

Orientalional and steric effects in linear alkanooates + *N*-Alkane mixtures

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ABSTRACT

The $\text{CH}_3(\text{CH}_2)_n\text{COO}(\text{CH}_2)_m\text{CH}_3$ + *n*-alkane mixtures have been investigated on the basis of an experimental database containing effective dipole moments of esters, and excess molar functions of the systems: enthalpies (H_m^E), volumes (V_m^E), isobaric heat capacities (C_{pm}^E) and isochoric internal energies (U_{vm}^E) and by means of the application of the Flory model and the Kirkwood-Buff formalism. The situation of the mixtures within the G_m^E (excess molar Gibbs energy) vs. H_m^E diagram has also been briefly considered. Results indicate that dispersive interactions are dominant and that steric effects can explain some differences between solutions containing heptane and isomeric esters. Proximity and orientational effects are also discussed in diester + hexane mixtures. In the case of systems with a given alkane and different isomeric polar compounds, orientational effects become weaker in the order: *n*-alkanone > dialkyl carbonate > *n*-alkanoate. Results from the Kirkwood-Buff formalism indicate that the number of ester-ester interactions decreases in systems with alkyl ethanoates when the alkyl size increases and that preferential solvation between polar molecules decreases as follows: dialkyl carbonate > *n*-alkanone > *n*-alkanoate.

1. Introduction

Esters are interesting compounds due to their many applications. It is well known that they are used in food and cosmetics industries where their pleasant odors and antifungal properties are important [1,2]. Bio-based polyesters, such as polyhydroxy alkanooates, are an alternative for petrochemical plastics since they can be synthesized by microbial cultures grown on renewable materials in clean environments [3–5]. On the other hand, monoalkyl esters of long chain fatty acids have gained interest as liquid biofuels in view of their great potential of CO₂ and SO₂ emission reductions [6–8].

Different versions of UNIFAC [9,10], DISQUAC [11,12] or the Nitta-Chao [13] models have been used for the theoretical characterization of *n*-alkanoate + alkane mixtures [14–19]. However, no systematic study is available in the literature about interactions in the mentioned solutions and on their structure. Such study is conducted in the present work by means of the Flory model [20] and the application of the formalism of the Kirkwood-Buff integrals [21–22]. Particularly, the considered esters are of the type $\text{CH}_3(\text{CH}_2)_n\text{COO}(\text{CH}_2)_m\text{CH}_3$: methyl alkanooates ($v = 0$; $u = 0-4$); ethyl ($v = 1$), propyl ($v = 2$) or butyl ($v = 3$) alkanooates ($u = 0-2$) and pentyl alkanooates ($v = 4$; $u = 0,1$). In addition,

proximity effects in systems with diesters are also investigated. This work is a continuation of previous research where the Flory model was applied for the study of mixtures containing the O and/or CO groups: ethers [23], or *n*-alkanones [24], or *n*-alkanals [24], or dialkyl carbonates [24,25] and alkanes. For the sake of comparison and in order to complete our study, the Kirkwood-Buff formalism has also been applied to some *n*-alkanone or dialkyl carbonate + heptane mixtures. Finally, it should be mentioned that, in the framework of the Flory model, some studies, mainly concerned with the correlation/prediction of excess molar volumes (V_m^E), of ester + alkane mixtures are available in the literature [15,26,27].

2. Theories

2.1. Flory model

A short summary of the essential hypotheses of the theory [20,28–30] can be encountered elsewhere [31]. The basic assumption of the model is that of random mixing. The Flory equation of state is:

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$$\frac{\widehat{P}\widehat{V}}{\widehat{T}} = \frac{\widehat{V}^{1/3}}{\widehat{V}^{1/3} - 1} - \frac{1}{\widehat{V}\widehat{T}} \quad (1)$$

where $\widehat{V} = V_m/V_m^*$, $\widehat{P} = P/P^*$ and $\widehat{T} = T/T^*$ are the reduced volume, pressure and temperature, respectively (V_m is the molar volume of the mixture). Equation (1) is valid for pure liquids and liquid mixtures. For pure liquids, the reduction parameters, V_m^* , P_i^* and T_i^* can be obtained from experimental data, such as density, α_{pi} (isobaric expansion coefficient) and κ_{Ti} (isothermal compressibility). Expressions for reduction parameters of mixtures have been given previously [31]. H_m^E values are determined from:

$$H_m^E = \frac{x_1 V_{m1}^* \theta_2 X_{12}}{\widehat{V}} + x_1 V_{m1}^* P_1^* \left(\frac{1}{\widehat{V}_{m1}} - \frac{1}{\widehat{V}} \right) + x_2 V_{m2}^* P_2^* \left(\frac{1}{\widehat{V}_{m2}} - \frac{1}{\widehat{V}} \right) \quad (2)$$

where all the symbols have their usual meaning [31]. The reduced volume of the mixture, \widehat{V} , is obtained from the equation of state. Therefore, the molar excess volume can be also calculated:

$$V_m^E = (x_1 V_{m1}^* + x_2 V_{m2}^*) (\widehat{V} - \varphi_1 \widehat{V}_{m1} - \varphi_2 \widehat{V}_{m2}) \quad (3)$$

2.2. Kirkwood-Buff integrals

In this formalism, the Kirkwood-Buff integrals are determined from [32,33]:

$$G_{ij} = \int_0^\infty (g_{ij} - 1) 4\pi r^2 dr \quad (4)$$

where, g_{ij} is the radial distribution function (probability of finding a molecule of species i in a volume element at the distance r of the center of a molecule of type j). Thus, g_{ij} provides information about the mixture structure at microscopic level. Values of G_{ij} can be interpreted as follows: positive values represent the excess of molecules of the type i in the space around a given molecule of kind j . That is, attractive interactions between molecules of i and j exist. Negative values of G_{ij} reveal that i - i and j - j interactions are predominant over i - j interactions [32,34]. The Kirkwood-Buff integrals can be derived from thermodynamic data such as chemical potential; partial molar volumes and isothermal compressibility factor. The resulting equations are [32,35]:

$$G_{ii} = RT\kappa_T + \frac{x_j \bar{V}_{mj}^2}{x_i V_m D} - \frac{V_m}{x_i} \quad (i, j = 1, 2) \quad (5)$$

$$G_{12} = G_{21} = RT\kappa_T - \frac{\bar{V}_{m1} \bar{V}_{m2}}{V_m D} \quad (6)$$

where R is the gas constant, x_i and \bar{V}_{mi} are the mole fraction and the partial molar volume of component i , respectively ($i = 1, 2$) and κ_T , the isothermal compressibility of the mixture. D is defined as:

$$D = 1 + \frac{x_1 x_2}{RT} \left(\frac{\partial^2 G_m^E}{\partial x_1^2} \right)_{P,T} \quad (7)$$

In this expression, G_m^E denotes the excess molar Gibbs energy. The G_{ij} integrals allow estimate the linear coefficients of preferential solvation [36]:

$$\delta_{ii}^0 = x_i x_j (G_{ii} - G_{ij}) \quad (8)$$

$$\delta_{ij}^0 = x_i x_j (G_{ij} - G_{ij})$$

which are useful quantities to determine the local mole fractions of the i species around the central j molecule [36].

3. Model calculations and results

Values of physical properties of n -alkanoates, required for calculations, are collected in Table 1. For other organic solvents considered, n -alkanes, n -alkanones and linear organic carbonates the values used have been taken from previous applications [25]. In order to calculate P_i^* , V_i^* , T_i^* ($i = A, B$) at $T \neq 298.15$ K, expressions provided in reference [37] for the temperature dependence of density, α_p and γ ($= \alpha_p/\kappa_T$) were used.

