to the importance of the ternary contribution to the mixture. The best agreement with experimental data was achieved by the symmetric equation of Knobloch Schwartz, with a 5.7% deviation, while the best asymmetric was that of Tsao Smith, with the alkane chosen as first component in the numbering. It can be observed that the dependence on the arrangement of the components varies in each equation.

TABLE IV Average percent deviations from the experimental values obtained with the empirical predictive methods listed above. For the asymmetric equations, three numberings of the components have been compared, in this order, 123, 231, 312

Predictive method		Percent deviation	
Kohler		14.5	
Jacob-Fitzner		15.6	
Colinet		14.3	
Knobloch-Schwartz		5.7	
Tsao-Smith	9.8	3.5	5.0
Toop	15.2	17.1	15.0
Scatchard	15.7	17.6	15.1
Hillert	7.4	17.1	15.0
Mathieson-Tynne	15.8	16.6	13.8

The Nitta Chao [12] group contribution model is based on the cell theory for thermodynamic properties of polar and non-polar liquids and their solutions, including excess properties, activity coefficients and PVT relations. The base of this model is the cell theory introduced by Flory [29], where the repulsive forces between molecules are expressed by means of a cell partition function, derived from the rigid spheres equation of state by Carnahan and Starling [30], and the quasi-chemical approximation of Guggenheim [31] is used. The interaction parameters for the groups involved in this mixture, ester, alkane and alkanol, were calculated by Fernández *et al.* [32], Ortega *et al.* [33] and Legido *et al.* [34].

The UNIFAC group contribution model was originally developed by Fredenslund *et al.* [35], using the UNIQUAC equation by Abrams and Praustniz [36] for a multicomponent mixture. The activity coefficient in this model is calculated as the addition of two terms. The first one is combinatorial and takes account of the differences of 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. The Tassios [13] version predicts only values for  $H_m^E$ . In the version of Larsen [14] the interaction parameters become temperature dependent, and the combinatorial term is modified. As a result this version can predict other properties, such as  $G_m^E$ , liquid-liquid equilibrium and vapour-liquid equilibrium. Gmehling [15] modified the temperature dependence of the parameters, recalculated interaction parameters using a wider database, and fitted them

TABLE V Average percent deviations, of the estimated ternary molar excess enthalpies using the described group contribution models, compared with the experimental data

<i>Model</i>	<i>Percent deviation</i>
Nitta-Chao	4.0
UNIFAC (Tassios)	14.9
UNIFAC (Larsen)	22.9
UNIFAC (Gmehling)	15.2

simultaneously to liquid–liquid equilibrium, vapour liquid equilibrium,  $H_m^E$  and  $\gamma^\infty$ . The parameters used in this work for prediction were, for every version of the model, those provided by the authors in the original works, except those of Gmehling version of UNIFAC, that were calculated by the same author in a later work [37].

Table V shows the percent deviations of the values predicted by the mentioned models. Best accuracy was yielded by the Nitta Chao model, with a 4,0% deviation from experimental data. This result improves definitely those obtained by the tested versions of UNIFAC, ranging from 14,9% of Tassios to 22,9% of Larsen.

## LIST OF SYMBOLS

$H_{m,1+2+3}^E$	Ternary excess molar enthalpy
$H_{m,(1+2)+3}^E$	Pseudobinary excess molar enthalpy
$H_{m,i+j}^E$	Binary excess molar enthalpy
$x$	Mole fraction
$A_m$	Parameter of correlation Eqs. (2) and (3)
$\Delta_{123}$	Ternary contribution
$B_i$	Parameter of correlation Eqs. (5), (6)
$C_i$	Parameter of correlation Eqs. (7), (8), (9)

## References

- [1] López, M., Paz Andrade, M. I., Peleteiro, J., Legido, J. L., Romani, L. and Pérez-Martell, E. (1992). *Thermochim. Acta*, **201**, 33.
- [2] López, M., Legido, J. L., Romani, L., Carballo, E., Pérez-Martell, E., Jiménez, E. and Paz Andrade, M. I. (1992). *J. Chem. Thermodynamics*, **24**, 205.
- [3] López, M., Paz Andrade, M. I., Legido, J. L., Romani, L., Peleteiro, J. and Jiménez, E. (1993). *Phys. Chem. Liq.*, **25**, 145.

