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EXCESS ENTHALPIES OF SOME TERTIARY AMINE + *n*-ALKANE OR CYCLOHEXANE MIXTURES

BRUNO MARONGIU * and SILVIA PORCEDDA
Dipartimento di Scienze Chimiche, via Ospedale 72, 09100-Cagliari (Italy)

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ABSTRACT

A Tian–Calvet-type calorimeter has been used to determine molar excess enthalpies H^E at 298.15 K as a function of concentration for mixtures containing *n*-heptane with *N,N*-dimethylpropylamine, *N,N*-dimethyldodecylamine, tripropylamine and tributylamine, and cyclohexane with *N,N*-dimethylethylamine, *N,N*-diemthylpropylamine, *N,N*-dimethylbutylamine and *N,N*-dimethyldodecylamine.

The data are examined on the basis of the group-contribution model which has been previously applied to mixtures of *N,N*-dialkylmethylamine with *n*-alkane (I. Ferino et al., Fluid Phase Equilibria, 9 (1982) 49). Using the same two alkyl group increments to account for intramolecular effects in the amines, and with one additional adjusted parameter (the enthalpy of interchange for N–cyclohexane contact), the model provides a fairly consistent description of the excess enthalpies as a function of composition.

The N–cyclohexane interchange parameters are slightly larger than the N–alkane parameters.

INTRODUCTION

In part 1 of this series [1], we investigated the thermodynamic properties of mixtures of *N,N*-dialkylmethylamines, $CH_3(CH_2)_{s-1}$–$N(CH_3)$–$(CH_2)_{t-1}CH_3$ (or $A_{s,t}$), with *n*-alkanes. We applied the group-contribution model of Kehiaian et al. [2,3] in the random-mixing approximation and determined the interchange enthalpy coefficients $C_{an,2}$ for the pair of group surfaces (a, n), where a represents the surface of the $-CH_2-$ or $-CH_3$ groups in *n*-alkyls or *n*-alkanes, and n the surface of the $>N-$ group in tertiary amines.

Our previous studies [1,4] have shown that the interchange enthalpy coefficents $C_{an,2}$ for tertiary amines, R_3N, are affected by the chain length of the *n*-alkyl substituents, R. The almost linear tertiary amines, $A_{s,t}$ were

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* Author to whom correspondence should be adressed.

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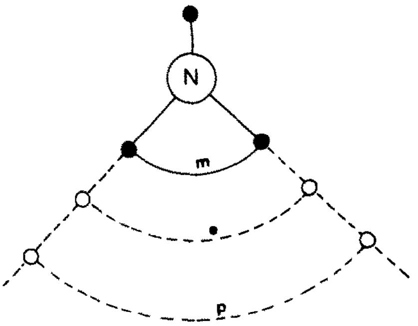

Fig. 1. Schematic representation of N,N-dialkylmethylamine molecules. In trimethylamine, there are only two C atoms which occupy level m and levels e and p are empty ($n^e = n^p = 0$); in N,N-diethylmethylamine, $n^e = 2$, $n^p = 0$; and in N,N-dimethylbutylamine, $n^e = 1$, $n^p = 1$, etc.

chosen to reduce this steric effect as much as possible. Indeed, it was found that the coefficients $C_{\text{an},2}$ for N,N-dialkylmethylamines can be represented by a relationship of the type

$$C_{\text{an},2} = C^0_{\text{an},2}(1 + n^e\sigma^e_{\text{an},2} + n^p\sigma^p_{\text{an},2} + \ldots) \tag{1}$$

where $C^0_{\text{an},2}$ is the interchange enthalpy coefficient for the base compound, trimethylamine ($s = t = 1$), and n^e and n^p represent the number of carbon atoms in the different 'levels' around the functional group $-\text{N(CH}_3\text{)}-$, e denoting ethyl, p, propyl, etc. (Fig. 1). The so-called alkyl-group increments $\sigma^R_{\text{an},2}$ are relatively small negative numbers.

