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Mixing thermodynamic properties of ester-containing solutions: A study on the ternary (methyl alkanoate (pentanoate and methanoate) + methanol) and the corresponding binaries. New contributions to the (ester + ester) interactions



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ABSTRACT

This work studies the volumetric (V_m^E) and energetic (H_m^E) properties resulting from the mixing processes of binary systems and the corresponding ternary of two methyl esters (methanoate and pentanoate) with methanol. The three binaries produce net endothermic mixing effects, with important energetic interactions, with maximum values of $H_m^E \cong 400 \text{ J} \cdot \text{mol}^{-1}$, for the (ester + ester) system. This produces expansive effects $V_m^E > 0$, but the binaries of the (methyl esters + methanol) give rise to contractions $V_m^E < 0$, due to the formation of molecular aggregates. The endothermicity in the mixing processes is a net effect which is justified by interactions of different nature, especially dipolar interactions and hydrogen bonds of the substances involved. The overall results in the ternary respond to the individual contributions of the binaries and the increment due to the simultaneous presence of the three compounds in the solution. The experimental results are correlated with our own model that gives a good representation of the properties of the solutions studied. The analysis of the behavior of the solutions is reinforced by spectral data obtained by ^1H NMR, supporting the structural model established. The application of UNIFAC to estimate the H_m^E in the ternary improves when one takes into account the individual contributions of the (ester + ester) interactions whose parameter are predetermined.

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1. Introduction

The line of work followed by our research team aims to understand the behavior of systems containing esters with alkanols, compounds present in some biodiesel. Some works in this field [1–7], have provided a large amount of experimental data of interest for studies into biofuels and the design of equipment. However, the experimental information produced is still insufficient, especially that referred to certain structural aspects of those solutions and their physicochemical behavior. Some of these points have been addressed in a previous work [8] on a ternary of two ethyl esters with dodecane, where interesting and useful information was presented about the mutual interactions between ethylic esters, which is also of value for the analysis proposed here.

One of the justifications of this line of work is that the growing demand for energy makes it necessary to find new sources and technologies, with less environmental impact. Hence, some

research focuses on searching for more environmentally-friendly fuels, which are less polluting and have better O/C ratios. This can be achieved by using additives that facilitate combustion and reduce emissions. Families of compounds such as ethers and alkanols have been tested as additives for gasoline [9–11] and biodiesel engines [12,13]. In some patents [14,15] methyl methanoate is proposed use as an additive in fuels, for its high O/C ratio. The advantage of using additives is that they can be used without significant changes in existing combustion systems. Another known alternative is to use bioalkanols and biodiesel, which can provide some environmental benefits [16], although they present less calorific power [17].

Our investigations on properties of solutions of compounds of this nature that may provide additional information are included in this research line. Mixing quantities were obtained, V_m^E and H_m^E at $T = 298.15 \text{ K}$ of the ternary (methyl pentanoate (1) + methyl methanoate (2) + methanol (3)) and their corresponding binaries. Methyl pentanoate was chosen as a candidate for study [18] forming part of a biodiesel produced by transesterification with methanol. The presence of methyl methanoate as an additive has already

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been exposed. We are especially interested in determining the behavior of (ester + ester) solutions, especially the nature of the interactions of (methyl pentanoate + methyl methanoate), which can provide information on the role of this additive in solution, to supplement a previous initial study [8], since there are very few studies on (ester + ester) solutions [19]. Studies in this field show that these solutions present very weak enthalpic effects, but that these reach significant levels when the esters have very different polarities, even without taking into account effects due to hydrogen bonds and their repercussions on the mixing processes of the alkyl alkanoates, mainly derived from the strongest organic acids (formic > acetic > etc.).

For the systems studied, the literature contains V_m^E [20] and H_m^E [21] data for the binary (methyl methanoate (2) + methanol (3)), which are used for purposes of comparison. However, data were not found for the two binaries containing methyl pentanoate. For purposes of clarification, the experimental values obtained are correlated with our own model that has produced good results in previous works [7,8], for which the parameters need to be identified. Conclusions about the behavior of these systems are supported by a spectral analysis obtained by $^1\text{H-NMR}$. Some aspect of the modeling, whose usefulness is interesting to optimize the processes mentioned, is carried out using the evaluation of results obtained by theoretical methods employed in process simulators, such as the UNIFAC method [22]. Special interest is to check if the numerical values of the HCOO/COOC interaction in binaries affect the results of solutions of more than two components.

2. Experimental

2.1. Materials

The products used, of high commercial quality, were supplied by Aldrich. The purity was verified by GC, giving values almost identical to those indicated by the manufacturer, see table 1. However, products were degassed by ultrasound for several hours and stored in topaz-colored bottles (over 0.3 nm Fluka molecular sieve), in the dark for several days to remove traces of moisture. Esters and methanol are hygroscopic, so the water content was determined by Karl-Fisher coulometric titration, approximating 50 ppm in all cases. After these operations, the quality of the products was verified again by GC and was found to have a slight improvement for some substances, compared to initial values. The most important characteristics of the products: refractive index n_D , and density ρ , at $T = 298.15$ K, are recorded in table 2, and are comparable to data published in the literature.

The apparatus were calibrated using bidistilled water [$\rho = 997.04 \text{ kg} \cdot \text{m}^{-3}$ ($T = 298.15$ K)] and degassed in our laboratory, and nonane [$\rho = 713.85 \text{ kg} \cdot \text{m}^{-3}$ ($T = 298.15$ K)], which was subjected to the same treatment indicated above for other products; the quality and the source of these substance are given in table 1.

TABLE 1
Pure compounds specifications.

Compound	CAS No.	Supplier	Purity w/w%		Analytical method
			Original	Final	
Methyl pentanoate	624-24-8	Aldrich	98.6	99.0	GC
Methyl methanoate	107-31-3	Aldrich	99.0	99.3	GC
Methanol	67-56-1	Aldrich	99.9	99.9	GC
TMS	75-76-3	Aldrich	99.9		GC
Cl_3CD	865-49-6	Aldrich	99.96		GC
Water	7732-18-15			<1 μS	Conductivity meter
Nonane	111-84-2	Aldrich	99.0	99.1	GC

TABLE 2

Experimental densities ρ , and refractive indices measured at $T = 298.15$ K and atmospheric pressure, of the pure compounds and comparison with those from literature.

Compounds	$\rho / \text{kg} \cdot \text{m}^{-3}$		n_D	
	Exp.	Lit.	Exp.	Lit.
Methyl pentanoate	884.78	884.66 ^c 884.58 ^e	1.3952	1.3948 ^c 1.3947 ^e
Methyl methanoate	966.28	966.8 ^b 965.85 ^c 966.4 ^d 966.18 ^e	1.3411	1.34074 ^b 1.3415 ^c 1.3412 ^e
Methanol	786.40	786.79 ^a 786.6 ^b 786.64 ^{c,d}	1.3261	1.3266 ^a 1.32640 ^b 1.32652 ^{c,d}

Uncertainties u are: $u(T) = \pm 0.02$ K, $u(n) = \pm 0.0002$, and $u(\rho) = \pm 0.02 \text{ kg} \cdot \text{m}^{-3}$

^a Reference [7].

^b Reference [20].

^c Reference [24].

^d Reference [25].

^e Reference [26].

