

EXCESS GIBBS FREE ENERGIES OF MIXTURES OF SUBSTANCES CONTAINING NITROGEN GROUPS

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ABSTRACT

Vapour–liquid equilibria for dimethylethylamine(1) + *n*-heptane or cyclohexane(2) and for *N,N,N',N'*-tetramethylalkanediamine(1) of general formula $(\text{CH}_3)_2\text{N}-(\text{CH}_2)_u-\text{N}(\text{CH}_3)_2$, with $u = 1, 2, 3$, + *n*-heptane(2) were determined at 298.15 K by head-space gas-chromatographic analysis of the equilibrated vapour phase withdrawn directly from the equilibration apparatus. Measurements on the test mixture, ethanol + cyclohexane, were also made.

Excess molar Gibbs free energies G^E were obtained by a least-squares treatment of the equilibrium x, y results. The G^E values are positive for all the systems and increase with the ratio of nitrogen to carbon atoms in the amine or diamine molecule. They also depend on the distance between the two N atoms in the diamines.

The experimental G^E values are compared with the predictions of a group contribution model in the random-mixing approximation.

INTRODUCTION

As a complement to previous works [1–3] and to continue our study on the thermodynamic properties of liquid organic mixtures (the TOM-Project [4–6]), undertaken to develop accurate group contribution models for predicting thermodynamic excess functions, molar excess Gibbs energies G^E and molar excess enthalpies H^E , here we report molar excess Gibbs energies at 298.15 K of dimethylethylamine, (A_{112}), (1) + *n*-heptane or cyclohexane(2) and of tetramethylalkane-diamines of general formula $(\text{CH}_3)_2\text{N}-(\text{CH}_2)_u-\text{N}(\text{CH}_3)_2$, (D_u), with $u = 1, 2, 3$, (1) + *n*-heptane (2).

In parts I and II of this series [1,3] we investigated the excess enthalpies of liquid mixtures of *N,N*-dialkylmethylamines, $\text{CH}_3(\text{CH}_2)_{s-1}\text{N}(\text{CH}_3)-$

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$(\text{CH}_2)_{l-1}\text{CH}_3$, with *n*-alkanes or cyclohexane. We showed that the experimental data can be correlated satisfactorily in terms of the random-mixing quasi-lattice group surface contribution theory [7] and determined the interchange enthalpy coefficients $C_{sn,2}$ ($s = a, c$) for the pair of group surfaces (an, cn) where *a* represents the surface of the CH_3- or $-\text{CH}_2-$ groups in *n*-alkyl or alkanes, *n* the surface of the $-\text{N}\langle$ group and *c* the surface of cyclohexane.

These previous studies have shown that for tertiary amines, R_3N , the interchange-energy coefficients $C_{an,l}$ and $C_{cn,l}$ for the *an* and *cn* contacts, are affected by the chain length of the alkyl substituents. Indeed, the coefficients $C_{sn,l}$ can be represented by the relationship

$$C_{sn,l} = C_{sn,l}^0 (1 + n^e \sigma_{sn,l}^e + n^p \sigma_{sn,l}^p + \dots) \quad (1)$$

where $l = 1, 2$, $C_{sn,l}^0$ are the interchange coefficients for the base compound, trimethylamine ($s = t = 1$) and n^e, n^p, \dots represent the numbers of carbon atoms in the different "levels" around the functional group $-\text{N}(\text{CH}_3)-$: *e*, denoting ethyl, *p*, propyl and so on (see Fig. 1 and ref. 1). The so-called alkyl-group increments $\sigma_{sn,l}^R$ are relatively small negative numbers.

One of the basic assumptions of group contribution theories, independent of the particular method used, is that each group is situated in a well-defined intramolecular environment. The above-mentioned steric effect exerted by alkyl groups is one of the many intramolecular factors which alter the values of the interchange parameters.

In polyfunctional molecules the proximity of two identical or different groups usually has quite a strong influence on the interchange-energy coefficients. This has already been demonstrated for molecules containing the following pairs of groups $-\text{O}-\dots-\text{O}-$ [8,9], $-\text{S}-\dots-\text{S}-$ [10] and $\text{Cl}-\dots-\text{Cl}$ [5,11].

The interchange Gibbs-energy coefficients $C_{an,1}$ are certainly not exempt from group proximity effects; Fredenslung et al. [12] have pointed out that the VLE properties of mixtures containing glycols cannot be predicted using the parameters for alcohol OH groups. The purpose of the present work was to investigate this "proximity effect" in molecular containing $\text{>N}-\dots-\text{N}\langle$ groups.

