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Thermodynamic study of the mixtures (butylbenzene + an alkane or + an alkyl ethanoate): experimental H_m^E and V_m^E values

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This article shows the experimental data of mixing properties for a set of nine binary mixtures formed by an aromatic hydrocarbon, butylbenzene, with several alkanes (C_7 to C_{12}) and several alkyl ethanoates (methyl to butyl). The excess enthalpies, H_m^E , were measured at $T = 298.15$ K for all systems, while the excess volumes, V_m^E , were obtained for the same set of systems but at two temperatures of 298.15 and 318.15 K. All systems studied presented endothermic effects with the excess enthalpy increasing regularly as the alkane chain-length increases, however in the mixtures with ethanoates the endothermicity decreases with the increase of the ester molecular weight. In this case V_m^E are positive for all systems except for those mixtures containing heptane or octane, which present $V_m^E < 0$. In both sets of mixtures the temperature effect on V_m^E is analysed. All experimental values are correlated with a suitable equation. Lastly, the UNIFAC model is applied to all the mixtures to estimate the H_m^E considering two versions, being necessary to recalculate the interaction parameters corresponding to methyl/aromatic and carboxylate/aromatic in the version of Dang and Tassios (*Ind. Eng. Chem. Des. Dev.*, **25**, 22, 1986). The estimation for the elected mixtures is acceptable.

Keywords: Excess enthalpy; Excess volumes; Alkane; Butylbenzene; Ethanoates; UNIFAC

1. Introduction

This article presents the experimental data obtained for a set of nine binary mixtures comprised of {butylbenzene + alkanes (heptane to dodecane) or +alkyl ethanoate (methyl to butyl)}. Specifically, for these mixtures excess molar volumes V_m^E at two temperatures, 298.15 and 318.15 K, and excess molar enthalpies H_m^E , at 298.15 K and atmospheric pressure were measured. This article is the first of a series on mixtures containing aromatic compounds in order to check the molecular interactions occurring in those mixtures, although some of them have been established previously [1–4], and thereby consider possible modifications in the UNIFAC group contribution model. Therefore, this article belongs to a wide project on which our research team is working using mixtures of alkanes with other second component, like esters [5,6], alkanols [7,8] and haloalkanes [9]. Even, in other papers we have already published H_m^E data for

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mixtures of dihaloalkanes (Cl, Br) with some of the aromatic compounds [10,11] of this project.

Alkylbenzenes represent a particularly interesting family of molecules for the purpose of testing group contribution models. They are weakly polar molecules of irregular shape alkylation of the benzene ring, reducing the aromatic fraction on molecules, produces a decrease in H_m^E . Therefore, in this series of studies we will attempt to add more data to the literature in order to clarify the behaviour of the mixtures mentioned.

Literature presents many data on mixtures containing aromatic compounds, especially benzene, toluene and ethylbenzene, with alkanes, however, there is insufficient data with propylbenzene or butylbenzene. Therefore we have decided to start studying the binary mixtures of (butylbenzene + alkanes) for which the literature only shows some data of H_m^E [12] and V_m^E [13] for the (butylbenzene + heptane) mixture at 298.15 K.

Finally, such as was indicated earlier, another objective proposed in this series of studies with aromatic compounds is to verify the predictive capacity of the UNIFAC engineering group contribution method, since we consider it to be of interest to study its application on mixtures containing a benzene ring. The oldest version of the model, with interaction parameters of Dang and Tassios [14], to predict the H_m^E will be applied and the results will be compared with those obtained using another version of the UNIFAC model, the one proposed by Gmehling *et al.* [15].

2. Experimental

The products used in this work were purchased from Fluka and Aldrich, and were of maximum purity. Before use, all substances were degassed with ultrasounds for several days and then stored in the dark on molecular sieves (Fluka, 0.3 nm), to remove the possible moisture. In order to characterise the quality of substances, the physical properties of pure compounds, density ρ and refractive index n_D , were measured at two temperatures of 298.15 and 318.15 K. The values obtained are shown in table 1 together with the values reported in literature at the same conditions, their comparison is acceptable in all cases.

