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Excess enthalpies of alkanediamines + benzene or + toluene mixtures
Predictions using group contribution models

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Abstract

The excess molar enthalpies of alkanediamine $H_2N-(CH_2)_u-NH_2$ $(u = 2, 3, 4)$ + benzene or toluene mixtures were measured using a Calvet microcalorimeter at 303.15 K. Group contribution models, Modified UNIFAC (Lyngby and Dortmund versions) and DISQUAC have been applied. The effects of the proximity of two NH_2 groups in these mixtures is analysed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Diamines, a particularly interesting and technically important class of molecules [1,2], have been investigated with a view to testing group contribution models and to analyse intramolecular effects, especially proximity effect. The thermodynamic properties of mixtures of symmetric tertiary diamines + n-alkanes or cyclohexane have been discussed recently [3–6]. For mixtures of primary alkanediamines, the available experimental data are very scarce and are limited to ethylenediamine. Molar excess volumes and molar excess enthalpies, of 1,2-ethanediamine (EDA) + benzene at 298.15 K have been measured in the past [7,8]. Isobaric liquid–vapour equilibrium have been investigated for EDA + benzene [8–11] and also for 1,3-propanediamine + benzene [9,12].

Following our systematic study of the thermodynamic properties of mixtures containing organic molecules [5–7], we present in this paper, data of molar excess enthalpies, H^E, of EDA, 1,3-propanediamine (PDA) and 1,4-butanediamine (BDA) with benzene and toluene at 303.15 K.

The purpose of this paper is the study of the excess properties of these mixtures and to compare the results in terms of several versions of UNIFAC that are available [13–15], DISQUAC, an extended quasi-chemical group contribution model [16], and to examine the proximity effect of NH_2 groups.

2. Experimental

Benzene and toluene and the diamines (purity greater than 99 mol%) were Fluka products, and were used without further purification.

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Excess molar enthalpies were measured at 303.15 K with a C 80 calorimeter (Setaram, France), a Calvet type microcalorimeter, with no vapour space. Mercury was used to separate the two cells which contained the liquids under study. The performance of the apparatus was checked by determining H^E of benzene + cyclohexane, at 298.15 K. Our results differ by less than 2% from those reported by Marsh [17].

3. Results

Experimental molar excess enthalpies H^E at 303.15 K are reproduced in Table 1. The results have been fitted to the smoothing equation

$$H^{E}_{\mathrm{exp}} = x_1(1 - x_1)\sum_{i=0}^{n-1} a_i(2x_1 - 1)^i \tag{1}$$

Table 1
Experimental molar excess enthalpies H^E at 303.15 K

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
EDA (1) + benzene (2)				EDA (1) + toluene (2)			
0.0	0.0	0.7422	1070.9	0.0	0.0	0.5035	1656.7
0.0985	579.8	0.8103	838.2	0.0589	453.3	0.6025	1566.4
0.1697	930.2	0.8923	536.7	0.0916	670.4	0.7089	1367.8
0.2514	1198.0	1.0	0.0	0.1470	975.4	0.8053	1059.6
0.303	1327.8			0.2037	1201.2	0.8515	863.4
0.4105	1449.0			0.2487	1363.4	0.9006	626.5
0.4904	1474.4			0.3036	1490.3	0.9502	332.9
0.5558	1421.0			0.3575	1579.5	1.0000	0.0
0.6657	1248.8			0.4236	1649.9		
PDA (1) + benzene (2)				PDA (1) + toluene (2)			
0.0	0.0	0.4371	1291.2	0.0	0.0	0.6017	1364.1
0.0621	340.3	0.5719	1232.2	0.0563	394.8	0.7047	1167.1
0.1024	539.3	0.7071	1010.7	0.0980	628.8	0.8016	878.5
0.1245	642.2	0.8046	739.2	0.1510	875.3	0.8519	692.3
0.1416	711.6	0.9097	375.8	0.2003	1074.0	0.9008	487.9
0.2122	954.2	1.0	0.0	0.2900	1315.3	0.9504	256.3
0.2480	1056.7			0.3952	1455.4	1.0	0.0
0.3462	1226.9			0.4948	1459.4		
BDA (1) + benzene (2)				BDA (1) + benzene (2)			
0.0	0.0	0.516	1097.5	0.0	0.0	0.4918	1280.4
0.0501	258.2	0.611	999.4	0.059	363.2	0.6126	1146.5
0.1017	468.8	0.7019	840.1	0.1005	580.2	0.7051	958.4
0.1498	650.5	0.8022	594.1	0.1537	797.1	0.8024	703.6
0.2003	792.9	0.851	470.9	0.2014	965.6	0.8509	536.1
0.3054	1010.9	0.9012	320	0.3012	1174.4	0.9017	364.7
0.4015	1102.7	1.0	0.0	0.4001	1291.2	1.0	0.0