3.1. Flory

Table 2 lists values of the interaction parameter X_{12} determined from the corresponding experimental H_m^E results at equimolar composition and 298.15 K following the method provided in reference [38]. Table 2 also includes the relative standard deviations for H_m^E defined as:

$$\sigma_r(H_m^E) = \left[\frac{1}{N} \sum \left(\frac{H_{m,exp}^E - H_{m,calc}^E}{H_{m,exp}^E} \right)^2 \right]^{1/2} \quad (9)$$

where N is the number of experimental data points (see Figs. 1-2). Figure S1 (supplementary material) shows the concentration dependence of X_{12} for a few systems. Such dependence has been determined according to the method explained in detail elsewhere [39]. Results provided by the model on V_m^E are collected in Table S1.

3.2. Kirkwood-Buff integrals

In these calculations, isothermal compressibilities of the mixtures were determined from $\kappa_T = \Phi_1 \kappa_{T1} + \Phi_2 \kappa_{T2}$ (where $\Phi_i = x_i V_{mi} / (x_1 V_{m1} + x_2 V_{m2})$ is the volume fraction of the component i of the system), i.e., ideal behaviour is assumed). This is a typical approach, which has not influence on the final calculations of the Kirkwood-Buff integrals [40]. Along calculations, G_m^E values were determined from the DISQUAC model using interaction parameters from the literature [18,41,42]. Results on $\delta_{ij}^0 = x_i x_j (G_{ij} - G_{ij})$ are collected in Table 3 (Figs. 3a,3b), together with the source of experimental data on V_m^E used.

4. Discussion

4.1. $CH_3(CH_2)_u COO(CH_2)_v CH_3$ (1) + n -alkane(2)

4.1.1. Systems with heptane

H_m^E results of this type of mixtures are positive indicating that interactions between like molecules are dominant. On the other hand, H_m^E values decrease along a given homologous series ($u = \text{constant}$ when v increases, e.g.). This can be explained assuming that: (i) interactions between ester molecules become weaker, as it is suggested by the corresponding partial excess molar enthalpies at infinite dilution of the n -alkanoate, $H_{m1}^{E,\infty}$, which also decrease along each considered series (Table 4); (ii) increasing steric effects, since the COO group becomes more sterically hindered when the ester size increases, and this leads to a decrease of the number of ester-ester interactions in the system in comparison to that of pure n -alkanoates [43]. Such effects are the cause of the decrease of the enthalpic parameters when the quasichemical approximation of DISQUAC was applied to the systems under study [19]. In addition, it has been suggested that the decrease of H_m^E might also be due to long n -alkanoates can form quasi-cycles [43]. We note that ester-ester interactions are stronger for the mixture including methyl ethanoate ($u = 0, v = 0$), characterized by the highest $H_{m1}^{E,\infty}$ value (8.3 kJ mol⁻¹) [44]. In fact, systems formed by this ester and n -alkane show LLE curves with relatively high upper critical solution temperatures (UCST), 241.7 K for the mixture with octane [45]. Solid-liquid equilibria measurements also reveal partial miscibility for the ethyl ethanoate + n -alkane systems at lower temperatures [19]. For example,

Table 1
Physical constants and Flory parameters^a of pure compounds at $T = 298.15$ K.

compound	$V_{mi}/\text{cm}^3 \text{ mol}^{-1}$	$\alpha_{pi}/10^{-3} \text{ K}^{-1}$	$\kappa_{Ti}/10^{-12} \text{ Pa}^{-1}$	$V_{mi}^*/\text{cm}^3 \text{ mol}^{-1}$	$P_i^*/\text{J cm}^{-3}$
methyl ethanoate	79.82 ^b	1.42 ^b	1143 ^b	60.16	653.7
ethyl ethanoate	98.47 ^c	1.41 ^d	1191 ^c	74.26	620.7
propyl ethanoate	115.72 ^e	1.27 ^f	1094 ^f	88.98	585.4
butyl ethanoate	132.60 ^e	1.17 ^f	1029 ^f	103.47	556.8
pentyl ethanoate	149.39 ^e	1.15 ^c	995 ^c	117.9	527.0
methyl propanoate	96.92 ^b	1.31 ^b	1077 ^b	74.10	620.3
ethyl propanoate	115.48 ^g	1.3 ^g	1157 ^g	88.41	571.5
propyl propanoate	132.65 ^h	1.21 ^h	1070 ^h	102.89	650.4
butyl propanoate	149.42 ⁱ	1.14 ⁱ	990 ⁱ	117.13	558.7
methyl butanoate	114.42 ^b	1.22 ^b	1031 ^b	88.63	588.1
ethyl butanoate	133.01 ^k	1.17 ^k	1000 ^k	103.72	572.9
methyl pentanoate	131.30 ^l	1.14 ^l	969 ^l	102.92	570.8
ethyl pentanoate	149.52 ^k	1.08 ^k	1200 ^k	118.30	428.6
methyl hexanoate	148.05 ^b	1.08 ^b	944 ^b	117.13	545.0
diethyl oxalate	136.29 ^m	1.1 ^m	770 ^m	107.50	684.6
diethyl malonate	152.81 ^c	0.937 ^c	707 ^c	123.77	602.3
diethyl succinate	168.25 ⁿ	1.04 ⁿ	718 ⁿ	133.97	681.1
diethyl glutarate	184.81 ^o	0.87 ^o	619 ^o	151.43	624.1
diethyl adipate	201.88 ^p	0.96 ^p	693 ^p	163.71	608.5
diethyl pimelate	218.77 ^q	0.86 ^q	634 ^l	179.57	600.2
diethyl sebacate	269.36 ^r	0.87 ^r	663 ^l	220.71	582.7

^a V_{mi} , molar volume; α_{pi} , isobaric expansion coefficient; κ_{Ti} , isothermal compressibility, V_{mi}^* , P_i^* , reduction parameters for volume and pressure, respectively;

^b [26];

^c [82];

^d [60];

^e [83];

^f [84];

^g [85];

^h [86,87]

ⁱ [88];

^j estimated using the Manzini-Crescenzi method [89];

^k [90];

^l [91];

^m [92,93];

ⁿ [94];

^o [95,96];

^p [97];

^q [95];

^r [98]

the UCST for the heptane solution is ≈ 200 K [19]. The weakening of the ester-ester interactions may be due to the weakening of the dipolar interactions involved. The effective dipole moment $\bar{\mu}_i$ is a useful magnitude to evaluate the impact of polarity on bulk properties [46–48]. For a compound with dipole moment in gas phase μ_i , $\bar{\mu}_i$ is defined according to [48]:

$$\bar{\mu}_i = \left[\frac{\mu_i^2 N_A}{4\pi\epsilon_0 V_{mi} k_B T} \right]^{1/2} \quad (10)$$

where N_A is the Avogadro's number, ϵ_0 the permittivity of the vacuum and k_B the Boltzmann's constant. While for a given series, here linear alkanates, μ_i varies only slightly with the chain length (Table S2), $\bar{\mu}_i$ shows a much greater variation (Table S2). For example, for $u = 0$ (alkyl ethanoates) or $v = 0$ (methyl alkanates), $\bar{\mu}_i$ decreases when the size of the ester increases, indicating that the dipolar interactions become weaker. The experimental results of the isobaric excess molar heat capacities, C_{pm}^E , for methyl alkanate + heptane systems support this statement. Thus, the solution with methyl ethanoate shows a W-shaped C_{pm}^E curve with positive values at the central part of the concentration range ($0.91 \text{ J mol}^{-1} \text{ K}^{-1}$) [49]. This is a typical feature of mixtures that, at the working temperature, 298.15 K, are not far from the UCST [50]. The same trend is observed for the mixtures propanone + dodecane [51], or dimethyl carbonate (DMC) + octane, or + nonane [52]. For systems with longer methyl n -alkanoates, the ($C_{pm}^E/\text{J mol}^{-1} \text{ K}^{-1}$) results become more negative when the ester size increases: -0.29