The V_m^E were calculated indirectly from density measurements, by using densities of pure components and those of the corresponding mixtures. Measurements were carried out using a vibrating-tube densimeter from Anton Paar, model DMA-58, operating at the constant temperature indicated earlier and at atmospheric pressure. The precision in the temperature control was of ± 0.01 K. The densimeter was calibrated using double-distilled water and nonane (Fluka) according to the standard procedure used in our laboratory for years (the reading error of ρ was ± 0.02 kg m⁻³). Molar fractions of the mixtures were calculated with an uncertainty better than $\pm 5 \times 10^{-5}$, while the uncertainty for V_m^E was $\pm 2 \times 10^{-9}$ m³ mol⁻¹.

The H_m^E were measured in a microcalorimeter type Calvet, model MS80D, from Setaram, but only at 298.15 K. The calorimetric equipment was regularly calibrated with a Joule effect. The uncertainty estimated for enthalpy measurements was ± 0.2 J mol⁻¹, which was calculated comparing the experimental results obtained for the standard mixture (cyclohexane + benzene) and those from literature [20], and of $\pm 2 \times 10^{-4}$ for the mole fractions.

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.

| Compound | T (K) | ρ (kg m^{-3}) | | n_D | |
|------------------|---------|-------------------------------|--|--------|--|
| | | Exp. | Lit. | Exp. | Lit. |
| Butylbenzene | 298.15 | 855.87 | 856.07 ^a 856.11 ^b | 1.4874 | 1.4874 ^{a,b} |
| | 318.15 | 839.71 | 839.80 ^c | 1.4793 | 1.4779 ^c |
| Heptane | 298.15→ | 679.32 | 679.51 ^a 679.46 ^b | 1.3853 | 1.3851 ^{a,b} |
| | 318.15→ | 662.06 | 662.32 ^d | 1.3756 | 1.3750 ^d |
| Octane | 298.15→ | 698.58 | 698.49 ^a 698.62 ^b | 1.3950 | 1.3950 ^{a,b} |
| | 318.15→ | 682.10 | 682.09 ^d | 1.3868 | 1.3855 ^d |
| Nonane | 298.15→ | 713.85 | 713.81 ^a 713.75 ^b | 1.4030 | 1.4031 ^{a,b} |
| | 318.15→ | 698.02 | 698.06 ^d | 1.3946 | 1.3939 ^d |
| Decane | 298.15→ | 726.03 | 726.25 ^a 726.35 ^b | 1.4097 | 1.4097 ^{a,b} |
| | 318.15→ | 710.71 | 711.43 ^d | 1.4008 | 1.4008 ^d |
| Dodecane | 298.15→ | 745.42 | 745.16 ^a 745.18 ^b | 1.4196 | 1.4195 ^{a,b} |
| | 318.15→ | 730.86 | 730.78 ^d | 1.4111 | 1.4110 ^d |
| Methyl ethanoate | 298.15→ | 927.05 | 927.90 ^a 927.30 ^b | 1.3589 | 1.3585 ^b |
| | 318.15→ | 900.07 | 900.20 ^d 900.10 ^e | 1.3480 | 1.3485 ^d 1.3490 ^e |
| Ethyl ethanoate | 298.15→ | 894.34 | 894.55 ^a 894.00 ^b | 1.3697 | 1.3704 ^f |
| | 318.15→ | 869.53 | 869.70 ^d 869.54 ^e | 1.3601 | 1.3595 ^d 1.3597 ^e |
| Propyl ethanoate | 298.15→ | 882.20 | 883.03 ^a 882.60 ^c | 1.3817 | 1.3828 ^{a,b,c} |
| | 318.15→ | 859.55 | 859.78 ^e | 1.3726 | 1.3721 ^e |
| Butyl ethanoate | 298.15→ | 876.26 | 876.36 ^a 876.06 ^b | 1.3919 | 1.3918 ^b 1.3920 ^c |
| | 318.15→ | 855.32 | 854.98 ^d 855.39 ^e | 1.3830 | 1.3823 ^d 1.3825 ^e |

^aRef. [16].^bRef. [18].^cValues interpolated from Ref. [18].^dRef. [19].^eRef. [5].^fRef. [17].