Table 2
Coefficients a_i and standard deviations $\sigma(H^E)$ for least-squares representation by Eq. (2) of H^E at 303.15 K

Mixtures	a_0	a_1	a_2	a_3	$\sigma(H^E)$ (J mol^{-1})
EDA (1) + benzene (2)	5861.907	−800.8348	376.4839		9
EDA (1) + toluene (2)	6620.739	−609.582	1343.407		5
PDA (1) + benzene (2)	5160.420	−828.450	164.5508		5
PDA (1) + toluene (2)	5854.1060	−980.5544	693.0809		5
BDA (1) + benzene (2)	4399.8550	−977.9154			5
BDA (1) + toluene (2)	5086.944	−1184.242	236.1792	−361.2933	5

The values of the coefficients a_i were determined by least-squares analysis and are reported in Table 2. The standard deviations $\sigma(H^E)$ are given by

$$\sigma(H^E) = \left[\sum_{i=1}^{N} \frac{(H^E_{i,\mathrm{cal}} - H^E_{i,\mathrm{exp}})^2}{N - n}\right]^{1/2} \qquad (2)$$

where N is the number of experimental points and n the number of coefficients.

4. Theory

The original UNIFAC [13] only predicts G^E, whereas modified UNIFAC (Larsen [14] and Gmehling [15]) can be used to predict G^E, H^E, and γ_i^∞.

In the DISQUAC model, the diamines are regarded as possessing two types of surfaces: type a, alkane (CH_3 or CH_2 group) and type n, nitrogen (NH_2 group). The geometrical parameters have been calculated as before [18]. The solvent, benzene (surface type b) is regarded as a homogeneous molecule and the toluene (surface type b and type a) have been estimated previously [19]. The three types of surfaces a, n and b generate a three pair of contact (a,n), (a,b) and (b,n). The equations used to calculate G^E and H^E are the same as previously reported [16]. The temperature dependence of the interchange parameters has been expressed in terms of dispersive (dis) and/or quasichemical (quac) interchange coefficients: $C_{\mathrm{an,l}}$ (dis or quac), where $l = 1$ (Gibbs energy)or $l = 2$ (enthalpy).

5. Discussion

Primary monoamines have been investigated previously [20] using the classical quasichemical model; the excess properties correlated successfully. The results show [21,22] that this class of amines is weakly associated through H-bonds of NH · · · N type and that this specific interaction is the main source of non ideality.

