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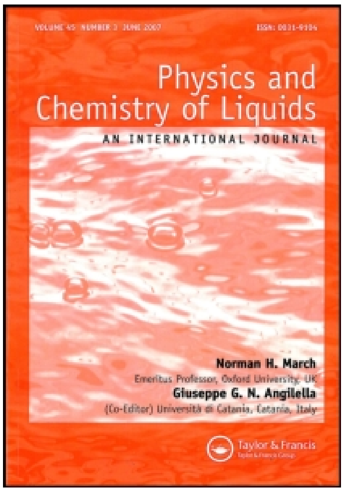

Physics and Chemistry of Liquids

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Thermodynamic properties of (ethylbenzene + an alkane or + an alkyl ethanoate): experimental H_m^E and V_m^E values

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In this work, we present the experimental values of excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, for a set of mixtures composed of ethylbenzene with several alkanes, from heptane to hexadecane, and the first four alkyl ethanoates. In all cases, measurements were made at the two temperatures of 298.15 and of 318.15 K. The mixtures of $C_6H_5C_2H_5 + C_nH_{2n+2}$ present endothermic effects that increase quasilinearly with *n*, and expansive effects that also increase with *n*, but quasiexponentially. The influence of temperature on these mixtures produces thermal indices $(\partial H_m^E/\partial T)_{p,x} < 0$ and $(\partial V_m^E/\partial T)_{p,x} < 0$. The aromatic mixtures with alkyl ethanoates, $C_6H_5C_2H_5 + CH_3COOC_vH_{2v+1}$, show a different behaviour. In this case, both the H_m^E and the V_m^E diminish quasiexponentially with the increase in *v*, resulting in $V_m^E < 0$ for mixtures with $v = 4$, and sigmoidal when $v = 3$. The rise in temperature produces a $(\partial H_m^E/\partial T)_{p,x} > 0$ and $(\partial V_m^E/\partial T)_{p,x} > 0$. In all cases, the experimental values were treated with a suitable polynomial equation that can simultaneously correlate the excess properties with liquid–vapour equilibria data. Finally, a prediction of the H_m^E values was made with two versions of the UNIFAC group contribution model, although it was necessary to recalculate parameters corresponding to the $CH_2/ACCH_2$ and $COOC/ACCH_2$ interactions for the groups of mixtures studied in the version of Dang and Tassios (Ind. Eng. Chem. Des. Dev. **25**, 22 (1986)), to obtain acceptable estimations.

Keywords: excess enthalpy; excess volumes; alkane; ethylbenzene; ethanoates; UNIFAC

1. Introduction

This article continues a series of works that study the behaviour of binary mixtures containing benzene derivatives with saturated hydrocarbons and esters, but analysing in this first part of the project only mixtures of alkyl ethanoates. Studies of systems with butyl and propylbenzene have been presented in previous papers [1,2], which provided experimental data of enthalpies H_m^E and excess volumes V_m^E for mixtures containing these compounds, giving an interpretation of their molecular behaviour. Regarding the modelling, previous works concluded that the UNIFAC group contribution model in the version of Gmehling *et al.* [3] did not give acceptable results for systems with alkanes and

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fair for systems containing alkyl ethanoates, while the simpler version of Dang and Tassios [4] was well adapted to the experimental data, and became increasingly valuable when new proposals were incorporated for the corresponding interaction parameters. One of the drawbacks of this latter version of the model was the loss of precision that occurs with increasing chain length of the compounds in the solution. Therefore, for this work, experimental data have been measured for other mixtures that can be used to confirm, or modify, the results obtained in the modelling. We therefore centred mainly on two points. On the one hand, to extend the model in an attempt to reduce the dependence on the molecular size of some compounds, and on the other hand, to study the effect of temperature, verifying how the model takes into account this magnitude to estimate the values in the same experimental direction. A prerequisite to modifying a theoretical model is to have experimental data of quality for reference purposes, which was one of the objectives of our research team. In the case of any model, and here in the case of UNIFAC, when unsuitable experimental data are used, interaction parameters are produced that do not adapt the model to the properties of the mixture. We therefore performed a preliminary analysis of data in the literature and confirmed their quality, ensuring that they were comparable with those obtained in this work, which enabled us to make better decisions about the modelling.

In research into liquid mixtures, there has always been considerable interest concerning studies into aromatic compounds, and the recent literature includes a significant amount of information on systems containing benzene derivatives. There is also quite a lot of information about ethylbenzene mixtures, which we analyse in this work. Hence, Figure 1(a) and (b) present, respectively, for mixtures $C_6H_5C_2H_5 + C_nH_{2n+2}$ and