(methyl propanoate); -0.75 (methyl octanoate) [49], and, similarly, -0.50 for the mixture with propyl butanoate [53]. Negative C_{pm}^E values are encountered in systems where dispersive interactions are dominant, e.g., benzene + n -alkane [54,55]. Inspection of Table 4 reveals that for a number of mixtures, the $H_{m1}^{E,\infty}$ values are quite similar (propyl, butyl propanoate or butanoate) and the same occurs for $\bar{\mu}_i$, while the H_m^E results are different. For example, $H_{m1}^{E,\infty}/\text{kJ mol}^{-1} \approx 4.4$ ($u=1, v=2$; $u=1, v=3$); $\bar{\mu}_i = 0.591$ ($u=1, v=2$); 0.562 ($u=1, v=3$) (Table 4) and $H_m^E/\text{J mol}^{-1} = 893$ ($u=1, v=2$) [56]; 758 ($u=1, v=3$) [57]. It suggests that structural effects may have a relevant impact on the H_m^E variation. In order to investigate this point, properties at constant volume are now considered, particularly the isochoric excess molar internal energy function, U_{Vm}^E , which can be obtained from the equation [47]:

$$U_{Vm}^E = H_m^E - T \frac{\alpha_p}{\kappa_T} V_m^E \quad (11)$$

where V_m^E is the excess molar volume, and α_p and κ_T are, respectively, the isobaric thermal expansion coefficient and the coefficient of isothermal compressibility of the considered system. The $T \frac{\alpha_p}{\kappa_T} V_m^E$ term describes the contribution from the equation of state (eos) term to H_m^E . If the needed data are not available, α_p and κ_T values can be calculated assuming that the mixtures behave ideally with regards to these properties. That is, $M^{id} = \Phi_1 M_1 + \Phi_2 M_2$; with $M_i = \alpha_{pi}$, or Such approximation is commonly acceptable. It is interesting to observe that $U_{Vm1}^{E,\infty}$ values are nearly constant for mixtures including alkyl propanoates ($u = 1$) with v

Table 2

Excess molar enthalpies, H_m^E , at equimolar composition and temperature T , for n -alkanoate (1) + n -alkane (2) mixtures. Values of the Flory interaction parameter, X_{12} , and of the relative standard deviations for H_m^E , $\sigma_r(H_m^E)$ (equation 9), are also included.

System	N^b	T/K	$H_m^E/J \text{ mol}^{-1}$	$X_{12}/J \text{ cm}^{-3}$	$\sigma_r(H_m^E)$	Ref.
methyl ethanoate + n -C ₇	15	298.15	1787	92.17	0.047	[14]
	18	318.15	1944	98.68	0.075	[99]
methyl ethanoate + n -C ₁₀	20	298.15	2062	100.56	0.084	[100]
methyl ethanoate + n -C ₁₂	21	298.15	2144	102.11	0.081	[59]
methyl ethanoate + n -C ₁₄	21	298.15	2363	110.44	0.113	[101]
methyl ethanoate + n -C ₁₆	20	298.15	2429	111.09	0.150	[15]
ethyl ethanoate + n -C ₇	18	298.15	1510	66.93	0.080	[102]
	15	318.15	1523	66.48	0.080	[99]
ethyl ethanoate + n -C ₈	18	298.15	1609	69.62	0.026	[60]
ethyl ethanoate + n -C ₁₀	18	318.15	1623	69.37	0.036	[60]
	18	298.15	1691	70.56	0.044	[60]
ethyl ethanoate + n -C ₁₂	17	318.15	1757	72.79	0.066	[60]
	20	298.15	1727	76.30	0.080	[59]
propyl ethanoate + n -C ₆	17	298.15	1120	45.60	0.055	[43]
propyl ethanoate + n -C ₇	13	298.15	1199	46.95	0.032	[43]
	16	318.15	1223	47.20	0.129	[99]
propyl ethanoate + n -C ₈	14	298.15	1281	48.69	0.052	[43]
	16	318.15	1303	48.90	0.064	[103]
propyl ethanoate + n -C ₁₀	15	298.15	1416	51.49	0.068	[103]
	14	318.15	1454	52.41	0.059	[103]
butyl ethanoate + n -C ₇	21	298.15	980	34.81	0.061	[104]
	18	318.15	989	34.70	0.075	[99]
butyl ethanoate + n -C ₁₀	20	298.15	1174	38.24	0.060	[104]
butyl ethanoate + n -C ₁₂	19	298.15	1303	40.95	0.057	[104]
butyl ethanoate + n -C ₁₄	19	298.15	1422	43.54	0.054	[104]
pentyl ethanoate + n -C ₇	17	298.15	828	27.20	0.086	[105]
	18	318.15	881	28.59	0.098	[99]
pentyl ethanoate + n -C ₉	18	298.15	947	28.87	0.097	[105]
	15	298.15	1424	63.31	0.059	[14]
methyl propanoate + n -C ₇	19	318.15	1514	65.89	0.042	[62]
	20	298.15	1539	66.64	0.094	[106]
methyl propanoate + n -C ₈	20	298.15	1689	70.27	0.072	[100]
methyl propanoate + n -C ₁₀	20	298.15	1837	74.28	0.069	[107]
methyl propanoate + n -C ₁₂	19	298.15	1940	76.86	0.088	[101]
methyl propanoate + n -C ₁₄	20	298.15	2027	78.36	0.078	[15]
methyl propanoate + n -C ₁₆	21	298.15	1036	42.28	0.047	[63]
ethyl propanoate + n -C ₆	16	298.15	1127	44.29	0.065	[102]
	17	318.15	1153	44.66	0.048	[62]
ethyl propanoate + n -C ₇	20	298.15	1307	47.86	0.072	[108]
	20	298.15	1430	50.84	0.069	[108]

Table 2 (continued)

