

***N*-ALKANOATE + *N*-ALKANE MIXTURES:  
FOLDING OF HYDROCARBON CHAINS OF *N*-ALKANOATES**

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## Abstract

The mixtures  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COO}(\text{CH}_2)_{v-1}\text{CH}_3$  ( $u = 5-13$ ,  $v = 1,2$ ;  $u = 1,2,3$ ;  $v = 3,4$ ;  $u = 1,2,4$ ,  $v = 5$ ) +  $n$ -alkane have been investigated on the basis of excess molar functions, enthalpy ( $H_m^E$ ), volume ( $V_m^E$ ), isobaric heat capacity ( $C_{pm}^E$ ), and isochoric internal energy ( $U_{Vm}^E$ ), and viscosity data, and by means of different models (Flory, Grunberg-Nissan and Bloomfield-Dewan). Solutions are characterized by weak orientational effects. Large structural effects are encountered in a number of systems, such as those containing pentane. The variation with the ester size of the difference between the standard enthalpy of vaporization at 298.15 K of an ester and that of the homomorphic alkane along an homologous series formed by methyl or ethyl  $n$ -alkanoates reveals the existence of structural changes in longer  $n$ -alkanoates, which lead to stronger interactions between them. A similar result is obtained from values of cohesive energy density. The variation of  $V_m^E$  values of the corresponding heptane mixtures supports this statement. The observed decrease of  $H_m^E$  for systems with a given  $n$ -alkane (heptane, e.g.) seems to be more related to the COO group is more sterically hindered than to interactional effects. The  $U_{Vm}^E(n)$  function ( $n$  is the number of C atoms in the  $n$ -alkane) shows a minimum for systems with esters characterized by ( $u \geq 4$ ,  $v = 1$ ); ( $u \geq 7$ ,  $v = 2$ ), or ( $u \geq 1$ ,  $v = 4,5$ ). A similar dependence of  $U_{Vm}^E(n)$  was encountered for  $n$ -alkane mixtures involving cyclic molecules (cyclohexane, benzene). This result suggests that certain  $n$ -alkanoates, in an alkane medium, can form quasi-cyclic structures. Viscosity data are well described by means of free volume effects only. For systems with butyl ethanoate or methyl decanoate, the variation of  $\Delta\eta(n)$  (deviation of dynamic viscosity) is consistent with that of  $U_{Vm}^E(n)$ , which supports the existence of the mentioned cyclic structures in these esters. The Flory model provides poor results on  $H_m^E$  for systems characterized by large structural effects. Results are improved when the model is applied to  $U_{Vm}^E$  data.

**Keywords:**  $n$ -alkanoates;  $n$ -alkanes; molar excess isochoric internal energy; thermophysical models; dispersive interactions; structural effects; folding

## 1. Introduction

Esters are interesting compounds in view of their many different applications. For example, they are used in food and cosmetics industries where their pleasant odors and antifungal properties are determinant [1,2]. Polyhydroxy alkanoates (PHA) are bio-based polyesters, which have become an alternative for petrochemicals since they can be synthesized by microbial cultures grown on renewable materials in clean environments [3-5]. PHAs have also medical applications [6,7]. On the other hand, biofuels, composed by long methyl or ethyl *n*-alkanoates have gained interest to replace petroleum fuels due to their small production costs, renewability and great potential to reduce harmful gas emissions [8-12].

In the previous work of this series [13], orientational and structural effects (i.e, effects related to different shape, size or free volume of the solution components) in the mixtures linear ester + *n*-alkane were investigated using excess molar functions, enthalpy ( $H_m^E$ ), volume ( $V_m^E$ ), isobaric heat capacity ( $C_{pm}^E$ ) and isochoric internal energy ( $U_{Vm}^E$ ), and by means of the application of the Flory model [14] and the Kirkwood-Buff formalism [15]. However, in the mentioned study only some esters of formula  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COO}(\text{CH}_2)_{v-1}\text{CH}_3$  were considered: methyl alkanoates ( $v = 1$ ;  $u = 1-5$ ); ethyl ( $v = 2$ ), propyl ( $v = 3$ ) or butyl ( $v = 4$ ) alkanoates ( $u = 1-3$ ) and pentyl alkanoates ( $v = 5$ ;  $u = 1,2$ ). The present work extends the research to similar mixtures involving longer *n*-alkanoates: methyl or ethyl alkanoates ( $u = 5-13$ ,  $v = 1,2$ ), or other esters not considered previously, (pentyl pentanoate, e.g.). This is important since in the decade of 1970, starting from some spectroscopic measurements [16,17], Dusart et al., on the basis of  $H_m^E$  [18],  $V_m^E$  [19] and viscosity [20] data for  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COOCH}_3$  ( $u = 1-5$ ) + heptane mixtures, explored the possibility of that some esters (e.g, methyl butanoate) may form quasi-cycles in such systems. The formation of these structures was ascribed to a weak intramolecular interaction between the C=O part of the ester group and an H atom of the terminal  $\text{CH}_3$  group of the alkyl chain of the *n*-alkanoate. Here, not only  $H_m^E$ ,  $V_m^E$  and viscosity data are taken into account, but also special attention is paid to  $U_{Vm}^E$ . We have demonstrated that this is a key thermodynamic function when investigating cyclic molecule + *n*-alkane mixtures which are characterized by two main features: (i) interactions are mainly of dispersive type (i.e. they arise from dispersion London forces); (ii) solutions with shorter *n*-alkanes show large structural effects [21,22]. Under these conditions, the variation of  $U_{Vm}^E$  with  $n$ , the number of C atoms in the *n*-alkane, depends on two competing contributions. The first leads to decreased values of  $U_{Vm}^E$ , and is due to a lower ability of longer *n*-alkanes to break interactions between cyclic molecules. The second is endothermic and arises from the breaking of correlations of molecular orientations of longer *n*-alkanes. If the first contribution is dominant, then  $U_{Vm}^E$  decreases when

$n$  is increased. This is the case of mixtures with chlorobenzene, bromobenzene, 1,2,4-trichlorobenzene, or 1-chloronaphthalene [21]. If the second contribution is dominant,  $U_{V_m}^E$  increases in line with  $n$ . This behavior is encountered in systems involving cyclohexane or benzene [22]:  $U_{V_m}^E$  decreases up to  $n = 8$  and from  $n \geq 10$  increases, which indicates that, for the solutions with longer  $n$ -alkanes, the second contribution to  $U_{V_m}^E$  is dominant. Finally, it must be remarked that, in order to complete our study, the present mixtures are also investigated by means of the following models: Flory [14], Grunberg-Nissan [23] and Bloomfield-Dewan [24].

## 2. Models

### 2.1 Flory's model

The essential hypotheses of the theory [14,25-27] can be found elsewhere [28]. The basic assumption of the theory is that of random mixing. The explicit expression of the Flory equation of state is:

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

where  $\hat{V}_m = V_m / V_m^*$ ;  $\hat{P} = P / P^*$  and  $\hat{T} = T / T^*$  stand for 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,  $V_{mi}^*$ ,  $P_i^*$  and  $T_i^*$  can be obtained from density,  $\alpha_{pi}$  (isobaric expansion coefficient) and  $\kappa_{Ti}$  (isothermal compressibility) data. Expressions for reduction parameters of mixtures can be found elsewhere [28].  $H_m^E$  values are obtained from:

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

where all the symbols have their usual meaning [28]. The reduced volume of the mixture,  $\hat{V}_m$ , is obtained from the equation of state. Therefore, the molar excess volume can be also calculated:

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

## 2.2 Viscosity models

### 2.2.1 Grunberg-Nissan equation

This equation, for the correlation of dynamic viscosity ( $\eta$ ) data, is [23]:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \quad (4)$$

where  $\eta_i$  stands for the dynamic viscosity of component i, and  $G_{12}$  is an adjustable parameter.

### 2.2.2 Bloomfield-Dewan's model

This theory [24] combines the absolute reaction rate model [29] with the free volume theory [30]. The former relates viscosity to the free energy required for a molecule to flow from an equilibrium position to a new one, overcoming the attractive interactions caused by its neighbours. The latter relates viscosity to the probability of occurrence of an empty neighboring site where a molecule can jump. Thus, dynamic viscosity can be determined from the equation:

$$\ln \eta = (x_1 \ln \eta_1 + x_2 \ln \eta_2) + \alpha \ln \eta_{fv} + \beta \ln \eta_{ar} \quad (5)$$

This means that the probability for viscous flow is calculated as the product of the probabilities of having the sufficient activation energy and of the existence of an empty site [24,31]. The parameters  $\alpha, \beta$  are weighting factors with values between 0 and 1. In the present application, calculations were performed assuming that  $\beta = 0$ , that is, neglecting the residual contribution to  $\eta$  and taking into account only free volume effects. In equation (5),  $\ln \eta_{fv}$  arises from free volume effects and it is obtained from the expression:

$$\ln \eta_{fv} = \frac{1}{\hat{V}_m - 1} - \frac{x_1}{\hat{V}_{m1} - 1} - \frac{x_2}{\hat{V}_{m2} - 1} \quad (6)$$

Here,  $\hat{V}_m$  and  $\hat{V}_{mi}$  are the reduced volumes of the mixture and of component i, respectively, defined as in the Flory model (see above) [28].

## 3 Model calculations and results

Values of physical properties of *n*-alkanoates, required for calculations, are collected in Table S1 (supplementary information; see also Table 1 of reference [13] for other *n*-alkanoates). For most of the *n*-alkanes considered, the values used have been taken from a previous application [32]. For tridecane, pentadecane and heptadecane, the corresponding values are also included in Table 1.

### 3.1 Flory's model

For the *n*-alkanoate + pentane, or + heptane or + pentadecane mixtures, Table 1 lists values of the interaction parameter  $X_{12}$  determined from experimental  $H_m^E$  data at equimolar composition and 298.15 K following the method provided in reference [33]. Experimental results on  $V_m^E$  at the same conditions are also compared with theoretical values in Table 1, which, in addition, contains the relative standard deviations for  $H_m^E$  defined as:

$$\sigma_r(H_m^E) = \left[ \frac{1}{N} \sum \left( \frac{H_{m,\text{exp}}^E - H_{m,\text{calc}}^E}{H_{m,\text{exp}}^E} \right)^2 \right]^{1/2} \quad (7)$$

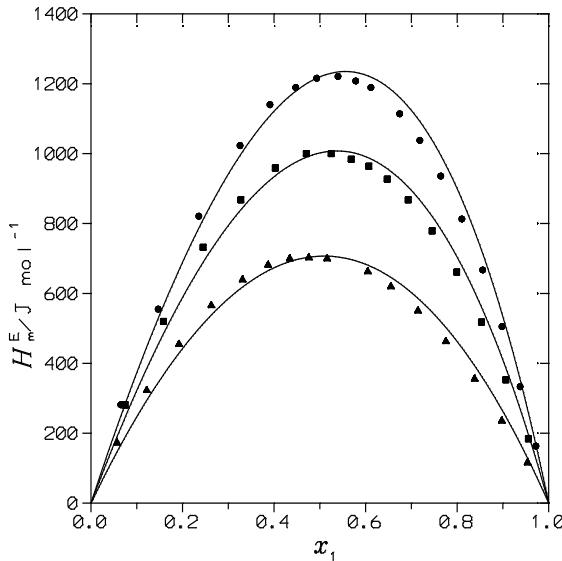
where  $N$  is the number of experimental data points. For the sake of completeness, Table S2 collects results for systems including other *n*-alkanes. A comparison between experimental  $H_m^E$  results and model calculations is shown in Figures 1-2 and S1.

**Table 1.** Excess molar enthalpies,  $H_m^E$ , volumes,  $V_m^E$ , and isochoric internal energies,  $U_{V_m}^E$ , at equimolar composition and 298.15 K, for *n*-alkanoate (1) + *n*-alkane (2) mixtures. Values of the Flory interaction parameter,  $X_{12}$ , and of the relative standard deviations for  $H_m^E$  and  $U_{V_m}^E$  ( $\sigma_r(H_m^E)$  and  $\sigma_r(U_{V_m}^E)$ ; see equation 7), are also included.