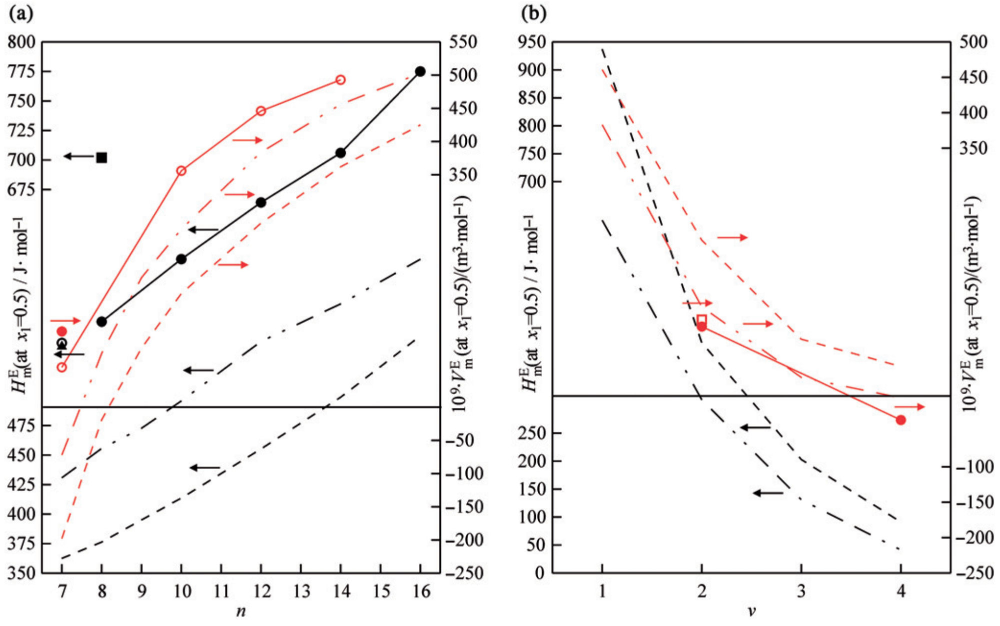

Figure 1. Equimolar H_m^E (black) and V_m^E (red) values from the literature as a function of chain-length for propylbenzene (–··–) [2] and butylbenzene (- - -) [1] at 298.15, and the values from the literature for ethylbenzene (colour online). (a) (▲) [5], (○) [6], (●) [7,8], (■) [9], (○) [10] and (●) [11]. (b) (●) [15,16], and (□) [14].

$C_6H_5C_2H_5 + CH_3COOC_uH_{2u+1}$, the equimolar values of H_m^E and V_m^E obtained in the literature. The equimolar values of H_m^E and V_m^E [1–2,5–11], represented in Figure 1(a) at 298.15 K for mixtures of alkanes, are distributed regularly as a function of n, with the exception of the H_m^E value by Murti *et al.* [9], which differed greatly from the other values and so is not considered here. The set of values seems to correspond to a linear representation between equimolar values of other groups that contain propyl [2] and butylbenzene [1], and, initially, those that form the line corresponding to the $C_6H_5C_2H_5 + C_nH_{2n+2}$ mixtures are coherent, except for the one corresponding to $n = 16$ [7]. In this case, because of the need for comparative H_m^E data, measurements are recorded where $n \geq 12$. Regarding the V_m^E values, the sequence of data presented by Grolier *et al.* [10] is acceptable, although the value of Diaz *et al.* [11], for the ethylbenzene + heptane system is slightly high. Regarding values obtained for the mixtures studied in other works [1,2], the curve traced with data, the literature trends to cut that of propylbenzene, but values for mixtures of ethylbenzene + C_8, o $+C_9$, or $+C_{16}$ are also missing. It is therefore clear that we must complete the database for V_m^E values. The literature compiles ethylbenzene + alkane data at other temperatures [12,13].

For the mixtures of $C_6H_5C_2H_5 + CH_3COOC_vH_{2v+1}$, the literature does not present H_m^E data, although V_m^E data are found for the $C_6H_5C_2H_5 + CH_3COOC_2H_5$ [14,15], or $+ CH_3COOC_4H_9$ [16] mixtures at $T = 298.15$ K, and also for the same esters but at other temperatures [17].

After carrying out this analysis and also taking into account the considerable age of the data, a continuation of the research first started by this project consolidates the database of H_m^E and V_m^E for a set of systems using as a common compound ethylbenzene and its binary mixtures with alkanes (C_7 to C_{16}) and alkyl ethanoates (methyl to butyl). Also, in line with the previous objective, it was decided to measure the excess quantities at the two temperatures, 298.15 and 318.15 K.

Finally, the literature presents isobaric liquid vapour equilibrium data (LVE) [18,19] for ethylbenzene + C_7, or + C_8. These data will be used to verify the value of a combined correlation procedure of mixing properties, which we will apply in this work.

2. Experimental

All compounds used in this work were supplied by companies offering products of maximum purity. Before use, all compounds were degasified with ultrasound and then kept in the dark for several hours on a 3 nm Fluka molecular sieve in order to remove any trace of moisture. The purity of all the liquids was verified by GC, with a HP6890 apparatus, giving values almost identical to those provided by the manufacturer. The final quality of the products was also compared by measuring some of the compounds' physical properties, such as density and refractive index, at the two temperatures considered in this work. For purposes of comparison, the values found for ethylbenzene (Aldrich) are recorded in Table 1, together with those presented in the literature, being acceptable to our results. The properties recorded for the alkanes and ethanoates coincided with those presented in previous work [1,2].

The values of V_m^E were calculated indirectly from density measurements using a DMA-58 Anton Paar vibrating-tube densimeter, with a reading error of $\pm 0.02\,\mathrm{kg\,m^{-3}}$. The apparatus was calibrated at the two working temperatures with bidistilled water, obtained in our laboratory with a conductance lower than $2\,\mu\mathrm{S}$ and nonane (Fluka).

Table 1. Physical properties of pure substances measured at $T = 298.15$ and 318.15 K and atmospheric pressure, where ρ and n_D denote the density and refractive index, respectively.

		ρ (kg m^{-3})		n_D	
Compound	T (K)	Exp.	Lit.	Exp.	Lit.
Ethylbenzene	298.15	862.37	862.64[a] 862.60[b]	1.4928	1.4932[a,b]
	318.15	844.57	845.00[b]	1.4834	1.4824[c]

Notes: [a]From [23]; [b]From [24]; [c]Values interpolated from [24].

The temperature T was achieved with a precision of ±0.01 K by the Peltier effect of the equipment, although an external ultrathermostat supplied water to the densimeter at a temperature of approximately $(T - 1)$K. The uncertainty in the calculations of V_m^E was $\pm 2 \times 10^{-9}$ m^3 mol^{-1}, while it was lower than $\pm 5 \times 10^{-5}$ for the molar fractions.

