Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 289–293

EXCESS MOLAR ENTHALPY OF BINARY MIXTURES OF HEXANE+ETHYL BENZENE, *o*-XYLENE, *m*-XYLENE AND *p*-XYLENE AT 298.15 K

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This paper reports excess molar enthalpies of the binary systems hexane+ethyl benzene, hexane+*o*-xylene, hexane+*m*-xylene and hexane+*p*-xylene at 298.15 K and atmospheric pressure, over the whole composition range. The data was measured directly using a Calvet microcalorimeter. The excess magnitude was correlated to a Redlich-Kister type equation for each mixture. Also, we will discuss the results for the four mixtures studied here and by comparison with the same binary systems but containing propyl propanoate as first component. Finally, we will correlate our results with the Nitta-Chao and the three UNIFAC theoretical approximations.

Keywords: *benzene based compounds, excess enthalpy, hexane, Nitta-Chao, UNIFAC*

Introduction

This work continues our studies about the excess thermodynamic properties for binary mixtures containing an aromatic hydrocarbon as component [1–3]. The mixtures measured here are very interesting from the theoretical point of view, because the hexane (a linear molecule without functional groups to generate interactions) is mixed with four compounds that have the same molecular mass and similar functional groups. So, the results obtained will indicate the influence of the position of the methyl groups on the intermolecular interactions. From the practical point of view, the mixtures presented here are especially important because they are widely used as solvents for dyes and colouring. Also, xylenes are used as raw material in plastic industry to make synthetic fibres and for aircrafts and vehicles.

Experimental

The chemicals employed were supplied by Fluka. Their mass purities were hexane (≥99.5%), ethyl benzene (≥99%), *o*-xylene (≥99%), *m*-xylene (≥99%) and *p*-xylene (≥99%). The substances were degassed by ultrasound and dried over molecular sieves (Sigma type 0.4 nm), otherwise used as supplied.

All the mixtures were prepared by mass using a Mettler AT 201 balance, the precision of the mole fraction is estimated to be better than $\pm 1\cdot 10^{-4}$. Excess molar enthalpies, H^E, were directly measured using a Calvet microcalorimeter connected to a Philips PM 2535 voltmeter. The inaccuracy of the excess enthalpy measurements was estimated to be 1%. Calibration was performed electrically using a Setaram EJP 30 stabilised current source and tested further with a hexane+cyclohexane (both Fluka ≥99.5%) mixture as recommended [4]. Details of the experimental procedure to measure H^E were described previously by Paz Andrade [5, 6].

Results

The measured excess molar enthalpies, H^E, of the binary systems can be represented by a Redlich-Kister type Eq. [7]

$$H^E = x_1 x_2 \sum_{K=0}^{m} A_K (2x_1 - 1)^K \tag{1}$$

where x_1 is the mole fraction of hexane, x_2 that of the other component of the binary mixture, and A_K denotes the polynomial coefficients. The degree of the polynomial Redlich-Kister equation was optimised by applying the F-test [8]. The coefficients A_K for Eq. (1) and the standard deviation, s, are given in Table 1 for the four mixtures measured here. In this work s is defined as,

$$s = \sqrt{\frac{\sum_{i=1}^{N} (Y_{cal} - Y_{\exp})^2}{N-1}} \tag{2}$$

where N is the number of data points, Y_{cal} is the calculated value and Y_{exp} is the experimental value.

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1388–6150/$20.00

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Table 1 Coefficients A_K and standard deviations, s, from the fit of H^E/J mol^{-1} with Eq. (1)

A_0	A_1	A_2	A_3	A_4	s
Hexane(x_1)+Ethyl Benzene(x_2)					
2096	–144.5				5.3
Hexane(x_1)+*o*-xylene(x_2)					
1707	0	325.8	0	–509.0	5.9
Hexane(x_1)+*m*-xylene(x_2)					
1500	–253.5	0	406.7		4.3
Hexane(x_1)+*p*-xylene(x_2)					
1252	–195.6	96.14	277.2		3.2