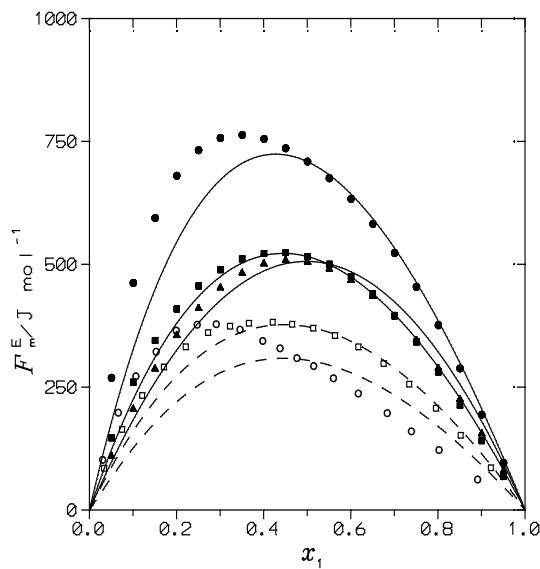
$n^a$	$N^b$	$H_m^E /$ $\text{J mol}^{-1}$	$X_{12} /$ $\text{J cm}^{-3}$	$\sigma_r(H_m^E)$	Ref.	$V_m^E /$ $\text{cm}^3 \text{mol}^{-1}$	Ref.	$U_{V_m}^E /$ $\text{J mol}^{-1}$	$X_{12} /$ $\text{J cm}^{-3}$	$\sigma_r(U_{V_m}^E)^c$		
											Exp.	Flory
methyl hexanoate + <i>n</i> -alkane												
5	21	721	27.50	0.189	57	-0.465	-0.257	59	842	31.86	0.128	
7	18	838	27.69	0.058	34	0.278	0.463	59	757	25.04	0.054	
15	18	1220	33.27	0.055	73	0.814	1.032	74	956	26.14	0.065	
methyl heptanoate + <i>n</i> -alkane												
5	20	631	23.00	0.193	57	-0.639	-0.540	58	800	28.69	0.117	
7	17	741	22.58	0.080	34	-0.082	-0.117	58	718	22.24	0.081	
15	17	1101	27.59	0.062	73	0.701	0.924	74	874	21.94	0.073	
methyl octanoate + <i>n</i> -alkane												
5	19	561	19.76	0.189	57	-0.826	-0.689	59	778	26.64	0.114	
7	17	645	18.93	0.089	34	-0.023	0.090	59	652	19.13	0.060	
15	16	1001	23.26	0.064	73	0.608	0.787	74	806	18.72	0.073	
methyl decanoate + <i>n</i> -alkane												
5	19	449	15.14	0.269	57	-1.070	-1.005	59	739	23.45	0.139	
7	20	550	14.81	0.106	34	-0.209	-0.154	59	612	16.40	0.087	
15	18	831	17.00	0.061	73	0.460	0.596	74	683	13.97	0.063	
methyl dodecanoate + <i>n</i> -alkane												
5	17	357	11.92	0.348	35	-1.251	-1.139	59	700	20.95	0.159	
7	17	442	11.26	0.096	35	-0.325	-0.436	59	537	13.49	0.055	
15	16	707	13.04	0.077	73	0.354	0.435	74	589	10.87	0.084	
methyl tetradecanoate + <i>n</i> -alkane												
5	18	305	10.11	0.354	35	-1.450	-1.609	59	709	20.02	0.139	
7	18	373	9.12	0.118	35	-0.467	-0.670	59	516	12.23	0.082	
15	18	597	10.12	0.085	73	0.273	0.286	74	506	8.58	0.092	

ethyl hexanoate + <i>n</i> -alkane											
5	18	406	14.97	0.195	45	-0.532	-0.514	45	549	19.77	0.103
7	17	655	20.08	0.084	45	0.222	0.341	45	592	18.17	0.080
15	17	1086	27.33	0.063	45	0.743	0.942	45	854	21.57	0.079
ethyl heptanoate + <i>n</i> -alkane											
5	17	302	11.21	0.232	45	-0.757	-0.745	45	506	17.65	0.115
7	17	530	15.43	0.070	45	0.091	0.122	45	510	14.86	0.043
15	17	944	21.95	0.095	45	0.645	0.774	45	739	17.36	0.113
ethyl octanoate + <i>n</i> -alkane											
5	19	234	8.77	0.258	46	-0.958	-0.914	46	491	16.38	0.129
7	17	437	12.16	0.041	46	-0.029	-0.028	46	445	12.37	0.013
15	17	783	17.07	0.129	46	0.572	0.654	46	599	13.09	0.141
ethyl decanoate + <i>n</i> -alkane											
5	17	151	6.19	0.316	46	-1.200	-1.174	46	482	15.24	0.118
7	19	300	7.92	0.035	46	-0.237	-0.284	46	370	9.63	0.034
15	17	582	11.29	0.106	46	0.435	0.449	46	444	8.62	0.126
ethyl dodecanoate + <i>n</i> -alkane											
5	13	99	4.65	0.336	46	-1.332	-1.330	46	467	13.94	0.084
7	18	251	6.31	0.115	46	-0.403	-0.430	46	375	9.10	0.089
15	18	437	7.72	0.132	46	0.314	0.331	46	333	5.89	0.155
ethyl tetradecanoate + <i>n</i> -alkane											
5	10	74	4.09	0.639	46	-1.472	-1.500	46	482	14.07	0.075
7	17	231	5.79	0.224	46	-0.477	-0.540	46	375	8.92	0.217
15	18	377	6.37	0.126	46	0.245	0.246	46	297	5.02	0.150
propyl ethanoate + <i>n</i> -alkane											
5	17	1024	44.16	0.257	75	0.131	0.544	75	990	42.72	0.196
7	17	1199	46.95	0.032	75	0.787	1.170	75	969	37.96	0.076
15	17	1718	58.18	0.074	75	1.167	1.628	75	1344	46.17	0.097
propyl propanoate + <i>n</i> -alkane											
5	17	670	26.96	0.249	75	-0.168	-0.263	75	714	28.55	0.220
7	17	893	31.76	0.091	75	0.562	0.668	75	736	26.19	0.082
15	17	1390	42.21	0.070	75	0.981	1.564	75	1078	33.12	0.129
propyl butanoate + <i>n</i> -alkane											
5	19	494	18.77	0.354	75	-0.379	-0.336	75	595	22.35	0.267
7	16	747	24.53	0.091	75	0.393	0.058	75	633	20.81	0.112
15	17	1192	32.76	0.046	75	0.865	1.097	75	915	25.49	0.064
butyl ethanoate + <i>n</i> -alkane											
5	18	789	31.65	0.157	55	-0.224	0.064	55	848	34.03	0.135
7	17	980	34.81	0.061	55	0.548	0.782	55	821	29.08	0.103
15	18	1447	43.49	0.075	55	0.996	1.283	55	1129	34.22	0.087
butyl propanoate + <i>n</i> -alkane											
5	15	577	21.91	0.193	55	-0.484	-0.290	55	706	26.61	0.098
7	18	758	24.89	0.100	55	0.359	0.492	55	654	21.52	0.102
15	18	1208	33.13	0.082	55	0.861	1.104	55	932	25.66	0.101
butyl butanoate + <i>n</i> -alkane											
5	15	400	15.10	0.320	55	-0.632	-0.690	55	568	20.58	0.167
7	17	565	17.43	0.159	55	0.190	0.131	55	510	15.95	0.151
15	17	1038	25.79	0.087	55	0.761	0.856	55	794	19.77	0.087
pentyl ethanoate + <i>n</i> -alkane											
5	16	636	24.21	0.217	56	-0.453	0.211	56	758	28.54	0.117
7	17	828	27.20	0.086	56	0.350	0.532	56	729	23.96	0.162
15	20	1305	35.43	0.081	56	0.882	1.068	56	1019	27.69	0.089
pentyl propanoate + <i>n</i> -alkane											
5	16	468	17.19	0.104	56	-0.631	-0.559	56	635	22.79	0.027
7	17	647	19.89	0.078	56	0.156	0.265	56	601	18.43	0.071
15	16	1056	26.51	0.071	56	0.764	0.930	56	809	20.46	0.090
pentyl pentanoate + <i>n</i> -alkane											
5	15	323	11.43	0.170	56	-1.026	-0.864	56	601	19.75	0.076
7	15	448	12.44	0.114	56	-0.050	0.327	56	463	12.85	0.092
15	19	771	16.79	0.087	56	0.612	0.652	56	575	12.55	0.138

<sup>a</sup>number of C atoms in the *n*-alkane; <sup>b</sup>number of data points



**Figure 1.**  $H_m^E$  for  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COOCH}_3$  (1) + pentadecane (2) systems at 298.15 K. Symbols, experimental results (for source of data, see Table 1): (●),  $u = 5$ ; (■),  $u = 7$ ; (▲);  $u = 11$ . Lines, Flory results using interaction parameters listed in Table 1.



**Figure 2.** Excess molar functions for  $\text{CH}_3(\text{CH}_2)_{12}\text{COOCH}_3$  (1) +  $n$ -alkane mixtures (2) systems at 298.15 K. Open symbols,  $F_m^E = H_m^E$  (see Table 1 for source of data): (○), pentane; (□), heptane. Full symbols,  $F_m^E = U_{Vm}^E$  (this work): (●), pentane; (■), heptane; (▲); pentadecane. Lines, Flory calculations using interaction parameters listed in Table 1: solid lines,  $U_{Vm}^E$ ; dashed lines,  $H_m^E$ .

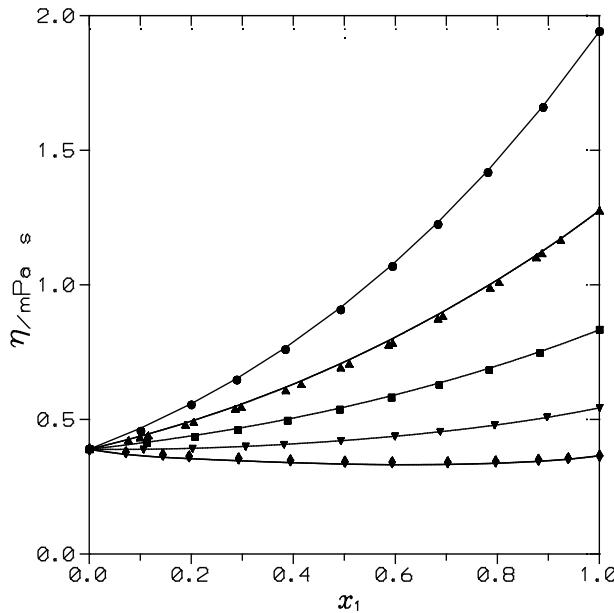
### 3.2 Viscosity models

Results from the application of the two viscosity models considered are collected in Table 2, which lists values of the relative deviations of dynamic viscosities,  $\sigma_r(\eta)$ , defined similarly to equation (7) (see also Figure 3).

**Table 2.** Dynamic viscosities ( $\eta$ ), deviations in absolute viscosity ( $\Delta\eta$ ), excess molar volumes,  $V_m^E$ , and deviations of molar Gibbs energy of activation,  $\Delta(\Delta G_m^*)$  (equation 11), for  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COO}(\text{CH}_2)_{v-1}\text{CH}_3$  (1) +  $n$ -alkane (2) mixtures at 298.15 K, and equimolar composition. Results from the application of the Bloomfield-Dewan's model with  $\beta = 0$  (see equation 5) and from the correlation of data using the Grunberg-Nissan's equation (equation 4) are also included.