Table 3
Interchange energy coefficients, dispersive $C^{\mathrm{dis}}_{st,l}$ and quasichemical $C^{\mathrm{quac}}_{st,l}$ ($z = 4$), for contact (s, t), CH_2 or CH_3 (type a), NH_2 (type n), benzene (type b)

Contact (s, t)	$C^{\mathrm{dis}}_{st,1}$	$C^{\mathrm{dis}}_{st,2}$	$C^{\mathrm{quac}}_{st,1}$	$C^{\mathrm{quac}}_{st,2}$
(a,n)	1.200	2.400	3.510	7.200
(a,b)	0.2598	0.5623	0.	0.
(b,n)	3.0	5.75	0.055	0.35

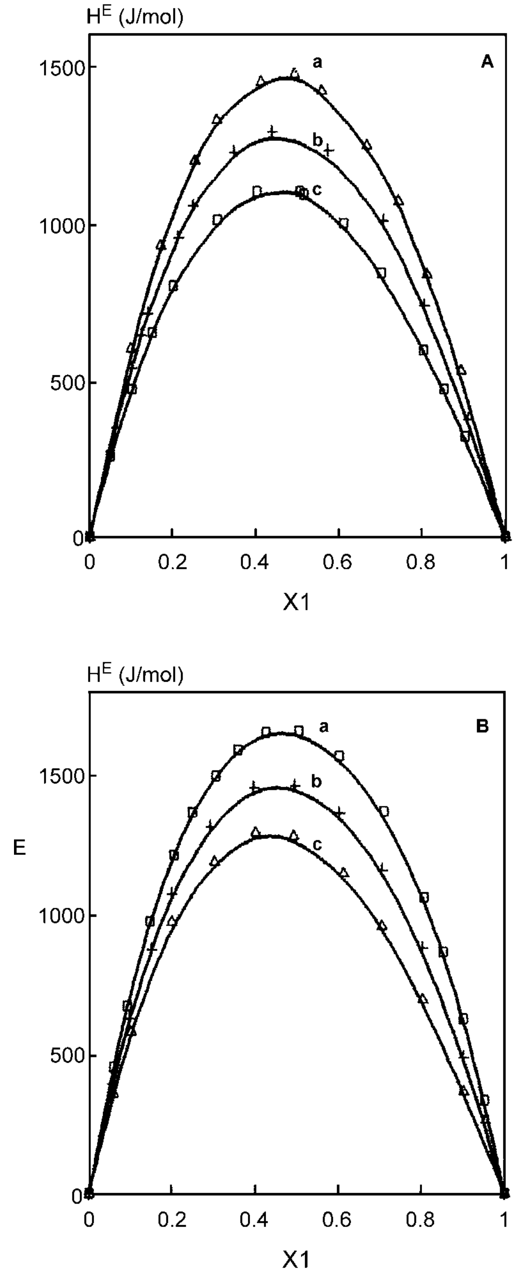

Fig. 1. Excess molar enthalpies, H^E, at 303.15 K of: (A) $H_2N-(CH_2)_u-NH_2$ (1) + benzene (2), (B) $H_2N-(CH_2)_u-NH_2$ (1) + toluene (2) (a) $u = 2$, (b) $u = 3$, (c) $u = 4$.

