

PREDICTION OF EXCESS FUNCTIONS OF SOME MULTICOMPONENT ORGANIC MIXTURES OF HYDROCARBONS WITH A GROUP CONTRIBUTION MODEL

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ABSTRACT

In order to study the performance of the Kehiaian–Guggenheim–Barker group contribution model on the characterisation of the excess molar functions of multicomponent organic mixtures, we present here the predictions of this model for the concentration dependence of three sets of G^E ternary data, eight sets of H^E ternary data, and one set of four- and another of five-component H^E data. The thirteen mixtures are formed for *n*-alkanes, cyclohexane and aromatic hydrocarbons and have been treated in the zeroth-order approximation of the theory. The ratio of the standard deviations between experimental and predicted excess molar enthalpies H^E or excess molar Gibbs functions G^E is less than 0.06 for all the systems. Since only the interaction parameters obtained from the binary systems are used and no new parameters are adjusted to perform the prediction, a satisfactory representation was reached in all cases.

INTRODUCTION

Because of the difficulties involved in the experimental measurement of the excess functions of multicomponent mixtures and in the time and effort required to obtain a meaningful set of multicomponent data, a lot of semiempirical equations have been developed for estimating multicomponent data from the data of the binary mixtures involved.

So, the excess enthalpy H^E in a ternary mixture is calculated as the sum of a binary and a ternary contribution:

$$H^E = \sum_{i < j} H_{ij}^E + H_T^E \quad (1)$$

The binary contribution, $\sum H_{ij}^E$, is calculated from the heat of mixing data of the three binary mixtures involved. The ternary contribution, H_T^E , has some adjustable ternary coefficients which are evaluated from ternary H^E data. When the ternary contribution is omitted, eqn. (1) is considered a predictive equation. Usually H^E is expressed as

$$H_{ij}^E = x_i x_j \sum_{k=0}^n A_k Z_{ij}^k / \sum_{l=0}^m B_l Z_{ij}^l, \quad B_0 = 1 \quad (2)$$

$Z_{i,j}$ is a composition variable which adopts different forms depending on the predictive method.

If the ternary contribution is included, eqn. (1) is considered a correlation equation. Some reviews on this topic are in refs. 1–4. We are interested in the prediction of excess functions of ternary mixtures using a group contribution method, particularly in terms of group surface interactions [5,6]. So we avoid the difficulties related to the choice of component 1 in the ternary mixture [3], and we carry out a test of the quality of the interaction parameters.

TERNARY SYSTEMS CONSIDERED

Table 1 lists all systems considered in this study; they are classified according to the number of different surfaces, or groups, present in the mixture.

The number of data points (N), the temperature (T) at which data were taken, the minimum (F_{\min}^E) and maximum (F_{\max}^E) values of the excess functions and the source of data are also indicated. All data are valid at atmospheric pressure. Some sets of data do not have enough data points to provide a meaningful description of the excess functions, but they are included, particularly those related to the excess Gibbs energy, G^E , to allow a more complete test of the method.

THEORETICAL MODEL

The equations used to predict G^E and H^E values were developed by Kehiaian and coworkers in 1978 according to a pseudo-lattice group contribution model in terms of group–surface interactions.

The molecules examined in this work are regarded as possessing the following types of contact surfaces: type a, aliphatic (CH_3 or $-\text{CH}_2-$); type b, benzene (C_6H_6 or phenyl C_6H_5-); type c, cyclohexane (C_6H_{12}).

Binary mixtures containing two of these surfaces have been treated by Kehiaian et al. in zero approximation [5], and thus predictions of the excess functions of the systems in Table 1 have been made in this approximation:

$$G^E = G_{\text{comb}}^E + G_{\text{int}}^{\text{E},\text{dis}} \quad (3)$$

$$H^E = H^{\text{E},\text{dis}}$$

where G_{comb}^E is the Flory–Huggins combinatorial term, containing the volume fraction $\phi_i = r_i x_i / \sum r_i x_i$, where x_i is the mole fraction and r_i is the total relative molecular volume of component i (see Table 2):

$$G_{\text{int}}^{\text{E},\text{dis}} = \left(\sum q_i x_i \right) \left(\xi_1 \xi_2 g_{12}^{\text{dis}} + \xi_1 \xi_3 g_{13}^{\text{dis}} + \xi_2 \xi_3 g_{23}^{\text{dis}} \right) \quad (4)$$