( $u,v$ )	$n$ - $C_n$	$N^a$	$\eta$ / mPa s	$\Delta\eta$ / mPa s	$\sigma_r(\eta)$ <sup>b</sup>	Ref. $\eta$	$V_m^E$ / $\text{cm}^3 \text{mol}^{-1}$	Ref. $V_m^E$	$G_{12}^c$	$\sigma_r(\eta)$ <sup>b</sup>	$\Delta(\Delta G_m^*)$ / J mol <sup>-1</sup>
(1,1)	7	11	0.343	-0.034	0.023	65	1.378	37	-0.376	0.006	-88
(2,1)	7	12	0.378	-0.035	0.014	20	0.973	37	-0.351	0.014	-144
(3,1)	7	9	0.416	-0.048	0.002	65	0.723	37	-0.399	0.008	-224
(4,1)	7	11	0.474	-0.051	0.010	20	0.489	37	-0.276	0.009	-158
(5,1)	7	9	0.539	-0.072	0.011	65	0.295	76	-0.218	0.005	-130
(7,1)	7	20	0.699	-0.133	0.015	65	-0.023	59	-0.032	0.005	-6
(9,1)	7	9	0.918	-0.247	0.011	65	-0.209	59	0.220	0.008	177
(1,1)	16	9	1.451	-0.276	0.108	77	1.695	77	1.178	0.050	1247
(1,4)	16	12	1.610	-0.266	0.050	77	1.064	77	0.434	0.016	473
(9,1)	16	9	2.338	-0.147	0.009	78	0.451	78	-0.136	0.003	-50
(11,1)	16	9	2.776	-0.142	0.016	78	0.358	78	-0.195	0.002	-109
(13,1)	16	9	3.321	-0.166	0.013	78	0.285	78	-0.165	0.002	-99
(2,3)	6	12	0.407	-0.059	0.022	79	0.341	79	-0.237	0.013	-141
(2,3)	7	9	0.476	-0.039	0.019	80	0.573	80	-0.197	0.018	-108
(2,3)	8	9	0.531	-0.046	0.008	80	0.712	80	-0.311	0.005	-168
(2,3)	10	11	0.697	-0.054	0.005	81	0.809	81	-0.255	0.003	-99
(2,3)	14	10	1.185	-0.175	0.027	81	0.941	81	-0.104	0.003	216

<sup>a</sup> $N$ , number of data points; <sup>b</sup>  $\sigma_r(\eta) = \left[ \frac{1}{N} \sum \left( \frac{\eta_{\text{exp}} - \eta_{\text{calc}}}{\eta_{\text{exp}}} \right)^2 \right]^{1/2}$ ; <sup>c</sup>adjustable parameter of the Grunberg-Nissan's equation (equation 4).



**Figure 3.** Viscosity,  $\eta$ , of  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COOCH}_3$  (1) + heptane (2) systems at 298.15 K. Points, experimental values (for source of data, see Table 2): ( $\blacklozenge$ ),  $u=1$ , ( $\blacktriangledown$ ),  $u=3$ ; ( $\blacksquare$ ),  $u=5$ ; ( $\blacktriangle$ ),  $u=7$ ; ( $\bullet$ ),  $u=9$ . Lines, results from the application of the Bloomfield-Dewan's model assuming  $\beta = 0$ .

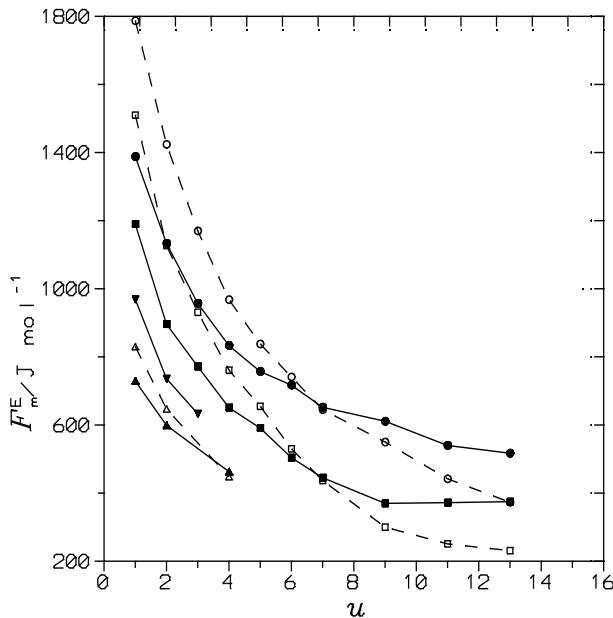
#### 4. Discussion

Below, values of the reported thermodynamic properties are given at equimolar composition and 298.15 K.



##### 4.1.1 Excess molar enthalpies

Firstly, mixtures including methyl ( $v = 1$ ) or ethyl ( $v = 2$ ) *n*-alkanoates are considered, since the corresponding available database is larger. These systems show positive values of  $H_m^E$ , which indicates that interactions between like molecules (i.e., interactions between molecules of the same type within the system) are dominant. If one assumes that  $u$  increases when  $v$  is constant, we note that  $H_m^E$  decreases (Tables 1, S2 and Figure 4). For example,  $H_m^E(v = 1)/\text{J mol}^{-1} = 1787(u = 1)$  [34]; 1424 ( $u = 2$ ) [34], 968 ( $u = 4$ ) [34], 645 ( $u = 7$ ) [34], 550 ( $u = 9$ ) [34]; 442 ( $u = 11$ ) [35]. On the other hand, it is remarkable that the observed decrease of  $H_m^E(v = 1)$  is sharper for systems with ( $u \leq 4$ ) and smoother for solutions with ( $u \geq 6$ ). Solutions with  $v = 2$  behave similarly (Figure 4). This reveals that dipolar interactions are relatively more important in mixtures including shorter *n*-alkanoates and that such interactions become weaker when the ester size increases [13]. Note that mixtures with methyl ethanoate show miscibility gaps at relatively high temperatures (the upper critical temperature solution of the system with octane is 241.7 K [36]).



**Figure 4.** Excess molar functions for  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COO}(\text{CH}_2)_{v-1}\text{CH}_3$  (1) + heptane (2) systems at equimolar composition and 298.15 K. Open symbols (joined by dashed lines),  $F_m^E = H_m^E$ : (○),  $v = 1$ ; (□),  $v = 2$ ; (Δ),  $v = 5$ . Full symbols (joined by solid lines),  $F_m^E = U_{Vm}^E$ : (●),  $v = 1$ ; (■),  $v = 2$ ; (▼),  $v = 3$ ; (▲),  $v = 5$ . Lines are for the aid of the eye. For source of data, see Tables 1, S2, S5 and reference [13].

Accordingly with this behaviour, the system methyl ethanoate + heptane shows a  $C_{pm}^E(x_1)$  curve with two negative minima at the extremes of the concentration range and positive values at its central part ( $0.91 \text{ J mol}^{-1} \text{ K}^{-1}$ ) [37], which is a typical feature of mixtures at temperature not far from the UCST [37]. For systems containing 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) [38], and  $-0.50$  for the mixture with propyl butanoate [39]. Similar trends are encountered in *n*-alkanoate + cyclohexane systems [40]. Note that negative values of  $C_{pm}^E$ , normally ascribed to order destruction, are encountered in systems characterized by dispersive interactions [41,42]. In addition, it should be also taken into account that the COO group becomes more sterically hindered when  $u$  increases ( $v = 1,2$ ), an effect that leads to decreased  $H_m^E$  values since entails a decrease in the number of ester-ester interactions in comparison to that of pure alkanoates [13,43]. The weakening of the ester-ester interactions may be also investigated by means of the partial excess molar enthalpies at infinite dilution of the *n*-alkanoate,  $H_{ml}^{E,\infty}$  (determined from  $H_m^E$  measurements over the whole concentration range, Table S3). For mixtures with methyl esters ( $v = 1$ ), this magnitude decreases up to  $u = 9$ , and it is constant for  $u = 11,13$  (Table S3):  $H_{ml}^{E,\infty}(v=1)/\text{kJ mol}^{-1} = 8.3 (u=1)$  [44];  $5.0 (u=3)$  [34];  $4.2 (u=5)$  [34];  $3.5 (u=7)$  [34];  $2.7 (u=11, 13)$  [35]. In the case of systems containing ethyl *n*-alkanoates ( $v = 2$ ), the dependence of  $H_{ml}^{E,\infty}$  with  $u$  is similar:  $H_{ml}^{E,\infty}(v=2)/\text{kJ mol}^{-1} = 7.0 (u=1)$  [45];  $4.5 (u=3)$  [45];  $2.7 (u=6)$  [45];  $2.0 (u=7)$  [46];  $1.5 (u=9, 11)$  [46]; and  $1.8 (u=13)$  [46]. In order to continue investigating the strength of the interactions between ester molecules, two magnitudes are now considered:  $\Delta\Delta H_{vap,i}$  and  $D_{ce,i}$ . The former is defined as the difference between the standard enthalpy of vaporization at  $298.15 \text{ K}$ ,  $\Delta H_{vap,i}$ , of a compound characterized by a polar group X (here, X = COO) and that of the homomorphic alkane [47]. The magnitude  $\Delta\Delta H_{vap,i}$  is useful to compare the relative changes in intermolecular forces of homomorphic compounds upon replacing a  $\text{CH}_2$  group by a given X group [47].  $D_{ce,i}$  is the density of cohesive energy determined from the equation [48]:

$$D_{cei} = \frac{\Delta H_{vap,i} - RT}{V_{mi}} \quad (8)$$

and describes the total strength of the solvent structure [48]. Values of  $\Delta H_{\text{vap},i}$  for the calculation of the magnitude  $\Delta\Delta H_{\text{vap},i}$  have been taken from [49-52] (see Table S4). Some results follow:  $\Delta\Delta H_{\text{vap},i}$  ( $v = 1$ )/kJ mol<sup>-1</sup> = 12.8 ( $u = 3$ ); 11.5 ( $u = 5$ ); 10.0 ( $u = 7$ ); 10.3 ( $u = 9$ ); 10.7 ( $u = 11$ ); 10.9 ( $u = 13$ ); and  $\Delta\Delta H_{\text{vap},i}$  ( $v = 2$ )/kJ mol<sup>-1</sup> = 11.1 ( $u = 3$ ); 10.2 ( $u = 5$ ); 8.1 ( $u = 7$ ); 9.0 ( $u = 9$ ); 8.7 ( $u = 11$ ). We note that  $\Delta\Delta H_{\text{vap},i}$  shows a minimum at  $u = 7$ , and then slightly increases, remaining roughly constant. This is an unexpected finding, and suggests the existence of some structural change in longer *n*-alkanoates which seems lead to stronger interactions between them. This effect is more pronounced for ethyl *n*-alkanoates. Values of  $D_{\text{ce},i}$  (Table S4) support this statement. Thus,  $D_{\text{cei}}(v = 1)$ /kJ mol<sup>-1</sup> = 321.6 ( $u = 3$ ); 307.7 ( $u = 5$ ); 297.3 ( $u = 7$ ); 299.6 ( $u = 9$ ); 301.4 ( $u = 11$ ); 300.8 ( $u = 13$ ), and  $D_{\text{ce}}(v = 2)$ /kJ mol<sup>-1</sup> = 302.2 ( $u = 3$ ); 295.8 ( $u = 5$ ); 285.4 ( $u = 7$ ); 292.0 ( $u = 9$ ); 291.3 ( $u = 11$ ). If one also takes into account the corresponding  $H_{\text{m}1}^{\text{E},\infty}$  values (see above), the observed decrease of  $H_{\text{m}}^{\text{E}}$  for systems with long chain esters seems to be more related to the COO group is more sterically hindered than to interactional effects. It is interesting to note that a similar variation of  $\Delta\Delta H_{\text{vap},i}$  and  $D_{\text{ce},i}$  is encountered for 2-alkanones (Table S4) and, therefore, it seems that a similar structural change may exist in longer 2-alkanones. It is pertinent to underline that dialkyl ethers behave “normally” and the magnitudes under consideration decreases when the size of the oxaalkane increases (Table S4). The negative values of  $\Delta\Delta H_{\text{vap},i}$  obtained for dialkylethers longer than dipropylether reveal that dispersive interactions in such oxaalkanes are dominant by far [47].