3. Results and discussion

Both excess quantities, H_m^E and V_m^E , represented generically by Y_m^E (J mol^{-1} or $\text{m}^3 \text{mol}^{-1}$), were correlated with a polynomial equation as follows:

$$Y_m^E = z(1-z) \sum_i A_{i-1} z^{i-1}, \quad (1)$$

where

$$z = \frac{x}{x + k(1-x)}. \quad (2)$$

The values of k -parameter will depend on the correlations to be made. This parameter is identified with the quotient of molar volumes of the pure substances i , $V_{m,i}^o$, denoted in this case by $k_v = V_{m,2}^o/V_{m,1}^o$, when the (x, V_m^E) pairs are correlated. For treatment of (x, H_m^E) values, Ortega *et al.* [21,22] also described in detail the use of k values obtained as a quotient of surface parameter $k_q = q_j/q_i$, corresponding to the substances i, j weighed with the quotient of both real molar volumes k_v and the volume parameters $k_r = r_j/r_i$. The volume parameters are determined using a group contribution method using the corresponding surface and volume group parameters shown in Bondi [23]. The expression used is

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

Table 2 shows the values calculated for k_v and k_h , according to the procedure indicated earlier for the nine binary systems considered in this work. The A_i coefficients obtained, which are also shown in table 2, were achieved by applying a least-squares procedure to each systems, establishing as objective function the minimisation of the standard deviation, $s(Y_m^E)$, of the corresponding excess quantities.

Figure 1(a) and (c) show, respectively, the experimental data of H_m^E at 298.15 K and V_m^E , measured at 298.15 and 318.15 K, for the binaries {butyl benzene(1)+alkanes (heptane to dodecane)(2)} and their fitting curves with equation (1). Figure 1(b) and (d) show the corresponding equimolar values for the same set of mixtures as a function of the hydrocarbon chain length. Literature [12] presents only three values of H_m^E at the same working temperature for the mixture (butylbenzene+heptane) which are represented in figure 1(a), while the corresponding interpolated value at $x_1=0.5$ is shown in figure 1(b); the agreement is acceptable. On the other hand, figure 1(c) and (d) show, respectively, analogous representations for the mixtures with alkanes, (x, V_m^E) and V_m^E (at $x_1=0.5$) measured at the two temperatures of 298.15 and 318.15 K. The comparison with the values found in the literature [13] for the mixture with heptane is good.

Figure 2(a)–(d) contain the same set of graphics described earlier but for the binary mixtures formed by {butyl benzene(1)+alkyl (methyl to butyl) ethanoate(2)}. Literature does not present any data for these mixtures.

The behavior of the mixtures ($C_6H_5C_4H_9 + C_nH_{2n+2}$) is similar to that of other systems containing aromatic compounds [1–4]. So, the excess enthalpies are positive in all cases increasing regularly with the alkane chain-length increases. The interaction between these two kinds of substances is probably due to three kinds of interactions: the relatively strong interaction between aromatic π -electrons (π - π interactions), and the aromatic–aliphatic and aliphatic–aliphatic interactions. The latter two are the main cause of the regular increase of H_m^E with the hydrocarbon chain-length increases. However, the H_m^E values obtained in this work for (butylbenzene + alkanes) are smaller than those obtained by other authors for mixtures of propylbenzene or ethylbenzene, because of the alkylation of the benzene ring, reducing the aromatic fraction on the molecules, producing a decrease in H_m^E .