TABLE 1

Systems used in this study

System ^a Number	Components	N	T (K)	$F_{\max}^{E, b}$ (J mol ⁻¹)	$F_{\min}^{E, b}$ (J mol ⁻¹)	Reference
1	$C_6H_6 + n-C_7 + n-C_{14}$	18	298.15	1156	344	Pfestorf et al. [7]
2	$C_6H_6 + n-C_{10} + n-C_{14}$	21	298.15	1180	325	Pfestorf et al. [7]
3	$C_6H_6 + C_6H_8 + n-C_{14}$	20	298.15	1196	695	Pfestorf et al. [7]
4	$C_6H_6 + C_6H_{12} + n-C_6$	49	298.15	920	210	Ridway and Butler [8]
5	$C_6H_6 + C_6H_{12} + n-C_7$	30	293.15	957	489	Brown et al. [9]
6	$C_6H_6 + C_6H_{12} + n-C_7$	18	298.15	916	153	Schainable et al. [10]
7	$C_6H_{12} + C_6H_8 + n-C_7$	18	298.15	602	107	Schainable et al. [10]
8	$C_6H_{12} + C_6H_8 + n-C_7$	24	293.15	703	111	Mathieson and Thynne [11,12]
9	$C_6H_6 + C_6H_{12} + n-C_6 + n-C_7$	15	293.15	987	531	Mathieson and Thynne [11,12]
10	$C_6H_6 + C_6H_{12} + n-C_6 + C_6H_8 + n-C_7$	17	298.15	820	674	Mathieson and Thynne [11,12]
11	$n-C_6 + C_6H_{12} + C_6H_6$	10	283.15	393	188	Li et al. [13]
12	$n-C_6 + C_6H_{12} + C_6H_6$	10	288.15	405	182	Li et al. [13]
13	$n-C_6 + C_6H_{12} + C_6H_6$	12	298.15	377	113	Li et al. [13]

^a Systems 1–3 include two different surfaces, 4–13 have three.^b For systems 1–9 F^E is H^E , for 11–13 F^E is G^E .

TABLE 2

Volumes r_i and total surfaces q_i

Formula	r_i	q_i
<i>n</i> -alkanes ($\alpha_{at} = 1$)		
<i>n</i> -C ₆ , CH ₃ -(CH ₂) ₄ -CH ₃	3.9871	3.3241
<i>n</i> -C ₇ , CH ₃ -(CH ₂) ₅ -CH ₃	4.5847	3.7897
<i>n</i> -C ₁₀ , CH ₃ -(CH ₂) ₈ -CH ₃	6.3773	5.1862
<i>n</i> -C ₁₄ , CH ₃ -(CH ₂) ₁₂ -CH ₃	8.7675	7.0483
Cyclohexane ($\alpha_{ct} = 1$)		
C ₆ H ₁₂	3.5187	2.5966
Benzene ($\alpha_{bt} = 1$)		
C ₆ H ₆	2.8248	2.0724
Toluene ($\alpha_{at} = 0.2846$, $\alpha_{bt} = 0.7154$)		
C ₆ H ₈ , C ₆ H ₅ -CH ₃	3.4760	2.5690

and

$$H^{E,\text{dis}} = \left(\sum q_i x_i \right) \left(\xi_1 \xi_2 h_{12}^{\text{dis}} + \xi_1 \xi_3 h_{13}^{\text{dis}} + \xi_2 \xi_3 h_{23}^{\text{dis}} \right) \quad (5)$$

where

$$g_{st}^{\text{dis}} = -\frac{1}{2} \sum_s \sum_t (\alpha_{st} - \alpha_{sj}) (\alpha_{ti} - \alpha_{tj}) g_{st}^{\text{dis}} \quad (6)$$

and

$$h_{st}^{\text{dis}} = -\frac{1}{2} \sum_s \sum_t (\alpha_{st} - \alpha_{sj}) (\alpha_{ti} - \alpha_{tj}) h_{st}^{\text{dis}} \quad (7)$$

g_{st}^{dis} and h_{st}^{dis} (Table 3) are dispersive interchange parameters, for Gibbs energy and enthalpy respectively, of the s - t contact, h_{st}^{disp} being independent of temperature and

$$\frac{g_{st}^{\text{disp}}}{RT} = \frac{g_{st}^{\circ}}{RT^{\circ}} + \frac{h_{st}^{\circ}}{RT^{\circ}} \left(\frac{T^{\circ}}{T} - 1 \right) \quad (8)$$

where T° is a reference temperature, generally 298.15 K, g_{st}° and h_{st}° are values of the interchange parameters at this temperature. Finally, α_{st} is the molecular surface fraction of surface type s (a, b, c) on a molecular surface of type i , q_i is the total relative molecular area (given in Table 2) of a