Next, we pay attention to the internal pressure ( $P_{\text{int},i}$ ), and, particularly to the ratio  $q_i = \frac{P_{\text{int},i}}{D_{\text{ce},i}}$ . The internal pressure is mainly determined by dispersive and weak dipolar interactions [48,53]. Values for *n*-alkanoates are listed Table S4. They were obtained using the expression:

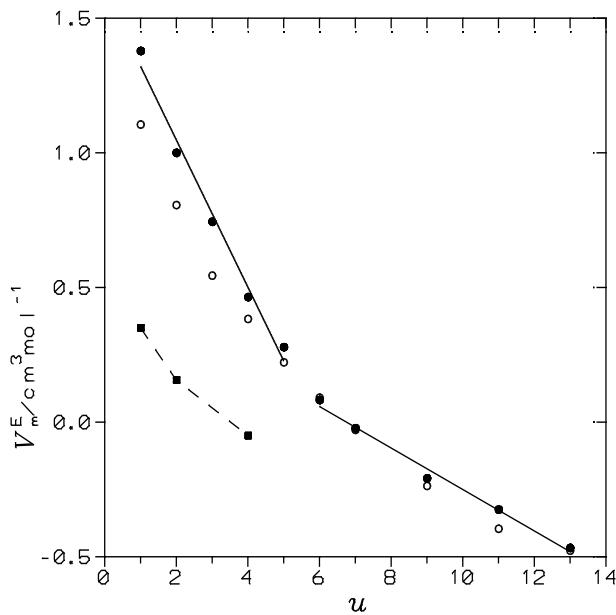
$$P_{\text{int},i} = \left[ \left( \frac{\partial U}{\partial V} \right)_T \right]_i = T \frac{\alpha_{p,i}}{\kappa_{T,i}} - p \quad (9)$$

With regards to  $q_i$ , for associated liquids,  $q_i \leq 0.8$ , i.e.,  $P_{\text{int},i} \leq D_{\text{ce},i}$  [53]. Values of  $q_i$  ranged between [1.0,1.2] are typical of hydrocarbons (Table S4) and of non-polar liquids [53] (see results for *n*-alkanes and oxaalkanes, Table S4). For *n*-alkanoates, their  $q_i$  values are encountered in the mentioned interval (Table S4), and one can assume that, in their mixtures with *n*-alkanes, interactions are mainly dispersive.

Systems including *n*-alkanoates with  $v = 3, 4$ , or  $5$  or *n*-alkanoates with  $u = \text{constant}$  also show decreasing positive  $H_m^E$  values when the ester size increases (Tables 1, S2 and Figure 4), which can be explained in similar terms that above. For example, in the case of solutions with alkyl propanoates,  $H_m^E(u = 2)/\text{J mol}^{-1} = 1424 (v = 1)$  [34];  $1127 (v = 2)$  [45];  $893 (v = 3)$  [54];  $760 (v = 4)$  [55];  $647 (v = 5)$  [56] and  $H_{m1}^{E,\infty}(u = 2)/\text{kJ mol}^{-1} = 5.4 (v = 1)$  [34];  $4.8 (v = 2)$  [45];  $4.4 (v = 3)$  [54];  $4.3 (v = 4)$  [55];  $3.4 (v = 5)$  [56].

#### 4.1.2 Excess molar volumes

Values of  $V_m^E$  for mixtures with methyl or ethyl *n*-alkanoate are represented in Figure 5 (see Table 2). Systems including a methyl *n*-alkanoate show  $V_m^E$  results which are negative from  $u \geq 7$ . Since the corresponding values of  $H_m^E$  are positive, this means that, for such solutions, the contribution to  $V_m^E$  from structural effects is dominant over that due to interactional effects. A similar trend is observed for solutions with ethyl alkanoates. Slightly negative  $V_m^E$  values are also encountered for the system containing pentyl pentanoate ( $-0.050 \text{ cm}^3 \text{ mol}^{-1}$  [56]).



**Figure 5.**  $V_m^E$  for  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COO}(\text{CH}_2)_{v-1}\text{CH}_3$  (1) + heptane (2) systems at equimolar composition and 298.15 K. Symbols: (●),  $v = 1$ ; (○),  $v = 2$ ; (■),  $v = 5$ ; Each solid line is the result from the linear fitting of the data for mixtures with  $(u = 1-5; v = 1)$  and with  $(u = 6-13; v = 1)$ , respectively. Dashed line is for the aid of the eye. For source of data, see Table 1 and reference [13].

It must be underlined that, along a given homologous series, e.g., mixtures with methyl *n*-alkanoates,  $V_m^E$  also decreases when the ester size is increased (Figure 5). This can be explained taking into account: (i) the positive interactional contribution to  $V_m^E$  decreases at this condition ( $H_m^E$  varies similarly); (ii) a more negative contribution to  $V_m^E$  from free volume effects, as it is indicated by the variation of the magnitude ( $\alpha_p(\text{ester}) - \alpha_p(\text{heptane})$ ) (Figure S2); (iii) the value of  $|V_{m1} - V_{m2}|$  also increases from  $u \geq 5$  and this also leads to a more negative contribution to  $V_m^E$ . In addition, the variation of this excess function is sharper for systems involving esters with  $u \leq 5$  ( $v = 1,2$ ) and much smoother for solutions with  $u \geq 6$  ( $v = 1,2$ ) (Figure 5). If one takes into account that structural effects are dominant for systems with longer alkanoates, and that increase with  $u$ , the latter variation of  $V_m^E$  can be explained in terms of an extra positive contribution to  $V_m^E$  due to the breaking of stronger interactions between molecules of such *n*-alkanoates, which might be related to the existence of quasi-cyclic structures of the mentioned esters.

#### 4.2 Systems with a given *n*-alkanoate

At this condition, both excess functions  $H_m^E$  and  $V_m^E$  increase with  $n$  (Tables 1 and S2) which is, say, the normal behavior. The important point is that a number of mixtures show positive  $H_m^E$  values and large and negative  $V_m^E$  results, which reveals the existence of strong structural effects. This occurs for some mixtures with pentane. For example,  $H_m^E / \text{J mol}^{-1} = 631$  ( $u = 6; v = 1$ ) [57]; 449 ( $u = 9, v = 1$ ) [57], 305 ( $u = 13, v = 1$ ) [35]; 302 ( $u = 6, v = 2$ ) [45], 151 ( $u = 9, v = 2$ ) [46]; 74 ( $u = 13, v = 2$ ) [46]; 638 ( $u = 1; v = 5$ ); 323 ( $u = 4; v = 5$ ) [56], and  $V_m^E / \text{cm}^3 \text{mol}^{-1} = -0.639$  ( $u = 6; v = 1$ ) [58];  $-1.070$  ( $u = 9, v = 1$ ) [59],  $-1.450$  ( $u = 13, v = 1$ ) [59];  $-0.757$  ( $u = 6, v = 2$ ) [45],  $-1.200$  ( $u = 9, v = 2$ ) [46];  $-1.472$  ( $u = 13, v = 2$ ) [46];  $-0.453$  ( $u = 1; v = 5$ ) [56];  $-1.026$  ( $u = 4; v = 5$ ) [56].

#### 4.3 Molar excess internal energy at constant volume.

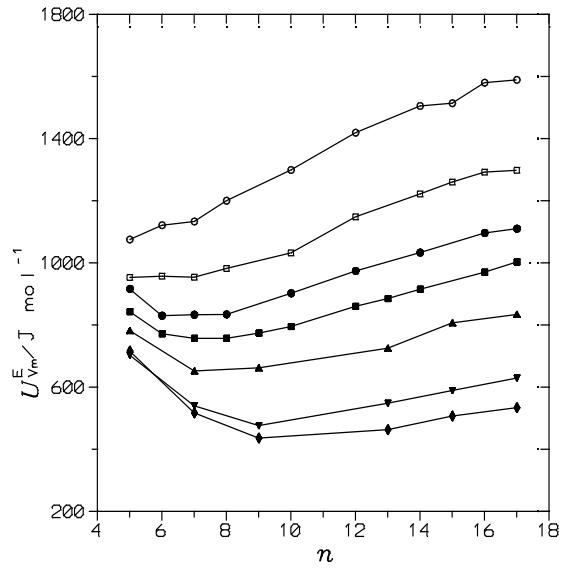
Since structural effects may become very important in the investigated mixtures, and such effects contribute meaningfully to  $H_m^E$ , it is pertinent to pay attention to the excess function  $U_{Vm}^E$ , which has been determined from the equation [60]:

$$U_{Vm}^E = H_m^E - T \frac{\alpha_p}{\kappa_T} V_m^E \quad (10)$$

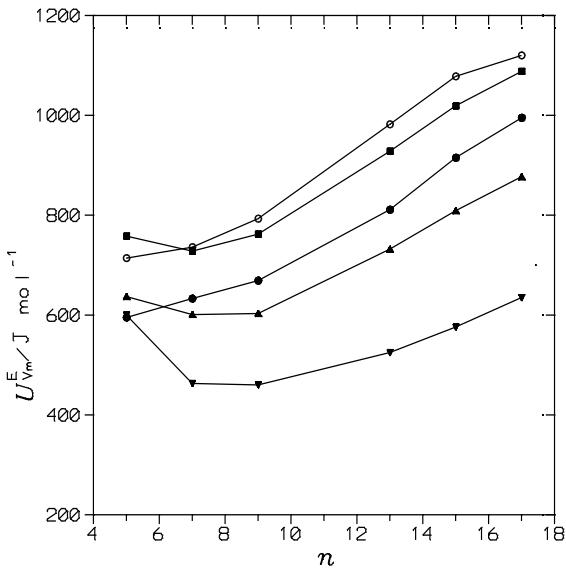
where  $\alpha_p$  and  $\kappa_T$  are, respectively, the isobaric thermal expansion coefficient and the coefficient of isothermal compressibility of the considered system. The  $T \frac{\alpha_p}{\kappa_T} V_m^E$  term describes the contribution from the equation of state (eos) term to  $H_m^E$ . When the needed data are not available,  $\alpha_p$  and  $\kappa_T$  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  $\kappa_{T_i}$  and,  $\phi_i = x_i V_{mi} / (x_1 V_{m1} + x_2 V_{m2})$ . This approximation is commonly acceptable. Results are listed in Tables 1, S2, and S5 (see Figures 6,7, S3). From these results some statements can be provided.

(i) In the systems methyl or ethyl alkanoate + heptane,  $U_{Vm}^E > H_m^E$  from  $u \geq 6$  ( $v = 1$ ) or from  $u \geq 7$  ( $v = 2$ ). This clearly reveals the relevance of the eos contribution to  $H_m^E$ . (ii)  $U_{Vm}^E$  (heptane) decreases when  $u$  is increased ( $v = 1,2$ ), but for larger  $u$  values, this magnitude varies smoothly ( $v=1$ ) or remains nearly constant ( $v = 2$ ) (Table 1, Figure 4). (iii) The values of  $U_{Vm}^{E,\infty}$  (heptane) (determined from  $U_{Vm}^E$  values over the whole concentration range) follow similar patterns than those of  $H_{m1}^{E,\infty}$  and are more or less constant from  $u \geq 7$ . Thus,  $U_{Vm1}^{E,\infty}$  (heptane)/kJ mol<sup>-1</sup>  $\approx 3$  ( $u \geq 7$ ;  $v = 1$ ); 2.1 ( $u \geq 7$ ;  $v = 2$ ) (Table S3). This suggests that, in such mixtures, the increasing of the steric hindrance of the COO group is more relevant than interactional effects on  $U_{Vm}^E$  values. Data for systems with alkyl ethanoate or propanoate or butanoate are scarce. Nevertheless, it seems clear that interactions between ester molecules become weaker when replacing, e.g., methyl by pentyl alkanoate. For example,  $U_{Vm1}^{E,\infty}$  (heptane)/kJ mol<sup>-1</sup> = 5.7 (methyl ethanoate); 3.7 (pentyl ethanoate) (Table S3). (v) An important result arises from the variation of  $U_{Vm}^E$  with  $n$  in systems with a given ester (Tables S2, S5, Figures 6,7 S3). In such a case,  $U_{Vm}^E$  increases with  $n$  in systems with methyl butanoate or propyl propanoate ( $u = 1,2,3$ ), while the  $U_{Vm}^E(n)$  function shows a minimum for systems with  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COO}(\text{CH}_2)_{v-1}\text{CH}_3$  from  $u \geq 4$  ( $v = 1$ ) or from  $u \geq 7$  ( $v=2$ ), or from  $u \geq 1$  ( $v=4,5$ ). A similar dependence for  $U_{Vm}^E(n)$  was encountered when investigating  $n$ -alkane mixtures with cyclic molecules such as cyclohexane, or benzene or cyclohexyl, or tetralin or cyclohexylbenzene [22]. That is, the existence of a minimum in the  $U_{Vm}^E(n)$  function for a given homologous series may be due to the involved  $n$ -alkanoate forms quasi-cyclic structures, probably by folding of the hydrocarbon chain on  $>\text{C}=\text{O}$ . The present treatment extends results from Dusart et al. using infrared techniques [16,17] and shows that the formation of quasi-cyclic structures of esters in  $n$ -alkane medium is a rather common behavior. Our study allows conclude that this phenomenon occurs weakly in systems with propyl

ethanoate [16,17], and that it might be present in solutions with methyl butanoate or ethyl heptanoate (Table S2 and S5).



