Correlation and prediction of mixing thermodynamic properties of ester-containing systems: Ester + alkane and ester + ester binary systems and the ternary dodecane + ethyl pentanoate + ethyl ethanoate

Noelia Pérez [a], Luís Fernández [a], Juan Ortega [a,*], Francisco J. Toledo [a], Jaime Wisniak [b]

[a] Laboratorio de Termodinámica y Fisicoquímica de Fluidos, Parque Científico-Tecnológico, Universidad de Las Palmas de Gran Canaria, Canary Islands, Spain
[b] Deparment of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

ABSTRACT

Excess thermodynamic properties V_m^E and H_m^E, have been measured for the ternary mixture dodecane + ethyl pentanoate + ethyl ethanoate and for the corresponding binaries dodecane + ethyl pentanoate, dodecane + ethyl ethanoate, ethyl pentanoate + ethyl ethanoate at 298.15 K. All mixtures show endothermic and expansive effects. Experimental results are correlated with a suitable equation whose final form for the excess ternary quantity M^E contains the particular contributions of the three binaries (i–j) and a last term corresponding to the ternary, all of them obtained considering fourth-order interactions. The fit goodness for all mixtures is good and comparable to others equations taken from the literature. In this work the dissolution model for the binaries and ternary is analyzed with a special attention to ester–ester binaries whose behaviour is discussed. The application of the UNIFAC group contribution model to estimate the H_m^E yields acceptable results for the binaries (with the exception of ester–ester) and for the ternary mixture.

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1. Introduction

Previous work by our group reported the behavior of various binary systems of esters with alkanes [1–3], alkanols [4–6] and haloalkanes [7–9]. It is especially interesting to quantify the solvent capacity of esters with different solutes, since these are often present as solutions in some sectors of the chemical industry, such as pharmacology and cosmetics. In some processes it is usual to find several esters in the same solution, although studies of the thermodynamics of solutions have not yet focused on ester–ester interactions. An accurate knowledge of the solute–solvent interactions, based on mixing properties, can be used to interpret the molecular structure of the solution, by defining some of the intermolecular relationships that cause effects that are transmitted during the mixing processes, and which also have implications on the modeling of their behavior. The first step must consist in a highly systematic and quality experimentation, in order to observe the relationships between analogous effects observed for sets of systems with homologous components.

There is much interest in research carried out on these systems, especially because of the value of these fluids in some industrial applications, such as the production of biofuels. It is, therefore, convenient to analyze these systems, and also those containing saturated hydrocarbons (both in theory and in practice) in depth. Our research group has already made certain contributions on the subject and has proposed a structural model for esters + alkanes that will be checked in this paper. Owing to the extensive database available for ester + alkane binary systems, it has been possible to use correlation/estimation models that can be applied for both purposes. So far, this model has been widely used to study binary systems [10], but not yet to ternary ones. The introduction of additional components to a binary system adds a new dimension to the complexity of the model and to the structural analysis of solutions. A complete modeling of solutions would be applicable to multicomponent systems, but there are insufficient data in the literature for systems of more than two components. One of our current projects is, therefore, to extend the application of the model, so it can be used in systems with a greater number of components, starting with ternaries. Here, we begin with the system (dodecane + ethyl pentanoate + ethyl ethanoate), electing an alkane of intermediate chain and two alkyl alkanoates, $H_{2u-1}C_{u-1}COOC_vH_{2v+1}$ (with $v = 2$), differentiated by the acid part, with $u = 2$ and 5. Experimental enthalpy H_m^E and excess molar volumes V_m^E data are reported and correlated for the binary systems, an extension is provided for ternary systems, and valuable up-to-date information on the ester–ester interaction. This study also includes an estimation of H_m^E using the UNIFAC group contribution method of Gmehling et al. [11,12].

2. Experimental

2.1. Materials

The dodecane used was from Fluka with a purity >98% w/w and both ethyl ethanoate and ethyl pentanoate were supplied by Aldrich, with a purity >99% w/w. Before use, products were degasified with ultrasound for several hours and stored in topaz colored glass bottles on a Fluka 0.3 nm molecular sieve to eliminate any traces of moisture. The quality of the products was confirmed by GC and by measuring other properties such as the density ρ, and the refractive index n_D. The results are in good agreement with the data reported in the literature (table 1). The water used to calibrate the apparatus was bidistilled in our laboratory and degasified before use, giving an electrical conductance lower than 1.5 μS. All the chemicals were used with the proper safety precautions.

2.2. Apparatus and procedures

The refractive index, n_D, of the pure products was measured using a 320 Abbe type refractometer from Zuzi with a precision of ±0.0002 units. It was thermostatized with a Polyscience 9012 circulating water bath with a temperature control of $(T \pm 0.005)$ K. The accuracy was first verified by taking recordings for water at the working temperature. The densities of both the pure compounds and the mixtures were measured with a DMA 60/602 Anton-Paar digital densimeter, with a temperature control of ±0.01 K, and the aforementioned thermostatic control. The uncertainties in the measurements of density were ±0.02 kg·m⁻³. The densimeter was first calibrated with bidistilled water and nonane as recommended previously [15]. The excess volumes V_m^E were calculated from the density values, as explained in the following section. The mixing enthalpies were measured directly using a Calvet MS80D calorimeter by Setaram (France), at a temperature of 298.15 K, calibrated by applying a Joule effect as described in previous publications [16], estimating an uncertainty in the H_m^E of 1%, and less than ±0.0002 for the mole fractions of binary systems, and slightly higher values for ternary systems.

The working procedure used in the experimentation with ternaries was similar to that used to measure the densities of the prepared synthetic solutions, and also for excess molar enthalpies. First, the mixing quantities were determined for the three binary systems and then, to obtain the corresponding property for the ternary system, ethyl ethanoate was added to the mixtures of (dodecane + ethyl pentanoate) prepared for this purpose with a known composition, thus constituting a pseudobinary system.

In this work, a 300 Hz Avance model ¹H NMR spectrometer by Bruker was used to take measurements at 293 K, using Cl₃CD in concentric capillaries to obtain lock. Paramagnetic displacements were measured in relation to the TMS signal ($\delta = 0$).