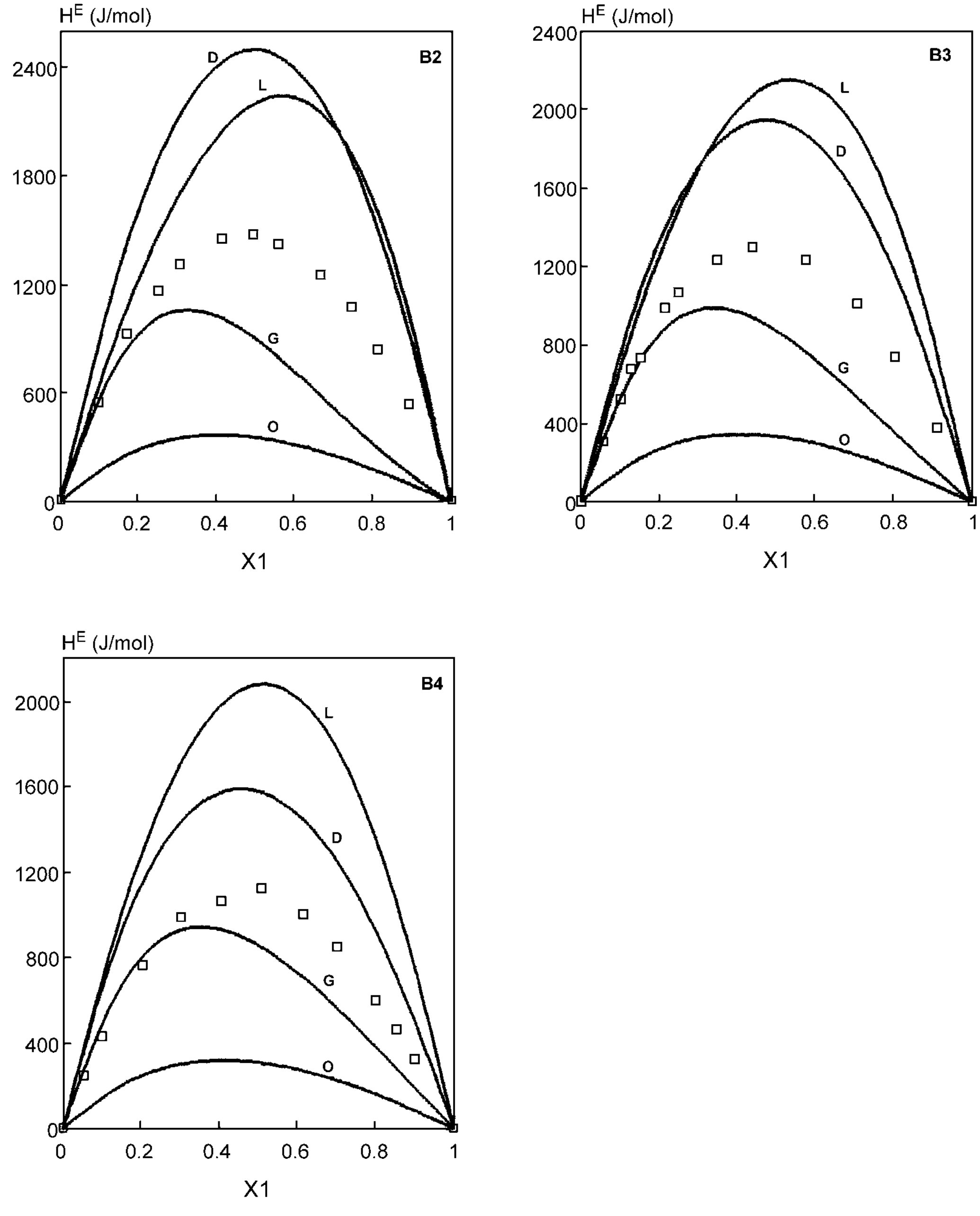

Fig. 2. Comparison of the theory with experiment for the molar excess enthalpy, H^E, at 303.15 K of: (B2) EDA (1) + benzene (2); (B3) PDA (1) + benzene (2); (B4) BDA (1) + benzene (2): points, our experimental results. Theoretical predictions with UNIFAC: (O) original UNIFAC, (L) Larsen, (G) Gmehling, (D) DISQUAC.

Recently [18] primary amines + *n*-alkanes have been reexamined in detail in terms of the DISQUAC model. The parameters used in this work are the same as those determined previously [18].

The thermodynamic properties of butylamine + benzene have been investigated previously [22,23]. These data are used to determine the interchange parameters of the contact (b,n). The dispersive