**Figure 6.**  $U_{Vm}^E$  of  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COOCH}_3$  (1) +  $n$ -alkane (2) systems at equimolar composition and 298.15 K vs.  $n$ , the number of C atoms in the  $n$ -alkane. Symbols: (O),  $u = 2$ ; ( $\square$ ),  $u = 3$ ; ( $\bullet$ ),  $u = 4$ ; ( $\blacksquare$ ),  $u = 5$ ; ( $\blacktriangle$ ),  $u = 7$ ; ( $\blacktriangledown$ ),  $u = 11$ ; ( $\blacklozenge$ ),  $u = 13$ . Lines are for the aid of the eye. Numerical data are listed in Tables S2 and S5.



**Figure 7.**  $U_{Vm}^E$  of  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COO}(\text{CH}_2)_{v-1}\text{CH}_3$  (1) +  $n$ -alkane (2) systems at equimolar composition and 298.15 K vs.  $n$ , the number of C atoms in the  $n$ -alkane. Symbols: (O),  $u = 1$ ;  $v = 3$ ; ( $\bullet$ ),  $u = 3$ ;  $v = 3$ ; ( $\blacksquare$ ),  $u = 1$ ;  $v = 5$ ; ( $\blacktriangle$ ),  $u = 2$ ;  $v = 5$ ; ( $\blacktriangledown$ ),  $u = 4$ ;  $v = 5$ . Lines are for the aid of the eye. Numerical data are listed in Tables S2 and S5.

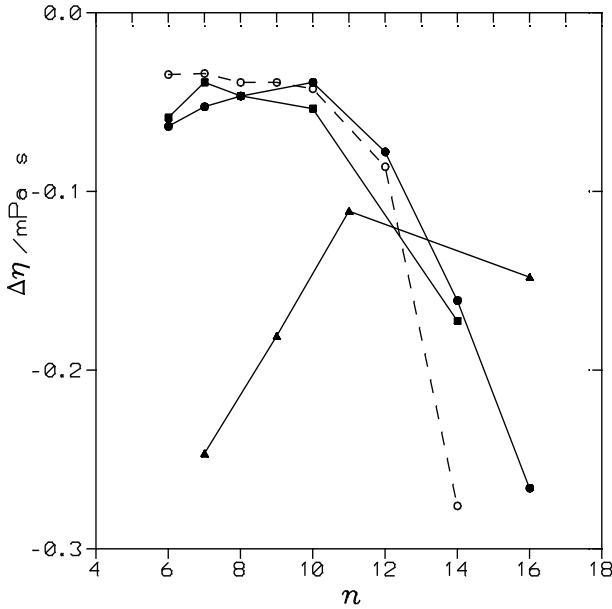
#### 4.4 Dynamic viscosities

Deviations of dynamic viscosity ( $\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2)$ ) of  $n$ -alkanoate +  $n$ -alkane mixtures are negative (Table 2, Figure 8), which is consistent with the fact that no specific

interactions exist between the system compounds [61,62]. The  $\Delta\eta$  values of  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COOCH}_3 + \text{heptane}$  mixtures decrease when  $u$  is increased (Table 3)). The same trend is observed for  $H_m^E$  (or  $U_{Vm}^E$ ) and  $V_m^E$ . It has been suggested that a certain correlation exists between  $\Delta\eta$  and  $V_m^E$ , these functions having opposite signs [63,64]. Indeed, this is held for systems with  $u = 1,3,5$ . However, the system containing methyl *n*-decanoate has negative values of  $\Delta\eta$  ( $-0.247 \text{ mPa}$  [65]) and of  $V_m^E$  ( $-0.154 \text{ cm}^3\text{mol}^{-1}$  [59]). It suggests that there is no clear relationship between such thermophysical magnitudes. On the other hand, the decreasing of  $U_{Vm}^E$  when  $u$  increases has been above related with a lower number of broken interactions between like molecules, and it cannot explain the corresponding increased negative values of  $\Delta\eta$ .

The Bloomfield-Dewans's model [24], assuming that  $\beta = 0$ , provides excellent results (Table 2) if one considers that they are obtained from volumetric data. Unfortunately, from this analysis, nothing can be stated about the possible formation of quasi-cyclic structures of *n*-alkanoates. In order to continue investigating this point, now it is paid attention to ester (fixed) + *n*-alkane systems. The data are scarce since they are only available for mixtures including methyl ethanoate, or butyl ethanoate or propyl propanoate or methyl decanoate (see Figure 8).

Inspection of Figure 8 shows that  $\Delta\eta$  is nearly constant for lower  $n$  values in the case of solutions with methyl acetate, decreasing for larger  $n$  values. The dependence of  $\Delta\eta$  with  $n$  is somewhat different for the mixtures including butyl ethanoate or methyl decanoate. In fact,  $\Delta\eta$  increases with  $n$  and decreases for larger  $n$  values. The large negative  $\Delta\eta$  result for the methyl ethanoate + hexadecane mixture can be explained taking into account that, at 298.15 K, this system is not far from its UCST which means that a large number of interactions between like molecules are broken upon mixing. It is remarkable that, in the case of systems with butyl ethanoate or methyl decanoate, the variation of  $\Delta\eta(n)$  is consistent with that of  $U_{Vm}^E(n)$ . This excess function decreases for low  $n$  values indicating that a lower number of ester-ester interactions are disrupted (consequently,  $\Delta\eta$  increases) and increases for large  $n$  values, which might be due to the quasi-cyclic structures of the alkanoate are good breakers of the correlations of molecular orientations of longer *n*-alkanes, leading to increased negative values of  $\Delta\eta$ . However, this statement should be taken with caution until more viscosity data for homologous series are available.



**Figure 8.**  $\Delta\eta$  results for  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COO}(\text{CH}_2)_{v-1}\text{CH}_3$  (1) + heptane (2) systems at 298.15 K. Symbols, experimental results (for source of data, see Table 2 and [82]): (O), ( $u = 1, v = 1$ ); (●), ( $u = 1, v = 4$ ); (■), ( $u = 2, v = 3$ ); (▲); ( $u = 9, v = 1$ ). Lines are for the aid of the eye.

With regards to the results obtained from the application of the Grunberg-Nissan equation [23], we note that it correlates very well the viscosity data under consideration (Table 2). The  $G_{12}$  parameter is usually negative, indicating that dispersive interactions are dominant [62,66,67], in agreement with our previous findings. Positive values of the parameter are encountered for the systems: methyl decanoate + heptane, or methyl ethanoate + hexadecane, or propyl propanoate + tetradecane (Table 2), which may be ascribed to size effects. In order to investigate this point, we have determined deviations of molar Gibbs energy of activation from the linear dependence with composition,  $\Delta(\Delta G_m^*)$ , according to the equation [68]:

$$\Delta(\Delta G_m^*) = \Delta G_m^* - x_1 \Delta G_{m1}^* - x_2 \Delta G_{m2}^* = RT[\ln(V_m \eta) - x_1 \ln(V_{m1} \eta_1) - x_2 \ln(V_{m2} \eta_2)] \quad (11)$$

Positive results of this magnitude have been also obtained for the same solutions mentioned above. Mixtures of benzene [68] or cyclohexane [69] and longer *n*-alkanes, or formed by long chain 1-alkanol and an amine [70,71] are also characterized by positive  $\Delta(\Delta G_m^*)$  results, which underlines the importance of size effects on this magnitude. Finally, it must be mentioned that for the series  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COOCH}_3$  + heptane, the function  $\Delta(\Delta G_m^*)$  shows a minimum at  $u = 3$ , in agreement with the finding of Dusart et al., who demonstrated the existence of quasi-cycles of methyl butanoate from viscosity data [20].

#### 4.5 Flory model

Inspection of Tables 1 and S2 shows that, for many of the considered systems, deviations between experimental and theoretical values of  $H_m^E$  are  $\leq 10\%$ , which suggests the existence of weak orientational effects. Large values of  $\sigma_r(H_m^E)$  are obtained for systems with pentane or for the mixtures ethyl tetradecanoate + heptane, or + nonane. For example,  $\sigma_r(H_m^E)$ (pentane) = 0.189 (methyl hexanoate); 0.269 (methyl decanoate); 0.354 (methyl tetradecanoate). Since orientational effects become weaker when the ester size increases along a given homologous series, the poorer results obtained for systems with methyl or ethyl decanoate, or methyl or ethyl tetradecanoate (Tables 1 and S2) cannot be ascribed to such effects, but to the existence of strong structural effects which largely contribute  $H_m^E$  (eos term), and that are not properly described by the model. This can be shown comparing  $H_m^E$  and  $U_{Vm}^E$  results (Tables 1, S2, S5). Thus,  $H_m^E$ (pentane)/J mol<sup>-1</sup> = 305 (methyl tetradecanoate) [35], 74 (ethyl tetradecanoate) [46] and, in the same sequence,  $U_{Vm}^E$ (pentane)/J mol<sup>-1</sup> = 709; 482. In order to examine the influence of the mentioned structural effects on Flory results, the model was applied to mixtures with pentane, heptane, or pentadecane using the corresponding  $U_{Vm}^E$  data. Results are listed in Table 1 (see Figure 2). A meaningful improvement is obtained for systems with pentane. We have determined the average standard relative deviation for  $H_m^E$  and  $U_{Vm}^E$ ,  $\bar{\sigma}_r(F_m^E)$  ( $F_m^E = H_m^E, U_{Vm}^E$ ), for each homologous series, according to the expression:

$$\bar{\sigma}_r(F_m^E) = \frac{1}{N_s} \sum \sigma_r(F_m^E) \quad (12)$$

where  $N_s$  is the number of systems of each series. The results are:  $\bar{\sigma}_r(H_m^E)$ (pentane) = 0.257 (methyl alkanoate); 0.330 (ethyl alkanoate); 0.287 (propyl alkanoate); 0.223 (butyl alkanoate); 0.164 (pentyl alkanoate), and in the same order,  $\bar{\sigma}_r(U_{Vm}^E)$ (pentane) = 0.133; 0.104; 0.228; 0.133, 0.073. For mixtures containing heptane or pentadecane, results are similar. It must be mentioned that the application of group contribution models for the characterization of the COO/aliphatic contacts in mixtures where strong structural effects may be present is quite difficult since the  $H_m^E$  values can largely change when increasing the alkane size in systems with a given ester. Compare, e.g.,  $H_m^E$ (ethyl tetradecanoate)/J mol<sup>-1</sup> = 74 (pentane); 231 (heptane), and 414 (pentadecane) [46]. Thus, solutions with pentane were discarded in an

application of the UNIFAC model to mixtures with butyl alkanoate [55]. In this framework, it should be mentioned that the Dortmund version of UNIFAC and DISQUAC models fail when describing  $H_m^E$  values of mixtures such as pentyl pentanoate + pentane [56].