3. Mathematical model used to correlate ternary data

A mathematical model was proposed to represent the thermodynamic quantities arising from the mixing process, the excess quantities, as a sum of the contributions of the effects of all the possible pth interactions of the n active fractions, where existing interactions follow the order $p = 2, 3, 4$. An excess generic property M^E, applied to a multicomponent system of n substances is written:

$$M_{n,4}^E = \sum_{p=2}^{4} \left[\sum_{i_1,i_2,i_3,i_4 \in \text{CR}*(n,4)} a_{i_1 i_2 i_3 i_4} z_{i_1} z_{i_2} z_{i_3} z_{i_4} \right] \quad (1)$$

where the parameters $a_{i_1 i_2 i_3 i_4}$, assigned to the generic expression (1), are the so-called *particular coefficients of influence* for the corresponding pth combinations. The expression $i_1 i_2 i_3 i_4 \in CR * (n, 4)$ indi-

cates the possible number of combinations with repetition of three substances taken in the interactional order 2, 3 and 4, in which the *active fractions* of the property studied participate. The *active fractions* z_i of each compound in a multicomponent system satisfy the relation $\sum z_i = 1$ and are related to the composition of the mixture by the following generic expression:

$$z_i = \frac{\upsilon_i x_i}{\sum_{j=1}^{n} \upsilon_j x_j} = \frac{\left(\frac{\upsilon_i}{\upsilon_1}\right) x_i}{\sum_{j=1}^{n} \left(\frac{\upsilon_j}{\upsilon_1}\right) x_j} = \frac{k^{i-1} x_i}{\sum_{j=1}^{n} k^{i-1} x_j} \quad (2)$$

where component 1 is chosen as a "*reference*". To the υ_i-value a parameter is assigned, which is related to the property studied, hence, parameter k^{i-1} that appears in expression (2) may have a different meaning, according to the property being correlated [16]. Hence, when the excess volumes V_m^E are correlated for a binary mixture $i + j$, this parameter is given a specific notation, such as k_υ^{j-i}, which is the ratio of the molar volumes of the compounds involved in the mixture at the working temperature $\upsilon_{m,i}^o(T)$, $k_\upsilon^{j-i} = \upsilon_{m,j}^o / \upsilon_{m,i}^o$. The enthalpies H_m^E are correlated with the parameter k_h^{j-i}, calculated from the following expression, see reference [16].

$$k_h^{j-i} = k_q^{j-i} \left(\frac{k_\upsilon^{j-i}}{k_r^{j-i}} \right)^{2/3} \quad (3)$$

where k_q and k_r are, respectively, the quotients of the surface parameters q_i and the parameters of molecular volume r_i, obtained for each pure substance i by the group contribution method proposed by Bondi [17].

The mathematical development of equation (1) for a ternary system, considering the successive contributions corresponding to interactions of second, third and fourth order is written as:

$$M_{3,4}^E = [a_{12}z_1 z_2 + a_{13}z_1 z_3 + a_{23}z_2 z_3] + [a_{112}z_1^2 z_2 + a_{113}z_1^2 z_3 + a_{221}z_2^2 z_1 +$$
$$a_{223}z_2^2 z_3 + a_{331}z_3^2 z_1 + a_{332}z_3^2 z_2 + a_{123}z_1 z_2 z_3] + [a_{1112}z_1^3 z_2 +$$
$$a_{1122}z_1^2 z_2^2 + a_{1222}z_1 z_2^3 + a_{1113}z_1^3 z_3 + a_{1133}z_1^2 z_3^2 + a_{1333}z_1 z_3^3 +$$
$$a_{2223}z_2^3 z_3 + a_{2233}z_2^2 z_3^2 + a_{2333}z_2 z_3^3 + a_{1123}z_1^2 z_2 z_3 + a_{1223}z_1 z_2^2 z_3 +$$
$$a_{1233}z_1 z_2 z_3^2] \quad (4)$$

This expression reminds us of the empirical model proposed by Wohl [18] to correlate values of Gibbs's function in multicomponent systems. After some algebraic work equation (4) reduces to

$$M_{3,4}^E = M_{2,4}^{E,(1-2)} + M_{2,4}^{E,(1-3)} + M_{2,4}^{E,(2-3)} + z_1 z_2 z_3 (C_0 + C_1 z_1 + C_2 z_2) \quad (5)$$

where $M_{2,4}^{E,(i-j)}$ refer to the specific contribution of the excess function of the binary system $(i–j)$ truncated to fourth order interactions. Each pair brings together the $C*(3,2)$, in other words, the combinations of three different compounds taken two-by-two. The C_i coefficients are the result of linear combinations of the *particular coefficients of influence* $a_{i_1 i_2 i_3 i_4}$. However, by applying equation (5) the C_i can be obtained by correlating the experimental data obtained for the different solutions formed at fixed composition (x_1, x_2, x_3, M^E). Equation (5) has a similar structure to others used to correlate the data for ternary systems [19–21] but differs from Cibulka's equation [19] in that it uses *active fractions* instead of mole fractions.

To apply equation (5), the pertinent data of the possible binary systems must first be correlated by a simplified form of this equation, which is derived by putting $z_3 = 0$ in (4), so that:

$$M_{2,4}^E = z_1 z_2 \sum_{i=0}^{2} A_i z_1^i = z_1 (1 - z_1)(A_0 + A_1 z_1 + A_2 z_1^2) \quad (6)$$

where the A_i are a linear combination of the *particular coefficients of influence* a_{ijk} of the binary system under consideration and can be obtained by a simple procedure of non-linear regression using the following objective function:

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TABLE 1

Properties of pure compounds at T = 298.15 K and atmospheric pressure.

Compound	Source	Mass fraction purity	ρ (kg·m^{-3})		n_D	
			Exp.	Lit.	Exp.	Lit.
Ethyl ethanoate	Aldrich	>0.99	894.34	894.55 [13]	1.3700	1.3698 [13]
				894.00 [14]		1.3704 [14]
				894.24 [3]		1.3700 [3]
Ethyl pentanoate	Aldrich	>0.99	869.28	868.98 [3]	1.3981	1.3980 [3]
Dodecane	Fluka	>0.98	745.10	745.18 [13,14]	1.4192	1.41949 [13]
						1.41952 [14]

Uncertainties u are: $u(T)$ = ±0.01 K, $u(n)$ = 0.0002, and $u(\rho)$ = ±0.02 kg·m^{-3}.