In Fig. 1 we present the measured H^E for hexane+ethyl benzene (round dots), hexane+*o*-xylene (square dots), hexane+*m*-xylene (triangle dots) and hexane+*p*-xylene (rhombus dots) at 298.15 K and atmospheric pressure. The lines on the data points represent the best fit of the Eq. (1) with the parameters summarised in Table 1 for each mixture. As observed, the data is positive for the four mixtures studied, in contrast with our previous results on similar mixtures with propyl propanoate as first component plus the three xylenes [3] and the ethyl benzene [9]. Some of the data presented here were previously measured by other authors and published in a national journal [10], both sets of data match very well but our curves, presented in Fig. 1, have more data and their maxima are not at equimolar composition as in Ref. [10].

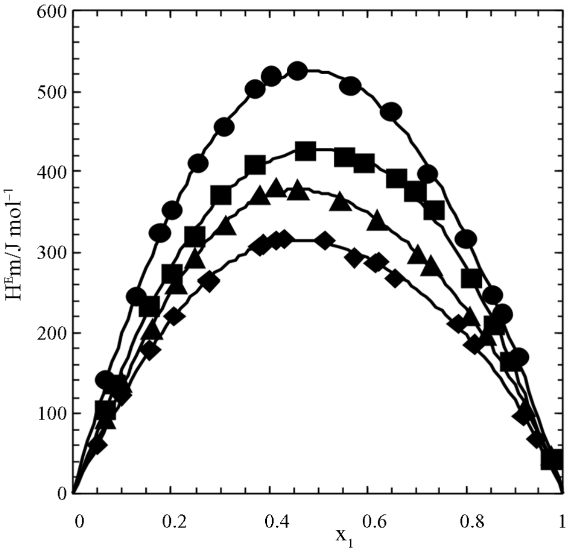

Fig. 1 Excess molar enthalpies $H^E$of: ● – hexane(x_1)+ethyl benzene, ■ – hexane(x_1)+*o*-xylene, ▲ – hexane(x_1)+*m*-xylene, ◆ – hexane(x_1)+*p*-xylene at 298.15 K. The lines are the best fit of the Redlich-Kister type equation with the corresponding parameters summarised in Table 1

Discussion

As it is well known, the excess molar enthalpy H^E is a measure of the rearrangement of the intermolecular forces that take place in the physical process of mixture. Thus, the observed positive H^E means that some intermolecular links present in the pure liquids are broken when they are mixed. So the interaction between two different molecules of our mixtures is feebler than that between equal molecules of any (or both) pure components. The interactions that get broken in our mixtures must be between the aromatic rings of the pure second compound due to the presence in between of the linear molecule of hexane, which does not present functional group that can interact with others. The absolute value of H^E will indicate the strength and the number of those broken interactions minus the strength and the number of the novel interactions, if any, between the molecules of the compounds forming the mixture. Higher positive value of H^E indicates more (or stronger) broken interactions. In this sense, we observe in Fig. 1 that the molecules with more intense intermolecular interactions when pure must be, in order: ethyl benzene, *o*-xylene, *m*-xylene and *p*-xylene. This result agrees with the assumption that those interactions are between the vertex of the aromatic rings, because the given order also indicates the number of vertexes of the aromatic ring free to interact in each kind of molecule. In the case of xylenes, the number of free vertices of the benzene ring is four for the three compounds, the differences in the H^E values would indicate that the position of the methyl groups is important to allow more or less benzene ring vertex interactions. In agreement with this assumption we must suppose that the H^E of the mixture hexane+benzene have to be higher in absolute value than those presented here, because the six vertex of the aromatic ring are free to interact. As we will observe below, this is the case for the last mentioned mixture from the data published in Ref. [1] (see below).