With regards to Flory results on  $V_m^E$ , the theory usually predicts the increase of this magnitude with  $n$  in systems involving a fixed  $n$ -alkanoate. However, for a number of systems, a decrease of the  $V_m^E$  is observed when replacing pentadecane by heptadecane (see results for mixtures with ethyl heptanoate, or pentyl pentanoate, Table S2). That is, the model overestimates the structural contribution to  $V_m^E$  in systems with heptadecane.

## 5. Conclusions

Interactions in the studied mixtures are of dispersive type. Large structural effects are encountered in a number of systems, e.g., in those containing pentane. The variations of  $\Delta\Delta H_{vap,i}$  and of  $D_{ce,i}$  with the ester size along homologous series formed by methyl or ethyl  $n$ -alkanoates reveal the existence of some structural change in longer  $n$ -alkanoates which leads to stronger interactions between them. This is supported by the variation of  $V_m^E$  values of the corresponding heptane mixtures. The observed decrease of  $H_m^E$  for this type of systems seems to be more related to the COO group is more sterically hindered than to interactional effects. The  $U_{V_m}^E(n)$  function shows a minimum for systems with esters characterized by ( $u \geq 4, v=1$ ); ( $u \geq 7, v=2$ ), or ( $u \geq 1, v=5$ ). That is, certain  $n$ -alkanoates, in an alkane medium, can form quasi-cyclic structures. Free volume effects are determinant for describing viscosity data of these mixtures. It is remarkable that, for systems with butyl ethanoate or methyl decanoate, the variation of  $\Delta\eta$  is consistent with that of  $U_{V_m}^E$ . which suggests that the quasi-cycles of the alkanoate are good breakers of the correlations of molecular orientations of longer  $n$ -alkanes. Results from the Flory model are rather poor for those systems with large structural effects. Better results for these mixtures are obtained when the model is applied using  $U_{V_m}^E$  data.

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## **SUPPLEMENTARY INFORMATION**

### ***N*-ALKANOATE + *N*-ALKANE MIXTURES: FOLDING OF HYDROCARBON CHAINS OF *N*-ALKANOATES**

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**TABLE 1**Physical constants and Flory parameters<sup>a</sup> of pure compounds at  $T = 298.15\text{ K}$ .

Compound	$V_{\text{mi}}/\text{cm}^3\text{ mol}^{-1}$	$\alpha_{pi}/10^{-3}\text{ K}^{-1}$	$\kappa_{Ti}/10^{-12}\text{ Pa}^{-1}$	$V_{\text{mi}}^*/\text{cm}^3\text{ mol}^{-1}$	$P_i^*/\text{J cm}^{-3}$
methyl hexanoate <sup>b</sup>	148.05	1.08	944	117.14	544.9
methyl heptanoate	164.73 <sup>c</sup>	1.04 <sup>c</sup>	889 <sup>d</sup>	131.17	550
methyl octanoate <sup>b</sup>	181.41	0.997	869	145.47	532
methyl decanoate <sup>b</sup>	214.56	0.939	814	173.72	524.6
methyl dodecanoate <sup>b</sup>	247.81	0.895	755	202.17	531
methyl tetradecanoate <sup>b</sup>	280.91	0.867	709	230.29	542
ethyl pentanoate <sup>e</sup>	149.52	1.08	992	118.30	518.5
ethyl hexanoate <sup>f</sup>	166.48	1.10	981	131.31	537.4
ethyl heptanoate <sup>f</sup>	183.09	1.04	934	145.79	523.6
ethyl octanoate <sup>g</sup>	199.80	1.02	904	159.61	527
ethyl decanoate <sup>g</sup>	232.57	0.96	848	187.96	518.5
ethyl dodecanoate <sup>g</sup>	266.11	0.94	814	215.43	525
ethyl tetradecanoate <sup>g</sup>	282.81	0.91	782	230.12	524
propyl butanoate	149.99 <sup>h</sup>	1.15 <sup>h,i</sup>	1006 <sup>d</sup>	117.39	556.4
butyl butanoate	166.78 <sup>j</sup>	1.04 <sup>j,k</sup>	911 <sup>d</sup>	132.80	536.8
pentyl propanoate	166.18 <sup>l</sup>	1.08 <sup>l,m</sup>	939 <sup>d</sup>	131.48	547.8
pentyl pentanoate	200.16 <sup>l</sup>	1.02 <sup>l,k</sup>	892 <sup>d</sup>	159.9	534.2
tridecane <sup>n</sup>	244.91	0.95	944	197.93	459.1
pentadecane <sup>n</sup>	277.66	0.91	882	225.93	464.5
heptadecane <sup>o</sup>	310.96	0.899	819	253.51	492.4

<sup>a</sup> $V_{\text{mi}}$ , molar volume;  $\alpha_{pi}$ , isobaric expansion coefficient;  $\kappa_{Ti}$ , isothermal compressibility,  $V_{\text{mi}}^*$ , $P_i^*$ , reduction parameters for volume and pressure, respectively; <sup>b</sup>[S1]; <sup>c</sup>[S2]; <sup>d</sup> estimated using the Manzini-Creszenci method [S3]; <sup>e</sup>[S4]; <sup>f</sup>[S5]; <sup>g</sup>[S6]; <sup>h</sup>[S7]; <sup>i</sup>[S8]; <sup>j</sup>[S9]; <sup>k</sup>[S10]; <sup>l</sup>[S9]; <sup>m</sup>[S11]; <sup>n</sup>[S12]; <sup>o</sup>[S13].

**TABLE S2**

Excess molar enthalpies,  $H_m^E$ , volumes,  $V_m^E$ , and isochoric internal energies,  $U_{Vm}^E$ , at equimolar composition and 298.15 K, 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 7), are also included.

$n\text{-C}_n$	$N^a$	$H_m^E /$ $\text{J mol}^{-1}$	$X_{12} /$ $\text{J cm}^{-3}$	$\sigma_r(H_m^E)$	Ref.	$V_m^E /$ $\text{cm}^3 \text{mol}^{-1}$	Ref.	$U_{Vm}^E /$ $\text{J mol}^{-1}$	
						Exp	Flory		
methyl heptanoate + $n$ -alkane									
5	21	631	23.00	0.193	S14	-0.639	-0.540	S15	800
6	20	684	22.58	0.080	S16	-0.139	-0.117	S16	722
7	18	741	22.94	0.073	S17	0.082	0.244	S15	718
8	17	778	22.97	0.081	S18	0.309	0.424	S18	685
9	17	845	24.00	0.074	S19	0.405	0.593	S15	721
10	20	886	24.39	0.092	S20	0.487	0.666	S20	735
12	20	967	25.51	0.077	S21	0.605	0.838	S21	778
13	18	1008	26.08	0.069	S22	0.665	0.847	S15	796
14	21	1050	26.72	0.084	S23	0.671	0.933	S23	835
15	18	1101	27.59	0.062	S24	0.701	0.924	S25	874
16	18	1115	27.59	0.067	S26	0.732	0.973	S26	880
17	18	1147	27.93	0.085	S27	0.739	0.859	S27	899
methyl octanoate + $n$ -alkane									
5	19	561	19.76	0.189	S14	-0.826	-0.689	S1	778
7	17	645	18.93	0.089	S17	-0.023	0.090	S1	652
9	16	756	20.14	0.085	S19	0.309	0.450	S1	662
13	18	902	21.67	0.055	S22	0.558	0.702	S1	725
15	16	1001	23.26	0.064	S24	0.608	0.787	S25	806
17	18	1046	23.55	0.057	S27	0.638	0.743	S27	834
methyl decanoate + $n$ -alkane									
5	19	449	15.14	0.269	S14	-1.070	-1.005	S1	739
7	20	550	14.81	0.106	S17	-0.209	-0.154	S1	612
9	16	639	15.32	0.125	S19	0.144	0.225	S1	595
12	12	722	15.72	0.146	S28	0.366	0.476	S1	607
13	18	756	16.08	0.092	S22	0.404	0.510	S1	627
14	12	789	16.46	0.085	S28	0.440	0.600	S28	648

TABLE S2 (continued)

15	18	831	17.00	0.061	S24	0.460	0.596	S25	683
16	12	829	16.68	0.071	S28	0.492	0.629	S28	671
17	18	885	17.51	0.070	S27	0.512	0.597	S27	714
<b>methyl dodecanoate + <i>n</i>-alkane</b>									
5	17	357	11.92	0.348	S29	-1.251	-1.139	S1	700
7	17	442	11.26	0.096	S29	-0.325	-0.436	S1	537
9	20	515	11.40	0.110	S30	0.114	-0.243	S1	476
13	18	640	12.35	0.104	S22	0.283	0.332	S1	548
15	16	707	13.04	0.077	S24	0.354	0.435	S25	589
17	18	749	13.31	0.086	S27	0.393	0.465	S27	629
<b>methyl tetradecanoate + <i>n</i>-alkane</b>									
5	18	305	10.11	0.354	S29	-1.450	-1.609	S1	709
7	18	373	9.12	0.118	S29	-0.467	-0.670	S1	516
9	20	425	8.85	0.128	S30	-0.097	-0.233	S1	456
13	18	531	9.46	0.092	S22	0.191	0.162	S1	463
15	18	597	10.12	0.085	S24	0.273	0.286	S25	506
17	20	639	10.42	0.094	S27	0.307	0.344	S27	534
<b>ethyl heptanoate + <i>n</i>-alkane</b>									
5	17	302	11.21	0.232	S5	-0.757	-0.746	S5	506
7	17	530	15.43	0.070	S5	0.091	0.122	S5	510
9	16	650	17.23	0.089	S5	0.325	0.460	S5	552
13	17	834	20.04	0.086	S5	0.578	0.698	S5	653
15	17	944	21.95	0.095	S5	0.645	0.774	S5	739
17	16	1022	23.06	0.062	S5	0.701	0.726	S5	791
<b>ethyl octanoate + <i>n</i>-alkane</b>									
5	18	234	8.77	0.258	S6	-0.958	-0.914	S6	491
7	17	437	12.16	0.041	S6	-0.029	-0.028	S6	445
9	16	535	13.39	0.083	S6	0.253	0.322	S6	458
13	17	695	15.66	0.102	S6	0.497	0.579	S6	538
15	17	783	17.07	0.129	S6	0.572	0.654	S6	599
17	17	876	18.50	0.202	S6	0.619	0.631	S6	671
<b>ethyl decanoate + <i>n</i>-alkane</b>									
5	17	151	6.19	0.316	S6	-1.200	-1.174	S6	482
7	19	300	7.92	0.035	S6	-0.237	-0.284	S6	370
9	19	356	8.14	0.075	S6	0.079	0.065	S6	332

TABLE S2 (continued)