No experimental G^E data were found in the literature for any compounds of this type. G^E values were determined from the composition of equilibrated vapour as measured by head-space gas chromatography (GC). The (*x, y*) results were processed by a mathematical method similar to that of Barker [13] for (*x, p*) data.

The GC technique, employed here to obtain isothermal vapour-liquid equilibria over the whole composition range, is simpler and faster than conventional static or dynamic methods of measurement. Moreover, in contrast to such techniques, purity of substances is not a critical factor and mixtures with unstable components can be investigated.

EXPERIMENTAL

The x, y data were obtained with a head-space gas-chromatographic technique in which an equilibration cell was combined with a gas chromatograph (Carlo Erba model HRGC 5300) for the analysis of the gas phase (air + vapour) at atmospheric pressure. The apparatus, assembled in our laboratory, and the procedure were described in detail in previous papers [14,15]. In most cases, the column was a 2 mm \times 2.5 m stainless steel tube packed with Porapak P. For the system N, N, N', N' -tetramethylmethane-diamine + n -heptane a Carbowax 20 M on Chromosorb WAW (4 mm \times 3 m) column was employed.

All chemicals were from Fluka and were the best grades available. They were used without further purification and their purities, as checked by gas-chromatographic analysis, were > 99 (mass)%.

It is noteworthy that the purity of substances is not a critical factor thanks to the GC technique employed in determining the vapour composition. All mixtures were prepared by weighing. The uncertainty in the liquid mole fraction x_i , after correction for buoyancy and evaporation, was estimated to be less than 0.05% of the lowest x_i .

The values of mole fraction y_1 in the vapour phase (the subscript 1 indicates tertiary amine or diamine) were obtained from

$$y_1 = \frac{1}{[1 + k(A_1/A_2)]} \quad (2)$$

where A_1/A_2 is the measured peak area ratio of the two components and k the response factor of the chromatograph for the mixtures under examination. The overall uncertainty in y_1 , resulting from the uncertainty in A_1/A_2 , was generally less than 1% of the lowest y_1 value.

The values of k for each mixture were determined by calibration analysis using the equation

$$k = \frac{(A_1/A_2)^0}{(n_1/n_2)} \quad (3)$$

where $(A_1/A_2)^0$ is the area ratio of the peaks obtained when a liquid or a vapour mixture of known composition (n_1/n_2 is the mole ratio) is injected into the chromatograph under the same condition as for the unknown samples.

We carried out a number of k determinations by injecting equal volumes of the two vapours equilibrated with the pure liquids at 298.15 K. Any dependence of k on composition or on the quantity injected, was less than the experimental uncertainty (1.5%).

The reliability of the apparatus and procedure were checked by carrying out measurements on the test mixture (ethanol + cyclohexane) over its entire composition range. Our results are compared in Fig. 1 with those of other

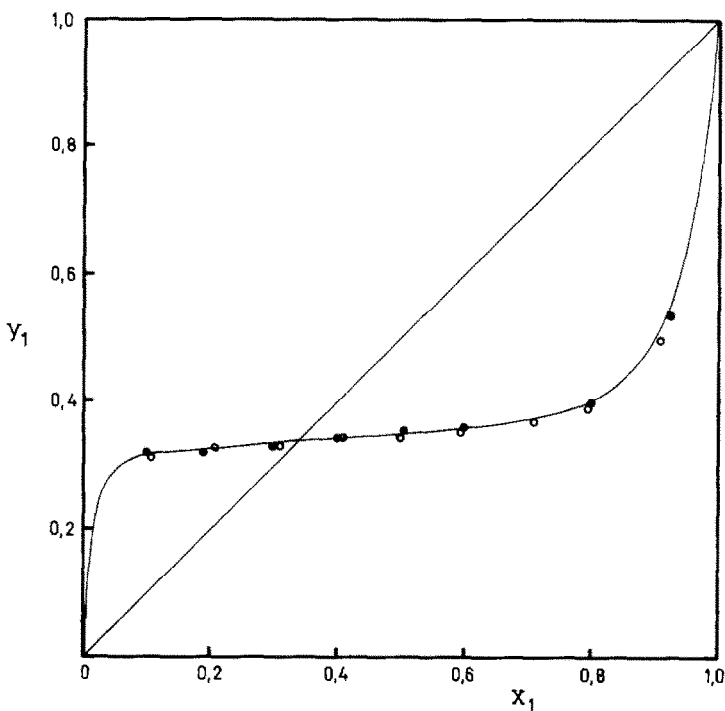


Fig. 1. Plot of y_1 against x_1 for ethanol+cyclohexane mixture at 298.15 K; experimental results, ●; present work; ○, ref. 17; full lines, calculated from eqn. (1).

authors [16,17] obtained using conventional techniques. The agreement is excellent.