TABLE 2

Experimental densities $\rho/(\text{kg·m}^{-3})$ and excess molar volumes $10^9 \cdot V_m^E/(\text{m}^3 \cdot \text{mol}^{-1})$ for (dodecane + an ethyl alkanoate) binary mixtures at 298.15 K and atmospheric pressure.

x_1	ρ (kg · m^{-3})	$10^9 \cdot V_m^E$ (m^3 · mol^{-1})	x_1	ρ (kg · m^{-3})	$10^9 \cdot V_m^E$ (m^3 · mol^{-1})
		x_1 Dodecane + $(1 − x_1)$ethyl pentanoate			
0.0505	858.92	185	0.6026	779.67	733
0.1024	849.09	329	0.6547	774.30	700
0.1522	840.25	447	0.6992	769.94	656
0.1998	832.32	534	0.7485	765.35	587
0.2496	824.53	603	0.7982	760.93	507
0.3013	816.70	699	0.8470	756.88	390
0.4039	802.81	753	0.8918	753.23	297
0.5020	790.76	779	0.9497	748.76	151
		x_1 Dodecane + $(1 − x_1)$ethyl ethanoate			
0.0970	860.06	582	0.6000	772.56	1336
0.1460	846.23	794	0.6909	764.45	1176
0.1976	833.46	985	0.7392	760.65	1061
0.2508	821.88	1152	0.7931	756.85	889
0.2979	812.79	1267	0.8213	754.91	812
0.3903	797.68	1398	0.8798	751.38	573
0.4943	783.92	1421	0.9374	748.08	351
		x_1 Ethyl pentanoate + $(1 − x_1)$ethyl ethanoate			
0.0482	892.36	21	0.6556	875.16	83
0.0954	890.53	41	0.6946	874.41	75
0.1480	888.63	57	0.7526	873.29	69
0.1941	887.05	70	0.7924	872.6	59
0.3047	883.64	88	0.8362	871.84	49
0.4000	881.02	96	0.8651	871.36	42
0.4921	878.73	97	0.9263	870.36	27
0.5717	876.92	92	0.9377	870.21	19

Uncertainties u are: $u(T)$ = ±0.01 K, $u(\rho)$ = ±0.02 kg·m^{-3}, $u(x)$ = ±0.0002, and $u(10^9 \cdot V_m^E)$ = ±2 m^3 · mol^{-1}.

$$s(M^E) = \sqrt{\sum_{i=0}^{N}\left(M_{i,\text{exp}}^E - M_{i,\text{cal}}^E\right)^2 \Big/ (N-1)} \qquad (7)$$

where N is the number of experimental points. The specific binary contributions of equation (5) $M_{2,4}^{E,(i-j)}$, are calculated for each binary using the coefficients of equation (6) but considering that the pairs $i–j$ are isolated in the ternary global system. To do this, the mole fractions x_i and the corresponding *active fractions* z_i must be normalized so that $x'_i + x'_j = 1$ and $z'_i + z'_j = 1$. In this work, the normalization proposed by Kohler [22] was used for the mole fractions, and found to have no effect on the *active fractions*, in other words: $z'_i = z_i$.

4. Presentation and treatment of experimental data

4.1. Excess molar volumes

The excess volumes of the binary and ternary solutions were determined from the results of the densities of mixtures prepared from known compositions, according to:
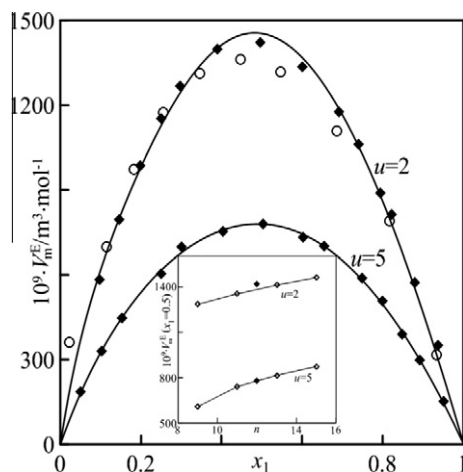
FIGURE 1. Experimental V_m^E values (♦) measured at 298.15 K and correlation curve using equation (6) for binaries $\{x_1C_nH_{2n+2}\ (n=12) + x_2C_{u-1}H_{2u-1}COOC_2H_5\ (u=2,5)\}$, and comparison with literature values (○, reference [23]). Inset shows the regularity of equimolar V_m^E values from reference [3] (◊) as a function of the hydrocarbon chain length for the two esters in the binaries {an alkane + ethyl ethanoate ($u=2$), or +ethyl pentanoate ($u=5$).

$$v^E = \sum_{i=1}^{3}\frac{x_i M_i}{\rho} - \sum_{i=1}^{3}\frac{x_i M_i}{\rho_i} \qquad (8)$$

where x_i, M_i, ρ_i, and ρ, are, respectively, the mole fraction, the molecular mass and the density of the pure compound i, and the density of the mixture. The uncertainty in the calculations of V_m^E for the binaries was of the order of $\pm 2 \cdot 10^{-9}$ m^3·mol^{-1}, and was somewhat greater for the ternaries, $\pm 5 \cdot 10^{-9}$ m^3·mol^{-1}. Table 2 shows the experimental data (x_i, ρ, V_m^E) for the three binary systems composed of the combination of dodecane (1), ethyl pentanoate (2) and ethyl ethanoate (3) at a temperature of 298.15 K. The experimental values of (x_i, V_m^E) for the binaries (1) + (2) and (1) + (3) are shown in figure 1. The results of the system (2) + (3) are discussed and shown in a separate section. The literature [23] only refers to the system dodecane + ethyl ethanoate at 298.15 K. These values, represented in figure 1, are similar to the experimental ones, except for the region of intermediate composition, which shows a difference of 7%. The paired values of the binaries are correlated with equation (6) using a least-squares procedure with the objective function showed by equation (7). The V_i coefficients (specific nomenclature for the correlation of volumes) and the value of the parameter k_v for each of the binary systems, according to a definition given in the previous section, are shown in table 3 together with the standard mean deviations of data. The quality of the fits is satisfactory and the corresponding correlation curves have been drawn up from the values obtained, which are also shown in figure 1. The inset in figure 1 shows the equimolar values for the two systems considered here, and their regular variation with the hydrocarbon chain, as can be expected from previous works.