H_m^E were measured directly in a Calvet MS80D calorimeter, from Setaram Lyon (France), calibrated by applying a Joule effect to a resistance of 1000.2 Ω located in the interior of a cell, using a known power source, EJ3 from Setaram, to simulate thermograms similar to those of the mixing processes. Different paired values (power, time) were applied to the calibration cell. The constant for the apparatus was obtained by linear regression of the pair values, energy supplied/area of response. The uncertainty estimated for the mixing enthalpy measurements was ±2 J mol^{-1}, evaluated by comparing the results with those obtained for the standard mixture cyclohexane + benzene [20]. The uncertainy for the molar fractions' data was of $\pm 2 \times 10^{-4}$.

3. Results and discussion

The experimental data of (x, V_m^E) and (x, H_m^E) for the set of mixtures containing ethylbenzene with alkanes and alkyl ethanoates, measured at $T = 298.15$ K and $T = 318.15$ K, were correlated with a simple polynomial equation, which used as a variable the so called 'active fraction' z_i, referred to one of the two components of the binary mixture. In turn, z_i is related to the composition x_i of the said component and of a parameter k, the value of which is fixed depending on whether V_m^E or H_m^E are correlated, as explained here. Equations for an excess generic quantity Y_m^E referred to the first compound and the corresponding relationship for $z_1 = \varphi(x_1)$ are, respectively:

$$Y_m^E = z_1(1 - z_1)\sum_i a_{i-1} z_1^{i-1}, \quad \text{being} \quad z_1 = \frac{x_1}{x_1 + k(1 - x_1)}, \tag{1}$$

where Y_m^E will give either V_m^E (m^3 mol^{-1}), or H_m^E (J mol^{-1}).

For the case of volumes, the k is identified with the quotient,

$$k_v(p, T) = \frac{V_{2,m}^o(p, T)}{V_{1,m}^o(p, T)} = \frac{M_2\rho_1(p, T)}{M_1\rho_2(p, T)} \cong \frac{r_2}{r_1}, \tag{2}$$

where $V_{i,m}^o$, M_i and ρ_i, are the molar volume, the molecular weight and the density of the component $i = 1, 2$, respectively. The value of k_v calculated in this way is quite similar to that obtained with volume parameters $r_i = \sum \upsilon_k^{(i)} R_k$, produced with a group contribution method, considering the volumes of the functional groups, given by Bondi [21]. This concept is not used to correlate the H_m^E, since if this mixing property is considered to depend directly on the contact surfaces between the compounds of the mixture, Equation (2) should establish relationships between the surfaces, or surface parameters q_i, where $q_i = \sum \upsilon_k^{(i)} Q_k$. Considering the surface/volume ratio of a spherical molecule, it is easy to establish a more appropriate relationship for the value of k, which we will identify as k_h, such that:

$$k_h = \frac{S_2^o}{S_1^o} = \left(\frac{q_2}{q_1}\right)\left(\frac{r_1}{r_2}\right)^{2/3}\left(\frac{V_{2,m}^o}{V_{1,m}^o}\right)^{2/3} = k_q\left(\frac{k_v}{k_r}\right)^{2/3}, \tag{3}$$

such that the values of k_v and k_h depend on the working conditions; in other words, on p and T. The values calculated for k_v and k_h using this procedure for each of the binary mixtures are presented in Table 2, together with the values of the A_i coefficients obtained for each of the systems, by linear regression of the experimental data to Equation (1). The objective function, proposed as the standard deviation of data, $s(Y_m^E)$, was minimised. Representations of experimental data of H_m^E and V_m^E together with the correlation curves for the mixtures of $C_6H_5C_2H_5 + C_nH_{2n+2}$ are shown in Figure 2(a) and (b), while Figure 3(a) and (b) represent data for $C_6H_5C_2H_5 + CH_3COOC_vH_{2v+1}$ ($v = 1$–4), in both cases at the two working temperatures studied here.

Figures 4(a) and (b) and 5(a) and (b) represent, respectively, the values of H_m^E and V_m^E at intermediate composition, as a function of the chain-length of the second component, and at the two temperatures, including also, for comparative purposes, the corresponding values for the same systems published in the literature. It can be observed that the values recorded in this work seem to present a better regularity than those reported previously, probably owing to the use of more modern equipment with clear technical improvements. The greatest difference is produced with the H_m^E values, Figure 4(a), in the $C_6H_5C_2H_5 + C_8$ system reported by Murti *et al.* [9], and mentioned previously, which has a much higher value than that recorded here or those reported by other authors [7]. A difference was detected in V_m^E (at $x = 0.5$), for the $C_6H_5C_2H_5 + C_7$ system, Figure 5(a), with values published by Diaz *et al.* [11], which also showed values for the set of mixtures of ethylbenzene, propylbenzene, or butylbenzene + alkanes at the two temperatures of 298.15 and of 318.15 K. For mixtures with ethanoates, Figure 5(b), the values almost coincide with those found in the literature [14–16].