DATA ANALYSIS

The experimental values of γ_1/γ_2 , the ratio of the activity coefficients of the constituents, were used in a non-linear least-squares procedure, similar to that described by Barker [13] for treatment of x -total pressure data. In our case, the sum S of the squares of residuals, extending over all n experimental points, to be minimized is

$$S = \sum_{k=1}^n (\ln(\gamma_1/\gamma_2)_{\text{exp}} - \ln(\gamma_1/\gamma_2)_{\text{calc}})^2 \quad (4)$$

The experimental γ_1/γ_2 ratio is given by

$$\left(\frac{\gamma_1}{\gamma_2}\right)_{\text{exp}} = \left(\frac{x_2}{x_1}\right) \left(\frac{A_1}{A_2}\right) \left(\frac{w_2}{w_1}\right) \left(\frac{p_2^*}{p_1^*}\right) \left(\frac{1}{k}\right) \quad (5)$$

TABLE 1

Vapour pressures, p^* , molar volumes, V^* , and second virial coefficients, B_{ii} , for pure compounds at 298.15 K, and cross virial coefficients B_{ij}

| Compound ^a | p^* (kPa) | V^* (cm ³ mol ⁻¹) | $-B_{ii}$ (cm ³ mol ⁻¹) | $-B_{ij}$ ^b (cm ³ mol ⁻¹) |
|-----------------------|--------------------|---|---|--|
| A ₁₁₂ | 140 ^c | 100.00 ^c | 1100 | 1400 ^d |
| D ₁ | 64 ^c | 72.90 ^c | 1000 | 2000 |
| D ₂ | 72 ^c | 150.34 ^c | 1200 ^e | 2100 |
| D ₃ | 80 ^c | 167.18 ^c | 1500 ^e | 2500 |
| Cyclohexane | 13.04 ^f | 108.74 ^g | 1700 ^h | — |
| Ethanol | 7.87 ^f | 58.68 ^g | 2400 ^h | 700 ^d |
| <i>n</i> -Heptane | 6.09 ^f | 147.70 ^g | 3020 ^h | — |
| Nitrogen | — | — | — | 100 ⁱ |

^a A₁₁₂ stands for dimethylethylamine, D₁ for tetramethylethylene diamine, D₂ for tetramethylethylenediamine, D₃ for tetramethylpropylenediamine.

^b Cross virial coefficients computed from ref. 21.

^c Unpublished values from our laboratory.

^d For mixtures with cyclohexane.

^e Estimated values.

^f Vapour pressures from ref. 22.

^g Molar volumes from ref. 23.

^h From ref. 24.

ⁱ From ref. 24; the same value applies for all mixtures including nitrogen.

The parameters of the function representing the activity coefficients in $(\gamma_1/\gamma_2)_{\text{calc}}$ are determined together with the product $(p_2^*/p_1^*)(1/k)$, treated as an adjustable parameter.

In eqn. (5), p_i^* is the vapour pressure of the i th pure component, and w_i a factor relevant to vapour phase non-ideality, which is calculated by taking into account the presence of air in the vapour phase.

In Table 1 are collected the values of the quantities V_i^* , p_i^* , B_{ii} and B_{ij} used in evaluating w_i , the expression for which is given elsewhere [14,15]. Although most virial coefficients, B_{ii} and B_{ij} , are estimated values and are subject to large uncertainties, the w_i terms differ from 1 by less than 2% and are partially compensating in the ratio w_2/w_1 (eqn. 5). The maximum deviations of y_1 , γ_1 and G^E from the values calculated with $w_1 = w_2 = 1$ (that is, neglecting vapour phase non-ideality) were 0.001, 2% and 5 J mol⁻¹, respectively.