The V_m^E's of the ternary were determined as described in Section 2.2. Starting with three synthetic binary mixtures with known

TABLE 3
Coefficients V_i and standard deviations, $10^9 \cdot s(V_m^E)$, obtained using equation (6) to correlate the excess molar volumes of (dodecane + an ethyl alkanoate) binary mixtures at 298.15 K.

System	V_0	V_1	V_2	k_v^{j-i}	$10^9 \cdot s(V_m^E)$	$10^9 \cdot s(V_m^E)^*$
Dodecane + ethyl pentanoate	2658	−602	2635	0.655	8	8
Dodecane + ethyl ethanoate	4086	−3669	11027	0.431	26	10
Ethyl pentanoate + ethyl ethanoate	344	−26	205	0.658	1	1

* Obtained by Redlich Kister.

TABLE 4
Experimental densities $\rho/(kg \cdot m^{-3})$ and excess molar volumes $10^9 \cdot V_{m,123}^E/m^3 \cdot mol^{-1}$ for the ternary mixture {x_1 dodecane + x_2 ethyl pentanoate + $(1 - x_1 - x_2)$ ethyl ethanoate} at 298.15 K at atmospheric pressure.

x_1	x_2	ρ (kg · m^{-3})	$10^9 V_{m,123}^E$ (m^3 · mol^{-1})	x_1	x_2	ρ (kg · m^{-3})	$10^9 V_{m,123}^E$ (m^3 · mol^{-1})
			$x_1' = 0.7855$				
0.0434	0.0119	877.17	311	0.3978	0.1087	798.20	1255
0.0795	0.0217	864.80	527	0.4728	0.1291	788.88	1214
0.1249	0.0341	851.38	722	0.5500	0.1502	780.78	1098
0.1671	0.0457	840.87	810	0.6311	0.1724	773.29	975
0.2053	0.0561	831.54	998	0.6661	0.1819	770.44	894
0.2415	0.0660	823.80	1112	0.6989	0.1909	767.92	811
0.3200	0.0874	809.61	1244	0.7237	0.1977	766.16	733
			$x_1' = 0.5267$				
0.0286	0.0257	881.91	245	0.2847	0.2559	816.72	1059
0.0510	0.0459	873.56	368	0.3102	0.2787	812.80	1057
0.0782	0.0703	864.22	522	0.3841	0.3451	802.92	986
0.1048	0.0942	856.01	648	0.4158	0.3737	799.09	963
0.1563	0.1405	842.15	853	0.4377	0.3934	796.57	952
0.1709	0.1536	838.81	874	0.4667	0.4195	793.53	907
0.2138	0.1922	829.41	995	0.4920	0.4421	791.08	854
			$x_1' = 0.2578$				
0.0136	0.0390	887.32	123	0.1171	0.3372	849.92	657
0.0241	0.0692	882.32	209	0.1457	0.4193	842.92	713
0.0383	0.1101	876.10	311	0.1636	0.4709	838.92	748
0.0496	0.1427	871.51	386	0.1822	0.5246	835.21	755
0.0633	0.1823	866.45	454	0.1904	0.5481	833.70	750
0.0890	0.2563	857.93	568	0.2047	0.5892	831.12	753
0.1047	0.3014	853.30	624	0.2157	0.6209	829.27	744

Uncertainties u are: $u(T) = \pm 0.01$ K, $u(\rho) = \pm 0.02$ kg·m^{-3}, $u(x) = \pm 0.0002$, and $u(10^9 \cdot V_m^E) = \pm 5$ m^{-3} mol^{-1}.

compositions of dodecane + ethyl pentanoate, known quantities of the third component, ethyl ethanoate, are added. Then the database shown in table 4 (x_1, x_2, ρ, V_m^E) was constructed and its correlation carried out by applying equation (5), where the terms corresponding to the specific contributions of the binaries $M_{2,4}^{E,(i-j)}$ were obtained for the compositions indicated in table 4, applying the normalization procedure described above, and the coefficients from table 3 implemented in equation (5). The volume data for the system were correlated by obtaining the C_i coefficients by minimizing the standard deviation, equation (7), adapted to ternary data. The results are shown in table 5. Calculation of the parameters k_v^{j-i} and k_h^{j-i} is worth a special mention here, and their introduction in the *active fractions* z_i that appear in the last term of equation (5), which correspond to the specific contribution of the ternary. For this work, taking dodecane as the substance of reference, the values of the volume parameter are: $k_v^{2-1} = v_{2,m}^o / v_{1,m}^o$ =0.655, $k_v^{3-1} = v_{3,m}^o / v_{1,m}^o$ =0.431, y $k_v^{3-2} = v_{3,m}^o / v_{2,m}^o = 0.658$.

Mathematical treatment of the ternary system generated a set of graphs that define the behavior of the solution under study more clearly. Thus, figure 2(a) shows the graph for the pseudobinaries of the values obtained from the experimentation, $V_{m,123}^E$, together with the correlation curves obtained with equation (5). Graph 2(b) shows the surface obtained with equation (5) for the function $V_{m,123}^E = f(x_1, x_2, x_3)$, together with the data from table 5. Figure 2(c) shows the composition isolines obtained after sectioning the surface of figure 2(b) by horizontal planes of constant volumes. A comparison of the goodness of fit of equation (5) and that of Cibulka [19] is shown in table 5, with similar values of standard deviation.