The study of symmetrical tertiary amines (tripropyl– and tributyl–) demonstrates that this steric effect is more accentuated in these cases.

By replacing the n-alkanes with other solvents, the number of surface types and, consequently, the number of interchange parameters is increased. For a systematic study, one should replace the n-alkanes with other homogeneous solvents, i.e. those having only one type of surface. The most typical are, in order of increasing 'activity', cyclohexane, benzene and tetrachloromethane. This study is concerned with N,N-dialkylmethylamine ($A_{s,t}$) + cyclohexane mixtures.

A survey of the literature revealed that experimental data are very scarce for this class of mixture. There is only one source, ref. 5, which gives the molar excess enthalpy H^E for dimethyldodecylamine + cyclohexane at 298.15 K. There are no liquid–vapour equilibrium data available in the literature. The most extensive investigation of the H^E values of symmetrical trialkylamines + n-alkanes is by Philippe et al. [6].

A theoretical discussion of the H^E data is presented here. The free-volume contribution was estimated by means of the Flory theory [7] and the difference in H^E is regarded as being because of a disorder contribution [8].

EXPERIMENTAL

The enthalpies of mixing were measured using a manually tilted Tian–Calvet (CRMT)-type calorimeter. The batch mixing cell and the experimental procedure are described elsewhere [9]. The calorimeter was

TABLE 1

Experimental values of the excess enthalpies, H^E, at 298.15 K, for binary mixtures of *N*, *N*-dialkylmethylamine or trialkylamine (1) + *n*-alkanes or cyclohexane (2)

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
$(CH_3)_2N(CH_2)_2CH_3 + C_7H_{16}$					
0.1007	78	0.7100	191		
0.3042	188	0.8900	92		
0.5000	228				
$(CH_3)_2N(CH_2)_{11}CH_3 + C_7H_{16}$					
0.0683	22	0.3987	63	0.7996	32
0.1506	43	0.5088	60	0.9132	14
0.2162	53	0.6190	52	0.9366	11
0.3542	62	0.7005	45		
$(CH_3CH_2CH_2)_3N + C_7H_{16}$					
0.1859	2.6	0.5310	3.2	0.8525	−1.6
0.2419	3.0	0.5975	2.5	0.8927	−1.8
0.3233	3.4	0.7154	0.8	0.9116	−1.7
$(CH_3CH_2CH_2CH_2)_3N + C_7H_{16}$					
0.0600	−2.0	0.5084	−3.4	0.8617	1.0
0.1473	−4.5	0.6126	−1.5	0.9205	0.8
0.2851	−6.0	0.7265	0.6		
$(CH_3)_2NCH_2CH_3 + C_6H_{12}$					
0.0792	120	0.4037	375	0.7448	284
0.2167	274	0.5893	368	0.8976	137
0.2993	332	0.6859	324		
$(CH_3)_2N(CH_2)_2CH_3 + C_6H_{12}$					
0.0991	129	0.6970	255		
0.3012	283	0.9017	103		
0.5005	318				
$(CH_3)_2N(CH_2)_3 + C_6H_{12}$					
0.1031	116	0.7018	212		
0.3000	249	0.8995	84		
0.4981	275				
$(CH_3)_2N(CH_2)_{11}CH_3 + C_6H_{12}$					
0.0981	177	0.3476	3245	0.6991	214
0.1517	238	0.4933	305	0.8295	131
0.2321	294	0.5877	270	0.9000	79

TABLE 2

Values of the coefficients a_i (J mol^{-1}) of eqn. (1) and standard deviation, $\sigma(H^E)$, eqn. (2), of the experimental molar excess enthalpies, H^E, for *N*,*N*-dialkylmethylamine or trialkylamine (1) + *n*-heptane or cyclohexane (2) mixtures at 298.15 K (m is the number of C atoms in the *n*-alkane and c-6 denotes cyclohexane)