System	N^b	T/K	$H_m^E/J \text{ mol}^{-1}$	$X_{12}/J \text{ cm}^{-3}$	$\sigma_r(H_m^E)$	Ref.
ethyl propanoate + n -C ₁₄	22	298.15	1541	53.64	0.056	[63]
propyl propanoate + n -C ₆	18	298.15	821	30.57	0.099	[56]
	16	298.15	893	31.76	0.091	[56]
propyl propanoate + n -C ₇	17	318.15	907	31.84	0.061	[62]
	17	298.15	944	32.46	0.076	[56]
propyl propanoate + n -C ₈	18	298.15	1068	34.98	0.056	[56]
propyl propanoate + n -C ₁₀	18	298.15	1068	34.98	0.056	[56]
butyl propanoate + n -C ₇	18	298.15	758	24.89	0.100	[57]
butyl propanoate + n -C ₉	16	298.15	871	26.66	0.073	[57]
	17	298.15	1169	46.00	0.064	[14]
methyl butanoate + n -C ₇	18	298.15	1241	47.33	0.041	[106]
methyl butanoate + n -C ₈	18	298.15	1376	50.10	0.072	[100]
methyl butanoate + n -C ₁₀	19	298.15	1494	52.66	0.076	[107]
methyl butanoate + n -C ₁₂	18	298.15	1583	54.33	0.064	[101]
methyl butanoate + n -C ₁₄	20	298.15	1665	55.84	0.057	[15]
methyl butanoate + n -C ₁₆	16	298.15	931	33.01	0.051	[102]
ethyl butanoate + n -C ₇	17	298.15	1101	36.65	0.113	[102]
ethyl butanoate + n -C ₉	18	298.15	968	34.60	0.073	[14]
methyl pentanoate + n -C ₇	17	298.15	1019	35.11	0.074	[106]
methyl pentanoate + n -C ₈	18	298.15	1140	37.25	0.068	[100]
methyl pentanoate + n -C ₁₀	20	298.15	1249	39.33	0.071	[107]
methyl pentanoate + n -C ₁₂	19	298.15	1329	40.77	0.061	[101]
methyl pentanoate + n -C ₁₄	21	298.15	1409	42.00	0.057	[15]
methyl pentanoate + n -C ₁₆	17	298.15	761	24.96	0.070	[102]
ethyl pentanoate + n -C ₇	17	298.15	895	27.23	0.062	[102]
ethyl pentanoate + n -C ₉	18	298.15	838	27.69	0.058	[14]
methyl hexanoate + n -C ₇	18	298.15	888	28.13	0.085	[106]
methyl hexanoate + n -C ₈	20	298.15	983	29.33	0.080	[100]
methyl hexanoate + n -C ₁₀	20	298.15	1083	31.00	0.075	[107]
methyl hexanoate + n -C ₁₂	20	298.15	1166	32.40	0.081	[101]
methyl hexanoate + n -C ₁₄	16	298.15	1233	33.24	0.064	[15]
methyl hexanoate + n -C ₁₆	20	303.15	1657	60.29	0.093	[64]
diethyl oxalate + n -C ₆	10	303.15	1693	57.64	0.100	[64]
diethyl malonate + n -C ₆	10	303.15	1614	51.54	0.068	[64]
diethyl succinate + n -C ₆	10	303.15	1405	43.03	0.089	[64]
diethyl glutarate + n -C ₆	12	303.15	1298	37.53	0.084	[64]
diethyl adipate + n -C ₆	12	303.15	919	23.23	0.033	[64]

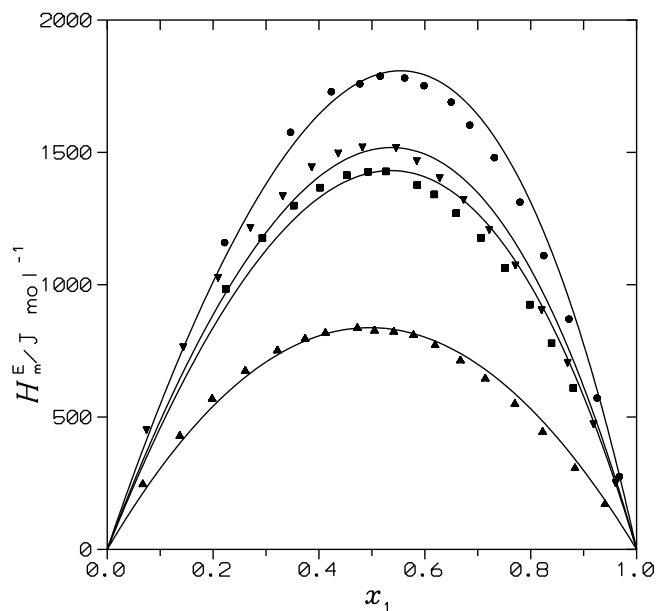


Fig. 1. H_m^E of n -alkanoate (1) + heptane (2) systems at 298.15 K. Points, experimental results: (●), methyl ethanoate [14]; (▼), ethyl ethanoate [102]; (■), methyl propanoate [14]; (▲), methyl hexanoate [14]. Solid lines, Flory calculations with interaction parameters listed in Table 2.

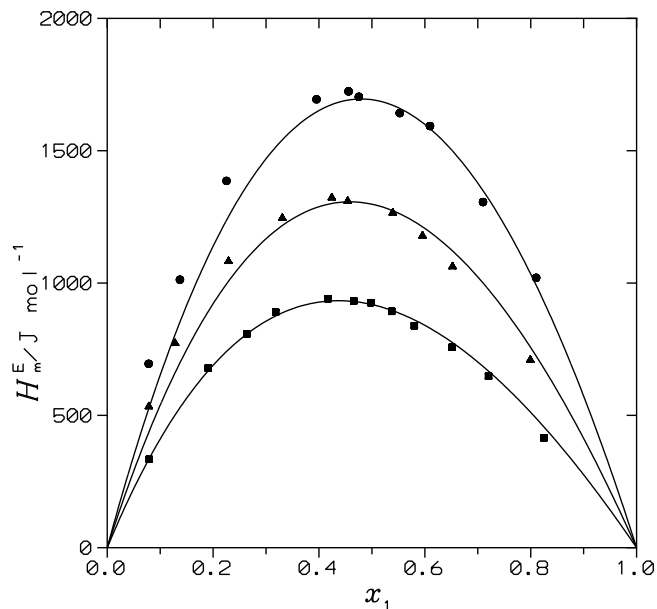


Fig. 2. H_m^E of diester (1) + hexane (2) systems at 303.15 K. Points, experimental results [64]: (●), diethyl malonate; (▲), diethyl adipate; (■), diethyl sebacate. Solid lines, Flory calculations with interaction parameters listed in Table 2.

= 1,2,3, or containing ethyl alkanoates ($v = 1$) with $u = 1,2$ (Table 4). In the former case, $U_{V_{m1}}^{E,\infty}(u = 1) \approx 3.7 \text{ kJ mol}^{-1}$ for $v = 1,2,3$ and $U_{V_{m1}}^{E,\infty}/J \text{ mol}^{-1} = 896$ ($v = 1$), 736 ($v = 2$), 654 ($v = 3$) (Table 4). This variation is probably due to increased steric effects (v increases) lead, as already mentioned, to a less number of ester-ester interactions in the system. In contrast, such effects are similar in solutions including an ester characterized by $u + v = 3$ ($u = 1, v = 2$, or $u = 2, v = 1$), or by $u + v = 4$ ($u = 4, v = 0$; $u = 0, v = 4$). It is remarkable that, e.g., the COO group is more sterically hindered in the mixture with butyl propanoate ($u = 1, v = 3$; $U_{V_{m1}}^{E,\infty}/J \text{ mol}^{-1} = 654$) than in solutions with methyl hexanoate ($u = 4, v = 0$) or pentyl ethanoate ($u = 0, v = 4$) ($U_{V_{m1}}^{E,\infty}/J \text{ mol}^{-1} = 729$). Note that

Table 3

Linear coefficients of preferential solvation, δ_{ij}^0 , at 298.15 K and composition x_1 for n -alkanoate (1), n -alkanone(1), or linear organic carbonate (1) + heptane (2) mixtures.