TABLE 3

Dispersive interchange parameters $g_{st}^{\circ}/RT^{\circ}$, $h_{st}^{\circ}/RT^{\circ}$ at $T^{\circ} = 298.15$ K

	ab	ac	bc
$g_{st}^{\circ}/RT^{\circ}$	0.2598	0.05123	0.2445
$h_{st}^{\circ}/RT^{\circ}$	0.5623	0.1533	0.5619

TABLE 4

Comparison of results of this study with experimental data (σ is the standard deviation)

System	$F_{\max}^E(\text{exp})$ (J mol ⁻¹)	$F_{\max}^E(\text{calc})$ (J mol ⁻¹)	$F_{\min}^E(\text{exp})$ (J mol ⁻¹)	$F_{\min}^E(\text{calc})$ (J mol ⁻¹)	σ (J mol ⁻¹)
1	1156	1142	344	294	66
2	1180	1164	325	293	39
3	1196	1150	695	702	56
4	920	934	210	300	52
5	957	928	489	506	22
6	916	957	153	164	30
7	602	622	107	122	24
8	703	623	111	132	26
9	987	958	531	509	24
10	820	861	674	704	29
11	393	409	188	208	25
12	405	404	182	198	20
13	377	382	113	121	17

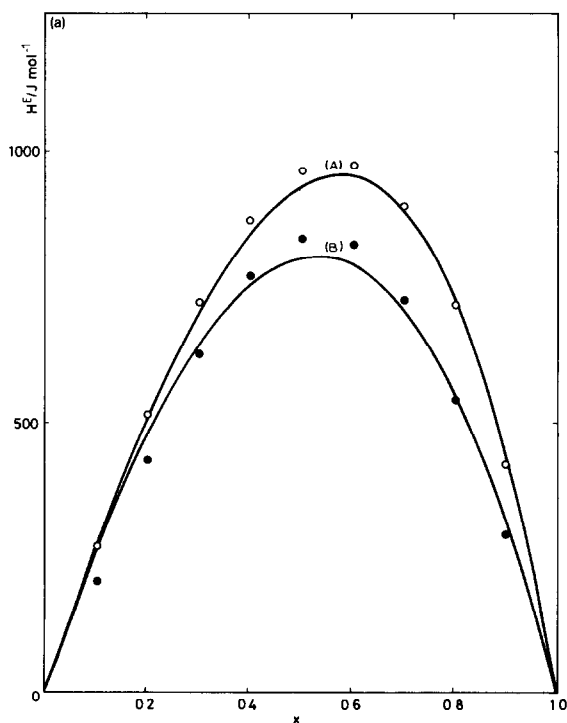


Fig. 1.(a) Comparison of theory with experiment for the molar excess enthalpy H^E at 293.15 K of benzene (1) + *n*-heptane (2) (curve A) and benzene (1) + cyclohexane (2) (curve B) mixtures vs. x_1 : —, predicted values (eqn. (5)). Experimental H^E results [9]: ○, *n*-heptane; ●, cyclohexane.

molecule of type i and $\xi_i = q_i x_i / \sum q_i x_i$ is the surface fraction of component i in the mixture.

RESULTS AND DISCUSSION

The parameters used are in Table 3. Although it seems that interchange coefficients related to the enthalpy of a-b and a-c interactions depend on the chain length [14-17], we have taken those calculated by Kehiaian et al. in 1978 [5] mainly because the higher n -alkanes (n -C₁₀, n -C₁₄) appear in two systems only.

Results of the comparison between experimental (maximum and minimum) and predicted values are given in Table 4. The standard deviations, σ , defined as

$$\sigma = \left[\frac{1}{N} \sum (F_{\text{calc}}^E - F_{\text{exp}}^E)^2 \right]^{\frac{1}{2}} \quad (9)$$

are also calculated.