Amine	m	a_0	a_1	a_2	a_3	a_4	$\sigma(H^E)$
Dimethylethylamine	c-6	1534	−108	47	16		0.65
Dimethylpropylamine	7	911	50	−16			0.32
	c-6	1270	−174	50			0.55
Dimethylbutylamine	c-6	1100	−211	−12			0.57
Dimethyldodecylamine	7	240	−92	71	−13	−51	0.54
	c-6	1210	−595	351	−159		0.49
Tripropylamine	7	14	−10	−21	−23		0.07
Tributylamine	7	−14	39	2	−16		0.14

calibrated by Joule effect and the calibration was repeated after each experiment.

The precision of our H^E measurements was generally better than 1%, as can be seen from the standard deviation values reported in Table 2. The reliability of the apparatus and procedure adopted were checked by performing H^E measurements on the test system benzene + cyclohexane. Our results differed by less than 2% from literature data [10] over the entire composition range. All measurements were carried out at an average temperature of 298.15 ± 0.10 K. The experimental H^E_{exp} values, reported in Table 1, were fitted to the smoothing equation

$$H^E_{\text{sm}} = x_1 x_2 \sum_i a_i (x_1 - x_2)^i \qquad (2)$$

where x_1 is the mole fraction of the amine and x_2 the mole fraction of the *n*-alkane or cyclohexane. The values of the coefficients a_i and the standard deviation $\sigma(H^E)$,

$$\sigma(H^E) = \left[(H_{\text{sm}} - H_{\text{exp}})^2 / (N - n) \right]^{1/2} \qquad (3)$$

where N is the number of experimental points and n the number of coefficients a_i, were determined by least-squares analysis and are reported in Table 2.

THEORY

Mixtures of tertiary amines with *n*-alkanes or cyclohexane are regarded as possessing three types of surfaces: type a, CH_3– and –CH_2– groups in *n*-alkane and in tertiary amines; type c, c–CH_2– in cyclohexane; and type n, N– in tertiary amines.

TABLE 3

Relative group increments for molecular volumes, $r_G = V_G/V_{CH_4}$, and areas, $q_G = A_G/A_{CH_4}$, calculated by Bondi's method [11] ($V_{CH_4} = 17.12 \times 10^{-6} m^3 mol^{-1}$ and $A_{CH_4} = 2.90 \times 10^5 m^2 mol^{-1}$)

Group	r_G	q_G
$-CH_3$	0.79848	0.73103
$-CH_2-$	0.59755	0.46552
N–	0.25290	0.07932

The geometric parameters, i.e. the total relative molecular volumes, r_i, the total relative molecular areas, q_i, and the molecular surface fractions α_{ai}, α_{ci} and α_{ni} of a, c or n surfaces on a molecule of type i of all the molecular species, were calculated additively from the group increments given by Bondi [11], methane being taken as the standard segment [2], see Table 3. Table 4 lists these parameters for all the compounds referred to in this paper.

In the random-mixing approximation, the molar excess enthalpy H^E is given by

$$H^E/RT = (q_1x_1 + q_2x_2)\ \xi_1\xi_2h_{12} \qquad (4)$$

where $\xi_1 = q_1x_1/(q_1x_1 + q_2x_2)$ is the surface fraction of component i.

For tertiary amine (1) + n-alkane (2) mixtures, the molecular interchange enthalpy parameter h_{12} is related to the group interchange parameter h_{an} by

$$h_{12} = \alpha_{ni}^2 h_{an} \qquad (5)$$

For tertiary amine (1) + cyclohexane (2) mixtures, h_{12} is related to the group interchange enthalpy parameters h_{ac}, h_{an} and h_{cn} by

$$h_{12} = \alpha_{n1}^2 h_{an} - \alpha_{n1}(h_{ac} + h_{an} - h_{cn}) + h_{ac} \qquad (6)$$

TABLE 4

Volumes, r_i, total surfaces, q_i, and molecular surface fractions α_{si} (s = a, c, n) of trialkylamines and solvents calculated from the group increments r_G and q_G given in Table 3