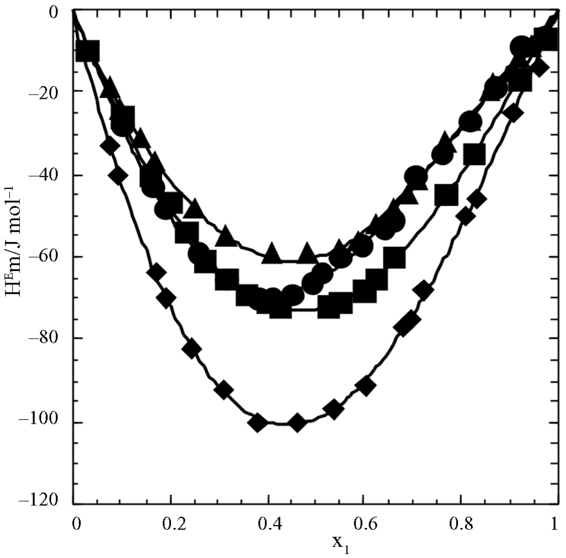

Fig. 2 Excess molar enthalpies H^E of: ● – propyl propanoate(x_1)+ethyl benzene [9], ■ – propyl propanoate(x_1)-+o-xylene [3], ▲ – propyl propanoate(x_1)+m-xylene [3], ◆ – propyl propanoate(x_1)+p-xylene [3] at 298.15 K. The lines are the best fit of the Redlich-Kister type equation

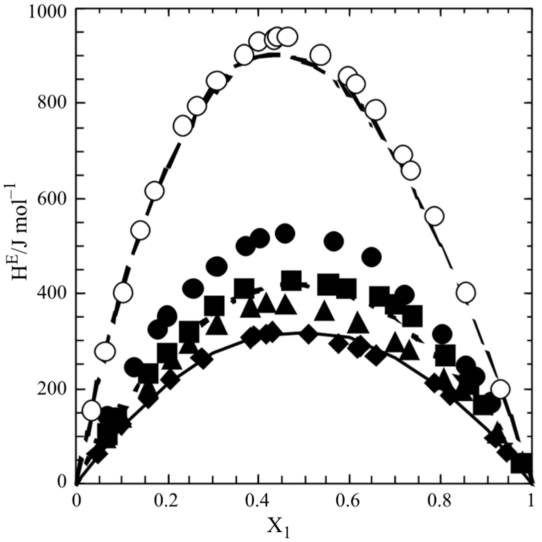

Fig. 3 Excess molar enthalpies H^E of: ○ – hexane(x_1)+benzene [1] (dashed line), ● – hexane(x_1)+ethyl benzene (dotted line), ■ – hexane(x_1)+o-xylene, ▲ – hexane(x_1)+m-xylene, ◆ – hexane(x_1)+p-xylene (continuous line) at 298.15 K. The lines correspond to the values obtained applying the Nitta-Chao model for each mixture

To compare the results presented here with those obtained for the same mixtures, but with propyl propanoate as first component [3, 9], we reproduce in Fig. 2 the data presented there. The first thing we observe in Fig. 2 is that the sign of H^E is negative, which indicates that novel interactions appear in these mixtures. In Ref. [3] we explain the data assuming that the novel interactions were between the aromatic ring and the carboxyl group of the propyl propanoate, which are stronger than the broken interactions between the benzene ring vertexes. Another important difference is the order of the H^E values between the different studied mixtures. Thus, the results reported in Refs [3, 9] present the order (in absolute value): p-xylene, ethyl benzene, o-xylene and m-xylene, which is different than the order observed here. If we assume that results presented in Fig. 2 are due only to the novel interaction less the broken ones, we can obtain the molar enthalpy of the carboxyl group-benzene ring interaction, by simply deducting the H^E values presented in Fig. 1 to those presented in Fig. 2. As a result, we will obtain the same order of compounds in absolute value than we find here, which agrees with the assumptions made before.

Now, we will correlate our results with the predictions given by the theoretical approximations of Nitta-Chao [11], UNIFAC I (Tassios version) [12], UNIFAC II (Larsen version) [13] and UNIFAC III (Gmehling version) [14]. The necessary data to perform the models for the involved functional groups were extracted from literature [14, 15]. Let us note that none of the four models presented distinguish between isomers of the same compound, and so only one curve can be obtained for the three different xylene mixtures. These theoretical models are usually used to compare the H^E data for binary and ternary mixtures [16].