The volumetric effects in these mixtures appear to be clearly explained by the interstitial accommodation in the case of molecules with $n \leq 8$, verifying that the coefficient $(\partial V_m^E/\partial T)_{p,x}$ is negative although the temperature effect diminishes as the hydrocarbon chain-length increases because of the relative decrease of empty spaces

Table 2. Coefficients A_i and k , and standard deviation SD, obtained in the correlations of experimental values using equation (1).

| Mixture | k_h | A_0 | A_1 | A_2 | $SD(H_m^E) \text{ J mol}^{-1}$ |
|--|-------|--------|---------|--------|---|
| $Y_m^E = H_m^E (\text{J mol}^{-1})$ | | | | | |
| $T = 298.15 \text{ K}$ | | | | | |
| $x_1\text{C}_6\text{H}_5\text{C}_4\text{H}_9 +$ | | | | | |
| $(1 - x_1)\text{C}_7\text{H}_{16}$ | 0.839 | 1212.4 | 365.0 | 170.7 | 3.0 |
| $(1 - x_1)\text{C}_8\text{H}_{18}$ | 1.119 | 1671.2 | -471.3 | 275.3 | 2.9 |
| $(1 - x_1)\text{C}_9\text{H}_{20}$ | 1.191 | 1839.3 | -700.2 | 350.1 | 3.1 |
| $(1 - x_1)\text{C}_{10}\text{H}_{22}$ | 1.339 | 1999.0 | -886.3 | 381.1 | 2.8 |
| $(1 - x_1)\text{C}_{12}\text{H}_{26}$ | 1.383 | 2263.6 | -1271.5 | 789.8 | 4.5 |
| $x_1\text{C}_6\text{H}_5\text{C}_4\text{H}_9 +$ | | | | | |
| $(1 - x_1)\text{CH}_3\text{CO}_2\text{CH}_3$ | 0.591 | 2359.0 | -810.6 | 5322.6 | 7.2 |
| $(1 - x_1)\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ | 0.711 | 1280.5 | 738.2 | -40.7 | 4.4 |
| $(1 - x_1)\text{CH}_3\text{CO}_2\text{C}_3\text{H}_7$ | 0.827 | 745.4 | -44.1 | 384.4 | 2.1 |
| $(1 - x_1)\text{CH}_3\text{CO}_2\text{C}_4\text{H}_9$ | 0.939 | 274.4 | 91.4 | 174.0 | 1.2 |
| | k_v | A_0 | A_1 | A_2 | $10^9 SD(V_m^E) \text{ m}^3 \text{ mol}^{-1}$ |
| $Y_m^E = 10^9 \cdot V_m^E (\text{m}^3 \text{ mol}^{-1})$ | | | | | |
| $T = 298.15 \text{ K}$ | | | | | |
| $x_1\text{C}_6\text{H}_5\text{C}_4\text{H}_9 +$ | | | | | |
| $(1 - x_1)\text{C}_7\text{H}_{16}$ | 0.941 | -746 | -119 | 198 | 3 |
| $(1 - x_1)\text{C}_8\text{H}_{18}$ | 1.043 | -81 | 34 | -46 | 1 |
| $(1 - x_1)\text{C}_9\text{H}_{20}$ | 1.146 | 471 | -316 | 161 | 2 |
| $(1 - x_1)\text{C}_{10}\text{H}_{22}$ | 1.249 | 832 | -301 | -36 | 4 |
| $(1 - x_1)\text{C}_{12}\text{H}_{26}$ | 1.457 | 1417 | -748 | 217 | 5 |
| $x_1\text{C}_6\text{H}_5\text{C}_4\text{H}_9 +$ | | | | | |
| $(1 - x_1)\text{CH}_3\text{CO}_2\text{CH}_3$ | 0.509 | 1516 | -38 | 1300 | 3 |
| $(1 - x_1)\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ | 0.627 | 745 | 330 | -50 | 5 |
| $(1 - x_1)\text{CH}_3\text{CO}_2\text{C}_3\text{H}_7$ | 0.738 | 326 | -65 | 119 | 2 |
| $(1 - x_1)\text{CH}_3\text{CO}_2\text{C}_4\text{H}_9$ | 0.845 | 160 | 55 | -77 | 1 |
| $T = 318.15 \text{ K}$ | | | | | |
| $x_1\text{C}_6\text{H}_5\text{C}_4\text{H}_9 +$ | | | | | |
| $(1 - x_1)\text{C}_7\text{H}_{16}$ | 0.947 | -1293 | 608 | -325 | 4 |
| $(1 - x_1)\text{C}_8\text{H}_{18}$ | 1.048 | -271 | -94 | 223 | 2 |
| $(1 - x_1)\text{C}_9\text{H}_{20}$ | 1.149 | 273 | -34 | 8 | 1 |
| $(1 - x_1)\text{C}_{10}\text{H}_{22}$ | 1.253 | 621 | 161 | -394 | 2 |
| $(1 - x_1)\text{C}_{12}\text{H}_{26}$ | 1.458 | 1284 | -396 | 5 | 6 |
| $x_1\text{C}_6\text{H}_5\text{C}_4\text{H}_9 +$ | | | | | |
| $(1 - x_1)\text{CH}_3\text{CO}_2\text{CH}_3$ | 0.515 | 1500 | 321 | 1004 | 3 |
| $(1 - x_1)\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ | 0.634 | 712 | 77 | 272 | 3 |
| $(1 - x_1)\text{CH}_3\text{CO}_2\text{C}_3\text{H}_7$ | 0.743 | 291 | 5 | 53 | 1 |
| $(1 - x_1)\text{CH}_3\text{CO}_2\text{C}_4\text{H}_9$ | 0.849 | 92 | 93 | -159 | 0 |