4.2. Excess molar enthalpies

Table 6 shows the experimental values for the excess molar enthalpies H_m^E of the binary systems studied here, and table 7 shows the values of the coefficients of the polynomial in "z" for the correlation expression, which has the same form as equation (6). This table also gives the values for the k_h^{j-i} parameters, calculated as shown previously. Graphical representations of this thermodynamic quantity are shown in figure 3. Data for the H_m^E of the dodecane + ethyl ethanoate system have been compiled in the literature at the same temperature [23], and show slight differences in the regions of intermediate composition. The authors mention the use of two different calorimeters to determine the mixing energies, but do not specify the interval that was measured with the two instruments; and the slight differences appearing in figure 3 could be attributed to the different sensitivities of the calorimeters used. The regularity of the equimolar values [H_m^E at $x = 0.5$] of the mixtures with the hydrocarbon chains corresponding to analogous systems [3] (see figure inset) confirms the goodness of fit of the data.

To obtain the $H_{m,123}^E$ data for the ternary mixture, three sets of measurements were carried on. The mixing energy of the ternary was obtained by adding ethyl ethanoate to binary mixtures of fixed compositions of dodecane + ethyl pentanoate (0.1845, 0.3973, 0.6471, in dodecane). Therefore, each point of the ternary is the enthalpic effect corresponding to a mixture of the fixed composition specified above, (as if it were only one compound), with the addition of ethyl ethanoate. Mathematically, the global effect is reflected by the following sum:

TABLE 5
Coefficients C_i and standard deviations $s(M^E)$ obtained using equation (5) and that of Cibulka [19] to correlate $10^9 \cdot V_{m,123}^E/(m^3 \cdot mol^{-1})$ and $H_{m,123}^E/(J \cdot mol^{-1})$ for the ternary mixture $\{x_1 \text{ dodecane} + x_2 \text{ ethyl pentanoate} + (1 - x_1 - x_2) \text{ ethyl ethanoate}\}$ at 298.15 K.

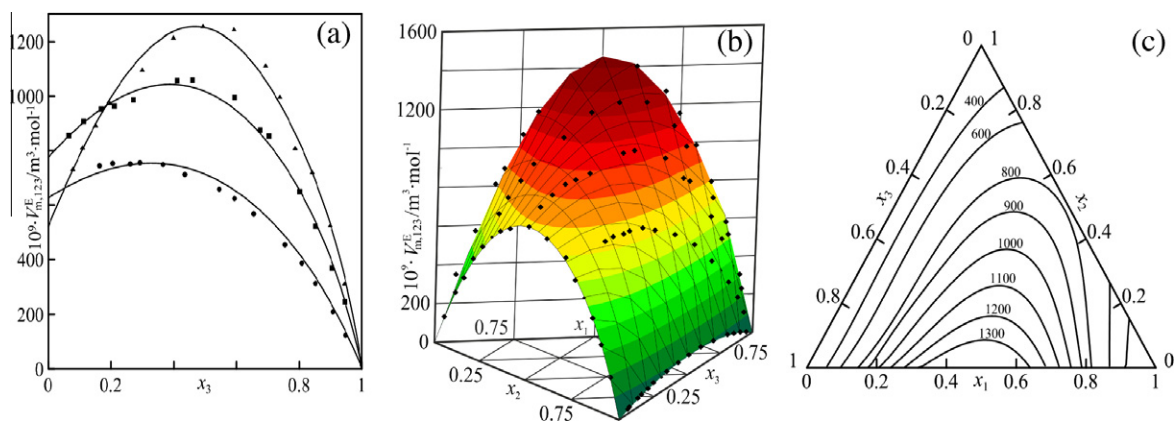|	Equation (5)					Cibulka [19]			
	C_0	C_1	C_2	k	$s(M^E)$	C_0	C_1	C_2	$s(M^E)$
v_{123}^E	1837	−3421	5035	$k_v^{2-1} = 0.655$ $k_v^{3-1} = 0.431$	$31 \cdot 10^{-9}$	1874	−9641	−1860	$23 \cdot 10^{-9}$
h_{123}^E	−3937	4548	11266	$k_h^{2-1} = 0.675$ $k_h^{3-1} = 0.456$	22	−5988	128	10914	23

FIGURE 2. (a) Plot of V_m^E for the pseudobinary mixture of the $(x_1 \text{ dodecane} + x_2 \text{ ethyl pentanoate} + x_3 \text{ ethyl ethanoate})$ ternary system for three initial binaries whose compositions are: (●) $x_1' = 0.2578$, (■) $x_1' = 0.5267$, (▲) $x_1' = 0.7855$ and the correlation by equation (5). (b) Plot of experimental (x_1, x_2, x_3, V_m^E) values and the surface obtained by equation (5). (c) Isolines corresponding to the horizontal projection of the V_m^E noted for the ternary using equation (5).

TABLE 6
Experimental excess molar enthalpies $H_m^E/(J \cdot mol^{-1})$ for (dodecane + an ethyl alkanoate) binary mixtures at 298.15 K and atmospheric pressure.

x_1	H_m^E (J · mol^{-1})	x_1	H_m^E (J · mol^{-1})	x_1	H_m^E (J · mol^{-1})
x_1 Dodecane + $(1 - x_1)$ethyl pentanoate					
0.0430	192	0.3181	916	0.5648	1032
0.0928	371	0.3511	961	0.6392	961
0.1433	540	0.3548	971	0.7228	826
0.1957	684	0.3978	1014	0.8127	621
0.2488	802	0.4460	1046	0.9036	375
0.3005	894	0.5012	1056		
x_1 Dodecane + $(1 - x_1)$ethyl ethanoate					
0.0232	236	0.2790	1628	0.4736	1868
0.0541	503	0.3296	1740	0.5534	1798
0.0898	771	0.3789	1817	0.6470	1612
0.1316	1031	0.4062	1849	0.7424	1309
0.1800	1279	0.4261	1859	0.8396	896
0.2292	1478	0.4718	1874	0.9339	423
x_1 Ethyl pentanoate + $(1 - x_1)$ethyl ethanoate					
0.0627	49	0.4144	152	0.6645	133
0.1347	89	0.4736	157	0.7376	114
0.2071	118	0.5198	154	0.8193	88
0.2799	139	0.5610	151	0.8904	58
0.3493	147	0.6071	145	0.9529	30

Uncertainties u are: $u(T) = \pm 0.005$ K, $u(x) = \pm 0.0002$, and $u(H_m^E) = \pm 1$ J · mol^{-1}.