2.2. Apparatus and procedures

The water content was determined by a Mettler C-20 Karl-Fisher titrator and a HP-6890N GC from Agilent was used for evaluate the quality of products. Densities of the pure compounds and mixtures were measured with an Anton Paar DMA 60/602 digital densimeter ($\rho \pm 0.02$) $\text{kg} \cdot \text{m}^{-3}$, maintaining the temperature at (298 ± 0.01) K using a 1166D Polyscience thermostatic water-bath. The densimeter was calibrated with water and nonane using a procedure described previously [23]. Densities were used to calculate the excess volumes of binaries [$(V_m^E \pm 2 \cdot 10^{-9}) \text{ m}^3 \cdot \text{mol}^{-1}$; $x \pm 0.0002$] and ternaries [$(V_m^E \pm 5 \cdot 10^{-9}) \text{ m}^3 \cdot \text{mol}^{-1}$; $x \pm 0.0005$]. Refractive indices ($n_D \pm 0.0002$) of the pure compounds were measured with a 302 Abbe refractometer by Zuzi. The apparatus was maintained at a constant temperature of (298.15 ± 0.01) K using a Polyscience 9012 circulating water-bath, and was calibrated with water, assigning as exact value that shown in ref [24]. The mixing enthalpies [$(H_m^E \pm 1\%) \text{ J} \cdot \text{mol}^{-1}$; $x \pm 0.0002$] at a temperature of (298 ± 0.01) K were measured directly with a MS80D Calvet conduction calorimeter by Setaram. Calibration was carried out by applying a Joule effect provided by an external power source, to simulate analogous thermograms to the mixing process. Correct functioning of the system was checked using the standard mixture of (cyclohexane + hexane) [27].

The working procedure followed to obtain the mixing quantities, V_m^E and H_m^E , of the ternaries was analogous to that used in a previous work [8]. By means of successive weighing, solutions ($\cong 40 \text{ cm}^3$) of known concentrations of (methyl pentanoate (1) + methanol (3)) were prepared. Each solution (considered as a

TABLE 3

Experimental densities in $\rho/(\text{kg} \cdot \text{m}^{-3})$ measured at $T = 298.15 \text{ K}$ and atmospheric pressure and excess molar volumes $10^9 \cdot V_m^E/\text{m}^3 \cdot \text{mol}^{-1}$ calculated for the binaries indicated below.

x_1	$\rho/\text{kg} \cdot \text{m}^{-3}$	$10^9 \cdot V_m^E/\text{m}^3 \cdot \text{mol}^{-1}$	x_1	$\rho/\text{kg} \cdot \text{m}^{-3}$	$10^9 \cdot V_m^E/\text{m}^3 \cdot \text{mol}^{-1}$	x_1	$\rho/\text{kg} \cdot \text{m}^{-3}$	$10^9 \cdot V_m^E/\text{m}^3 \cdot \text{mol}^{-1}$
<i>(x₁Methyl pentanoate + x₂methyl methanoate)</i>								
0.0000	966.28	0	0.3493	919.84	294	0.7258	895.50	207
0.0555	956.19	75	0.4011	915.46	302	0.7765	893.24	171
0.1040	948.47	129	0.4572	911.17	302	0.8360	890.80	123
0.1464	942.39	170	0.5000	908.17	299	0.9031	888.23	70
0.2093	934.27	229	0.5539	904.69	288	1.0000	884.78	0
0.2537	929.22	257	0.6081	901.55	264			
0.3106	923.46	279	0.6522	899.15	246			
<i>(x₁Methyl pentanoate + x₂methanol)</i>								
0.0000	786.40	0	0.2480	837.51	−32	0.7472	875.67	−28
0.0235	793.56	−4	0.3040	844.36	−36	0.7884	877.42	−25
0.0620	803.85	−10	0.3501	849.28	−39	0.7982	877.81	−23
0.0741	806.78	−12	0.4499	858.16	−41	0.8786	880.85	−15
0.1314	818.95	−19	0.5121	862.75	−41	0.9630	883.66	−4
0.1512	822.61	−22	0.6073	868.69	−38	1.0000	884.78	0
0.2017	830.95	−28	0.6865	872.86	−34			
<i>(x₁Methyl methanoate + x₂methanol)</i>								
0.0000	786.40	0	0.3219	863.26	−72	0.7815	939.62	−73
0.0337	795.73	−12	0.3906	876.73	−79	0.8533	949.01	−59
0.0833	808.80	−27	0.4946	895.61	−85	0.8968	954.39	−46
0.1557	826.74	−46	0.5416	903.58	−87	0.8968	954.39	−46
0.1900	834.77	−52	0.6467	920.31	−87	0.9357	959.02	−32
0.2499	848.14	−62	0.7271	932.10	−81	1.0000	966.28	0

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

TABLE 4

Experimental excess molar enthalpies $H_m^E/\text{J} \cdot \text{mol}^{-1}$ measured directly at $T = 298.15 \text{ K}$ and atmospheric pressure for the binaries indicated below.

x_1	$H_m^E/\text{J} \cdot \text{mol}^{-1}$	x_1	$H_m^E/\text{J} \cdot \text{mol}^{-1}$	x_1	$H_m^E/\text{J} \cdot \text{mol}^{-1}$
<i>(x₁Methyl pentanoate + x₂methyl methanoate)</i>					
0.0272	59	0.2533	379	0.5232	409
0.0583	112	0.2946	401	0.6056	366
0.0932	171	0.3096	413	0.6943	304
0.1292	230	0.3486	422	0.7968	219
0.1720	291	0.3982	431	0.8656	145
0.2104	340	0.4522	431	0.9300	84
<i>(x₁Methyl pentanoate + x₂methanol)</i>					
0.0244	83	0.2640	736	0.5081	1091
0.0512	169	0.2993	819	0.5867	1095
0.0839	277	0.3336	876	0.6887	1006
0.1195	383	0.3670	921	0.7931	812
0.1562	485	0.3861	947	0.8868	533
0.1920	578	0.4156	990	0.9570	240
0.2279	665	0.4625	1053		
<i>(x₁Methyl methanoate + x₂methanol)</i>					
0.0200	75	0.3086	914	0.5783	1196
0.0487	179	0.3501	987	0.6460	1178
0.0833	311	0.3644	1010	0.7178	1105
0.1225	441	0.3943	1054	0.7842	984
0.1670	577	0.4077	1074	0.8517	808
0.2135	703	0.4572	1131	0.9098	584
0.2613	817	0.5127	1179	0.9505	339

Uncertainties u are: $u(T) = \pm 0.01 \text{ K}$, $u(x) = \pm 0.0002$, and $u(H_m^E) = \pm 0.01$.

pseudocomponent) was then used to determine the excess property, V_m^E or H_m^E , of a pseudobinary system, now using the methyl methanoate as a second component. In this way, series of data are obtained whose compositions obeying a constant ratio of x_1/x_3 .

For the structural analysis of the pure compounds and solutions, a 300 MHz Bruker ^1H NMR spectrometer was employed to take measurements at $T = 293 \text{ K}$, using Cl_3CD (see table 1) in concentric capillaries to achieve the lock. Chemical shifts were measured in relation to the signal of TMS ($\delta = 0$) (see table 1), dissolved in Cl_3CD .