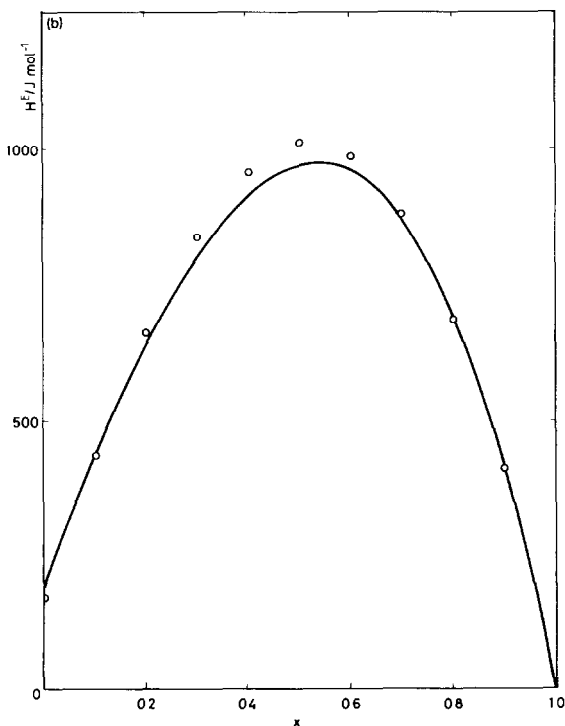


Fig. 1.(b) Comparison of theory with experiment for the molar excess enthalpy H^E of benzene (1) + cyclohexane (2) + n -heptane (3) mixture vs. x_1 at 293.15 K and $x_2/x_3 = 0.3333$: —, predicted values (eqn. (5)); experimental results from Brown et al. [9].

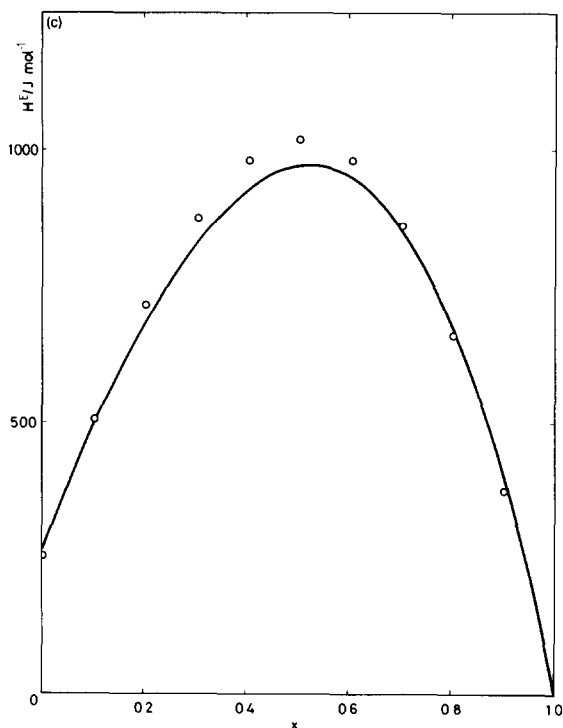


Fig. 1.(c) Comparison of theory with experiment for the molar excess enthalpy H^E of benzene (1) + cyclohexane (2) + *n*-heptane (3) mixture vs. x_1 at 293.15 K and $x_2/x_3 = 0.6666$: —, predicted values (eqn. (5)); experimental results from Brown et al. [9].

Systems 1, 2 and 3 have two different surfaces and there is only one interaction, aliphatic–benzene, type a–b. In these ternary systems, the binary systems involved are $C_6H_6 + n-C_7$, $C_6H_6 + n-C_{14}$, $C_6H_6 + n-C_{10}$, $C_6H_8 + n-C_{14}$, and $C_6H_8 + C_6H_6$ with the following maximum values of H^E ($J mol^{-1}$): 900, 1200, 1100, 680 and 68 respectively. So these ternary mixtures have heats of mixing with maxima of the same magnitude as those of binary mixtures with the higher H^E , which also occur in system 3. This means that surface effects or structure-breaking effects, characteristic of the substitution of benzene by toluene, which reduce H^E , are not important in comparison with the increasing amount of aromatic surface [18].

System 1 is not well represented, probably for the following reasons: (a) Patterson's effect [14–17] is present in benzene + *n*-alkanes mixtures for the higher *n*-alkanes (ten or more carbon atoms). This effect is also the more important in system 3 because the predicted H^E to $C_6H_6 +$ toluene is acceptable ($60 J mol^{-1}$ in the maximum); (b) In this model the heat of mixing in a binary mixture of two *n*-alkanes is assumed to be zero. Note that the maximum values of H^E to $n-C_6 + n-C_{12}$, $n-C_8 + n-C_{16}$, $n-C_7 + n-C_{16}$ and $n-C_6 + n-C_{16}$ are respectively 40, 80, 110 and $125 J mol^{-1}$.