Compound	r_i	q_i	α_{ai}	α_{ci}	α_{ni}
$(CH_3)_2NCH_2CH_3$	3.2459	2.7379	0.9710	0.0000	0.0290
$(CH_3)_2N(CH_2)_2CH_3$	3.3484	3.2034	0.9752	0.0000	0.0248
$(CH_3)_2N(CH_2)_3CH_3$	4.4410	3.6690	0.9784	0.0000	0.0216
$(CH_3)_2N(CH_2)_{11}CH_3$	9.2213	7.3931	0.9892	0.0000	0.0107
$(CH_3CH_2CH_2)_3N$	6.2340	5.0655	0.9843	0.0000	0.0156
$(CH_3CH_2CH_2CH_2)_4N$	8.0266	6.4621	0.9877	0.0000	0.0123
C_6H_{12}	3.5187	2.5966	0.0000	1.0000	0.0000
$CH_3(CH_2)_5CH_3$	4.5847	3.7897	1.0000	0.0000	0.0000

TABLE 5

Alkyl-group increments, $\sigma^{R}_{sn,l}$ (s = a, c), for calculation of the interchange energy coefficients given in Table 6, by means of eqns. (1) and (8) ($l = 1$ or 2 and $C^{0}_{an,l}$ and $C^{0}_{cn,l}$ are the coefficients of trimethylamine)

l	$C^{0}_{an,l}$	$C^{0}_{cn,l}$	$\sigma^{e}_{sn,l}$	$\sigma^{p}_{sn,l}$
1	52	53 [a]	−0.024 [a]	
2	184	187	−0.034	−0.017

[a] Estimated values.

Over a limited temperature range, the interchange parameters $h_{cn,2}$ may be represented by

$$h_{cn} = C_{cn,2}(T_0/T) \tag{7}$$

where $C_{cn,2}$ is the enthalpy coefficient for contact cn and $T = 298.15$ K, the scaling temperature. The coefficients $C_{ac,2}$ and $C_{an,2}$ are defined by similar equations [2,3].

Tertiary amines + n-alkane

The interchange enthalpy coefficients $C_{an,2}$ derived from eqn. (1) using the alkyl-group intercrements $\sigma^{R}_{an,2}$ in Table 5 are given in Table 6.

The predicted dependence of H^{E} at 298.15 K and $x_1 = 0.5$ on s and t is reported in Table 7 and compared with experimental results. The agreement is quite satisfactory. The shape of the experimental H^{E} curves are reproduced well by the model, see Fig. 2.

It should be noted that these parameters cannot be used to predict the behaviour of tripropyl- and tributylamine + *n*-heptane mixtures where the steric effect is accentuated. This is clearly shown by applying eqn. (1) to tripropylamine + *n*-heptane and to tributylamine + *n*-heptane ($n^{e} = 3$, $n^{p} = 3$). The calculated H^{E} ($x_1 = 0.5$ and $T = 298.15$ K) values are, respectively,

TABLE 6

Interchange energy coefficients, $C_{an,1}$ and $C_{cn,1}$ (Gibbs energy) and $C_{an,2}$ and $C_{cn,2}$ (enthalpy), at 298.15 K for *N,N*-dialkylmethylamine + *n*-alkane or cyclohexane mixtures calculated by means of eqns. (1) and (8) using the alkyl-group increments, $\sigma^{R}_{sn,l}$, from Table 5

s	t	$C_{an,1}$	$C_{an,2}$	$C_{cn,1}$	$C_{cn,2}$
1	1	52	184	53	187
1	2	51	178	52	181
1	⩾ 3	51	175	52	178
2	2	50	171	51	174
2	⩾ 3	50	168	51	171
⩾ 3	⩾ 3	50	165	51	168