3. Presentation and correlation of experimental data

Table 3 shows the experimental values of (x_1, ρ, V_m^E) at $T = 298.15 \text{ K}$ for the binaries (methyl pentanoate (1) + methanol (3)), (methyl methanoate (2) + methanol (3)), and (methyl pentanoate (1) + methyl methanoate (2)). The empirical formulation is given for: $\text{H}_{2u-1}\text{C}_u\text{OOCH}_3$ ($u = 1, 5$) for the methyl esters and $\text{CH}_3(\text{OH})$ for methanol. Table 4 shows the corresponding values of (x_1, H_m^E) for the same binaries. Values of the mixing properties are recorded graphically in figure 1(a) and (b). Both data sets were correlated by a polynomial equation as a function of the composition of one of the compounds of the studied system. If the referenced compound is the first-mentioned, the equation is:

$$Y_m^E = z_1 z_2 \sum_{i=0}^2 A_i z_1^i = z_1 (1 - z_1) (A_0 + A_1 z_1 + A_2 z_1^2 + A_3 z_1^3), \quad (1)$$

where

$$z_i = \frac{v_i x_i}{\sum_{j=1}^n v_j x_j} = \frac{k^{i-1} x_i}{x_i + \sum_{i=2}^n k^{i-1} x_i} \quad (2)$$

corresponding to the variable called the *active fraction* of the property considered. For the moment, no single significance is assigned to the “ k ” ratio, as its meaning depends on the property to which it is applied, although this parameter is known to be associated with the nature of the compounds in solution. Hence, when equation (1) is applied to volumes, this ratio between two compounds $i - j$ is identified by the quotient of molar volumes of the substances: $k^{j-i} \equiv v_j^{j-i} = v_j^0/v_i^0$. The parameters k^{j-i} of the three binaries are not independent of each other, and obey the relationship: $k^{3-2} k^{2-1} = k^{3-1}$, regardless of the property under study.

Correlation of H_m^E values for the binaries is also carried out with equation (1), but now the v_i parameters of equation (2) are associated with a characteristic of the compounds that produce the energetic effects in the mixing process. With this hypothesis, enthalpic results are largely a consequence of the contact surfaces of the molecules. That is, to advance the theoretical version of the model (equation (1)) is particularly interesting to define the meaning of

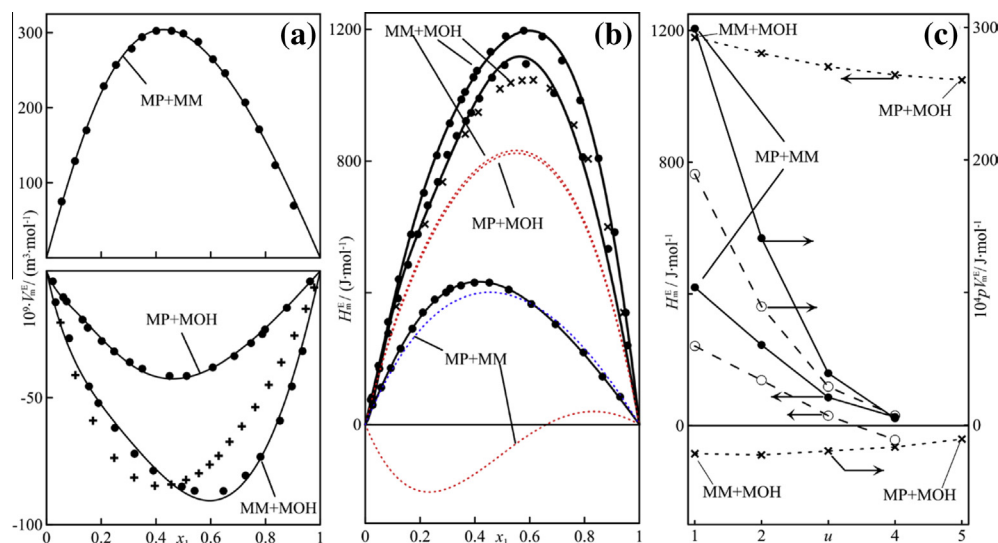


FIGURE 1. Plot of mixing properties for binary solutions formed by: methyl pentanoate (MP), methyl methanoate (MM), Methanol (MOH). (a) Experimental V_m^E values (●) at $T = 298.15$ K for binaries MP(1)+MM(2), MP(1)+MOH(3), MM(2)+MOH(3) and the correlation curves by equation (1); (×) values from ref [20]. (b) Experimental H_m^E values (●) at $T = 298.15$ K for binaries MP(1) + MM(2), MP(1) + MOH(3), MM(2) + MOH(3) and the correlation curves by equation (1); (×) values from ref [21]. (●●●●●) H_m^E values by UNIFAC [22], (●●●●●) H_m^E values by UNIFAC [recalculated]. (c) Variation of equimolar H_m^E and $p V_m^E$ values at $T = 298.15$ K as a function of u [$H_{2u-1}C_uOOC_2H_5$], (●), Experimental values for MP + methyl alkanolate, (○), Experimental values for (ethyl pentanoate + ethyl alkanolate), (×) Experimental values for (methyl alkanolate + MOH).

TABLE 5

Coefficients A_i and standard deviations $s(Y_m^E)$ obtained for equation (1) in the correlation of excess molar properties obtained at $T = 298.15$ K and atmospheric pressure of the binaries formed by two methyl esters and methanol.

Binary system	A_0	A_1	A_2	A_3	k^{j-i}	$s(Y_m^E)$
	$Y_m^E = 10^9 \cdot V_m^E / m^3 \cdot mol^{-1}$					
(Methyl pentanoate (1) + methyl methanoate (2))	617	951	218	0	0.473	4
(Methyl pentanoate (1) + methanol (3))	−93	181	−479	0	0.310	1
(Methyl methanoate (2) + methanol (3))	−333	506	−923	0	0.656	2
	$Y_m^E = H_m^E / J \cdot mol^{-1}$					
(Methyl pentanoate (1) + methyl methanoate (2))	1006	1478	−248	0	0.506	3
(Methyl pentanoate (1) + methanol (3))	234	11839	−27845	29462	0.352	20
(Methyl methanoate (2) + methanol (3))	2339	6590	−12460	14111	0.695	11

the ratio k^{j-i} and fix for the property under study. One method that can be used is to calculate the parameter k^{j-i} by considering it to be the quotient of normalized values of Van der Waals volumes for the case of k_v^{j-i} mentioned previously, and of surfaces for the case of the own parameter of H_m^E , k_h^{j-i} . The simplest approach is to propose that the molecule generates a spherical envelope in its Brownian motion, resulting in a geometric ratio of surface/volume. Therefore, it is useful to identify the ratio, for example, with the parameters calculated by Bondi's method [28], which, in turn, are normalized values corresponding to the Van der Waals surface and volume, see table S1 (supplementary material), as shown below:

$$\left[\frac{\text{surface}}{\text{volume}} \right]_{\text{geometric}} = \left[\frac{\text{surface}}{\text{volume}} \right]_{\text{theoretical}}, \quad (3)$$

$$\left[\frac{S_i}{V_i} \right]_{\text{geometric}} = \left[\frac{q_i}{(r_i)^{2/3}} \right]_{\text{theoretical}}$$

For two substances $i - j$:

$$k_h^{j-i} = \frac{S_i}{S_j} = \frac{q_i}{q_j} \cdot \left(\frac{r_j V_i}{r_i V_j} \right)^{2/3} = k_q^{j-i} \left(\frac{k_v^{j-i}}{k_r^{j-i}} \right)^{2/3} \quad (4)$$

this corresponds to a correction of theoretical ratios k_q and k_r , since these parameters themselves do not take into account changes in temperature, nor do they vary with the regioisomers. Another method proposed in the literature to obtain these ratios directly is that suggested by Connolly [29,30], in which molecular surface and volume are calculated independently. Table S1 records the values obtained for pure components and the k^{j-i} values for the binaries studied, showing the numerical similarity among the values obtained by different methods. The methodology proposed by us above presents minor differences with the Bondi parameters method, with the advantage that the temperature variations and differences between regioisomers are considered.