Analysing together the results represented in Figures 2–5, we can establish that the mixing processes of these compounds are carried out endothermically, $H_m^E > 0$, for all the ethylbenzene + alkane mixtures and with expansive effects, $V_m^E > 0$, being the thermal coefficients $(\partial H_m^E/\partial T)_{p,x} < 0$ and $(\partial V_m^E/\partial T)_{p,x} < 0$. We can observe from Figures 4 and 5 quite a regular increase in excess properties with alkane chain-length, quasilinear for the H_m^E and parabolic for the V_m^E. However, in the case of the mixtures of ethylbenzene + alkyl ethanoates an opposite tendency can be observed, decreasing the H_m^E and V_m^E with the ester chain-length increasing. The influence of temperature is positive on the H_m^E values for all these mixtures but changes sign, and the thermic coefficient goes from being positive for the ethylbenzene + methyl ethanoate system, to negative for the other systems. This can be explained by the influence of the increased chain-length of the ester, with the consequent increase in permanent dipole moment of alkyl ethanoate. In general, the behaviour of these mixtures can be described as being similar to that observed in previous works for

Table 2. Coefficients A_i and k, and standard deviation s, obtained in the correlation of experimental values using Equation (1).

Mixture	k_h	A_0	A_1	A_2	$s(H^E_m)$ (J mol^{-1})
$Y^E_m = H^E_m$ (J mol^{-1})					
$T = 298.15$ K					
$xC_6H_5C_2H_5 +$					
$(1-x)\ C_7H_{16}$	1.307	2441	−569	−26	3
$(1-x)\ C_8H_{18}$	1.449	2752	−1144	217	3
$(1-x)\ C_9H_{20}$	1.589	3066	−1674	461	4
$(1-x)\ C_{10}H_{22}$	1.748	3415	−2378	685	4
$(1-x)\ C_{12}H_{26}$	2.021	3899	−3089	900	7
$(1-x)\ C_{14}H_{30}$	2.307	4557	−4288	1539	7
$(1-x)\ C_{16}H_{34}$	2.598	5176	−5750	2651	4
$xC_6H_5C_2H_5 +$					
$(1-x)\ CH_3CO_2CH_3$	0.764	1939	−111	449	3
$(1-x)\ CH_3CO_2C_2H_5$	0.922	786	−54	129	2
$(1-x)\ CH_3CO_2C_3H_7$	1.070	363	−391	90	2
$(1-x)\ CH_3CO_2C_4H_9$	1.217	12	−762	483	2
$T = 318.15$ K					
$xC_6H_5C_2H_5 +$					
$(1-x)\ C_8H_{18}$	1.503	2819	−1767	887	4
$(1-x)\ C_{10}H_{22}$	1.735	3391	−2303	645	5
$(1-x)\ C_{12}H_{26}$	2.018	3910	−3502	1455	6
$(1-x)\ C_{14}H_{30}$	2.306	4555	−4282	1535	7
$(1-x)\ C_{16}H_{34}$	2.596	5014	−5441	2187	10
$xC_6H_5C_2H_5 +$					
$(1-x)\ CH_3CO_2CH_3$	0.770	2080	−325	777	5
$(1-x)\ CH_3CO_2C_2H_5$	0.926	1096	−404	421	4
$(1-x)\ CH_3CO_2C_3H_7$	1.074	437	4	−318	2
$(1-x)\ CH_3CO_2C_4H_9$	1.219	367	−1807	1476	1

Mixture	k_v	A_0	A_1	A_2	$10^9\ s(V^E_m)$ (m^3 mol^{-1})
$Y^E_m = 10^9 \cdot V^E_m$ (m^3 mol^{-1})					
$T = 298.15$ K					
$xC_6H_5C_2H_5 +$					
$(1-x)\ C_7H_{16}$	1.199	393	−328	97	2
$(1-x)\ C_8H_{18}$	1.329	1005	−542	177	4
$(1-x)\ C_9H_{20}$	1.459	1610	−1145	529	5
$(1-x)\ C_{10}H_{22}$	1.529	1946	−1190	369	4
$(1-x)\ C_{12}H_{26}$	1.857	2716	−2611	1495	5
$(1-x)\ C_{14}H_{30}$	2.123	3388	−3628	1936	5
$(1-x)\ C_{16}H_{34}$	2.389	4000	−4780	2657	4
$xC_6H_5C_2H_5 +$					
$(1-x)\ CH_3CO_2CH_3$	0.649	1179	117	224	2
$(1-x)\ CH_3CO_2C_2H_5$	0.800	514	−172	−51	2
$(1-x)\ CH_3CO_2C_3H_7$	0.941	87	−237	59	1
$(1-x)\ CH_3CO_2C_4H_9$	1.077	−10	−248	80	0

(*continued*)

Table 2. Continued.

Mixture	k_v	A_0	A_1	A_2	$10^9\, s(V_m^E)$ ($m^3\, mol^{-1}$)
$T = 318.15$ K					
$xC_6H_5C_2H_5 +$					
$(1-x)$ C_7H_{16}	1.205	39	318	−257	1
$(1-x)$ C_8H_{18}	1.332	1106	−782	345	7
$(1-x)$ C_9H_{20}	1.462	1738	−1490	835	4
$(1-x)$ $C_{10}H_{22}$	1.593	1969	−1189	269	5
$(1-x)$ $C_{12}H_{26}$	1.854	2493	−1672	608	7
$(1-x)$ $C_{14}H_{30}$	2.119	3236	−3385	1800	6
$(1-x)$ $C_{16}H_{34}$	2.384	3635	−3428	1220	6
$xC_6H_5C_2H_5 +$					
$(1-x)$ $CH_3CO_2CH_3$	0.655	1252	24	396	3
$(1-x)$ $CH_3CO_2C_2H_5$	0.807	383	−47	−59	1
$(1-x)$ $CH_3CO_2C_3H_7$	0.946	−5	−75	−19	1
$(1-x)$ $CH_3CO_2C_4H_9$	1.081	−55	−261	160	1