TABLE 7
Coefficients H_i and standard deviations $s(H_m^E)$ obtained from equation (5) to correlate excess molar enthalpies for (dodecane + an ethyl alkanoate) binary mixtures.
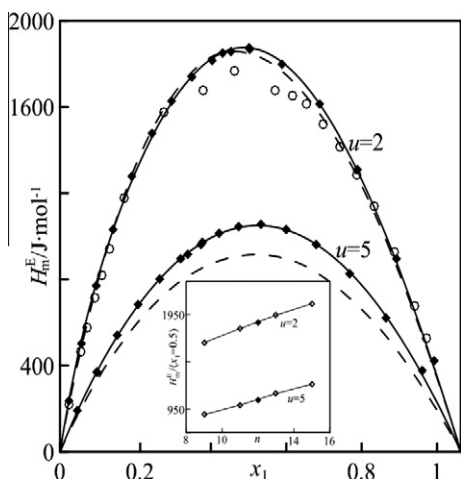
System	H_0	H_1	H_2	k_h^{j-i}	$s(H_m^E)$	$s(H_m^E)^*$
Dodecane + ethyl pentanoate	3141	793	2106	0.675	6	7
Dodecane + ethyl ethanoate	5392	−2148	10058	0.456	14	14
Ethyl pentanoate + ethyl ethanoate	624	−290	537	0.676	1	2

* Obtained by Redlich Kister.

binary dodecane + ethyl pentanoate and ethyl ethanoate, considering these three blocks of data at fixed compositions for the specified binary. Finally, figure 4(c) represents the isolines corresponding to projections of the variation in compositions on a triangular diagram for different constant values of excess molar enthalpies, isoenthalpic lines.

5. Behavior of the alkane + ester + ester systems

Some conclusions can be drawn from the results of the experimental determination of the volumetric and energetic mixing quantities, at 298.15 K, for the ternary system dodecane + ethyl pentanoate + ethyl ethanoate, and its three binaries, with the purpose of proposing a structural model for their behavior. For the case of the alkane + ester solutions, dodecane + ethyl ethanoate, or +ethyl pentanoate, the graphs of V_m^E and H_m^E show symmetrical data distributions with expansive and endothermic effects, respectively, throughout the range of compositions. The decreasing tendency of the binary mixing properties defined empirically by $C_{12}H_{26} + H_{2u-1}C_{u-1}COOC_2H_5$ ($u = 2,5$), shown in figures 1 and 3, can be attributed to a decrease in the permanent dipolar moment $\mu \cdot 10^{30}/(C \cdot m)$

$$H_{m,123}^E = H_m^{E(pseudo,3+12)} + (1 - x_3)H_m^{E(12)} \qquad (10)$$

The enthalpic data calculated are shown in table 8 as a function of the real compositions of each of the mixture components and were correlated using equation (5), following the same procedure as indicated for volumes. The values of the C_i coefficients, calculated as explained in Section 4.1 are reported in table 5. The correlation was used to construct figure 4(a)–(c), including the resulting surface $H_{m,123}^E = f(x_1, x_2, x_3)$, figure 4(b). Figure 4(a) shows the representation of the energetic effect of the pseudobinary system, composed of the

FIGURE 3. Experimental H_m^E values (♦) measured at 298.15 K and correlation curve using equation (6) for binaries {$x_1C_nH_{2n+2}$ ($n = 12$) + $x_2C_{u-1}H_{2u-1}COOC_2H_5$ ($u = 2, 5$)}, and comparison with literature values (○, reference [23]). Inset shows the regularity of equimolar H_m^E values from reference [3] (◇) as a function of the hydrocarbon chain length for the two esters in the binaries {an alkane + ethyl ethanoate ($u = 2$), or +ethyl pentanoate ($u = 5$)}.

[24] associated with the −COO− group (5.94 for $u = 2$, 5.84 for $u = 5$), owing to the increased length of the acid chain of the alkanoate u, as a consequence of the reduced dipole-dipole interactions in the pure substances, and also in the mixtures. This is more extreme in the latter owing to the formation of empty intermolecular spaces because of the greater distance between these permanent dipoles (similar to that shown for ester–ester in figure 6). Nonetheless, the pronounced

difference previously shown for the dipolar moments of the ethyl alkanoates does not completely explain the quantitative difference between the mixing properties, which correspond, for example, to >1000 J·mol^{-1} for H_m^E of mixtures of the hydrocarbon with ethyl ethanoate and with ethyl pentanoate. This behavior supports our initial proposal of the model [1,2] for systems with compounds of the same chemical nature.

Ester–ester: A specific comments can explain the behavior of ester–ester mixtures, for which mixing properties studied result be expansive and endo/exothermic, to depend on the acid/alkanoic chain length of the alkanoate. Very few studies are available in the literature about the properties of solutions of oxygenated compounds of the same chemical nature, except for some alkanol–alkanol solutions [25]. We must also consider the solutions of reference, alkane–alkane [26,27], for which the excess process have very small values. In these systems, the contractive effects increase with the size difference of the hydrocarbon chains, so that the ester–ester solutions cannot be explained solely by the coupling of different-sized molecules. The small values for excess properties of alkane–alkane mixtures are a consequence of slight changes in the Van der Waals forces, but in the ester–ester systems, the H_m^E can increase by up to 20 fold, revealing the existence of energetic effects that must be taken into account in the mixing process.