In the treatment of the ternary, a previous consideration is taken into account, that the values of k_v^{j-i} and k_h^{j-i} for the three binaries are not independent, in each property obeying the relationships: $k_v^{3-2} k_v^{2-1} = k_v^{3-1}$ and $k_h^{3-2} k_h^{2-1} = k_h^{3-1}$.

Experimental data of the binaries are correlated with equation (1), using a non-linear regression procedure that optimizes the following objective function (OF):

$$OF = s(Y_{m,i}^E) = \left[\sum_i (Y_{m,i,\text{exp}}^E - Y_{m,i,\text{cal}}^E)^2 / (N - 1) \right]^{0.5} \quad (5)$$

To obtain an expression that is applicable to the ternaries, the origins of equation (1) must be considered. This corresponds to a generalization for multicomponent systems, comprised by n substances, which generate a recurrent expression that condenses in:

$$Y_{m,i}^E = \sum Y_{m,n-1,N}^{E(i_1-i_2-i_3 \dots i_{n-1})} + T_n \cdot P_N, \quad (6)$$

where N is the order of the molecular interaction considered and the term $Y_{m,n-1,N}^{E(i_1-i_2-i_3 \dots i_{n-1})}$ represents the partial contribution of the excess property Y_m^E owing to the interaction of $(n - 1)$ different species to a maximum order of interaction N . On the contrary, each

TABLE 6

Experimental densities $\rho/(\text{kg} \cdot \text{m}^{-3})$ and excess molar volumes $10^9 \cdot V_{m,123}^E/\text{m}^3 \cdot \text{mol}^{-1}$ for the ternary mixture (x_1 methyl pentanoate + x_2 methyl methanoate + x_3 methanol) obtained at $T = 298.15$ K and atmospheric pressure.

x_1	x_2	$\rho/\text{kg} \cdot \text{m}^{-3}$	$10^9 \cdot V_{m,123}^E/\text{m}^3 \cdot \text{mol}^{-1}$	x_1	x_2	$\rho/\text{kg} \cdot \text{m}^{-3}$	$10^9 \cdot V_{m,123}^E/\text{m}^3 \cdot \text{mol}^{-1}$
$x'_1 = 0.2442$							
0.0000	1.0000	966.28	0	0.0949	0.6112	915.09	28
0.0097	0.9605	961.26	–11	0.1189	0.5130	902.25	35
0.0190	0.9224	956.25	–9	0.1417	0.4194	890.13	35
0.0352	0.8557	947.43	–3	0.1560	0.3609	882.62	31
0.0480	0.8035	940.51	3	0.1679	0.3122	876.39	26
0.0595	0.7561	934.22	11	0.1890	0.2261	865.47	13
0.0716	0.7069	927.72	16	0.2055	0.1583	856.93	–2
0.0827	0.6611	921.67	22	0.2177	0.1083	850.65	–13
$x'_1 = 0.4031$							
0.0000	1.0000	966.28	0	0.2057	0.4898	901.41	109
0.0209	0.9481	958.88	15	0.2182	0.4586	898.04	106
0.0418	0.8963	951.68	31	0.2597	0.3558	887.35	86
0.0585	0.8548	945.98	47	0.3020	0.2508	877.03	54
0.0769	0.8093	939.94	60	0.3225	0.1999	872.27	31
0.1018	0.7475	931.91	79	0.3436	0.1476	867.43	11
0.1121	0.7218	928.62	88	0.3570	0.1143	864.43	–4
0.1451	0.6401	918.60	104	0.3788	0.0603	859.62	–26
0.1802	0.5529	908.44	111				
$x'_1 = 0.5922$							
0.0000	1.0000	966.28	0	0.3563	0.3983	895.80	151
0.0320	0.9460	957.92	32	0.3806	0.3573	892.49	135
0.0630	0.8936	950.16	68	0.4481	0.2433	883.90	81
0.0980	0.8345	941.91	107	0.4179	0.2943	887.60	110
0.1213	0.7952	936.81	124	0.4692	0.2077	881.36	64
0.1456	0.7542	931.64	145	0.4909	0.1710	878.87	41
0.1793	0.6972	924.89	165	0.5292	0.1064	874.57	8
0.2438	0.5883	913.16	182	0.5521	0.0677	872.10	–14
0.2970	0.4985	904.50	178	0.5610	0.0527	871.23	–30
0.3199	0.4598	901.04	169				
$x'_1 = 0.7818$							
0.0000	1.0000	966.28	0	0.3973	0.4918	905.54	260
0.0506	0.9353	955.31	75	0.4191	0.4639	903.40	255
0.0785	0.8996	949.82	110	0.4848	0.3799	897.52	223
0.1181	0.8489	942.53	157	0.5488	0.2980	892.37	180
0.1753	0.7758	933.10	209	0.5893	0.2462	889.40	145
0.2286	0.7076	925.27	246	0.6185	0.2089	887.35	120
0.2836	0.6372	918.11	263	0.6698	0.1433	884.00	66
0.3239	0.5857	913.33	269	0.7028	0.1010	881.92	34
$x'_1 = 0.8879$							
0.0000	1.0000	966.28	0	0.4309	0.5092	907.81	277
0.0473	0.9461	956.79	68	0.4743	0.4597	904.27	266
0.0928	0.8943	948.38	142	0.5584	0.3639	898.15	230
0.1403	0.8402	940.79	188	0.6482	0.2616	892.48	173
0.2139	0.7564	930.50	240	0.6933	0.2103	889.95	135
0.2638	0.6995	924.38	264	0.7383	0.1590	887.59	92
0.3317	0.6222	916.97	283	0.7692	0.1238	886.03	64
0.3953	0.5497	910.90	282	0.8152	0.0714	883.80	24

Uncertainties u are: $u(T) = \pm 0.01$ K, $u(\rho) = \pm 0.02$ kg \cdot m $^{-3}$, $u(x) = \pm 0.0005$, $u(10^9 \cdot V_{m,123}^E) = \pm 5$ m $^3 \cdot$ mol $^{-1}$. x_1 o x_2 : mixing compositions referenced to compound 1 or 2, respectively. x'_1 : composition of compound 1 in the pseudobinary. ρ : density of ternary mixture. $V_{m,123}^E$: excess volumes for ternary mixture.