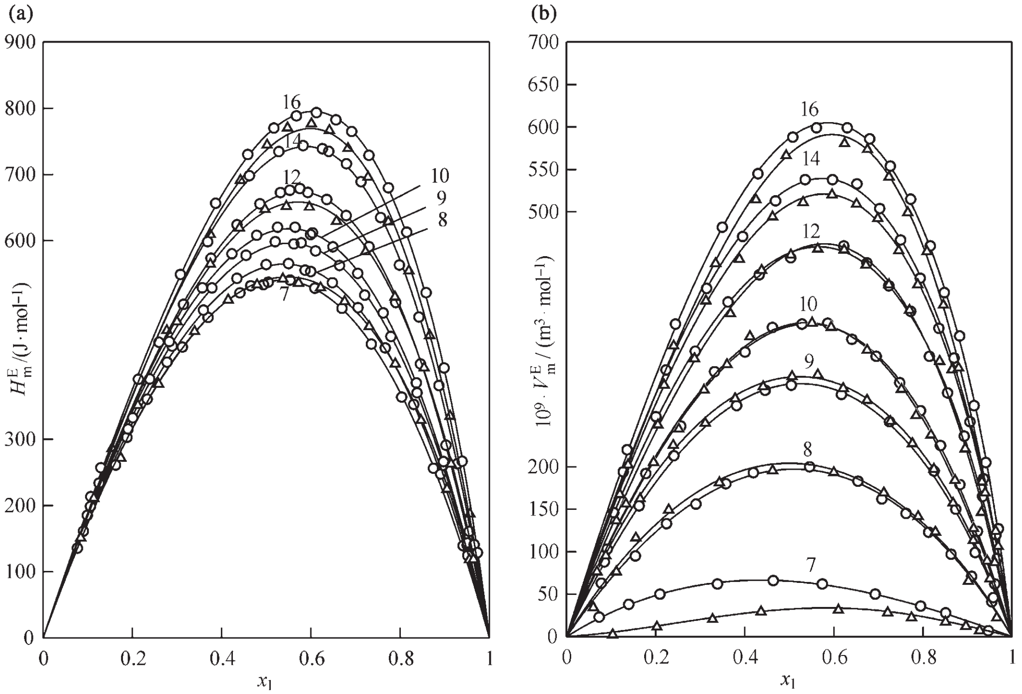

Figure 2. Plots of experimental values and correlation curves for binary mixtures $\{xC_6H_5C_2H_5 + (1-x)C_nH_{2n+2}\}$. (a) H_m^E experimental values at 298.15 K (○) and (△) 318.15 K. (b) Comparison between V_m^E experimental values at two temperatures, 298.15 K (○) and (△) 318.15 K. Labels indicate the *n* values.

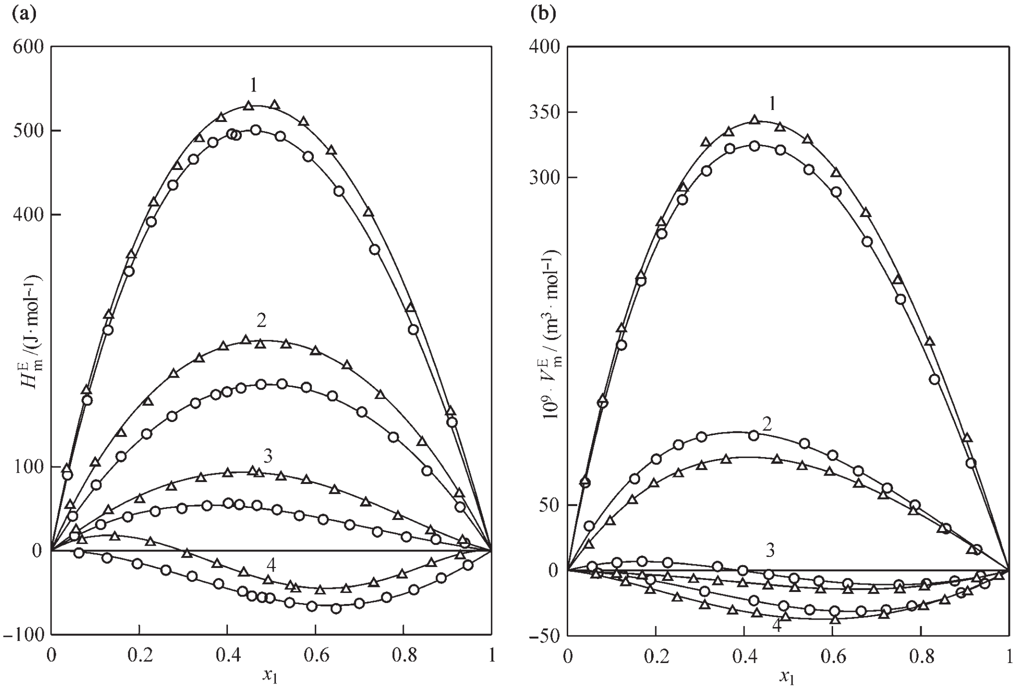

Figure 3. Plots of experimental values and correlation curves for binary mixtures $\{xC_6H_5C_2H_5 + (1-x)CH_3CO_2C_vH_{2v+1}\}$. (a) H_m^E experimental values at 298.15 K (○) and (△) 318.15 K. (b) Experimental values of V_m^E at 298.15 K (○) and (△) 318.15 K. Labels indicate the v values.

propylbenzene [2] and butylbenzene [1], and the considerations made in the said works are also applicable here.