between molecules. On the other hand, for (butylbenzene + alkyl ethanoates) mixtures, in addition to the interactions found in aromatic + alkanes systems, we must further consider the possibility of a dipole-dipole interaction between the dipoles of different ethanoates, $\text{CH}_3\text{CO}_2\text{C}_v\text{H}_{2v+1}$, $\mu \times 10^{30}/(\text{Cm})$, (5.60 for $v=1$; 5.94 for $v=2$; 5.97 for $v=3$; 6.40 for $v=4$) [17] and those of aromatic hydrocarbons, in spite of the small dipole moment of butylbenzene, $\mu = 1.2 \times 10^{-30} \text{ Cm}$ [17]. All these comments could explain the fact that the mixing enthalpies and excess volumes of esters with butylbenzene diminish with an increase in the ethanoate alkanolic part, such as is shown in figure 2(b) and (d). The temperature effect on V_m^E is very small in these mixtures and presents a change of

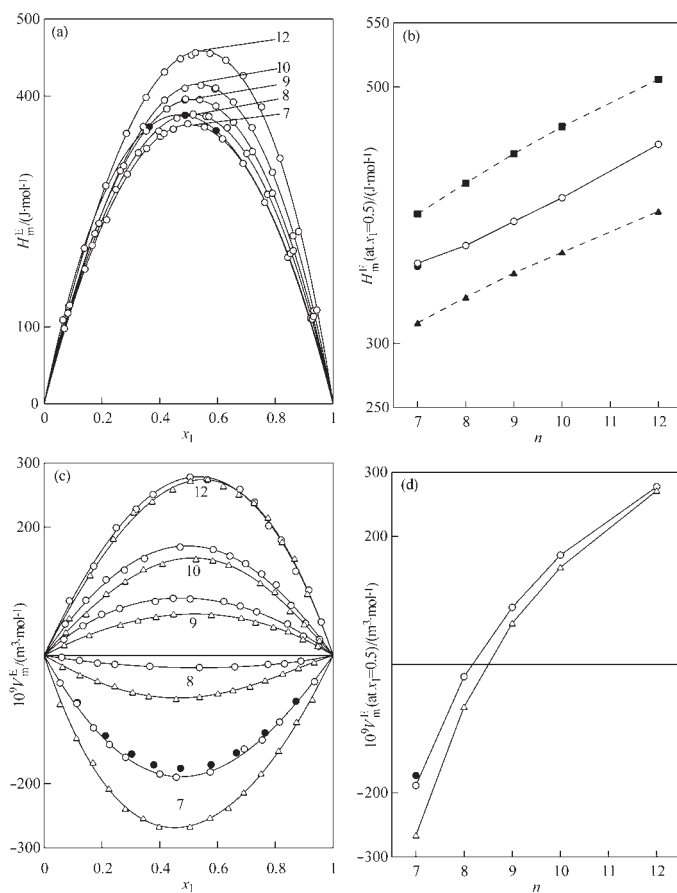


Figure 1. Plots of experimental values and correlation curves for binary mixtures $\{x_1\text{C}_6\text{H}_5\text{C}_4\text{H}_9 + (1-x_1)\text{C}_n\text{H}_{2n+2}\}$. (a) H_m^E experimental values (\circ), and those (\bullet) from literature [12]; labels indicate the n -values. (b) H_m^E equimolar values as a function of n , and comparison with values by UNIFAC, (\blacksquare) [14] and (\blacktriangle) [15]. (c) Comparison between V_m^E experimental values at two temperatures, 298.15 K (\circ), 318.15 K (\triangle), and those from literature [13]; labels indicate the n -values. (d) Representation of equimolar V_m^E values at two temperatures 298.15 K (\circ), 318.15 K (\triangle), as a function of n , and those from literature [13].