of these excess quantities can be reduced, in turn, to the $Y_{m,n-1,N}^E$ and reach the corresponding binary interactions. The term $T_n \cdot P_N$ essentially represents the multiple product of the *active fractions* of the n substances and a polynomial, for which the degree is determined by N . The general form of T_n , expressed in terms of the *active fractions* z_i , using a generalized form of expression (2), becomes:

$$T_n = \frac{\prod_{i=2}^n k_{i1} \prod_{i=1}^n x_i}{[x_1 + \sum_{i=2}^n k_{i1} x_i]^n} \quad (7)$$

for the case that concerns us here, with $n = 3$ an interactional order of 4 or 5 appears to be sufficient. By considering the terms corresponding to the $Y_{m,2,5}^{E(i-j)}$ of equation (6), it is necessary to take into account the contributions due to the possible combinations $C^*(3,2)$ of three substances taken two by two, $i - j$, using

interactions of up to the fifth-order to reproduce the tendency of the properties obtained by experimentation. By applying model (6), and the term T_n of the equation (7), to the case of a ternary with the specified number of interactions, we obtain the following expression:

$$Y_{m,2,5}^E = \sum_{m,2,5} Y_{m,2,5}^{E(i_1-i_2-i_3 \dots -i_{n-1})} + z_1 z_2 z_3 (C_0 + C_1 z_1 + C_2 z_2 + C_3 z_1^2 + C_4 z_2^2 + C_5 z_1 z_2). \quad (8)$$

Optimization of the C_i parameters is carried out by a non-linear procedure, analogous to that used in adjustment of the binaries, and using the same OF as that used for the binaries. In this work it was necessary to consider a high degree of interaction (fifth order) due to the complex distribution of experimental points

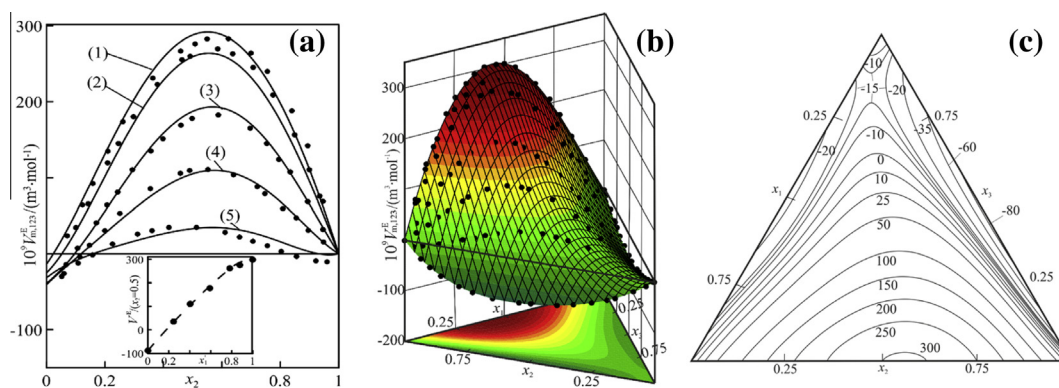


FIGURE 2. Plot of excess volumes for ternary solutions formed by: methyl pentanoate (MP), methyl methanoate (MM), methanol (MOH). (a) Projections of experimental $V_{m,123}^E$ values and correlation curves on the x_2 - $V_{m,123}^E$ plane obtained for different constant ratios x_1/x_3 [(1) 7.92; (2) 3.58; (3) 1.45; (4) 0.68; (5) 0.32]. Inset represents the regular variation of equimolar (at $x_2 = 0.5$) $V_{m,123}^E$ values as function of x_1 . (b) 3D-plot for the surface $V_{m,123}^E = V_{m,123}^E(x_1, x_2, x_3)$ obtained by equation (8) and the corresponding experimental values $V_{m,123}^E$ obtained for the ternary at $T = 298.15$ K. (c) Isolines corresponding to the horizontal projections of the surface of $V_{m,123}^E = V_{m,123}^E(x_1, x_2, x_3)$ represented in (b) for constant values of $V_{m,123}^E$ which are indicated by the labels in $10^3 \cdot \text{m}^3 \cdot \text{mol}^{-1}$.

TABLE 7

Coefficients C_i of equation (8) and standard deviation $s(V_m^E)$ obtained in the correlation of mixing properties for the ternary (methyl pentanoate (1) + methyl methanoate (2) + methanol (3)) at $T = 298.15$ K.

Property	k^{-1}	k^{-3}	C_0	C_1	C_2	C_3	C_4	C_5	$s(V_m^E)$
$10^3 \cdot V_{m,123}^E$	0.473	0.310	1674	-46388	-52421	23604	34995	76439	10
$H_{m,123}^E$	0.506	0.352	35613	-123531	-85039	142709	96878	180734	25

resulting from different interactional effects. In previous work, with solutions containing esters and alkanes, an interaction degree of fourth order was considered sufficient.

3.1. Excess volumes

Representations of (x, V_m^E) data by curves corresponding to the binaries in study, obtained with equation (1) and the coefficients resulting from applying the afore-mentioned procedure, table 5, are shown, respectively, in figure 1(a). Regarding the volumetric analysis, it is noteworthy that solutions of (methyl pentanoate (1) + methyl methanoate (2)) present expansive effects $V_m^E > 0$, which are three times higher in absolute value than those of (methyl methanoate (2) + methanol (3)) and six times higher than those of (methyl pentanoate (1) + methanol (3)), see figure 1(c). The appearance of weak interactions, see also enthalpic results, together with steric impediments owing to the size differences between the hydrocarbon chains of the two esters, are reflected in higher volumetric expansions. By contrast, the volumetric effects of the binaries (methyl esters + methanol) give rise to contractions, with $V_m^E < 0$, which increase (decrease in absolute value) with the alkanolic chain length of ester, being $(dV_m^E/du)_{p,T} > 0$. These observations suggest the presence of molecular aggregates in the systems chosen. A study was found in the literature [20] for the system (methyl methanoate (2) + methanol (3)) at $T = 298.15$ K, for which the V_m^E data are represented in figure 1(a). In the comparison, it can be observed that our values are clearly asymmetrical to those reported by Polak and Lu, although the correlation curve in their paper is quite similar to ours; this would suggest that the molar fraction of the data presented by these authors is incorrect.

The densities of the ternaries (methyl pentanoate (1) + methyl methanoate (2) + methanol (3)) were measured as described in Section 2.2. Binary mixtures of the methyl methanoate with 5

pseudocompounds are produced by synthetically mixing the two remaining products at predetermined compositions x_1' . Table 6 collects the direct experimental data (x_1, x_2, ρ) and the calculated values of $V_{m,123}^E$. Slight volumetric contractions are observed in the areas corresponding to low ester composition, arising from the reduction in V_m^E values resulting in the mixed of the two binaries of (methyl alkanooate + methanol), see figure 2(a). The inset figure represents the change in $V_{m,123}^E$ (at $x_2 = 0.5$) as a function of the composition of the five pseudobinaries x_1' , with a quasi-linear relation. This variation is justified by the relative increase in methyl pentanoate in the ternary solution.

The mathematical treatment of volumes in the ternary was done by applying equation (8). The C_i coefficients are shown in table 7, together with the standard deviations, OF defined by equation (5). The surface $V_m^E = V_m^E(x_1, x_2, x_3)$ generated by equations (1) and (8), using the k_v^{j-i} of the corresponding $i - j$ pair, is represented in 3D in figure 2(b). The correlation curve shown in Figure 2(a) represents the projection of this surface on the plane x_2 - $V_{m,123}^E$. Figure 2(c) shows the isolines of different $V_{m,123}^E$ projected on the compositions-plane. It can be observed that this amount does not increase monotonously as the composition of methanol in the solution diminishes. There is a local minimum in the interior of the surface at values around $x_1 \approx x_2 \approx 0.1$ for both esters, and a high methanol concentration, shown by a confluence of level curves at the specified composition. As mentioned previously, there are contractive effects in the regions close to the binaries of methyl esters with methanol, in the superior vertex of the triangular representation of figure 2(c).