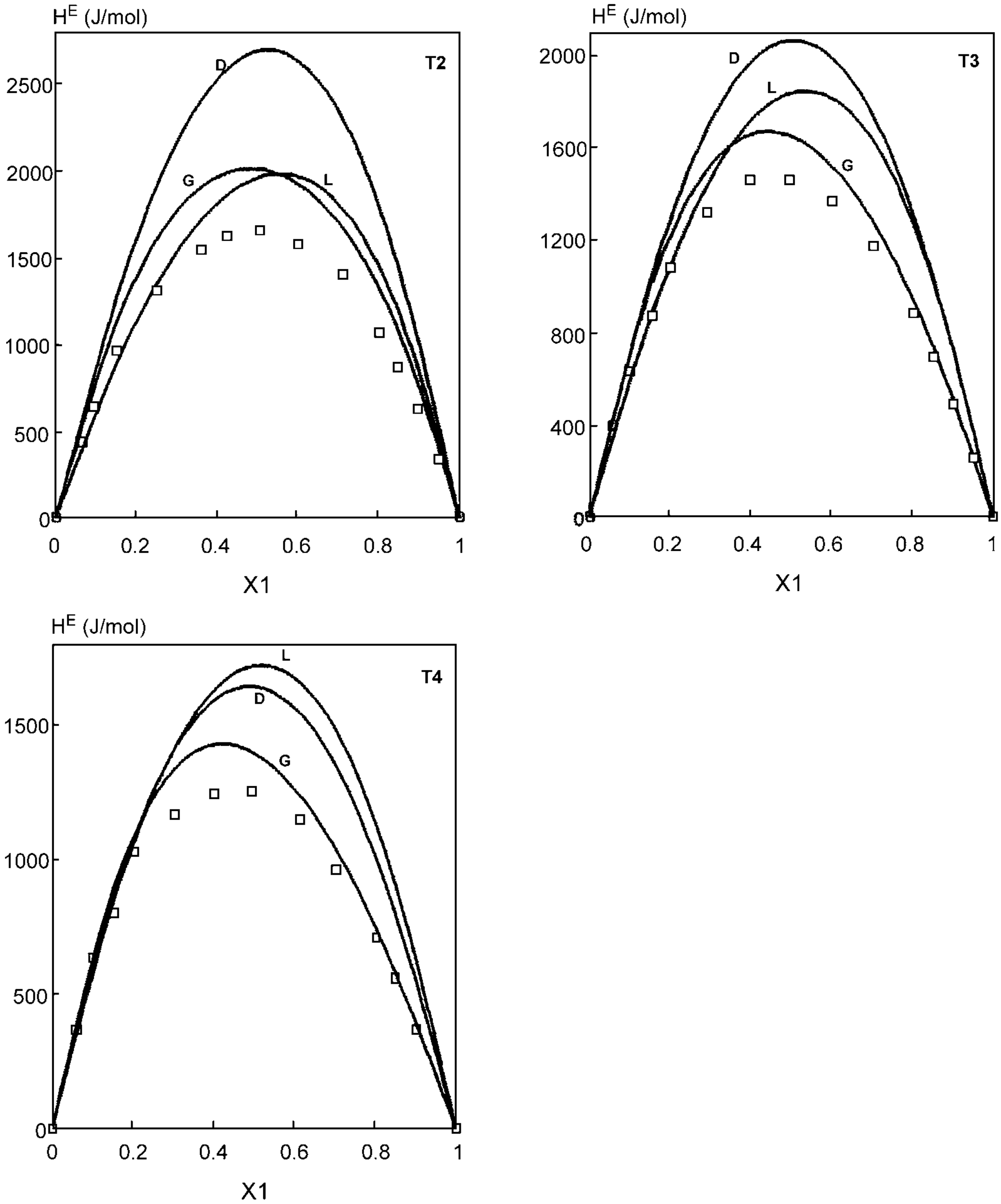

Fig. 3. Comparison of the theory with experiment for the molar excess enthalpy, H^E, at 303.15 K of: (T2) EDA (1) + toluene (2); (T3) PDA (1) + toluene (2); (T4) BDA (1) + toluene (2): points, our experimental results. Theoretical predictions with UNIFAC: (L) Larsen, (G) Gmehling, (D) DISQUAC.

coefficients and the quasichemical coefficients have been adjusted to the G^E and H^E of butylamine + benzene [23]. The values of the interchange coefficient parameters of the contact (a,b) are reported elsewhere [16]. Using the parameters of butylamine + benzene, we calculated H^E for the alkanediamine + benzene, or + toluene. The values of the interchange coefficients used in this work are reported in Table 3.