sign depending on the ethanoate chain. So, the volumetric coefficient $(\partial V_m^E/\partial T)_{p,x}$ is positive in the case of methyl ethanoate, but becomes negative for butyl ethanoate due to the increase of the dipole moments of ethanoates.

4. Application of UNIFAC

The other objective proposed in this series of articles is to verify the utility of the UNIFAC group contribution model to predict the enthalpy data. So, two versions of that method were applied, the original by Dang and Tassios [14], and that of Gmehling *et al.* [15]. The first of the two models mentioned did not give good results for binary systems of this study, such as is shown in figure 1(b). In binaries (butylbenzene + alkanes) the application of the version by Dang and Tassios [14]

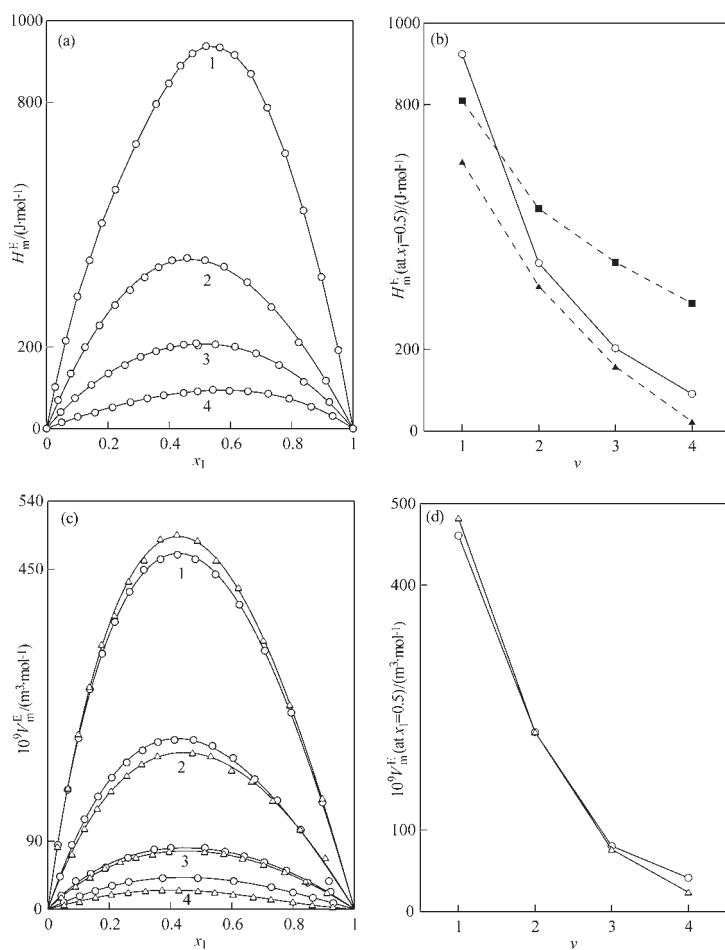


Figure 2. Plots of experimental values and correlation curves for binary mixtures of $\{x_1\text{C}_6\text{H}_5\text{C}_4\text{H}_9 + (1-x_1)\text{CH}_3\text{CO}_2\text{C}_v\text{H}_{2v+1}\}$. (a) H_m^E experimental values (\circ); labels indicate the ν -values. (b) H_m^E equimolar values as a function of ν ; and comparison with values by UNIFAC (\blacksquare) [14] and (\blacktriangle) [15]. (c) Comparison between V_m^E experimental values at two temperatures, 298.15 K (\circ), 318.15 K (\triangle); labels indicate the ν -values. (d) Representation of equimolar V_m^E values at two temperatures, 298.15 K (\circ) and 318.15 K (\triangle), as a function of n .