Systems 4, 5, 7 and 8 have three surfaces and there are also three types of interactions: aliphatic–benzene, type a–b; aliphatic–cyclohexane, type a–c; benzene–cyclohexane, type b–c. The binary systems involved are $C_6H_6 + n-C_6$, $C_6H_{12} + n-C_6$, $C_6H_6 + C_6H_{12}$, $C_6H_{12} + n-C_7$ and $C_6H_8 + C_6H_{12}$ with the following maximum values of H^E ($J mol^{-1}$): 860, 220, 800, 250 and 630 respectively. Here ternary mixtures have heats of similar magnitude to those of the two corresponding binaries involved with higher H^E .

In system 4, a poor prediction for H^E is obtained when the benzene concentration is low. There are differences between experimental and calculated values of 30% and more. So when $x_1 = 0.07$ (component 1, benzene) and $x_2 = 0.1$ (component 2, cyclohexane) the experimental value is $210 J mol^{-1}$ and the calculated value is $278 J mol^{-1}$, the contribution of the a–b interaction being about 60%. In system 5 when $x_1 = 0.81$ and $x_2 = 0.07$ the experimental value is $649 J mol^{-1}$ and the calculated value is $657 J mol^{-1}$,

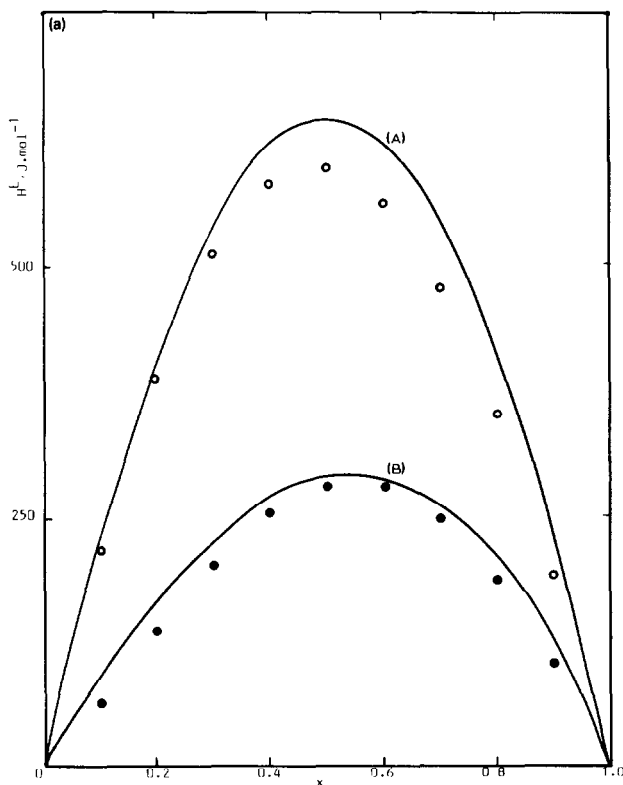


Fig. 2.(a) Comparison of theory with experiment for the molar excess enthalpy H^E at 293.15 K of cyclohexane (1) + toluene (2) (curve A) and cyclohexane (1) + *n*-heptane (2) (curve B) mixtures vs. x_1 : —, predicted values (eqn. (5)). Experimental H^E results: ○, toluene (Mathieson et al. [11,12]); ●, *n*-heptane (Brown et al. [9]).