Since there is very little information about ester/ester mixtures in the literature [28–31], the present study fills the missing gaps for non-existent mixtures in the databases. Hence, in figure 5 the H_m^E's and the V_m^E's of the binary system {ethyl pentanoate ($u = 5$) + ethyl ethanoate ($u = 2$)} are represented together with the results obtained for mixtures with other members of the series $H_{2u-1}C_{u-1}COOC_2H_5$, with $u = 3$ and $u = 4$, showing a regular decrease in the mixing quantities with the increase in u, giving place

TABLE 8
Excess molar enthalpies $H_m^{E(pseudo,3+12)}/(J \cdot mol^{-1})$ for the pseudobinary mixtures and for the ternary {x_1 dodecane + x_2 ethyl pentanoate + $(1 - x_1 - x_2)$ethyl ethanoate} $H_{m,123}^E/(J \cdot mol^{-1})$, using equation (10) at 298.15 K and atmospheric pressure.

x_1	x_2	$H_m^{E(pseudo,3+12)}$ (J·mol^{-1})	$H_{m,123}^E$ (J·mol^{-1})	x_1	x_2	$H_m^{E(pseudo,3+12)}$ (J·mol^{-1})	$H_{m,123}^E$ (J·mol^{-1})
			x'_1=0.6471				
0.5891	0.3212	299	1167	0.2068	0.1128	968	1273
0.5391	0.2939	498	1292	0.1855	0.1011	930	1203
0.4858	0.2649	682	1397	0.1683	0.0918	882	1130
0.4286	0.2337	842	1473	0.1503	0.0820	836	1057
0.3761	0.2051	952	1506	0.1345	0.0733	778	976
0.3306	0.1803	1010	1497	0.1190	0.0649	725	900
0.2927	0.1596	1029	1460	0.0959	0.0523	620	761
0.2593	0.1414	1025	1407	0.0787	0.0429	545	661
0.2304	0.1256	1003	1342				
			x'_1=0.3973				
0.3649	0.5538	149	1078	0.1586	0.2407	627	1031
0.3347	0.5081	272	1125	0.1427	0.2165	615	978
0.3096	0.4699	373	1162	0.1275	0.1935	593	918
0.2883	0.4376	445	1179	0.1137	0.1726	561	851
0.2694	0.4089	501	1187	0.1017	0.1543	523	782
0.2497	0.3791	549	1185	0.0906	0.1376	489	720
0.2285	0.3468	589	1171	0.0795	0.1207	448	651
0.2092	0.3176	614	1147	0.0644	0.0978	388	552
0.1908	0.2896	628	1114	0.0457	0.0694	301	417
0.1751	0.2657	629	1075				
			x'_1=0.1845				
0.1730	0.7657	150	763	0.0689	0.3051	368	612
0.1603	0.7094	227	795	0.0612	0.2707	351	568
0.1465	0.6481	286	805	0.0542	0.2399	331	523
0.1334	0.5902	330	803	0.0481	0.2129	302	472
0.1204	0.5327	364	790	0.0427	0.1889	274	425
0.1077	0.4764	384	765	0.0362	0.1602	235	363
0.0968	0.4283	390	733	0.0312	0.1380	206	316
0.0869	0.3848	388	696	0.0267	0.1182	174	269
0.0776	0.3436	381	656				

Uncertainties u are: $u(T)$ = ±0.005 K, $u(x)$ = ±0.00035, and $u(H_m^E)$ = ±2 J·mol^{-1}.
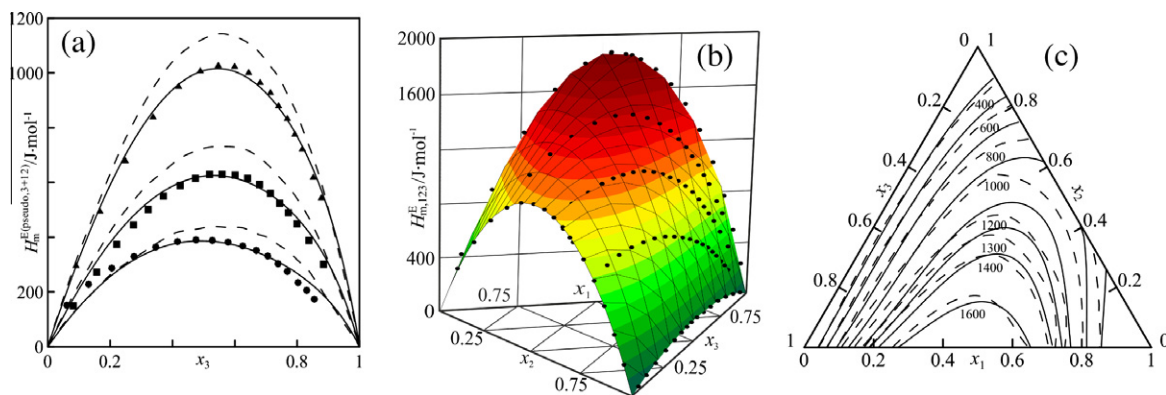
FIGURE 4. (a) Plot of H_m^E for the pseudobinary mixture of the (x_1 dodecane + x_2 ethyl pentanoate + x_3 ethyl ethanoate) ternary system for three initial binaries whose compositions are: (●) $x_1' = 0.1845$, (■) $x_1' = 0.3973$, (▲) $x_1' = 0.6471$ and the correlation obtained by equation (5). (b) Plot of experimental ($x_1, x_2, x_3, H_{m,123}^E$) values and the surface obtained by equation (5). (c) Isolines corresponding to the horizontal projection of the H_m^E noted for the ternary using equation (5), and predictions by the UNIFAC method [11,12] (- - -).
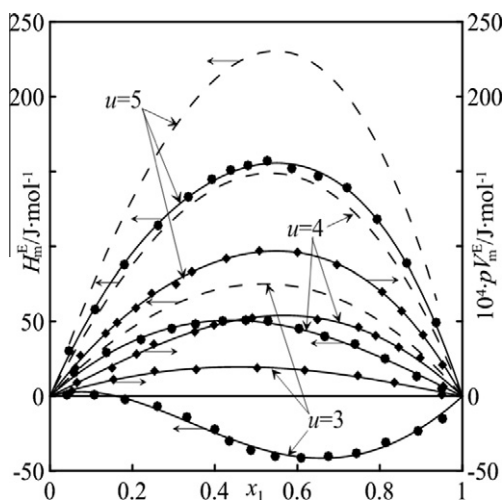

FIGURE 5. Plot of experimental points (x_1, H_m^E) (●) and ($x_1, p V_m^E$) (♦) for binaries {x_1 ethyl ethanoate + x_2 an ethyl alkanoate (propanoate, $u = 3$; butanoate, $u = 4$; pentanoate, $u = 5$)} and the correlations by equation (6). (- - -) Predictions of H_m^E by UNIFAC [11,12].