System	x_1	$\delta_{11}^0/\text{cm}^3 \text{ mol}^{-1}$	$\delta_{12}^0/\text{cm}^3 \text{ mol}^{-1}$	Ref.
methyl ethanoate (1) + n -C ₇ (2)	0.2	85.0	-0.4	[59]
	0.4	181.5	-45.1	
	0.6	134.7	-160.1	
	0.8	74.9	-122.9	
methyl ethanoate (1) + n -C ₁₂ (2)	0.2	78.7	18.0	[59]
	0.4	163.8	5.0	
	0.6	309.9	-106.5	
	0.8	463.1	-573.0	
methyl hexanoate (1) + n -C ₇ (2)	0.2	38.1	-10.0	[58]
	0.4	45.6	-31.1	
	0.6	28.3	-43.1	
	0.8	7.8	-31.6	
ethyl ethanoate (1) + n -C ₇ (2)	0.2	71.1	-3.6	[59]
	0.4	121.6	-38.2	
	0.6	105.9	-82.0	
	0.8	34.9	-61.7	
butyl ethanoate (1) + n -C ₇ (2)	0.2	57.5	-10.6	[59]
	0.4	71.9	-38.0	
	0.6	44.9	-52.1	
	0.8	13.2	-35.6	
ethyl propanoate (1) + n -C ₇ (2)	0.2	61.6	-6.7	[102]
	0.4	90.3	-36.3	
	0.6	66.0	-60.5	
	0.8	21.3	-43.7	
propanone (1) + n -C ₇ (2)	0.2	164.6	-9.0	[77]
	0.4	303.9	-80.4	
	0.6	317.1	-206.8	
	0.8	80.7	-122.4	
3-pentanone (1) + n -C ₇ (2)	0.2	85.1	-8.2	[109]
	0.4	113.9	-40.9	
	0.6	77.5	-63.2	
	0.8	24.2	-43.2	
dimethyl carbonate (1) + n -C ₇ (2)	0.2	163.8	-13.9	[110]
	0.4	515.9	-181.4	
	0.6	875.2	-726.1	
	0.8	96.5	-184.2	
diethyl carbonate (1) + n -C ₇ (2)	0.2	102.7	-17.2	[111]
	0.4	146.2	-72.2	
	0.6	88.8	-96.2	
	0.8	22.8	-56.2	

there is no meaningful difference between the $U_{V_{m1}}^{E,\infty}$ values of these systems ($\approx 3.7 \text{ kJ mol}^{-1}$ (Table 4)). The excess molar volumes V_m^E are also positive (Table S1) and change in line with the H_m^E results. Some examples follow, $V_m^E/\text{cm}^3 \text{ mol}^{-1} = 1.384$ (methyl ethanoate); 0.295 (methyl hexanoate) [58], and, in the same order, $H_m^E/J \text{ mol}^{-1} = 1787$; 838 [14]. It is possible to conclude that the main contribution to V_m^E arises from interactional effects. The positive values of $(\frac{\Delta V_m^E}{\Delta T})_p/\text{cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ agree with such statement: 0.024 (ethyl ethanoate) [59,60], $6.0 \cdot 10^{-3}$ (methyl propanoate) [49,61], or $3.0 \cdot 10^{-3}$ (propyl propanoate) [56,62].

4.1.2. Systems with a given n -alkanoate

In this case, both excess functions H_m^E and V_m^E increase with the size of the n -alkane (Tables 2 and S1). That is, the variation of V_m^E can be ascribed to an increase of the corresponding interactional effects. For the mixtures listed in Table S1 (see Fig. 4), $U_{V_{m1}}^{E,\infty}$ changes similarly. However, some previous calculations show that such variation is not hold for systems with long methyl alkanoates. This matter deserves a careful investigation and will be considered in a forthcoming work.

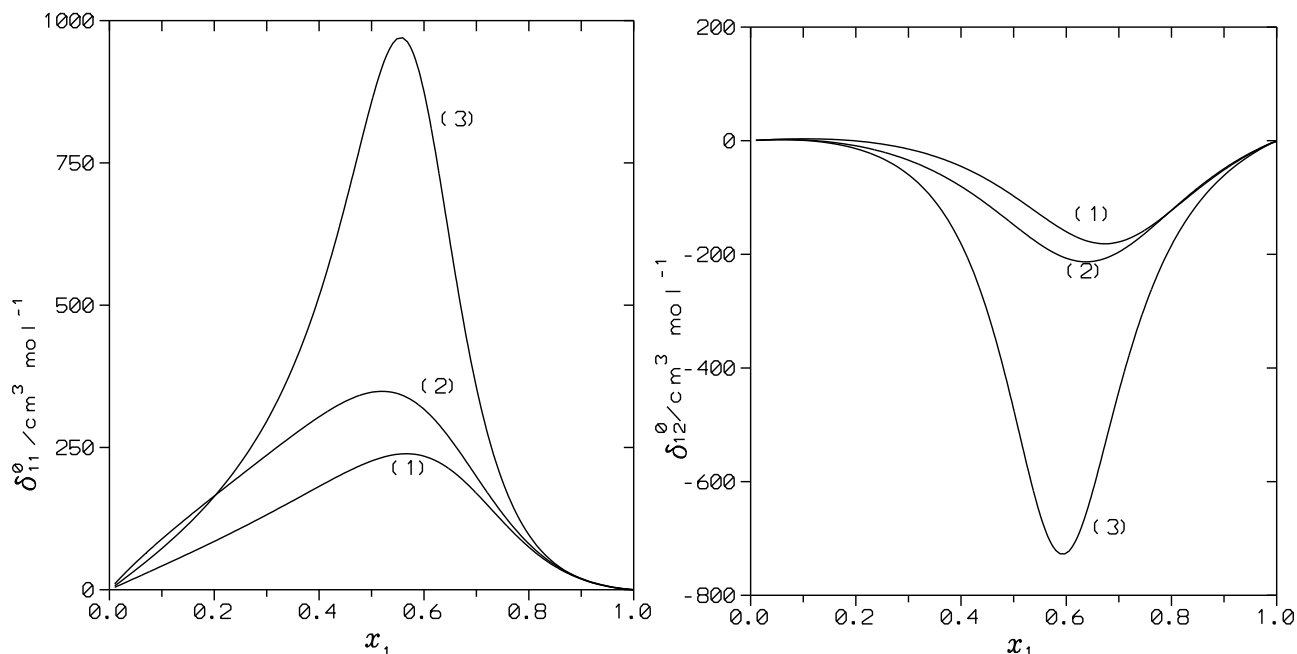


Fig. 3. Linear coefficients of preferential solvation, δ_{ij}^0 , for polar compound (1) + heptane (2) systems at 298.15 K: (1), methyl ethanoate; (2), propanone; (3), dimethyl carbonate. Fig. 3a, δ_{11}^0 ; Fig. 3b, δ_{12}^0 .