13	17	499	10.06	0.140	S6	0.343	0.362	S6	390
15	17	582	11.29	0.106	S6	0.435	0.449	S6	444
17	17	650	12.19	0.086	S6	0.491	0.451	S6	487
<i>ethyl dodecanoate + n-alkane</i>									
5	13	99	4.65	0.336	S6	-1.332	-1.330	S6	467
7	18	251	6.31	0.115	S6	-0.403	-0.430	S6	375
9	16	297	6.31	0.110	S6	-0.048	-0.054	S6	312
13	17	385	7.09	0.111	S6	0.232	0.248	S6	310
15	18	437	7.72	0.132	S6	0.314	0.331	S6	333
17	17	476	8.12	0.130	S6	0.379	0.333	S6	349
<i>ethyl tetradecanoate + n-alkane</i>									
5	10	74	4.09	0.639	S6	-1.472	-1.500	S6	482
7	17	231	5.79	0.224	S6	-0.477	-0.540	S6	375
9	17	276	5.73	0.169	S6	-0.146	-0.149	S6	231
13	17	348	6.16	0.106	S6	0.176	0.169	S6	291
15	18	377	6.37	0.126	S6	0.245	0.246	S6	297
17	18	414	6.74	0.102	S6	0.296	0.271	S6	314
<i>propyl propanoate + n-alkane</i>									
5	17	670	26.96	0.249	S7	-0.168	-0.263	S7	714
7	17	893	31.76	0.091	S7	0.562	0.668	S7	736
9	17	1019	34.15	0.075	S7	0.753	1.089	S7	793
13	16	1269	39.55	0.064	S7	0.932	1.448	S7	982
15	17	1390	42.21	0.070	S7	0.981	1.564	S7	1078
17	17	1464	43.38	0.068	S7	1.041	1.457	S7	1120
<i>propyl butanoate + n-alkane</i>									
5	19	494	18.77	0.354	S7	-0.379	-0.336	S7	595
7	16	747	24.53	0.091	S7	0.393	0.508	S7	633
9	17	855	26.07	0.080	S7	0.616	0.805	S7	669
13	17	1065	30.07	0.064	S7	0.803	1.019	S7	811
15	17	1192	32.76	0.046	S7	0.865	1.097	S7	915
17	17	1294	34.53	0.059	S7	0.901	1.011	S7	995
<i>butyl propanoate + n-alkane</i>									
5	15	577	21.91	0.193	S31	-0.484	-0.290	S31	706
7	18	760	24.95	0.100	S31	0.359	0.492	S31	655
9	16	874	26.75	0.073	S31	0.571	0.805	S31	701

TABLE S2 (continued)

13	18	1094	30.87	0.080	S31	0.791	1.032	S31	843
15	18	1208	33.13	0.082	S31	0.861	1.104	S31	932
17	17	1318	35.18	0.074	S31	0.922	1.033	S31	1011
<b>butyl butanoate + <i>n</i>-alkane</b>									
5	15	400	15.10	0.320	S31	-0.632	-0.690	S31	568
7	17	565	17.43	0.159	S31	0.190	0.131	S31	510
9	17	679	19.15	0.084	S31	0.407	0.475	S31	556
13	18	918	23.55	0.057	S31	0.679	0.769	S31	703
15	17	1038	25.79	0.098	S31	0.761	0.856	S31	794
17	18	1160	27.98	0.087	S31	0.804	0.844	S31	893
<b>pentyl ethanoate + <i>n</i>-alkane</b>									
5	16	636	24.21	0.217	S9	-0.453	-0.211	S9	758
7	17	828	27.19	0.086	S9	0.350	0.532	S9	728
9	18	947	28.84	0.097	S9	0.612	0.807	S9	761
13	16	1186	33.13	0.073	S9	0.814	1.010	S9	928
15	20	1305	35.43	0.081	S9	0.882	1.068	S9	1019
17	15	1412	37.27	0.119	S9	0.971	1.003	S9	1088
<b>pentyl propanoate + <i>n</i>-alkane</b>									
5	16	469	17.19	0.104	S9	-0.631	-0.559	S9	635
7	17	647	19.89	0.078	S9	0.156	0.265	S9	601
9	17	739	20.76	0.087	S9	0.449	0.584	S9	603
13	18	945	24.47	0.061	S9	0.670	0.849	S9	732
15	16	1056	26.51	0.070	S9	0.764	0.930	S9	809
17	18	1154	28.18	0.061	S9	0.830	0.879	S9	877
<b>pentyl pentanoate + <i>n</i>-alkane</b>									
5	15	323	11.43	0.170	S9	-1.026	-0.864	S9	601
7	15	448	12.44	0.114	S9	-0.050	-0.037	S9	463
9	18	536	13.78	0.099	S9	0.249	0.327	S9	460
13	16	692	15.57	0.076	S9	0.528	0.581	S9	525
15	19	771	16.79	0.087	S9	0.612	0.654	S9	575
17	16	862	18.17	0.082	S9	0.682	0.632	S9	635

<sup>a</sup>number of data points

**TABLE S3**

Excess partial molar functions at infinite dilution of the first compound,  $F_{m1}^{E,\infty}$ , and at 298.15 K for *n*-alkanoate (1) + heptane (2) mixtures:  $F = H$  (enthalpy) or  $U_V$  (isochoric internal energy)

<i>n</i> -alkanoate	$H_{m1}^{E,\infty}$ /kJ mol <sup>-1</sup>	Ref.	$U_{V,m1}^{E,\infty}$ /kJ mol <sup>-1</sup>
methyl ethanoate	8.3	S32	5.7
methyl propanoate	5.4	S17	4.3
methyl butanoate	5.0	S17	4.0
methyl pentanoate	4.5	S17	3.8
methyl hexanoate	4.2	S17	3.5
methyl heptanoate	4.0	S17	3.4
methyl octanoate	3.5	S17	3.1
methyl decanoate	3.3	S17	3.1
methyl dodecanoate	2.7	S29	3.0
methyl tetradecanoate	2.7	S29	3.0
ethyl ethanoate	7.0	S5	5.1
ethyl propanoate	4.8	S5	3.7
ethyl butanoate	4.5	S5	3.7
ethyl pentanoate	3.9	S5	3.1
ethyl hexanoate	3.6	S16	3.2
ethyl heptanoate	2.7	S5	2.4
ethyl octanoate	2.0	S6	2.1
ethyl decanoate	1.5	S6	2.0
ethyl dodecanoate	1.5	S6	2.0
ethyl tetradecanoate	1.8	S6	2.5
propyl ethanoate	5.6	S33	4.6
propyl propanoate	4.4	S7	3.7
propyl butanoate	3.7	S7	3.1
butyl ethanoate	5.4	S31	4.5
butyl propanoate	4.3	S31	3.8
butyl butanoate	3.6	S31	3.4
pentyl ethanoate	4.5	S9	3.7
pentyl propanoate	3.4	S7	3.2
pentyl pentanoate	2.9	S9	3.0

**TABLE S4**

Standard enthalpies of vaporization at 298.15 K,  $\Delta H_{\text{vap},i}$ ,  $\Delta\Delta H_{\text{vap},i}$  ( $= \Delta H_{\text{vap},i}$  (pure compound)  $- \Delta H_{\text{vap},i}$  (isomeric alkane)); molar volumes,  $V_{\text{mi}}$ , density of cohesive energy,  $D_{\text{cei}}$  (equation 10), internal pressures,  $P_{\text{int},i}$  (equation 11)<sup>a</sup> and  $q_i$  ( $= P_{\text{int},i}/D_{\text{cei}}$ ).

compound	$\Delta H_{\text{vap},i}$ / kJ mol <sup>-1</sup>	Ref.	$\Delta\Delta H_{\text{vap},i}$ / kJ mol <sup>-1</sup>	$V_{\text{mi}}$ / cm <sup>3</sup> mol <sup>-1</sup>	Ref.	$D_{\text{cei}}$ / MPa	$P_{\text{int},i}$ / MPa	$q_i$
methyl ethanoate	32.29	S34		79.82	S1	373.5	370.3	0.99
methyl butanoate	39.28	S34	12.8	114.42	S1	321.6	352.7	1.10
methyl pentanoate	43.10	S34	11.5	131.30	S2	309.4	350.7	1.13
methyl hexanoate	48.04	S34	11.5	148.05	S1	307.7	341.1	1.11
methyl heptanoate	51.62	S34	10.1	164.73	S10	298.3	348.7	1.17
methyl octanoate	56.41	S34	10.0	181.41	S1	297.3	342.0	1.15
methyl decanoate	66.75	S34	10.3	214.56	S1	299.6	343.8	1.15
methyl dodecanoate	77.17	S34	10.7	247.81	S1	301.4	353.3	1.17
methyl tetradecanoate	86.98	S34	10.9	280.90	S1	300.8	364.6	1.21
ethyl butanoate	42.68	S34	11.1	133.01	S35	302.2	348.7	1.15
ethyl pentanoate	47.01	S34	10.4	149.39	S35	298.1	324.5	1.09
ethyl hexanoate	51.72	S34	10.2	166.48	S5	295.8	334.2	1.13
ethyl heptanoate	55.8	S35	9.4	182.09	S5	292.8	331.9	1.13
ethyl octanoate	59.5	S36	8.1	199.80	S6	285.4	336.3	1.18
ethyl decanoate	70.5	S37	9.0	232.97	S6	292.0	337.4	1.16
ethyl dodecanoate	80.	S38	8.7	266.11	S6	291.3	344.2	1.18
2-butanone	34.79	S34		90.14	S39	385.8	333.7	0.86
2-pentanone	38.46	S34	12.0	107.46	S40	334.8	324.9	0.97
2-hexanone	43.1	S41	11.5	124.16	S42	327.2	306.3	0.94
2-heptanone	47.1	S41	10.6	140.76	S43	317.7	326.0	1.03
2-octanone	51.8	S44	10.3	157.45	S45	313.2	341.5	1.10
2-decanone	60.9	S46	9.5	190.55	S47	306.6	335.8	1.10
2-dodecanone	71.83	S34	10.3	223.87 <sup>b</sup>		309.7		
diethyl ether	27.19	S34	0.76	104.74	S48	259.6	250.6	0.97
dipropyl ether	35.68	S34	-0.9	137.68	S49	259.1	261.0	1.01
dibutyl ether	44.56	S34	-1.8	170.45	S50	261.4	280.2	1.07
dipentyl ether	54.50	S34	-1.9	203.40	S51	267.9	286.9	1.07
dihexyl ether	64.10	S34	-2.3					
pentane	26.43	S34		116.11	S45	206.3	220.1	1.07

TABLE S4 (continued)

hexane	31.56	S33	131.57	S45	221.0	230.4	1.04
heptane	36.57	S33	147.45	S52	231.2	256.2	1.11
octane	41.49	S33	163.52	S53	238.6	266.5	1.12
nonane	46.41	S33	179.69	S45	244.5	274.6	1.12
decane	51.38	S33	195.90	S53	249.6	282.2	1.13
dodecane	61.51	S33	228.47	S53	258.4	289.6	1.12
tridecane	66.43	S33	244.91	S54	261.1	299.9	1.15
tetradecane	71.30	S33	261.09	S53	263.6	302.8	1.15
pentadecane	76.11	S33	277.66	S54	265.2	307.5	1.16
hexadecane	81.38	S33	294.04	S53	268.3	305.3	1.14

<sup>a</sup>values of the physical constants needed to determine internal pressure are listed in Table1 and

in references [S55-S57]; <sup>b</sup>estimated value from molar volumes of lower 2-alkanones

**TABLE S5**

Excess molar enthalpies,  $H_m^E$ , volumes,  $V_m^E$ , and isochoric internal energies,  $U_{V_m}^E$ , at equimolar composition and 298.15 K, for *n*-alkanoate (1) + *n*-alkane (2) mixtures.