3.2. Excess enthalpies

Experimental values of (x_1, H_m^E) for the three binaries studied here, measured at $T = 298.15$ K, are recorded in table 4 and their representations are shown in figure 1(b). All the processes are

TABLE 8

Excess enthalpies $H_m^{E(2-1,3)}/J \cdot mol^{-1}$ for the pseudobinary mixtures whose composition is indicated and excess enthalpies, $H_{m,123}^E/J \cdot mol^{-1}$, for the ternary (methyl pentanoate (1) + methyl methanoate (2) + methanol (3)) measured at $T = 298.15$ K and atmospheric pressure.

x_1	x_2	$H_m^{E(2-1,3)}/J \cdot mol^{-1}$	$H_{m,123}^E/J \cdot mol^{-1}$	x_1	x_2	$H_m^{E(2-1,3)}/J \cdot mol^{-1}$	$H_{m,123}^E/J \cdot mol^{-1}$
$x'_1 = 0.2231$							
0.0335	0.8498	647	750	0.0925	0.5855	1069	1353
0.0343	0.8463	695	800	0.1068	0.5214	1046	1373
0.0377	0.8312	746	861	0.1232	0.4480	978	1356
0.0416	0.8135	806	934	0.1387	0.3785	876	1301
0.0469	0.7900	868	1012	0.1555	0.3032	741	1218
0.0532	0.7618	928	1091	0.1730	0.2249	583	1113
0.0606	0.7286	983	1169	0.1900	0.1488	376	958
0.0693	0.6898	1033	1245	0.2056	0.0788	172	802
0.0799	0.6421	1063	1308				
$x'_1 = 0.3631$							
0.0804	0.7786	736	943	0.2042	0.4377	858	1383
0.0881	0.7574	781	1008	0.2281	0.3719	788	1374
0.0977	0.7310	826	1077	0.2507	0.3096	702	1347
0.1098	0.6977	871	1153	0.2711	0.2533	598	1294
0.1249	0.6561	905	1226	0.2968	0.1827	448	1211
0.1419	0.6092	923	1288	0.3231	0.1102	276	1107
0.1602	0.5588	926	1338	0.3461	0.0468	121	1011
0.1811	0.5012	906	1372				
$x'_1 = 0.4619$							
0.0987	0.7864	644	864	0.2401	0.4802	802	1338
0.1091	0.7638	687	931	0.2644	0.4275	762	1353
0.1218	0.7363	729	1001	0.2909	0.3702	703	1353
0.1363	0.7049	768	1072	0.3214	0.3042	612	1330
0.1529	0.6690	801	1142	0.3518	0.2383	497	1283
0.1720	0.6276	825	1209	0.3828	0.1712	361	1216
0.1930	0.5821	835	1266	0.4143	0.1030	216	1141
0.2163	0.5317	827	1310	0.4412	0.0448	87	1072
$x'_1 = 0.4848$							
0.1103	0.7725	654	892	0.2691	0.4449	757	1337
0.1216	0.7492	691	953	0.3085	0.3637	665	1330
0.1342	0.7232	742	1031	0.3509	0.2762	536	1292
0.1538	0.6827	784	1116	0.3939	0.1875	377	1226
0.1766	0.6357	809	1190	0.4331	0.1067	213	1146
0.2012	0.5850	823	1257	0.4617	0.0477	89	1084
0.2328	0.5198	809	1311				
$x'_1 = 0.6623$							
0.1668	0.7482	553	809	0.3523	0.4680	671	1211
0.1844	0.7216	594	877	0.4046	0.3891	621	1241
0.2077	0.6864	633	951	0.4580	0.3084	538	1240
0.2362	0.6434	663	1025	0.5182	0.2175	419	1214
0.2689	0.5940	681	1093	0.5693	0.1404	297	1170
0.3063	0.5375	688	1158	0.6206	0.0629	163	1115
$x'_1 = 0.7786$							
0.2334	0.7002	465	718	0.4889	0.3721	444	973
0.2615	0.6641	492	775	0.5529	0.2898	374	972
0.2953	0.6207	511	831	0.6205	0.2030	277	948
0.3339	0.5711	520	881	0.6870	0.1176	162	905
0.3808	0.5109	514	926	0.7469	0.0407	57	865
0.4322	0.4449	489	957				

Uncertainties u are: $u(T) = \pm 0.01$ K, $u(x) = \pm 0.0005$, and $u_e(H_{m,123}^E) = 0.02$. x_1 o x_2 : mixing compositions referenced to compound 1 or 2, respectively. x'_1 : composition of compound 1 in the pseudobinary. $H_{m,123}^E$: excess enthalpy for ternary mixture. $H_m^{E(2-1,3)}$: excess enthalpy for the binary formed by the compound 2 and the pseudobinary (methyl pentanoate (1) + methanol (3)).

endothermic, with $H_m^E > 0$, but quantitatively different because of the type of interactions taking place. In addition to the results for the binaries (methyl-ester + methanol), those obtained for (ester + ester) binaries are also of interest, see figure 1(b), with a maximum close to $400 J \cdot mol^{-1}$ in the case of (methyl pentanoate (1) + methyl methanoate (2)). In figure 1(c), the equimolar H_m^E of these systems are compared with others previously published and those obtained additionally to explain the behavior of the mixtures, although not formed part of this work. It can be observed that the increase in ester chain, R_1COO-R_2 , both the acid part R_1 or the alkanolic R_2 , weaken the (dipole + dipole) interactions, with a resulting drop in the H_m^E values. This decrease also occurs with

systems of (esters + alkanols), as shown in figure 1(b). The H_m^E data for the binary (methyl methanoate (2) + methanol (3)) differ from those presented by other authors [21] by around $150 J \cdot mol^{-1}$; the numerical values in that cited study are similar to those given for the binary (methyl pentanoate (1) + methanol (2)). The data were correlated with equation (1) using the parameter k_h^{i-1} established by equation (4), with a good quality of fit.

Because of possible relevance of these binaries in some of the processes indicated in the introduction, the H_m^E were estimated by the UNIFAC method [22]. As can be observed in figure 1(b), the estimation of that property for (ester + ester) system is contrary to real values, with the distribution adopting a sigmoidal