TABLE 7

Molar excess enthalpies, H^E, at 298.15 K and equimolar composition ($x_1 = 0.5$) for N,N-dialkylmethylamine (1) + n-heptane or cyclohexane (2) mixtures. Comparison of direct experimental results (exp.) with values calculated (calc.) using the coefficients $C_{an,2}$ and $C_{cn,2}$ for trimethylamine and the alkyl-group increments $\sigma^R_{an,2} = \sigma^R_{cn,2}$ from Tables 5 and 6

Amine (1)	Solvent (2)	$H^E(x_1 = 0.5)$ (J mol^{-1})		Source of experimental data
		Calc.	Exp.	
Dimethylpropylamine	C_7H_{16}	232	228	This work
Dimethyldodecylamine	C_7H_{16}	63	60	This work
Dimethylethylamine	C_6H_{12}	384	384	This work
Dimethylpropylamine	C_6H_{12}	317	318	This work
Dimethylbutylamine	C_6H_{12}	275	275	This work
Dimethyldodecylamine	C_6H_{12}	313	302	This work
			318	Ref. 5

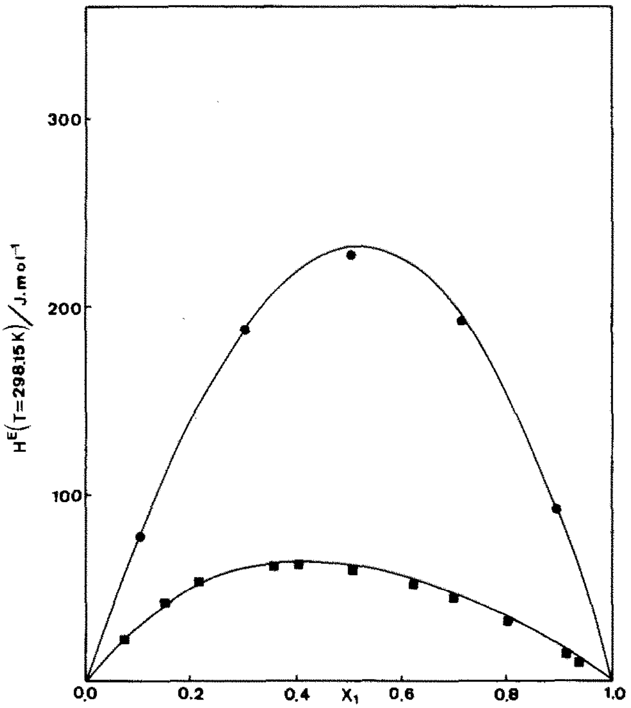

Fig. 2. Comparison of theory with experiment for the molar excess enthalpy values, H^E, at 298.15 K for N,N-dialkylmethylamine (1) + n-heptane (2) mixtures versus x_1, the mole fraction of amine: full lines, predicted values; points, experimental H^E results; ●, dimethylpropylamine; ■, dimethyldodecylamine.

103 J mol^{-1} and 70 J mol^{-1}, whereas the corresponding experimental values are 3.5 J mol^{-1} and -3.6 J mol^{-1}.

A consistent description of amine molecules which are very hindered sterically requires additional measurements and the use of DISQUAC, an extended quasi-chemical pseudo-lattice group contribution model [12,13].

Tertiary amines + cyclohexane

It appears that for tertiary amines containing short (less than six C atoms) alkyl groups adjacent to the N atoms, the interchange coefficients of the (a, c) contact can be neglected, i.e. $C_{\mathrm{ac},2} = 0$.

Because $C_{\mathrm{cn},2}$ had been found to depend on the size, s and t, of the alkyl substituents, we expected that $C_{\mathrm{cn},2}$ would also depend on s and t, and assumed a relationship of the same type as eqn. (1), namely

$$C_{\mathrm{cn},2} = C^{0}_{\mathrm{cn},2}(1 + n^{\mathrm{e}}\sigma^{\mathrm{e}}_{\mathrm{cn},2} + n^{\mathrm{P}}\sigma^{\mathrm{P}}_{\mathrm{cn},2} + \ldots) \qquad (8)$$

Unfortunately no H^{E} data are available in the literature for the trimethylamine + cyclohexane base system (it should be noted that trimethylamine is a gas at 298.15 K under normal pressure). Consequently, it was not possible to calculate the interchange coefficients $C_{\mathrm{cn},2}$ for trimethylamine directly.