4. Simultaneous correlation of VLE-H_m^E data

As mentioned in the Introduction, mixtures with aromatic compounds are frequently used for purposes of reference in the field of thermodynamics of solutions, resulting in a significant number of publications in the literature that include experimental data of their properties. Hence, for the mixtures studied here, isobaric VLE data of mixtures of $C_6H_5C_2H_5 + C_7$ [18] and $C_6H_5C_2H_5 + C_8$ [19] have been obtained from the literature to correlate the experimental data with the H_m^E values, considering the following thermodynamic relationship:

$$\frac{-H_m^E}{RT} = T\left[\frac{\partial(G_m^E/RT)}{\partial T}\right]_{p,x,\ldots}. \qquad (4)$$

For the non-dimensional Gibbs function, a similar expression to Equation (1) was used, making the coefficients temperature-dependent, such that:

$$\frac{G_m^E}{RT}(x_1, T) = z_1(1-z_1)\left[\left(\frac{A_{00}}{T} + A_{01}\right) + \left(\frac{A_{10}}{T} + A_{11}\right)z_1 + \left(\frac{A_{20}}{T} + A_{21}\right)z_1^2\right], \qquad (5)$$

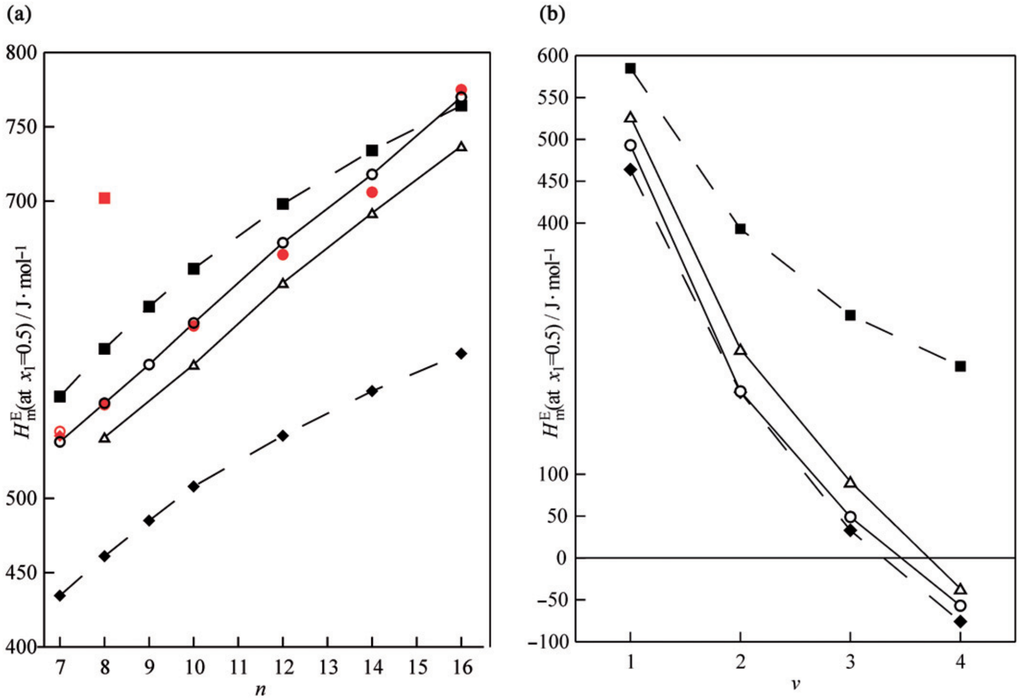

Figure 4. H_m^E equimolar values as a function of chain-length, determined in this work at 298.15 K (○) and 318.15 K (△) and comparison with values by UNIFAC (■) [4] and (◆) [3]. (a) Values from the literature (◆) [5], (○) [6], (●) [7–8], (■) [9] (colour online).

but in which, now $z_1 = x_1/(x_1 + k_g(1 - x_1))$, an equation that establishes the dependence $z_1(x_1)$ through a parameter k_g that must be determined. From Equation (5), the activity coefficients can also be determined with the expression

$$\ln \gamma_i = z_1(1 - z_1)\sum_{i=0}^{2} a_i z_1^i + (1 - x_i)\left(\sum_{i=0}^{3}(i + 1)b_i\right)k\left(\frac{z_1}{x_1}\right)^2. \tag{6}$$

The mathematical derivative of Equation (5), considering relationship (4), can be used to obtain a final expression for H_m^E, similar to that proposed initially with Equation (1); in other words,

$$H_m^E = Rz_1(1 - z_1)\left(A_{00} + A_{10}z_1 + A_{20}z_1^2\right), \tag{7}$$

producing a relationship between both types of coefficients $a_i = RA_{i0}$. The correlation of data can be carried out by two procedures. One of them uses a simultaneous fit of the corresponding excess quantities with Equations (5–7). The other, simpler procedure, is by stages, involving first the correlation of $x - H_m^E$, and calculating the a_i coefficients of Equation (1), or the A_{i0} via Equation (7). Then, in a second step, with the A_{i0} and the VLE data, $x_i - \gamma_i - (G_m^E/RT)$, the A_{i1} coefficients are calculated and parameter k_g of Equations (5) or (6). In all cases, Marquardt's algorithm [22] was used for non-linear