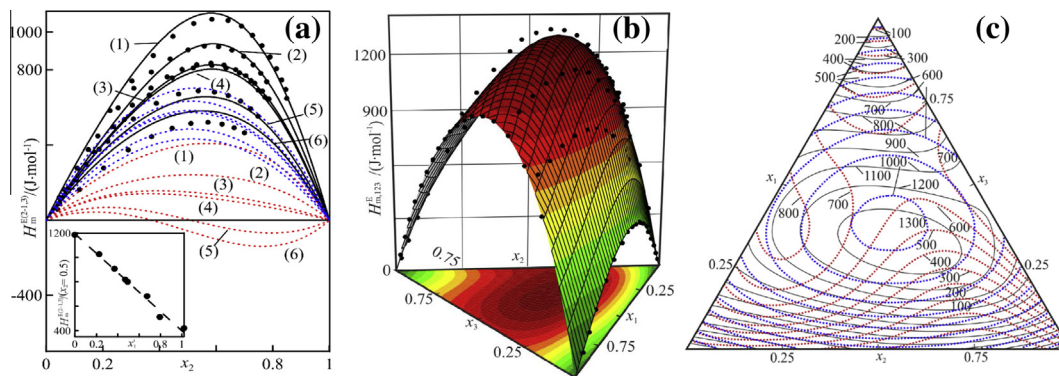


FIGURE 3. Plot of excess enthalpies for ternary solutions formed by: methyl pentanoate (MP), methyl methanoate (MM), methanol (MOH). (a) Plot of $H_m^{E(2-1,3)}$ obtained by addition of MM (2) on the binary MP + MOH (1,3) whose compositions are: (1) $x_1' = 0.223$, (2) $x_1' = 0.363$, (3) $x_1' = 0.462$, (4) $x_1' = 0.485$, (5) $x_1' = 0.6623$, (6) $x_1' = 0.7786$. Inset represents the regular variation of equimolar (at $x_2 = 0.5$) $H_m^{E(2-1,3)}$ values as function of x_1' . (b) 3D-Plot for the surface $H_m^{E(2-1,3)} = H_{m,123}^E(x_1, x_2, x_3)$ obtained by equation (8) and the corresponding experimental values $H_{m,123}^E$ obtained for the ternary at $T = 298.15$ K. (c) Isolines corresponding to the horizontal projections of the surface of $H_{m,123}^E = H_{m,123}^E(x_1, x_2, x_3)$ represented in (b) for constant values of $H_{m,123}^E$ which are indicated by the labels in $J \cdot mol^{-1}$. (•••••) Excess enthalpies by UNIFAC [22], (•••••) excess enthalpies by UNIFAC [recalculated].

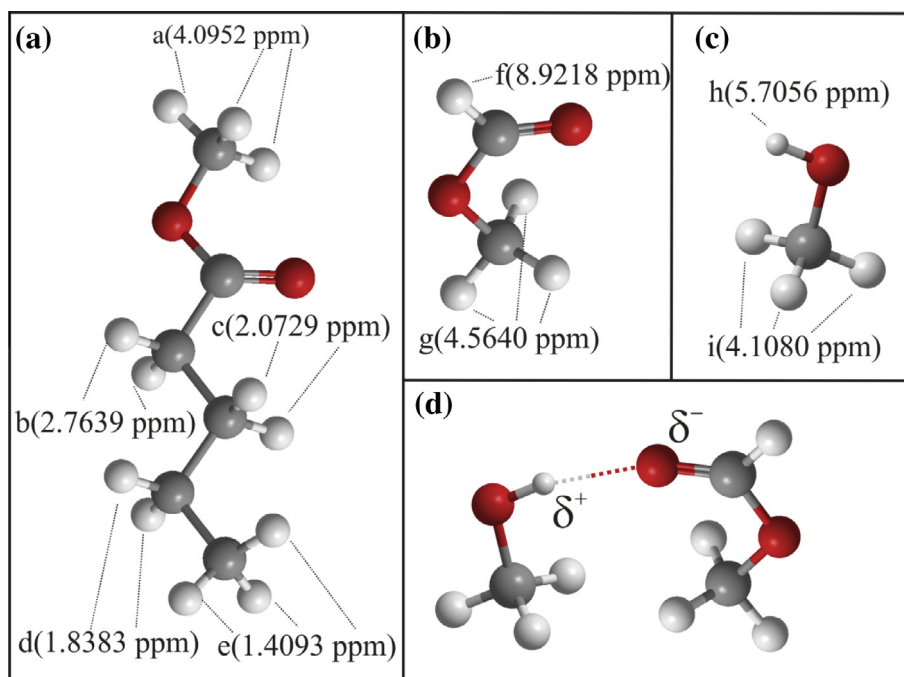


FIGURE 4. Molecular representation of pure compounds indicating the identifiers of the protons. In brackets the chemical shifts, δ /ppm, of each proton are indicated (CH₂ and CH₃ groups are indicated with an average value). (a) methyl pentanoate, (b) methyl methanoate, (c) methanol, (d) heteroassociation between (methyl methanoate (2) + methanol (3)).

form. The theoretical representation of the H_m^E for the (methyl ester + methanol) is not acceptable either, giving values 30% lower than experimental values, as the model does not take into account the acid chain length of the methyl alkanoate. The results suggest that the group contribution model must consider the specific interaction, since in some cases is quantitatively significant.

Table 8 shows the experimental data for the ternary ($x_1, x_2, H_{m,123}^E$) measured at $T = 298.15$ K, also showing the specific net energetic effect $H_m^{E(2-1,3)}$ resulting from adding methyl methanoate (2) to the pseudocompound, which is a synthetic solution of (methyl pentanoate (1) + methanol (3)); from which, six different solutions were prepared x_1' . Figure 3(a) shows a graphical

representation of that effect, for which $H_m^{E(2-1,3)} > 0$, in all cases. The inset figure shows that the variation in these enthalpic effects (at $x_2 = 0.5$) with the composition of the pseudocompound x_1' is quasilinear, with a negative slope, opposed to the volumes, see figure 2(a). Finally, the global numerical values of the ternary $H_{m,123}^E$, are calculated by

$$H_{m,123}^E = H_m^{E(2-1,3)} + (x_1 + x_3)H_{m,x_1=x_1'}^{E(1,3)}, \quad (9)$$

where $H_{m,x_1=x_1'}^{E(1,3)}$ is the mixing enthalpy of the binary (methyl pentanoate (1) + methanol (3)) at each composition x_1' obtained by interpolation of the correlation function calculated previously

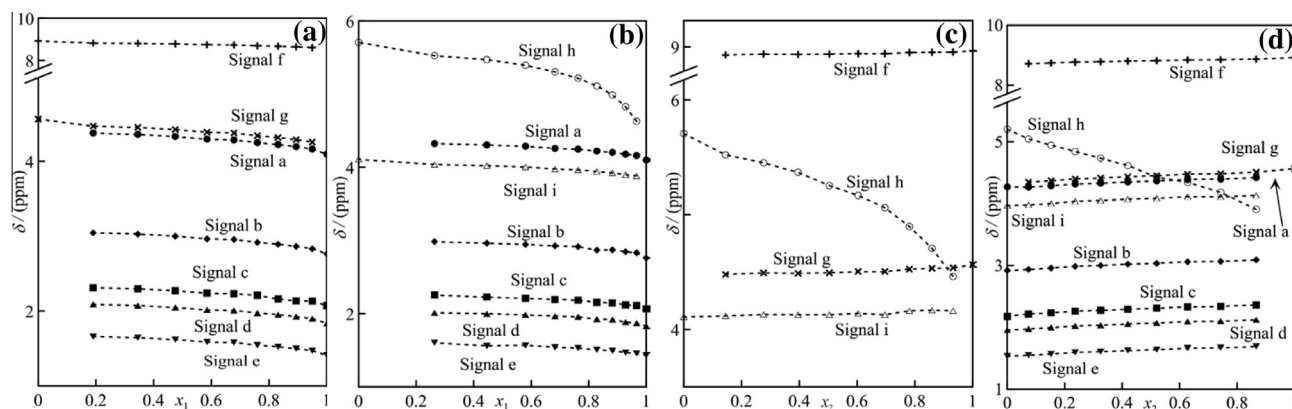


FIGURE 5. Chemical shifts δ /(ppm), obtained by ^1H RMN, for the binary solutions: (a) (methyl pentanoate(1) + methyl methanoate (2)), (b) (methyl pentanoate (1) + methanol (3)), (c) (methyl methanoate (2) + methanol (3)), and for the ternary (d) (methyl pentanoate (1) + methyl methanoate (2) + methanol (3)). The identifiers of each proton/protons are the corresponding to those indicated in figure 4. (●) signal a, (◆) signal b, (■) signal c, (▲) signal d, (▼) signal e, (+) signal f, (×) signal g, (○) signal h, (△) signal i.