gave place to enthalpy values higher than experimental. On the contrary, the version of Gmehling *et al.* [15] estimated smaller values the differences being close to 100 J mol^{-1} in both the cases. The estimations carried out with the same methods in binaries of (butylbenzene + alkyl ethanoates) are more or less similar although in this case the predictions by Gmehling *et al.* [15] are closer to experimental but also slightly smaller, behaviour quasi-identical to the (butylbenzene + alkanes) systems. We think that for both versions of UNIFAC model the interaction parameters should be changed, however it would be convenient to enlarge the database in order to get a set of adequate parameters. One possibility is to take the chain length of the compounds into account. This aspect would be more complicated for the Gmehling version because it is necessary to have values of other properties like VLE, LLE, etc. However, in this work we

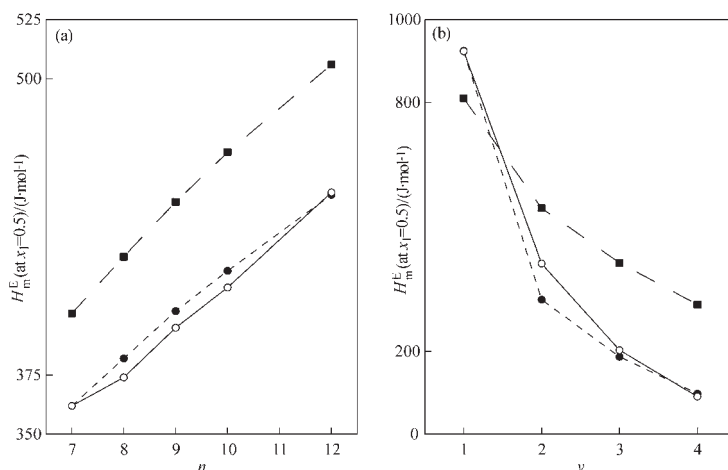


Figure 3. Comparison between the equimolar excess enthalpies obtained in this work (○), and those estimated by UNIFAC, by using parameters from [14] (■), and using the parameters recalculated in this work (●). (a) For $\{x_1\text{C}_6\text{H}_5\text{C}_4\text{H}_9 + (1-x_1)\text{C}_n\text{H}_{2n+2}\}$, (b) for $\{x_1\text{C}_6\text{H}_5\text{C}_4\text{H}_9 + (1-x_1)\text{CH}_3\text{CO}_2\text{C}_v\text{H}_{2v+1}\}$.

attempted to recalculate the interaction parameters corresponding to the CH_2/ACH pair using the version by Dang and Tassios [14], but only using the set of values obtained in this work for (butylbenzene + alkanes) mixtures. The Marquardt algorithm [24] for non-linear functions with a least-square procedure was used in order to minimize the deviations between the experimental and theoretical values. Regression made on a lot of experimental values generated the following primary interaction parameters for mixtures with aromatics: $a_{\text{CH}_2/\text{ACH}} = -2.03$ and $a_{\text{ACH}/\text{CH}_2} = 21.18$. Now the representation of excess enthalpies with the UNIFAC model yielded the values shown in figure 3(a), the valuation is good.

The same procedure was applied to (butylbenzene + ethanoates) mixtures in order to get, in this case, better values for the pair $\text{ACH}/\text{CH}_3\text{COO}$. The new parameters obtained are $a_{\text{ACH}/\text{CH}_3\text{COO}} = 2.30$ and $a_{\text{CH}_3\text{COO}/\text{ACH}} = 24.10$. The results for these systems, shown in figure 3(b), are also good.

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