In Fig. 3 we plot experimental results for H^E with the curves obtained from the Nitta-Chao model [11]. In this figure, we have included for comparison the data for the binary mixture hexane+benzene previously published by us [1], which presents a higher value of H^E than the mixtures studied here as expected (see above). In Fig. 3 the continuous line is for the mixture hexane+xylenes, the dashed line corresponds to the mixture hexane+ethyl benzene, and the dotted line to hexane+benzene. As observed, the agreement between the experimental data and the results from the Nitta-Chao model is good in sign and shape for all. The absolute value obtained from this model for the mixture hexane+benzene is less than a 4% lower than the measured value, which indicates a very good agreement. For the hexane+ethyl benzene mixture the prediction is around a 20% lower than the measured values, while for the hexane+xylene mixture the curve from the model match nearly exactly with the measured data for the mixture hexane+p-xylene (that with the lowest measured H^E value).

In Fig. 4 we present the theoretical curves obtained using the UNIFAC I model [12]. Also, we include the data for the mixture hexane+benzene [1]. As in Fig. 3 the continuous line is for the mixture hexane+xylenes, the dashed line corresponds to the mix-

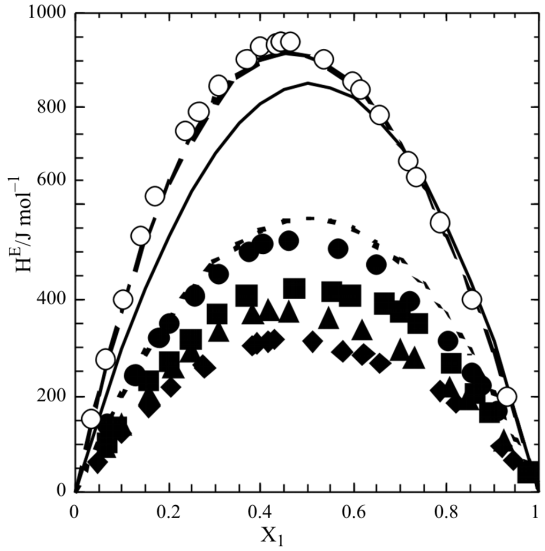

Fig. 4 Excess molar enthalpies H^E of: ○ – hexane(x_1)+benzene [1] (dashed line), ● – hexane(x_1)+ethyl benzene (dotted line), ■ – hexane(x_1)+*o*-xylene, ▲ – hexane(x_1)+*m*-xylene, ◆ – hexane(x_1)+*p*-xylene (continuous line) at 298.15 K. The lines correspond to the values obtained applying the UNIFAC I model (Tassios version) for each mixture

ture hexane+ethyl benzene, and the dotted line to hexane+benzene. In that figure we observe that the model approximates the measured data in the case of the mixtures hexane+benzene (less than a 2.5% higher the measured one) and hexane+ethyl benzene (around a 7% lower the measured one). Although, the model does not reflect the data measured for the different hexane+xylene mixtures, the results obtained from UNIFAC I are around the double than the measured data for the hexane+*o*-xylene mixture (which presents the higher value of H^E among the three xylene mixtures).

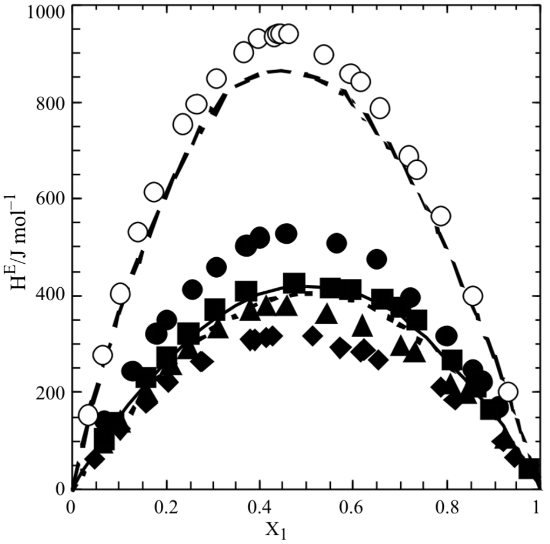

Fig. 5 Excess molar enthalpies H^E of: ○ – hexane(x_1)+benzene [1] (dashed line), ● – hexane(x_1)+ethyl benzene (dotted line), ■ – hexane(x_1)+*o*-xylene, ▲ – hexane(x_1)+*m*-xylene, ◆ – hexane(x_1)+*p*-xylene (continuous line) at 298.15 K. The lines correspond to the values obtained applying the UNIFAC III model (Gmehling version) for each mixture