4.2. $\text{CH}_3\text{CH}_2\text{COO}(\text{CH}_2)_u\text{COOCH}_2\text{CH}_3$ + hexane mixtures

The data needed to conduct a discussion in similar terms that above are not available and only enthalpic data will be here considered. Nevertheless, some quite general trends can be outlined. Firstly, it is to be noted that the inclusion of a second COO group in the aliphatic chain of the *n*-alkanoate leads to higher H_m^E values in alkane solutions. Thus, $H_m^E(\text{hexane})/\text{J mol}^{-1} = 1036$ (ethyl propanoate) [63] < 1657 (diethyl oxalate, $T = 303.15$ K) [64] which can be ascribed to interactions between diester molecules are stronger as the corresponding $H_{m1}^{E,\infty}$ values reveal: $H_{m1}^{E,\infty}(\text{hexane})/\text{kJ mol}^{-1} = 5.7$ (ethyl propanoate) [63] < 9.1 (diethyl oxalate) [64]. It is interesting to note that although the $\bar{\mu}_i$ value of diethyl malonate (0.796) is higher than that of butyl propanoate (ester of similar size, 0.565, Table S2), indicating that dipolar interactions between diester molecules are stronger, the $\bar{\mu}_i$ values of other alkanates are rather similar: 0.555 (diethyl succinate), 0.585 (ethyl hexanoate) (Table S2). This underlines that some additional effect must be considered in order to explain the stronger interactions between diester molecules. Such effect is the so-called proximity effect and is also encountered, e.g., in alkane mixtures with dioxaalkanes [65], or dichloroalkanes [66], or with diketones [67]. In the case of hexane systems, $H_m^E/\text{J mol}^{-1} = 1254$ (2-butanone) [68]; 1600 (2,3-butanedione, $T = 303.15$ K) [67], and 496 (1-chlorobutane) [69], 1245 (1, 4-dichlorobutane) [70]. On the other hand, the H_m^E results of $\text{CH}_3\text{CH}_2\text{COO}(\text{CH}_2)_u\text{COOCH}_2\text{CH}_3$ + hexane mixtures at 303.15 K decrease when *u* increases ($u \geq 1$): $H_m^E/\text{J mol}^{-1} = 1707$ ($u = 1$) > 919 ($u = 8$) [64]. Such variation can be linked to a progressive weakening of the proximity effect, i.e., to weaker ester-ester interactions at the mentioned condition. In fact, the ($H_{m1}^{E,\infty}/\text{kJ mol}^{-1}$) values change in the same order [64]: 11.5 ($u = 1$) > 4.8 ($u = 8$). Mixtures with hexane and dichloroalkanes behave similarly: 1616 (dichloroethane) [71]; 990 (1, 6-dichlorohexane) [70]. Nevertheless, the system with $u = 0$, shows a H_m^E value (1658 J mol^{-1}) slightly lower than that corresponding to the mixture with $u = 1$. It is to be mentioned that diketone + hexane mixtures at 303.15 K behave differently: H_m^E values decrease when replacing 2,3-butanedione by 2,4-pentadione but the system with 2,5-hexanedione shows a miscibility gap at the mentioned temperature [67]. This

has been explained in terms of the percentage of enol form of 2,5-hexanedione in hexane is higher than for the other two diketones [67].

4.3. Comparison with other mixtures

For solutions with a given *n*-alkane, e.g. decane, UCST/K changes in the order: 255 (methyl ethanoate, estimated from data from [45]) < 266.8 (propanone) [72] < 286.6 (DMC) [73]. It is remarkable that the $\bar{\mu}_i$ value of DMC (0.391, [24]) is lower than those of acetone (1.281 [24]), or of methyl ethanoate (0.737 (Table S2)). This suggests that non-random mixing is not only determined by polarity [74] and that other effects (polarizability, size of the polar group) may also contribute to non-random effects. It is known that internal pressure ($P_{\text{int}} = (T\alpha_p/\kappa_T) - p$) is a magnitude mainly determined by dispersive interactions and weak dipole-dipole interactions, and that $P_{\text{int}}V_m$ is a measure of the London dispersive energies [25,75]. Here we have, $P_{\text{int}}V_m/\text{kJ mol}^{-1} = 35.46$ (DMC), 29.53 (methyl ethanoate); 24.27 (acetone). That is, dispersive interactions are meaningfully more relevant in DMC, the compound characterized by a larger dipolar polarizability: $7.7 \cdot 10^{-24}$ (DMC); $6.9 \cdot 10^{-24}$ (methyl ethanoate); $6.6 \cdot 10^{-24}$ (acetone) (all values in cm^3) [76]. The values of $H_{m1}^{E,\infty}$ and $U_{Vm1}^{E,\infty}$ for the mixtures with heptane change similarly to the UCST results given above: $H_{m1}^{E,\infty}/\text{kJ mol}^{-1} = 8.3$ (methyl methanoate) [44] < 9.1 (propanone) [77] < 9.5 (DMC) [78] and $U_{Vm1}^{E,\infty}/\text{kJ mol}^{-1} = 5.7$ (methyl methanoate) < 7.1 (propanone) < 8.1 (DMC) (Tables 4,5). One can conclude that interactions between like polar molecules become weaker in the sequence: DMC > propanone > methyl ethanoate. The variation of H_m^E and U_{Vm}^E is different. Thus, $H_m^E(\text{heptane})/\text{J mol}^{-1} = 1988$ (DMC) [78] > 1787 (methyl ethanoate) [14] > 1676 (propanone) [77] and $U_{Vm}^E(\text{heptane})/\text{J mol}^{-1} = 1632$ (DMC) > 1390 (propanone) > 1362 (methyl ethanoate). The two latter values together with the lower $U_{Vm1}^{E,\infty}$ result for the system with methyl ethanoate suggest that a larger neat number of interactions between like molecules are broken upon mixing in this solution than in the mixture with acetone. Similar trends are observed for systems with diethyl carbonate, 3-pentanone or ethyl propanoate (Tables 4,5). Finally, it should be remarked that for systems with a given *n*-alkane, the differences $|U_{Vm}^E(\text{CH}_3\text{COO}(\text{CH}_2)_u\text{CH}_3) - U_{Vm}^E(\text{CH}_3\text{CO}(\text{CH}_2)_u\text{CH}_3)|$ are lower than

Table 4

Excess molar functions at equimolar composition and 298.15 K: enthalpies, H_m^E , volumes, V_m^E , and isochoric internal energies, $U_{V_m}^E$, and excess molar functions at infinite dilution of the alkanooate at 298.15 K: enthalpies, $H_{m1}^{E,\infty}$, and internal energies, $U_{V_{m1}}^{E,\infty}$, for $\text{CH}_3(\text{CH}_2)_u \text{COO}(\text{CH}_2)_v \text{CH}_3$ (1) + heptane (2) mixtures. The effective dipolar moments, $\bar{\mu}_1$, of n -alkanoates are also given (see Table S2).