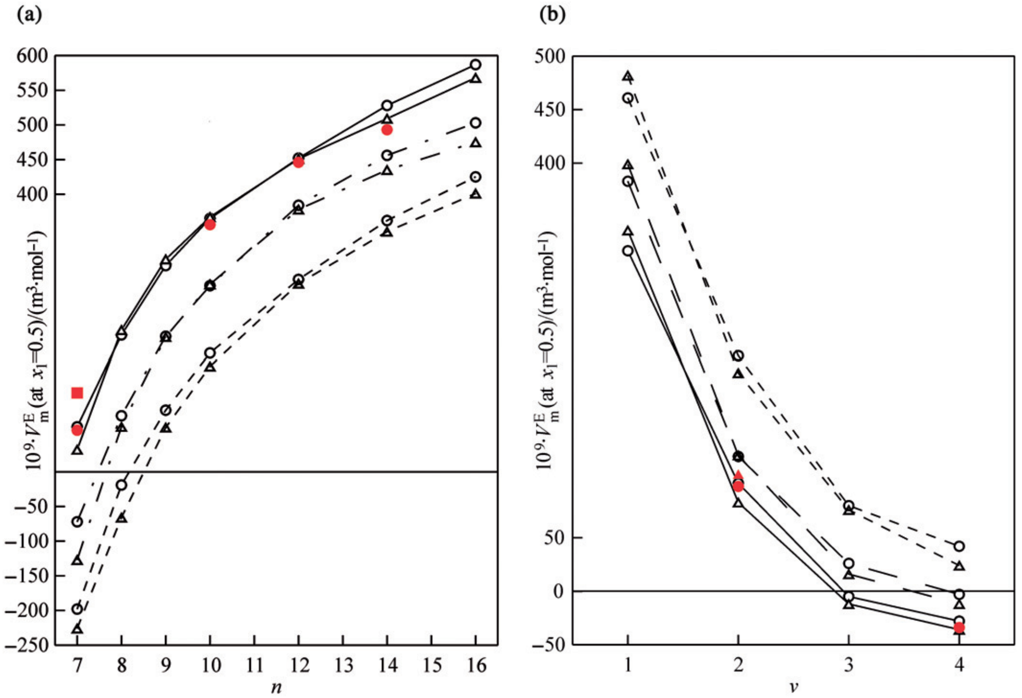

Figure 5. Equimolar values of V_m^E as a function of chain length at 298.15 K (○) and (△) 318.15 K, for mixtures of ethylbenzene (—), propylbenzene (–·–) [2] and butylbenzene (----) [1] with alkanes or ethanoates. (a) Values from the literature at 298.15 K (●) [10] and (■) [11]. (b) Values from the literature at 298.15 K (●) [15–16], and (▲) [14] (colour online).

functions, minimising the sum of the standard deviations *s*, established as an objective function, *OF*:

$$OF = \sum_{i=1}^{2} s(\gamma_i) + \sum_{j=1}^{N} s\left(\frac{G_m^E}{RT}\right)_j. \tag{8}$$

The values found for these correlations are shown in Table 3. Figure 6(a) and (b) represent the VLE data from the literature together with the correlations obtained for the G_m^E/RT function. The correlations are acceptable in all cases.

5. Application of the UNIFAC model

Figure 4(a) and (b) include the values estimated for the two versions of the UNIFAC using the original interaction parameters, obtaining different results in each case. Hence, the version of Gmehling *et al.* [3] gives lower and very different values to experimental ones for the set of ethylbenzene + alkanes, Figure 4(a). However, the version of Dang and Tassios [4] produces slightly higher values, but the differences are less. For mixtures of ethylbenzene + alkyl ethanoates, the version of Dang and Tassios [4] gives H_m^E values far from experimental ones, while the version of Gmehling *et al.* [3] produces quite

Table 3. Parameters in the correlation of VLE data and H_m^E using Equation (5–7).

	Ethylbenzene + heptane	Ethylbenzene + octane
k	1.666	1.398
A_{00}	293.64	331.00
A_{01}	−0.4799	−0.4778
A_{10}	−68.51	−137.64
A_{11}	−0.1112	0.0828
A_{20}	−3.16	26.17
A_{21}	0.1095	−0.0575
$s(\gamma_1)$	0.019	0.009
$s(\gamma_2)$	0.006	0.011
$s(G_m^E/RT)$	9×10^{-4}	0.005
$s(H_m^E)$ (J mol^{-1})	3	3

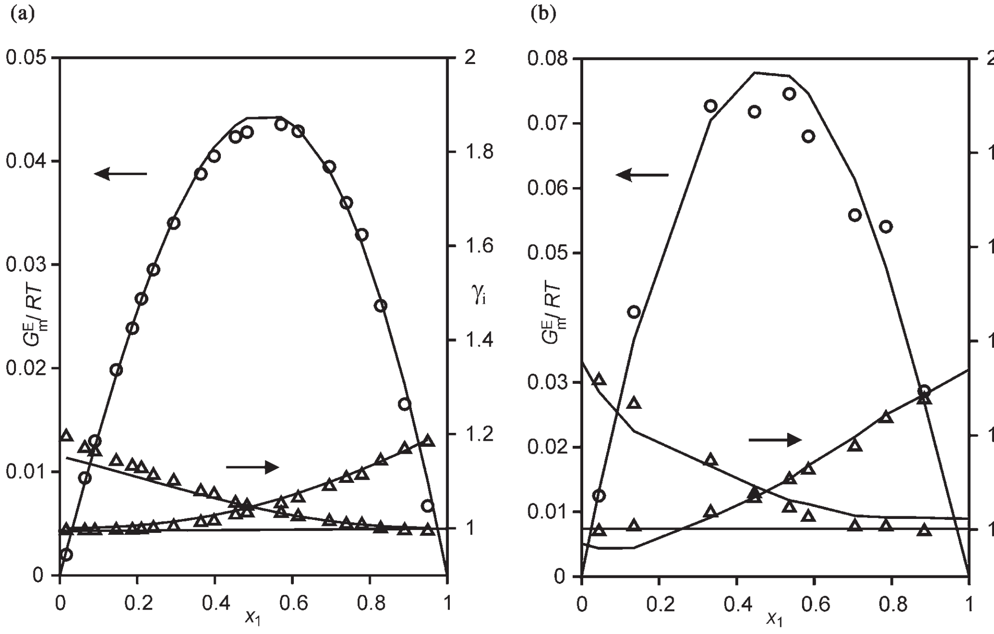

Figure 6. Results obtained in correlation of data of isobaric VLE, $G_m^E(x, T)/RT$ (○) and γ_i (△) *vs.* x_1, using Equations (5–7) for: (a) {ethylbenzene + heptane} [18], (b) {ethylbenzene + octane} [19].