The data obtained from the UNIFAC II model is not presented because the agreement with the measured data is not good, this model gives always values of H^E very much lower than those measured, although positives. In Fig. 5 we plot the curves obtained from the UNIFAC III theoretical model (Gmehling version) [14], also including the hexane+benzene data [1]. As in Figs 3 and 4 the continuous line is for the mixture hexane+xylenes, the dashed line corresponds to the mixture hexane+ethyl benzene, and the dotted line to hexane+benzene. In this case, the model reproduces quite well the data for the hexane+xylene mixtures, but for the other two mixtures plotted in this figure, the model predicts lower values of H^E than those measured (around a 10% lower for hexane+benzene and around a 20% lower for hexane+ethyl benzene).

Other theoretical models as DISQUAC or Equation of State methods based in the Corresponding States Techniques will be applied to the data in a next paper.

Conclusions

We present here measurements of excess molar enthalpies H^E, in the binary mixtures {hexane+ethyl benzene, +*o*-xylene, +*m*-xylene and +*p*-xylene} at 298.15 K and atmospheric pressure. The data is compared with previous measurements of H^E for similar systems with propyl propanoate as first component. The results are discussed in terms of the formation and rupture of intermolecular interactions. Finally, we analyse our data using the theoretical approximations of Nitta-Chao and the three UNIFAC versions. The model that match better with all measured data is that of Nitta-Chao, while UNIFAC II (Larsen version) is the worst model to reproduce the measured data.

References

1 H. Casas, L. Segade, C. Franjo and E. Jiménez, J. Chem. Eng. Data, 45 (2000) 445.
2 S. Freire, L. Segade, S. García Garabal, J. Jiménez de Llano, M. Domínguez and, E. Jiménez, J. Therm. Anal. Cal., 70 (2002) 243.
3 M. Domínguez-Pérez, J. Jiménez de Llano, L. Segade, O. Cabeza, C. Franjo and E. Jiménez, Thermochim. Acta, 420 (2004). 45.
4 K. N. Marsh, Recommended Reference Materials for the Realisation of Physicochemical Properties, Blackwell Scientific Publications, Oxford, 1987.
5 M. I. Paz Andrade, S. Castromil and M. D. C. Baluja, J. Chem. Thermodyn., 2 (1970) 775.

6 M. I. Paz Andrade, Les Développements récents de la Microcalorimétrie et de la Thermogénese, C. N. R. S., París, 1967.
7 O. Redlich and A. T. Kister, Ind. Eng. Chem., 40 (1948) 341.
8 P. R. Bevington and D. K. Robinson, Data Reduction and Error Analysis for the Physical Sciences, 2nd Ed. McGraw-Hill, Singapore, 1994.
9 O. Cabeza, M. Domínguez-Pérez, E. Rilo, L. Segade, J. Jiménez de Llano, C. Franjo and E. Jiménez. Submitted to Fluid Phase Equilibria
10 M. D. C. Baluja-Santos, Acta Cient. Compostelana, 7 (1970) 3.
11 T. Nitta, E. A. Turek, R. A. Greenkorn and K.C. Chao, AIChE Journal, 23 (1977) 144.
12 P. J. Stathis and D. P. Tassios, Ind. Eng. Chem. Process. Des. Dev., 24 (1985) 701.
13 B. L. Larsen, P. Rasmussen and A. Fredenslund, Ind. Eng. Chem. Res., 26 (1987) 2274.
14 J. Gmehling, J. Li and M. Schiller, Ind. Eng. Chem. Res., 32 (1993) 178.
15 J. J. Christensen, R. L. Rowley and R. M. Izatt, Handbook of heats of mixing: Supplementary volume, Ed. Wiley, New York 1988.
16 F. Allal and A. Dahmani, J. Therm. Anal. Cal., 73 (2003) 961