- [4] López, M., Legido, J. L., Jiménez, E., Romani, L., Carballo, E. and Paz Andrade, M. I. (1993). *Chem. Thermodynamics*, **25**, 321.
- [5] López, M., Legido, J. L., Romani, L., Peleteiro, J. and Paz Andrade, M. I. (1993). *J. Chem. Eng. Data*, **38**, 238.
- [6] López, M., Carballo, E., Legido, J. L., Salgado, J., Vijande, J. and Paz Andrade, M. I. (1995). *J. Chem. Thermodynamics*, **27**, 1281.
- [7] López, M., Carballo, E., Legido, J. L., Salgado, J., Vijande, J. and Paz Andrade, M. I. (1995). *J. Chem. Thermodynamics*, **27**, 879.
- [8] Redlich, O. and Kister, A. T. (1948). *Ind. Eng. Chem.*, **40**, 341.
- [9] Cibulka, I. (1982). *Collect. Czech. Chem. Commun.*, **47**, 1414.
- [10] Nagata, I. and Tamura, K. (1990). *J. Chem. Thermodynamics*, **22**, 279.
- [11] Piñeiro, M. M., Cominges, B. E., Legido, J. L., García-Garabal, S., López, M. and Paz Andrade, M. I. (1998). *J. Thermal Anal.*, **52**, 799.
- [12] Nitta, T., Turek, E., Greenkorn, R. A. and Chao, K. C. (1977). *AIChE J.*, **23**, 144.
- [13] Dang, D. and Tassios, D. P. (1986). *Ind. Eng. Chem. Process. Dev.*, **25**, 22.
- [14] Larsen, B. L., Rasmussen, P. and Fredenslund, A. (1987). *Ind. Eng. Chem. Res.*, **26**, 2274.
- [15] Weidlich, U. and Gmehling, J. (1987). *Ind. Eng. Chem. Res.*, **26**, 1372.
- [16] Kohler, F. (1960). *Monatsh. Chem.*, **91**, 738.
- [17] Jacob, K. T. and Fitzner, K. (1977). *Thermochim. Acta*, **18**, 197.
- [18] Colinet, C. (1967). Thesis University of Grenoble, France.
- [19] Knobloch, J. B. and Schwartz, C. E. (1962). *J. Chem. Eng. Data*, **7**, 386.
- [20] Tsao, C. C. and Smith, J. M. (1953). *Chem. Eng. Prog. Symp. Series*, **49**, 107.
- [21] Toop, G. W. (1965). *Trans. TMS-AIME.*, **223**, 850.
- [22] Scatchard, G., Ticknor, L. B., Goates, J. R. and McCartney, E. R. (1952). *J. Am. Chem. Soc.*, **74**, 3721.
- [23] Hillert, M. (1980). *Calphad*, **4**, 1.
- [24] Mathieson, A. R. and Tynne, J. C. (1956). *J. Chem. Soc.*, p. 3708.
- [25] Paz Andrade, M. I. (1967). "Les Développements Récents de la Microcalorimétrie et de la Thermogénèse", 1st edn. CNRS, Paris.
- [26] Bevington, P. (1969). *Data Reduction and Error Analysis for the Physical Sciences*. McGraw-Hill, New York.
- [27] Brown, I., Fock, W. and Smith, F. (1964). *Aust. J. Chem.*, **17**, 1106.
- [28] Marquardt, D. W. (1963). *J. Soc. Indust. Appl. Math.*, **2**, 431.
- [29] Flory, P. J., Orwoll, R. A. and Vrij, A. (1964). *J. Am. Chem. Soc.*, **86**, 3507.
- [30] Carnahan, N. F. and Starling, K. E. (1969). *J. Chem. Phys.*, **51**, 635.
- [31] Guggenheim, E. A. (1952). *Mixtures*, Clarendon Press, Oxford.
- [32] Fernández, J., Legido, J. L., Paz Andrade, M. I. and Pias, L. (1990). *Fluid Phase Eq.*, **55**, 293.
- [33] Ortega, J. and Legido, J. L. (1994). *Fluid Phase Eq.*, **95**, 175.
- [34] Legido, J. L., Vijande, J., Cominges, B. E., García, J., Iglesias, T. P., García Garabal, S. and Fernández, J. (1998). *Fluid Phase Eq.*, **148**, 49.
- [35] Fredenslund, A., Gmehling, J. and Rasmussen, P. (1977). *Vapor-Liquid Equilibria using UNIFAC*. Elsevier, New York.
- [36] Abrams, D. S. and Prausnitz, J. M. (1975). *AIChE J.*, **21**, 16.
- [37] Gmehling, J., Jiding, L. and Schiller, M. (1993). *Ind. Eng. Chem. Res.*, **32**, 178.