Property		$u = 0$ ethanoate	$u = 1$ propanoate	$u = 2$ butanoate	$u = 3$ pentanoate	$u = 4$ hexanoate
$v = 0$ methyl	$H_m^E / \text{J mol}^{-1}$	1787 ^a	1424 ^b	1170 ^b	968 ^b	835 ^b
	$V_m^E / \text{cm}^3 \text{ mol}^{-1}$	1.378 ^c	0.973 ^c	0.723 ^c	0.489 ^c	0.295 ^d
	$U_{V_m}^E / \text{J mol}^{-1}$	1388	1141	960	826	729
	$H_{m1}^{E,\infty} / \text{kJ mol}^{-1}$	8.3 ^a	5.4 ^b	5.0 ^b	4.5 ^b	4.2 ^b
	$U_{V_{m1}}^{E,\infty} / \text{kJ mol}^{-1}$	5.7	4.3	4.0	3.8	3.5
	$\bar{\mu}_1$	0.737	0.661	0.615	0.588	0.519
	$H_m^E / \text{J mol}^{-1}$	1510 ^e	1127 ^e	931 ^e	761 ^e	
$v = 1$ ethyl	$V_m^E / \text{cm}^3 \text{ mol}^{-1}$	1.105 ^f	0.803 ^c	0.542 ^c	0.383 ^c	
	$U_{V_m}^E / \text{J mol}^{-1}$	1190	896	772	660	
	$H_{m1}^{E,\infty} / \text{kJ mol}^{-1}$	7.0 ^e	4.8 ^e	4.5 ^e	3.9 ^e	
	$U_{V_{m1}}^{E,\infty} / \text{kJ mol}^{-1}$	5.1	3.7	3.7	3.1	
	$\bar{\mu}_1$	0.700	0.591	0.581		
	$H_m^E / \text{J mol}^{-1}$	1199 ^g	893 ^h	749 ⁱ		
	$V_m^E / \text{cm}^3 \text{ mol}^{-1}$	0.787 ^f	0.540 ^h	0.385 ⁱ		
$v = 2$ propyl	$U_{V_m}^E / \text{J mol}^{-1}$	969	736	n.a.		
	$H_{m1}^{E,\infty} / \text{kJ mol}^{-1}$	5.6 ^g	4.4 ^h	3.7 ⁱ		
	$U_{V_{m1}}^{E,\infty} / \text{kJ mol}^{-1}$	4.6	3.7			
	$\bar{\mu}_1$	0.633	0.591	0.562		
	$H_m^E / \text{J mol}^{-1}$	980 ^j	758 ^k			
	$V_m^E / \text{cm}^3 \text{ mol}^{-1}$	0.562 ^f	0.359 ^k			
	$U_{V_m}^E / \text{J mol}^{-1}$	818	654			
$v = 3$ butyl	$H_{m1}^{E,\infty} / \text{kJ mol}^{-1}$	5.4 ^j	4.3 ^k	3.6		
	$U_{V_{m1}}^{E,\infty} / \text{kJ mol}^{-1}$	4.5	3.8			
	$\bar{\mu}_1$	0.622	0.565	0.563		
	$H_m^E / \text{J mol}^{-1}$	828 ^l	646 ^l			
	$V_m^E / \text{cm}^3 \text{ mol}^{-1}$	0.347 ^l	n.a.			
	$U_{V_m}^E / \text{J mol}^{-1}$	729				
	$H_{m1}^{E,\infty} / \text{kJ mol}^{-1}$	4.47 ^l	3.4 ^l			
$v = 4$ pentyl	$U_{V_{m1}}^{E,\infty} / \text{kJ mol}^{-1}$	3.7	n.a.			
	$\bar{\mu}_1$	0.586	0.585			

^a [44];^b [14];^c [49];^d [58];^e [102];^f [59];^g [43];^h [56];ⁱ [112];^j [104];^k [57];^l [105]

that between the corresponding H_m^E data (Fig. 4). That is, the eos contribution to H_m^E is higher in systems with n -alkanoates.

4.4. Results from the application of models

4.4.1. Flory

Firstly, we note that the X_{12} parameter is positive for all the investigated mixtures (Table 2), indicating that interactions between like molecules are prevalent. On the other hand, X_{12} and H_m^E change in line. For example, in systems with heptane and alkyl ethanoate, both H_m^E and X_{12} decrease with the length of the alkyl term (Table 2) and this may be ascribed to the weakening of interactions between ester molecules. In contrast, for butyl ethanoate or methyl pentanoate + heptane mixtures, H_m^E practically remains unchanged, and the same occurs for the corresponding interaction parameters. From the $\sigma_r(H_m^E)$ values listed in Table 2, we have determined the mean value, $\bar{\sigma}_r(H_m^E)$, for the systems involving n -alkanoates ($T = 298.15$ K), according to the equation:

$$\bar{\sigma}_r(H_m^E) = \left(\sum \sigma_r(H_m^E) \right) / N_S \quad (12)$$

where N_S is the number of systems ($N_S = 58$). The result is $\bar{\sigma}_r(H_m^E) = 0.070$ and this points out that orientational effects are rather weak in this type of solutions. In terms of the model, it is quite difficult to make distinction between mixtures which differ by the monoester, except, perhaps, in the case of systems including methyl ethanoate, where orientational effects seem to be stronger. Thus, $\bar{\sigma}_r(H_m^E) = 0.095$ (methyl ethanoate; $N_S = 5$); 0.057 (ethyl ethanoate; $N_S = 4$); 0.057 (propyl ethanoate; $N_S = 4$); 0.052 (butyl ethanoate; $N_S = 4$); 0.091 (pentyl ethanoate; $N_S = 2$). The latter result may be consequence of experimental inaccuracies. Systems including diesters ($T = 303.15$ K), behave similarly to those with monoesters since $\bar{\sigma}_r(H_m^E) = 0.078$ ($N_S = 6$). At 318.15 K, for mixtures with monoesters, $H_m^E = 0.069$ ($N_S = 12$). That is, in such narrow temperature range, orientational effects remain, in practice, unchanged. It is interesting to consider the position of the investigated mixtures within the G_m^E (excess molar Gibbs energy) vs. H_m^E diagram [79,80]. It is well known that systems characterized by dispersive interactions are situated between the lines $G_m^E = 1/3H_m^E$ and $G_m^E = 1/2H_m^E$, while those where dipolar interactions are prevalent are encountered between the lines $G_m^E = 1/2H_m^E$

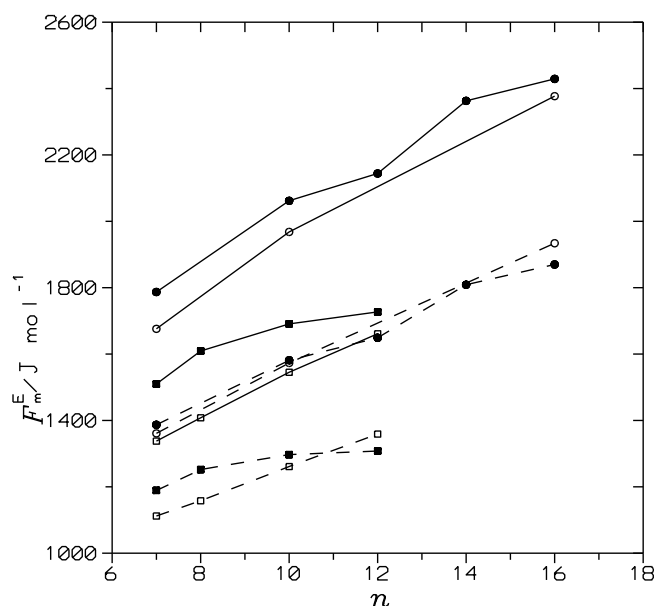


Fig. 4. Excess molar functions, F_m^E , at equimolar composition and 298.15 K of linear alkanolate or alkanone + n -alkane mixtures vs. n , the number of C atoms of the alkane. Lines are for the aid of the eye: solid lines, H_m^E ; dashed lines, U_m^E . Symbols: (●), methyl ethanoate; (○), propanone; (■), ethyl ethanoate; (□), 2-butanone. For source of experimental H_m^E data, see Tables 2 and 5. Numerical values of U_m^E are given in Tables S1 and S3.

Table 5

Excess molar functions at equimolar composition at 298.15 K: enthalpies, H_m^E , volumes, V_m^E , and isochoric internal energies, U_m^E , and excess molar functions at infinite dilution of the polar compound at 298.15 K: enthalpies, $H_{m1}^{E,\infty}$, and internal energies, $U_{m1}^{E,\infty}$, for n -alkanone (1) or linear organic carbonate (2) + heptane (2) mixtures.