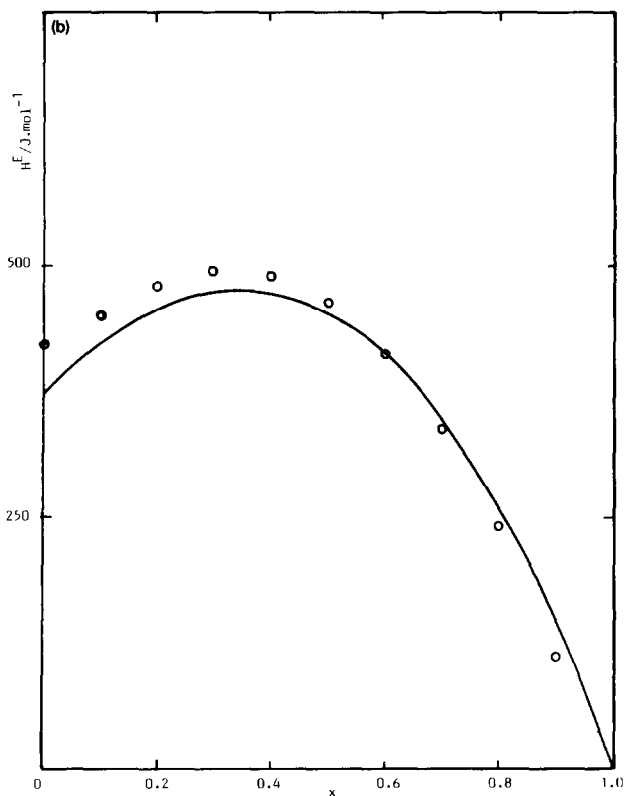


Fig. 2.(b) Comparison of theory with experiment for the molar excess enthalpy H^E at 293.15 K of cyclohexane (1)+toluene (2)+*n*-heptane (3) mixture vs. x_1 and $x_2/x_3 = 0.3333$: —, predicted values (eqn. (5)); experimental results from Mathieson et al. [11,12].

the contribution of the a - b interaction being about 70%. These contributions agree with the rather symmetric curve for benzene + *n*-heptane. However, it is clear that in the first case the contribution is too large, perhaps because the activity of the benzene molecule must be reduced by the presence of cyclohexane in the mixture. In the second case, the concentration of cyclohexane being similar, this is not found because the concentration of benzene is larger than before and the a - b interaction is more relevant, so the prediction is better and systems 5-7 are well reproduced. Results for the ternary mixtures benzene + cyclohexane + *n*-heptane and cyclohexane + toluene + *n*-heptane, both at 293.15 K, are plotted in Figs. 1(b), 1(c), and Figs. 2(b), 2(c) respectively for two different constant concentration ratios: $x_2/x_3 = 0.3333$ in Figs. 1(b) and 2(b), and $x_2/x_3 = 0.6666$ in Figs. 1(c) and 2(c). We can see the good prediction of these ternary systems, the differences between experimental and predicted values being of a similar magnitude to those in the binary systems involved (Figs. 1(a) and 2(a)).

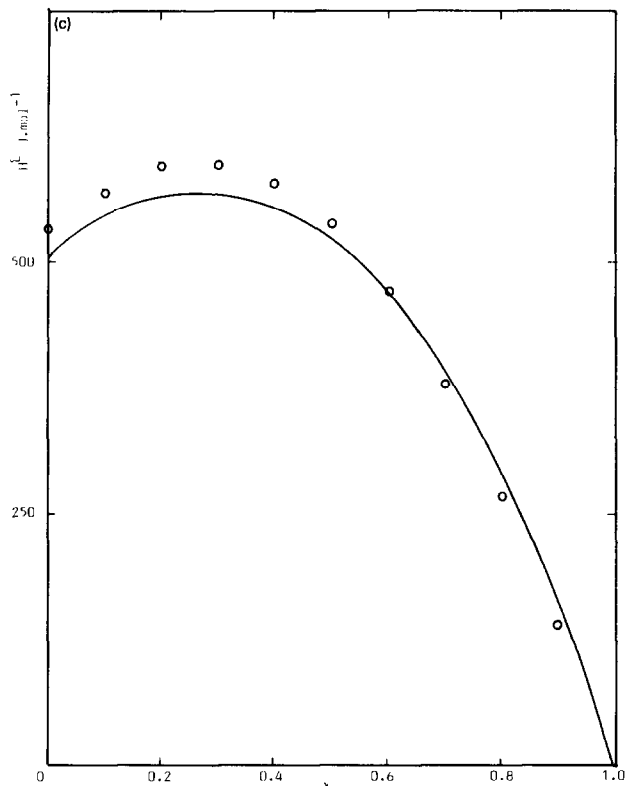


Fig. 2.(c) Comparison of theory with experiment for the molar excess enthalpy H^E at 293.15 K of cyclohexane (1)+toluene (2)+*n*-heptane (3) mixture vs. x_1 and $x_2/x_3 = 0.6666$: —, predicted values (eqn. (5)); experimental results from Mathieson et al. [11,12].

There are not enough points for systems 9 and 10 with more than three components. This is also valid for systems 11–13. In these, the binaries involved are $C_6H_6 + n-C_6$, $C_6H_{12} + n-C_6$ and $C_6H_6 + C_6H_{12}$ with maxima in G^E of 400, 100 and 325 $J mol^{-1}$ respectively, the first of which is near the maximum value of system 13. Finally, it must be said that the results we have obtained are similar to those calculated with empirical equations such as Toop's or Hillert's equations [3].

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