good estimations. To avoid confusion, the values of the theoretical model have only been shown for 298.15 K and not for 318.15 K, although it could be said that the two versions of the UNIFAC model, the one of Dang and Tassios [4] and that of Gmehling *et al.* [3], produce $(\partial H_m^E/\partial T)_{p,x} < 0$, in the same experimental direction as for mixtures with alkanes, with temperature having only a minimum influence with the second version. For mixtures with ethanoates, the version of Gmehling *et al.* [3] gives rise to $(\partial H_m^E/\partial T)_{p,x} > 0$, similar to experimental values, while the version of Dang and Tassios [4] gives a thermic coefficient of opposite sign.

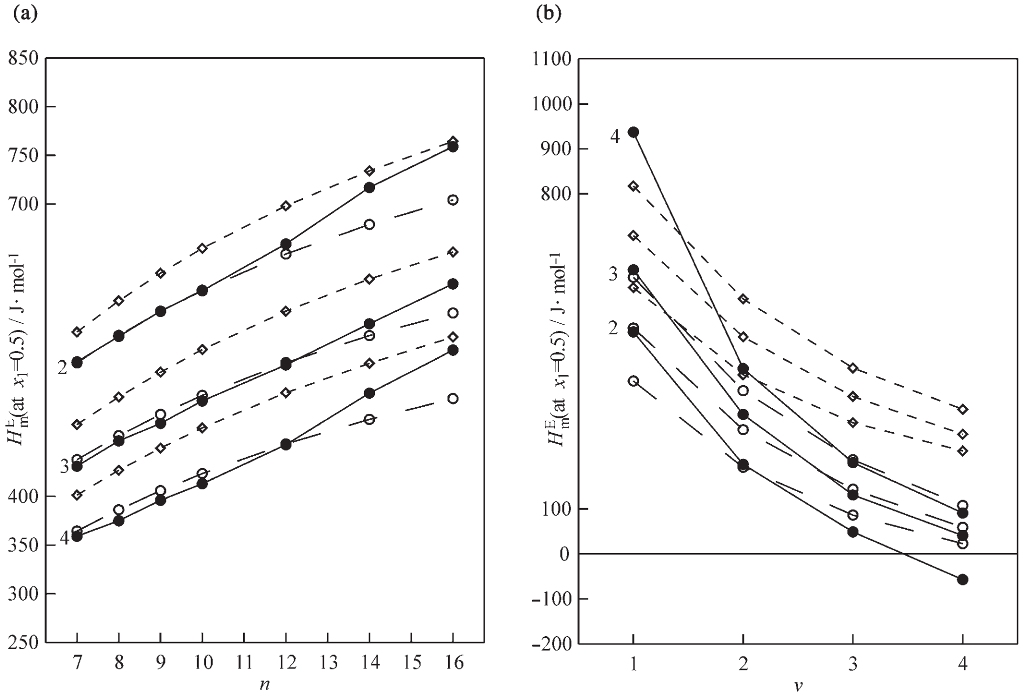

Figure 7. Variation of equimolar excess enthalpies H^E_m(●), at $T = 298.15\,K$ and theoretical estimations by original-UNIFAC [4] (◇) and original-UNIFAC with a pair of global average parameters (○) for ethylbenzene ($u = 2$), propylbenzene ($u = 3$) and butylbenzene ($u = 4$) mixtures: (a) $\{xC_6H_5C_2H_5 + (1 - x)\ C_nH_{2n+2}\}$; (b) $\{xC_6H_5C_2H_5 + (1 - x)\ CH_3CO_2C_vH_{2v+1}\}$.

Taking all these considerations into account, application of the UNIFAC model with interaction parameters from the literature, in the two versions, that of Dang and Tassios [4] and that of Gmehling *et al.* [3], to the H^E_m data of this work, can be considered to not give acceptable results, with the exception of application of the version of Gmehling *et al.* [3] to ethylbenzene + alkyl ethanoate systems, which reproduce acceptably experimental data, see Figure 4(b). Because of this, the interaction parameters for $ACCH_2/CH_2$ and $ACCH_2/COOC$ were calculated again, but only for the Dang and Tassios version [4], since that of Gmehling *et al.* [3] requires other experimental information that are not currently available. A database was developed using the ethylbenzene mixtures of this work, those of propylbenzene [2] and those of butylbenzene [1] with alkanes and with ethanoates. Marquardt's algorithm [22] was used with a least-squares method, minimising the standard deviation of experimental data, as an objective function. The pair of values obtained for the $ACCH_2/CH_2$ interaction was:

$$a_{CH_2/ACCH_2} = -13.61, \quad a_{ACCH_2/CH_2} = 48.36.$$

These values were used to calculate the interaction, $ACCH_2/COOC$, obtaining the following pair of mean values:

$$a_{CH_3COO/ACCH_2} = 75.41, \quad a_{ACCH_2/CH_3COO} = -9.65.$$

Figure 7(a) compares the experimental data of $H_{\mathrm{m}}^{\mathrm{E}}(x=0.5)$ obtained for the alkylbenzene + alkane mixtures and those estimated by the UNIFAC model. A substantial improvement was observed in the estimated values using the parameters obtained in the aforementioned recalculation, compared to application of the model with the parameters obtained from the original version. The same consideration applies for alkylbenzene + alkyl ethanoate systems, as observed in Figure 7(b).

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