to $H_m^E < 0$ when $u = 3$. Initially, this result can be justified by the increase in u producing a decrease in the dipolar moment associated

with the carboxylate group (mentioned previously), resulting in a weakening of the dipole-dipole attractions, both in the pure compound and the mixture. However, this would be more pronounced in the mixture, owing to the greater distance between these dipoles and the empty intermolecular spaces that are formed, see figure 6(a). The greater destabilization of the mixture, as u increases, in comparison to that of the pure compound, confirms the values of $H_m^E > 0$ and $V_m^E > 0$. However, the exception to this rule is an exothermic process in the mixture of ethyl propanoate + ethyl ethanoate, which can be qualitatively explained by the coexistence of two phenomena: the existence of empty spaces in the liquid network of the mixture, caused by an asymmetric structure which is formed by minimizing the internal energy and maximizing the dipole-dipole interactions. This results in a folding of the –CH$_3$ in β of the ethyl propanoate, which enter to occupy the inside, giving rise to an exothermic effect caused by an increase in Van der Waals forces, which also increase the contact surfaces. This phenomenon is not observed in mixtures with butanoate and ethyl pentanoate, because of the preference of these to adopt the zig-zag formation, which minimizes both the angular and torsional tension.

To verify these assumptions, a spectral study was carried out of ^{1}H NMR, to observe the paramagnetic displacements δ of the protons of three methylenes and one methyl group of ethyl pentanoate, [signals a, b, c, d in figure 6(b)], and a methyl group of ethyl ethanoate (signal e) as the proportion of the ethanoate is increased,
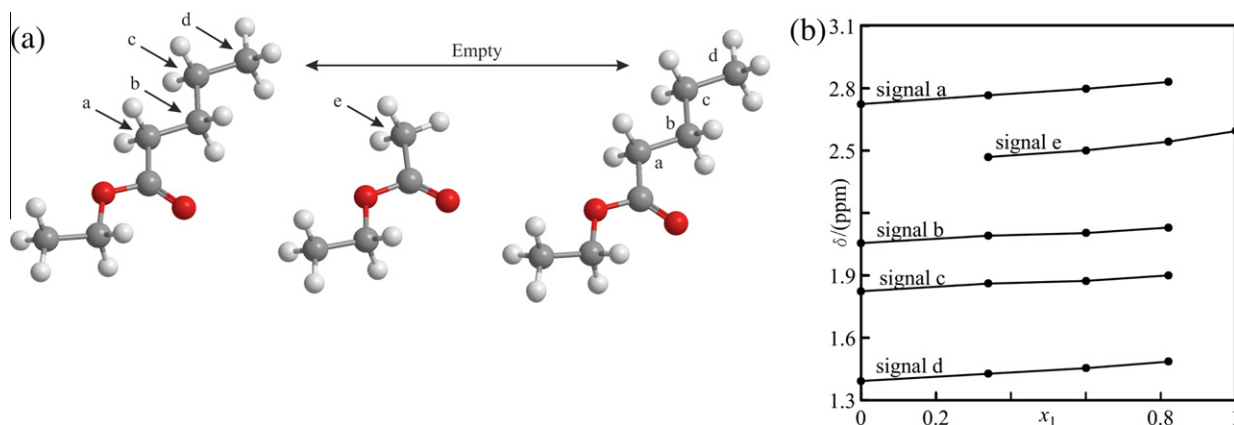
FIGURE 6. (a) Plot of the solution molecular structure formed by ethyl pentanoate + ethyl ethanoate with the identification of each of functional groups. (b) Shift of peaks in the ^{1}H NMR spectra referenced to the TMS signal (δ 0.000) for ethyl pentanoate + ethyl ethanoate mixture. Signal a = C$_\alpha$H$_2$, b = C$_\beta$H$_2$, c = C$_\gamma$H$_2$, d = C$_\delta$H$_3$, for ethyl pentanoate; and e = C$_\alpha$H$_3$ of ethyl ethanoate. Other signals of the ^{1}H NMR spectra are omitted because of overlapping.

showing that the greatest density of dipoles appears in the mixtures with the smallest molecular size, i.e. lower values of u.

Ester–ester–alkane: The ternary solution presents net expansive and endothermic global effects for every composition. The surfaces represented in figures 2 and 4 present absolute maxima, which coincide with that of the dodecane + ethyl ethanoate system. The ternary contribution is positive except in the regions rich in dodecane, in which it is greatly diminished, even reaching negative values. The incidence of the ternary contribution is greater in regions closer to the ester–ester system, corresponding to around 15% of the total. The behavior observed seems to suggest that the properties obtained for the ternary solution are dominated by the binary effects.

6. Estimation of the mixing enthalpies with UNIFAC

The UNIFAC group contribution method [11,12] was applied with the original parameters for the two binary mixtures dodecane + ethyl alkanoate. As shown in figure 3, the results are qualitatively acceptable, although in the case of the dodecane + ethyl pentanoate mixture, the estimates of H_m^E are slightly lower than experimental values. This result has also been demonstrated in previous works [2,3], since the UNIFAC method becomes less accurate with the increasing chain length of the compounds, in particular, of the esters. However, estimation of the enthalpies for the mixture with ethanoates is excellent since the method presents a set of exclusive parameters for compounds containing the COOC/CH$_2$ interaction.

Estimates made for ester–ester systems present significant discrepancies, showing this method to be somewhat ineffective for these systems. As seen in figure 5, the estimated values are quantitatively higher than the experimental ones for the mixtures ethyl pentanoate, or ethyl butanoate + ethyl ethanoate, and do not reproduce the sigmoidal form of the ethyl propanoate + ethyl ethanoate system. It is evident that the interactions considered by the UNIFAC method for the CH$_3$COO- and -CH$_2$COO- groups cannot be zero and, possibly, the definition for a single group of the form -COO- should be used.

For the ternary mixture, UNIFAC provides an acceptable qualitative description of the H_m^E. Quantitatively, the estimates are more accurate in zones rich in ethyl ethanoate (high values of x_3), although slightly higher. At values of fixed compositions of ethyl ethanoate, the estimates improve with increased dodecane composition, and this behavior coincides with that of the corresponding binary mixtures. To summarize, this method can acceptably predict the behavior of the ternary system selected here, although it is limited by the deficient description of the ester–ester system.

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