The experimental H^{E} values at $x_1 = 0.5$ were first used to adjust $C_{\mathrm{cn},2}$ for each individual mixture of tertiary amine ($\mathrm{A}_{s,t}$) + cyclohexane, see Table 7. Assuming that the alkyl-group increments for cyclohexane are the same as for n-alkane, $\sigma^{\mathrm{R}}_{\mathrm{cn},2} = \sigma^{\mathrm{R}}_{\mathrm{an},2}$, and applying eqn. (8), $C_{\mathrm{cn},2}$ was calculated.

In Table 7, the equimolar values of H^{E} for dialkylmethylamine + cyclohexane as a function of s and t are reported. The agreement is quite satisfactory and shows that the H^{E} values of amine + cyclohexane systems can be calculated using the coefficients of n-alkane systems by slightly increasing the coefficient of the base compound.

DISCUSSION

The shapes of the calculated curves are satisfactorily reproduced for the systems examined in Fig. 3. This proves that the random-mixing approximation is suitable for describing such systems where unspecific interaction between $>\!\mathrm{N}-$ and cyclohexane occurs.

The best evidence for the reliability of our approach follows from the very reasonable values of the derived alkyl-group increments. The increments are relatively small negative numbers essentially reflecting the weakening of N---N interactions due to steric hindrance of the alkyl group in the N,N-dialkylmethylamines.

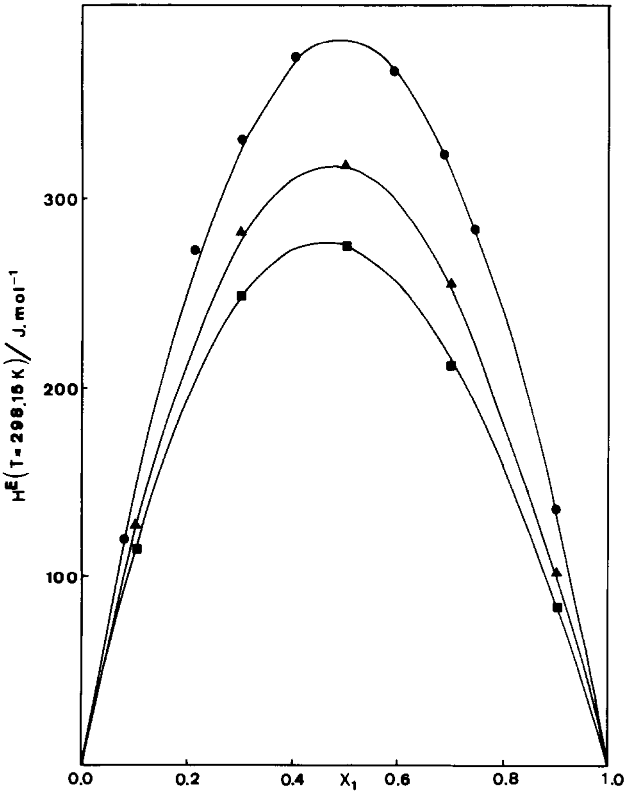

Fig. 3. Comparison of theory with experiment for the molar excess enthalpy values, H^E, at 298.15 K of *N*,*N*-dialkylmethylamine (1) + cyclohexane (2) mixtures versus x_1, the mole fraction of amine: full lines, predicted values; points, experimental H^E results; ●, dimethylethylamine; ▲, dimethylpropylamine; ■, diemethylbutylamine.

Much stronger steric effects are present in the symmetrical trialkylamines, for which eqn. (1) cannot be used to predict the excess enthalpies.

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