for the binary 1–3 (equation (1)). Data for the ternary, shown in table 8, are positive and are correlated with equation (8), using for the binary contributions (corresponding to the first summand $H_{m,2.5}^E(i_1-i_2-i_3-\dots-i_{n-1})$ of equation (8)), the equation (1) and the coefficients exposed in table 5. The C_i coefficients of the ternary are determined as described previously, see table 7. Although the quality of fit is considered to be acceptable, some differences are observed in figure 3(a) with experimental values. Figure 3(b) shows the surface $H_{m,123}^E = H_{m,123}^E(x_1, x_2, x_3)$ represented by function (8) obtained in the fit, with an absolute maximum in the interior ($x_1 = 0.204$, $x_2 = 0.438$), reflected by the presence of closed isenthalpics that appear in the triangular diagram of figure 3(c).

The UNIFAC group contribution model transfers the errors made in the binary estimation, already discussed, resulting in inadequate predictions, as shown by the isolines (in red) of the triangular representation.

4. ^1H NMR spectral analysis

A ^1H NMR spectral study was carried out and the chemical shifts δ of protons were observed, for the different compounds studied. The values of these are recorded on the corresponding structures of figure 4(a) to (c), which also shows the characteristic identifier for each signal. Similarly, the corresponding study was also conducted for the binary and ternary mixtures, at known compositions, and the results are shown in figure 5(a) to (d). Diamagnetic or paramagnetic shifts $\Delta\delta$ versus composition for the binary of the two methyl alkanoates (figure 5(a)) are weak, associated with a slight change in polarity of the medium. The two solutions of (methyl ester + methanol), figure 5(b) and (c), show, respectively, small diamagnetic and paramagnetic shifts as the composition of the ester increases, justified by the increase in polarity mentioned, and the anisotropies of the $-\text{COO}-$ groups. In the same figures it can be observed that the hydroxylic proton of methanol presents significantly pronounced diamagnetic shifts ($\Delta\delta$) with the alkanoate composition (signal h), related to an effect of hydrogen bond heteroassociation $\text{OH}\cdots\text{OOC}$, see figure 4(d). This binding is weak compared to the autoassociation of the alkanol molecules, shifting toward greater intensities of magnetic field (reduction of δ).

The ternaries were measured for a constant ratio (methyl pentanoate + methanol), generating a pseudocompound, as indicated previously in the determination of properties, to which known quantities of methyl methanoate were added later. The results of

the chemical shifts are shown in figure 5(d) relative to the composition x_2 , of the methyl methanoate. As expected, the signal of all the protons is transferred (note the slight increase in paramagnetic shifts) as the methanoate composition increases. The exception to this is seen by the signal corresponding to the proton of $-\text{OH}$ of alkanol that does so diamagnetically (signal h), partially attributable to the anisotropy of the carbonyl group (see figure 5(d)). The chemical shift in the ternary can be observed to be quantitatively inferior to that of both binaries (figure 5(b) and (c)), reflecting a weaker heteroassociation effect compared to the binaries.

5. Conclusions

The properties of H_m^E and V_m^E have been determined experimentally for the ternary comprised of two methyl alkanoates (methanoate and pentanoate) and methanol, and for the corresponding binaries. The data obtained have given rise to the following discussions and conclusions, depending on the nature of the compounds in the solutions.

5.1. (Ester + Ester)

The mixing process of methyl pentanoate with methyl methanoate produces $H_m^E > 0$ and $V_m^E > 0$, mainly resulting from the (dipole + dipole) interactions and the rupture of the hydrogen bonds of the methyl methanoate (autoassociation). Figure 1(c) collects some equimolar H_m^E values using other binaries (ethyl alkanoates) different to those from this work. All this will be the subject of future research. Using the UNIFAC method HCOO/COOC interactions were calculated (distinguishing between the ethanoate and non-ethanoate groups) substantially modifying the representation of the model, see figure 1(b) for the (methyl pentanoate (1) + methyl methanoate (2)) mixture. Obviously, the values found affected positively in the estimation of the energetic interaction of the ternary, as shown in figure 3(c). In summary, the group contribution method should be adequately modified to evaluate the different interactions when compounds of the same chemical nature give place to specific interaction. Spectral data obtained with ^1H NMR are coherent with these deductions since, as the amount of pentanoate is reduced, the paramagnetic shifts of the signal are partly due to the decreased polarity of the solution. The weaker interactions, together with the impediment due to the size of the acid chain of the methyl pentanoate, cause empty

spaces to appear between the molecules in the solution, giving rise to volumetric expansions in these mixtures.

5.2. (Ester + Alkanol)

In the binaries of (methyl methanoate or methyl pentanoate + methanol), the volumetric effects of contraction are noteworthy, and the energetic effects resulting from the mixing process, which in this case would be the algebraic sum of positive (endo) and negative (exo) energetic interactions, the latter characteristic of an aggregation process or a molecular heteroassociation in the final solution. The spectral study by ^1H NMR confirms this grouping by showing the formation of pseudo-hydrogen bonds, which are weaker than those corresponding to the auto-association with alkanol. In figure 5(b), signal h (corresponding to the hydroxylic proton) presents a reduction in the chemical shift in the mixture of (methyl pentanoate (1) + methanol (3)), while in figure 5(c), the slope ($d\delta/dx_1$), corresponding to (methyl methanoate (2) + methanol (3)) is greater than in the previous case, as to be expected. The UNIFAC model does not take into account the specific interactions of these mixtures.

5.3. (Ester + Ester + Alkanol)

In the ternary solution it is necessary to compute the interactions belonging to the pure components, and also those of the binaries. Moreover, the coexistence of molecules from three different species produces a synergy, with differences in the real thermodynamic quantities in the order of those to be expected by summing the effects of the binaries. Figures S1a and S1b (supplementary material) represent, respectively, the values of $\Delta V_{m,123}^E$ and $\Delta H_{m,123}^E$, which, mathematically, correspond to the last summand of equation (8). These quantities constitute the individual contribution in each of the specified quantities ($V_{m,123}^E$ and $H_{m,123}^E$) due to the simultaneous presence of three components. Hence, the contribution of $\Delta V_{m,123}^E$ to the global volumetric effect is small and, generally, positive and decreases with increasing composition of methyl pentanoate, to reach even negative values (see figure S1a). However, the specific contribution of $\Delta H_{m,123}^E$ to the overall energetic calculation is more significant (see figure S1b) and, in most cases, corresponds to 11% of the total amount. This is reflected in an internal maximum in the function $H_{m,123}^E = H_{m,123}^E(x_1, x_2, x_3)$, see figure 3(c).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jct.2015.02.019>.

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