System	H_m^E /J mol ⁻¹	V_m^E /cm ³ mol ⁻¹	U_m^E /J mol ⁻¹	$H_{m1}^{E,\infty}$ /kJ mol ⁻¹	$U_{m1}^{E,\infty}$ /kJ mol ⁻¹
propanone (1) + n -C ₇ (2)	1676 ^a	1.129 ^a	1362	9.1 ^a	7.1
2-butanone (1) + n -C ₇ (2)	1338 ^b	0.794 ^c	1112	7.5 ^b	6.1
2-pentanone (1) + n -C ₇ (2)	1135 ^b	0.614 ^d	963	6.3 ^b	5.3
3-pentanone (1) + n -C ₇ (2)	1078 ^b	0.519 ^c	931	5.8 ^b	5.0
2-hexanone (1) + n -C ₇ (2)	1055 ^e	0.375 ^f	948	6.6 ^e	5.7
DMC (1) + n -C ₇ (2)	1988 ^g	1.158 ^h	1632	9.5 ^g	8.1
DEC (1) + n -C ₇ (2)	1328 ⁱ	0.736 ^j	1102	7.1 ⁱ	6.0

^a [77];

^b [113];

^c [114];

^d [115];

^e [116];

^f [117];

^g [78];

^h [110];

ⁱ [118];

^j [111]

and $G_m^E = H_m^E$. Solutions where association effects are dominant are situated above the line $G_m^E = H_m^E$. In the present case, the situation of the mixtures within this diagram is slightly above the line $G_m^E = 1/2H_m^E$ and this remarks the relevance of dispersive interactions. Some examples follow for heptane mixtures at 298.15 K using G_m^E values determined

according to the DISQUAC model with interaction parameters from the literature [18] and H_m^E results listed in Table 2. Thus, $G_m^E/H_m^E = 969/1787 = 0.542$ (methyl ethanoate); $770/1510 = 0.510$ (ethyl ethanoate); $554/980 = 0.565$ (butyl ethanoate); $639/1127 = 0.567$ (ethyl propanoate).

On the other hand, $\bar{\sigma}_r(H_m^E)$ values for systems including linear organic carbonates (DMC, DEC; $N_S = 8$) or n -alkanones (propanone, 2-butanone, 2-pentanone, 2-hexanone or 3-pentanone; $N_S = 10$) are, respectively, 0.109 [24] and 0.156 [25]. The DISQUAC model has been also used to determine G_m^E values of linear organic carbonate, or n -alkanone + heptane mixtures [41,42] in order evaluate G_m^E/H_m^E using enthalpic data listed in Table 4. Thus, $G_m^E/H_m^E = 0.663$ (propanone), 0.603 (DMC); 0.663 (3-pentanone); 0.593 (DEC). This set of results allow to conclude that orientational effects become weaker in the sequence n -alkanone > organic carbonate > n -alkanoate, which is confirmed by the $\bar{\sigma}_r(H_m^E)$ values for systems including homomorphic polar molecules shown in Fig. 5. Accordingly with these results, the variation of the ratio $(X_{12}(x_1)/X_{12}(x_1 = 0.5))$ is sharper for mixtures with n -alkanones, DMC or DEC than for solutions containing n -alkanoates (Figure S1).

The Flory model has been shortly applied to the mixtures 2,3-butanedione or 2,4-pentadione + hexane ($T = 303.15$ K) [67] and the results are: $X_{12}/J \text{ cm}^{-3} = 78.66$ (2,3-butanedione); 37.84 (2,4-pentadione) and, in the same order, $\sigma_r(H_m^E) = 0.067, 0.148$.

4.4.2. Kirkwood-Buff integrals

Firstly, we note that for $\text{CH}_3\text{COO}(\text{CH}_2)_\nu\text{CH}_3$ (1) + heptane (2) mixtures at 298.15 K the δ_{11}^0 values decrease when ν is increased. This result reveals that the number of ester-ester interactions decreases in systems with alkyl ethanoates when the ester size increases and supports the previous statement about that the observed H_m^E decrease at this condition is partially due to a lower number of interactions between n -alkanoate molecules in the mixture. Similar trends are observed in systems with methyl or ethyl alkanooates (Table 3). The effect linked to the increasing of the n -alkane size in systems with a given alkanooate is shown in the mentioned Table by means of the results for the methyl ethanoate (1) + dodecane (2) mixture. The most relevant feature of such results is that the δ_{11}^0 curve is skewed towards higher x_1 values, which is consistent with the fact that the critical composition of the LLE curves of methyl acetate + n -alkane mixtures becomes also shifted to higher concentrations of the alkanooate when the alkane size increases [19,45].

The comparison with results for systems containing n -alkanones or organic carbonates shows a decreasing of δ_{11}^0 in the sequence: organic carbonate > n -alkanone > n -alkanoate (Fig.s 3a, 3b). This is consistent with the fact that, at 298.15 K, the mixtures with DMC or propanone are closer to the corresponding UCST than the solution with methyl ethanoate.

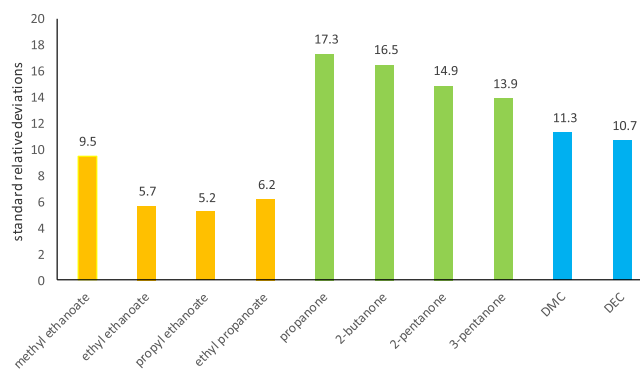


Fig. 5. Standard relative deviations (%) between experimental H_m^E results and values calculated according to the Flory model for polar compound + n -alkane systems at 298.15 K: n -alkanoates (Table 2); n -alkanones [24]; dialkyl carbonates [25].

Finally, some tentative calculations have been conducted for the system 2,3-butanedione + heptane assuming ideal volume of mixing and using G_m^E values from reference [81]. In this case, at equimolar composition and 298.15 K, $\delta_{11}^0 = 1600 \text{ cm}^3 \text{ mol}^{-1}$, which reveals that interactions between ketone molecules are here much more probable than in the solution with 2-butanone.

5. Conclusions

The investigated mixtures are mainly characterized by dispersive interactions and by steric effects. The former is supported by: (i) slightly positive or negative values of C_{pm}^E ; (ii) the situation of the systems within the G_m^E vs. H_m^E diagram; (iii) results from the Flory model. The theory cannot make a meaningful distinction between systems with a given n -alkane and which differ by the n -alkanoate. Steric effects are determinant to explain the observed differences between H_m^E (or U_{vm}^E) values of solutions formed by heptane and isomeric n -alkanoates. Orientational effects are also weak in diester + hexane mixtures. It has been shown that, when isomeric polar compounds are considered, the orientational effects become weaker in the sequence: n -alkanone > dialkyl carbonate > n -alkanoate. The application of the Kirkwood-Buff formalism reveals that the number of ester-ester interactions decrease in systems with alkyl ethanoates when the alkyl size increases and that preferential solvation between polar molecules decreases in the order dialkyl carbonate > n -alkanone > n -alkanoate.

CRedit authorship contribution statement

Juan Antonio González: Conceptualization, Formal analysis, Methodology, Writing – review & editing. **Fernando Hevia:** Formal analysis, Investigation, Validation, Writing – original draft. **Luis Felipe Sanz:** Conceptualization, Software, Validation, Writing – original draft. **Daniel Lozano-Martín:** Methodology, Investigation, Supervision, Validation. **Isaías García de la Fuente:** Investigation, Supervision, Writing – original draft. **José Carlos Cobos:** Conceptualization, Formal analysis, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Supplementary materials

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