<i>n</i> -C <sub><i>n</i></sub>	$H_m^E$ / J mol <sup>-1</sup>	Ref.	$V_m^E$ / cm <sup>3</sup> mol <sup>-1</sup>	Ref.	$U_{V_m}^E$ / J mol <sup>-1</sup>
methyl propanoate + <i>n</i> -alkane					
5	1191	S14	0.444	S1	1075
6	1345	S16	0.825	S16	1121
7	1425	S17	1.000	S1	1133
8	1535	S18	1.123	S18	1200
10	1685	S20	1.252	S20	1299
12	1831	S21	1.318	S21	1419
14	1930	S23	1.322	S23	1505
15	1966	S58	1.396	S25	1514
16	2019	S26	1.362	S26	1580
17	2065	S27	1.411	S27	2589
methyl butanoate + <i>n</i> -alkane					
5	979	S14	0.098	S1	953
6	1100	S16	0.528	S16	957
7	1170	S17	0.744	S26	954
8	1239	S18	0.865	S18	982
10	1351	S20	1.003	S20	1032
12	1483	S21	1.075	S21	1148
14	1577	S23	1.111	S23	1222
15	1626	S58	1.136	S25	1260
16	1661	S26	1.153	S26	1292
17	1690	S27	1.168	S27	1298
methyl pentanoate + <i>n</i> -alkane					
5	830	S124	-0.328	S15	918
6	894	S16	0.235	S16	830
7	968	S17	0.464	S15	833
8	1018	S18	0.617	S18	834
10	1139	S20	0.769	S20	902
12	1240	S21	0.853	S21	974
14	1325	S23	0.913	S23	1033
16	1406	S26	0.966	S26	1096
17	1436	S27	0.9733	S27	1110

TABLE S5 (continued)

methyl hexanoate + *n*-alkane

5	721	S14	-0.465	S1	843
6	782	S16	0.037	S16	772
7	838	S17	0.278	S1	757
8	888	S18	0.442	S18	757
9	936	S19	0.537	S1	774
10	982	S20	0.612	S20	795
12	1081	S21	0.716	S21	860
13	1123	S22	0.755	S1	885
14	1163	S23	0.780	S23	915
16	1233	S26	0.827	S26	970
17	1278	S27	0.829	S27	1003

ethyl pentanoate + *n*-alkane

5	501	S5	-0.344	S5	592
7	762	S5	0.383	S5	651
9	895	S5	0.609	S5	712
13	1118	S5	0.816	S5	862
15	1217	S5	0.874	S5	939
17	1322	S5	0.921	S5	1018

ethyl hexanoate + *n*-alkane

5	406	S5	-0.532	S5	547
7	655	S5	0.222	S5	591
9	778	S5	0.452	S5	642
13	980	S5	0.676	S5	768
15	1086	S5	0.743	S5	850
17	1177	S5	0.791	S5	916

propyl ethanoate + *n*-alkane

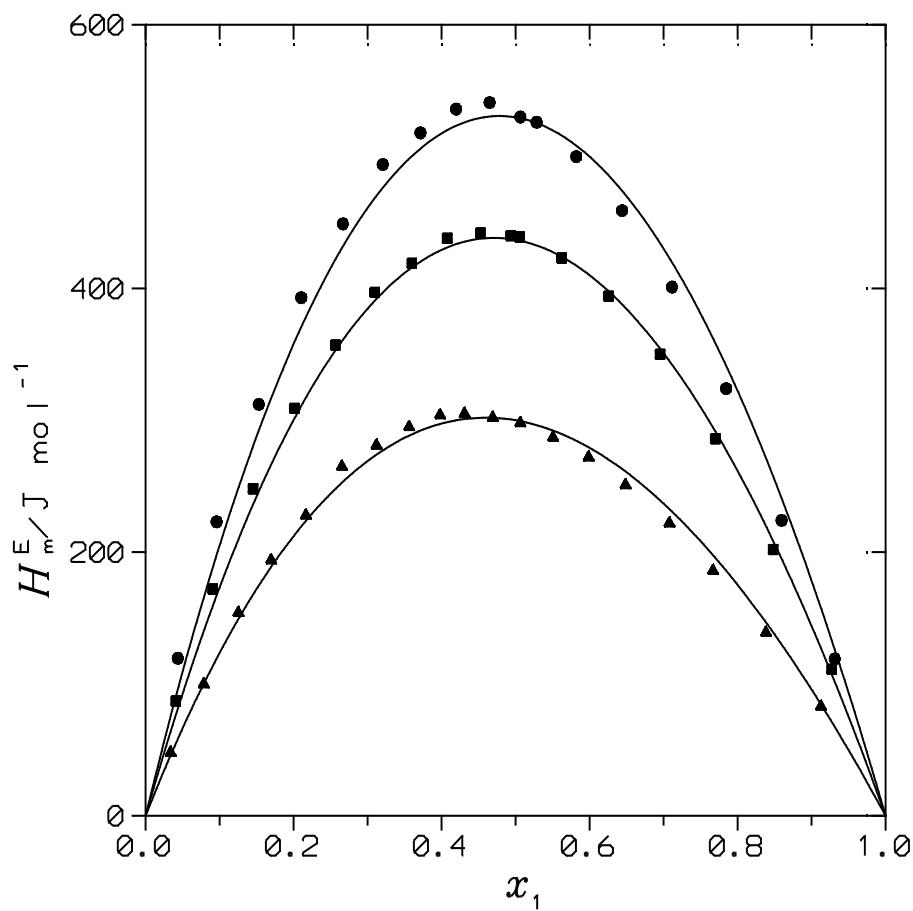
5	1024	S7	0.131	S7	990
7	1199	S7	0.819	S7	969
9	1335	S7	0.964	S7	1145
13	1601	S7	1.144	S7	1239
15	1718	S7	1.167	S7	1344
17	1867	S7	1.211	S7	1466

butyl ethanoate + *n*-alkane

5	789	S31	-0.224	S31	848
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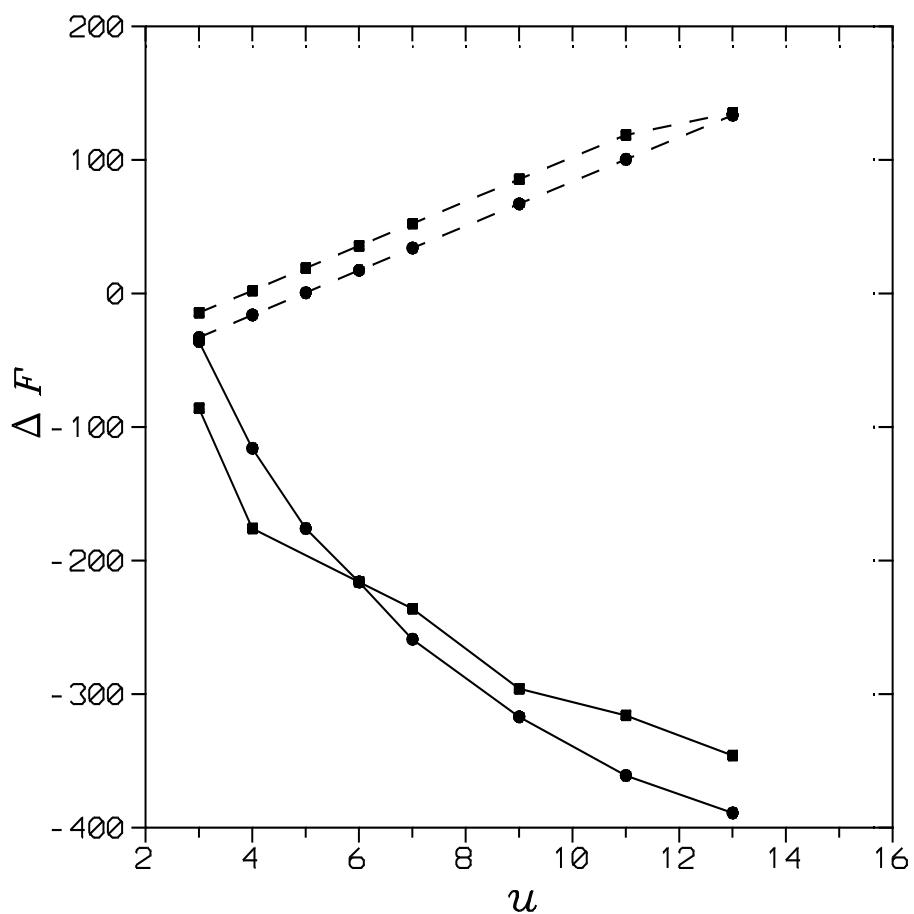
TABLE S5 (continued)

7	980	S31	0.548	S31	821
9	1123	S31	0.754	S31	887
13	1347	S31	0.935	S31	1053
15	1447	S31	0.996	S31	1129
17	1575	S31	1.053	S31	1226



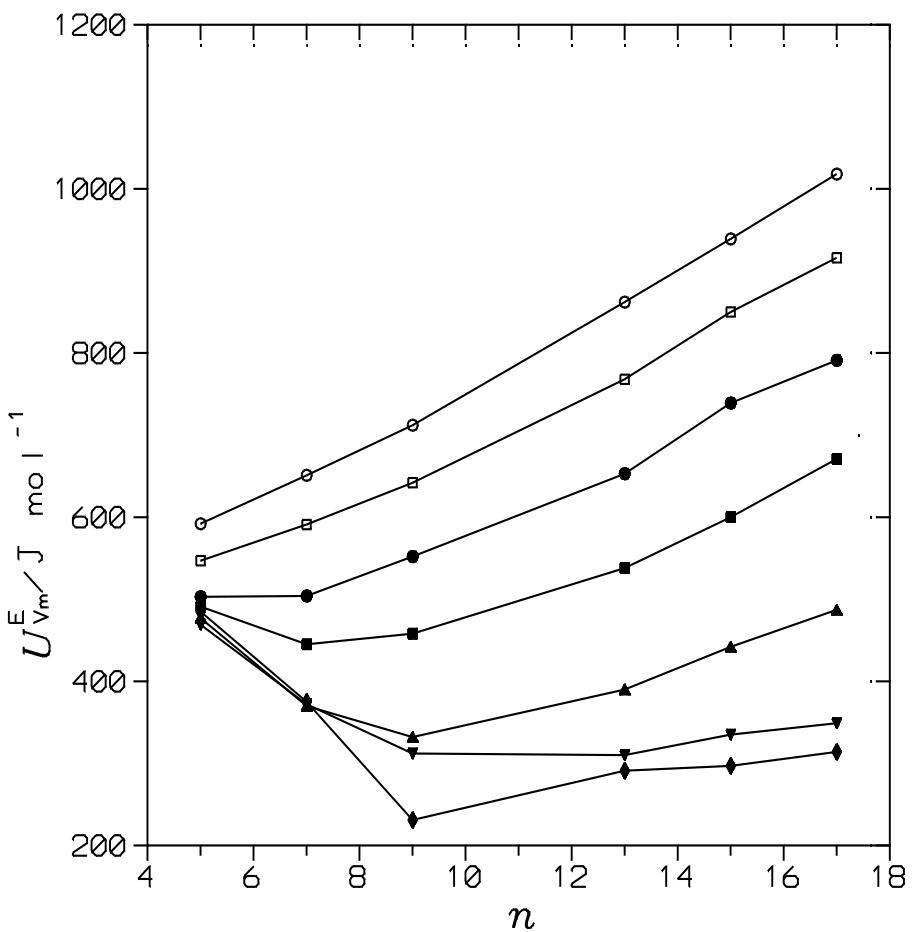
**Figure S1**

$H_m^E$  for  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COOCH}_2\text{CH}_3$  (1) + heptane (2) systems at 298.15 K. Symbols, experimental results (for source of data, see Table S2): (●),  $u = 6$ ; (■),  $u = 7$ ; (▲),  $u = 9$ . Lines, Flory results using interaction parameters listed in Table S2.



**Figure S2**

Differences between isobaric expansion coefficients or molar volumes of pure compounds in the mixtures  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COO}(\text{CH}_2)_{v-1}\text{CH}_3$  (1) + heptane (2) at 298.15 K. Symbols: ( $\bullet$ ),  $\Delta F / \text{K}^{-1} = (\alpha_{p1} - \alpha_{p2})10^3$ ; ( $\blacksquare$ ),  $\Delta F / \text{cm}^3 \text{mol}^{-1} = V_{m1} - V_{m2}$ . Solid lines, methyl alkanoates, dashed lines ethyl alkanoates. For source of data, see Table S2 and [S55].



**Figure S3**

$U_{Vm}^E$  of  $\text{CH}_3(\text{CH}_2)_{u-1}\text{COOCH}_2\text{CH}_3$  (1) +  $n$ -alkane (2) systems at equimolar composition and 298.15 K and atmospheric pressure vs.  $n$ , the number of C atoms in the  $n$ -alkane. Symbols: (O),  $u = 4$ ; ( $\square$ ),  $u = 5$ ; ( $\bullet$ ),  $u = 6$ ; ( $\blacksquare$ ),  $u = 7$ ; ( $\blacktriangle$ ),  $u = 9$ ; ( $\blacktriangledown$ ),  $u = 11$ ; ( $\blacklozenge$ ),  $u = 13$ . Numerical data are listed in Tables S2 and S5.

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