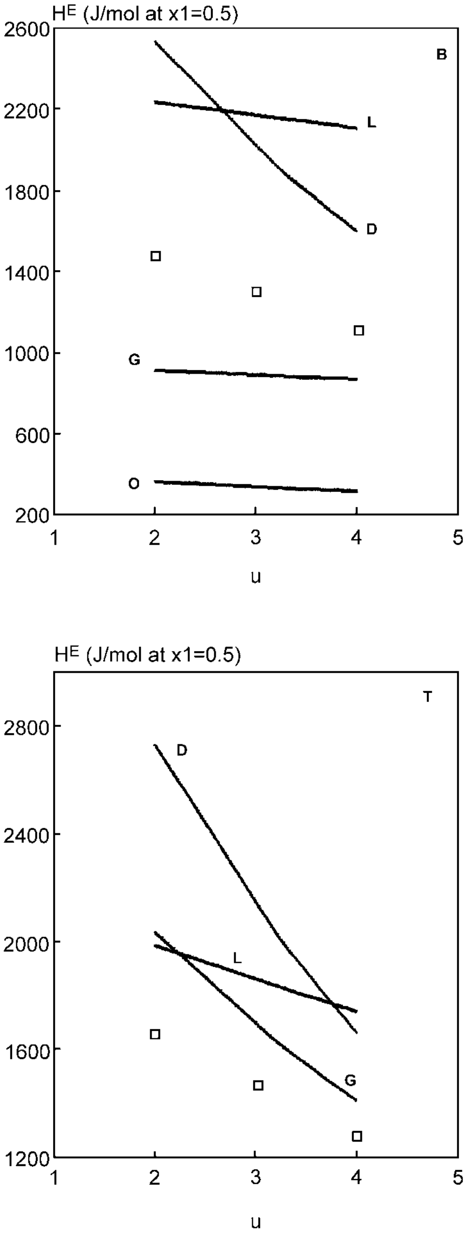

Fig. 4. Comparison of the theory with experiment for the equimolar excess enthalpy, H^E $(x_1 = 0.5)$, at 303.15 K, versus u, the number of NH_2 group of: (B) diamine (1) + benzene (2), (T) diamine (1) + toluene (2): points, our experimental results. Theoretical predictions with UNIFAC: (O) original UNIFAC, (L) Larsen, (G) Gmehling, (D) DISQUAC.

The H^E values for alkanediamine + benzene, or + toluene are positive and decrease with increasing the distance u between NH_2 groups.

Fig. 1 shows the experimental curves of H^E at 303.15 K. The H^E values for alkanediamine + benzene, or + toluene are positive and decrease with increasing the distance u between NH_2 groups.

Using the parameters of original UNIFAC [13] and modified UNIFAC [14,15], we calculated H^E for the alkanediamine + benzene, or + toluene.

Figs. 2 and 3 show the experimental and theoretical curves of H^E at 303.15 K. The modified UNIFAC (Gmehling) model gives slightly better results than the other versions.

The predicted dependence of H^E at 303.15 K and $x_1 = 0.5$ on the chain length of diamine, u is represented in Fig. 4 and compared with our experimental values.

It may be seen from Fig. 4 that the H^E decreases with the "distance u" between the NH_2 group and tends towards the limiting values of the monoamine + n-alkane.

The modified UNIFAC version gives better predictions for H^E than the original. The difficulties in representing complex systems such as diamines are not surprising because a simple group contriburion method is not able to account for intramolecular proximity effects, i.e., the influence on a group from nearby groups on the same molecule.

The most interesting result of our study is the confirmation of proximity effects in linear diamines, quite similar to the effect observed in dichloroalkanes [24,25], acetals [26] and dibromoalkanes [27].

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