RESULTS

The experimental x_1 and A_1/A_2 values, together with the calculated values of y_1 and G^E , are collected in Table 2, while Table 3 gives the a_i

TABLE 2

Experimental values of the liquid phase mole fraction, x_1 , and chromatographic peak area ratios of vapour (A_1/A_2) calculated values of vapour phase mole fraction y_1 and excess molar Gibbs energies G^E at 298.15 K

| x_1 | A_1/A_2 | y_1 | G^E (J mol ⁻¹) | x_1 | A_1/A_2 | y_1 | G^E (J mol ⁻¹) |
|---|-----------|--------|---------------------------------|--------|-----------|--------|---------------------------------|
| $(\text{CH}_3)_2\text{N}-\text{CH}_2-\text{CH}_3$ (A_{112}) + C_6H_{12} | | | | | | | |
| 0.0410 | 0.368 | 0.5017 | 11 | 0.4931 | 7.184 | 0.9517 | 42 |
| 0.0889 | 0.817 | 0.6919 | 21 | 0.6019 | 10.989 | 0.9678 | 37 |
| 0.2055 | 2.070 | 0.8499 | 38 | 0.6999 | 16.653 | 0.9786 | 31 |
| 0.3036 | 3.370 | 0.9022 | 44 | 0.7977 | 27.602 | 0.9870 | 24 |
| 0.3950 | 4.911 | 0.9310 | 44 | 0.8976 | 59.932 | 0.9939 | 14 |
| 0.9484 | 124.05 | 0.9971 | 7 | | | | |
| $(\text{CH}_3)_2\text{N}-\text{CH}_2-\text{CH}_3$ (A_{112}) + C_7H_{16} | | | | | | | |
| 0.0481 | 0.279 | 0.3718 | 19 | 0.5960 | 6.632 | 0.9336 | 100 |
| 0.1334 | 0.832 | 0.6384 | 49 | 0.6973 | 9.980 | 0.9549 | 86 |
| 0.2106 | 1.398 | 0.7479 | 72 | 0.8073 | 17.287 | 0.9735 | 63 |
| 0.3041 | 2.202 | 0.8237 | 91 | 0.9055 | 38.651 | 0.9880 | 34 |
| 0.4031 | 3.276 | 0.8742 | 103 | 0.9556 | 85.311 | 0.9945 | 17 |
| 0.4978 | 4.628 | 0.9076 | 106 | | | | |
| $(\text{CH}_3)_2\text{N}-\text{CH}_2-\text{N}(\text{CH}_3)_2$ (D_1) + C_7H_{16} | | | | | | | |
| 0.0997 | 0.468 | 0.5858 | 63 | 0.5965 | 4.582 | 0.9326 | 172 |
| 0.1998 | 0.994 | 0.7502 | 113 | 0.6865 | 6.381 | 0.9507 | 152 |
| 0.3003 | 1.609 | 0.8294 | 150 | 0.7854 | 9.998 | 0.9680 | 116 |
| 0.3980 | 2.329 | 0.8756 | 172 | 0.8664 | 17.002 | 0.9890 | 76 |
| 0.4950 | 3.241 | 0.9074 | 180 | | | | |
| $(\text{CH}_3)_2\text{N}-(\text{CH}_2)_2-\text{NCH}_3$ (D_2) + C_7H_{16} | | | | | | | |
| 0.1558 | 0.049 | 0.7146 | 93 | 0.6027 | 0.303 | 0.9393 | 160 |
| 0.1974 | 0.064 | 0.7658 | 111 | 0.7093 | 0.462 | 0.9594 | 132 |
| 0.2988 | 0.104 | 0.8416 | 145 | 0.8027 | 0.730 | 0.9739 | 94 |
| 0.4168 | 0.163 | 0.8928 | 167 | 0.9015 | 1.607 | 0.9880 | 47 |
| 0.5236 | 0.236 | 0.9234 | 170 | | | | |
| $(\text{CH}_3)_2\text{N}-(\text{CH}_2)_3-\text{N}(\text{CH}_3)_2$ (D_3) + C_7H_{16} | | | | | | | |
| 0.1051 | 0.0146 | 0.6405 | 59 | 0.6044 | 0.141 | 0.9451 | 136 |
| 0.1996 | 0.0294 | 0.7820 | 100 | 0.7034 | 0.210 | 0.9624 | 114 |
| 0.3024 | 0.0474 | 0.8526 | 130 | 0.8100 | 0.361 | 0.9778 | 80 |
| 0.4013 | 0.0694 | 0.8944 | 145 | 0.9007 | 0.743 | 0.9891 | 44 |
| 0.5020 | 0.0995 | 0.9239 | 147 | | | | |
| $\text{CH}_3-\text{CH}_2-\text{OH}$ + C_6H_{12} | | | | | | | |
| 0.1011 | 0.262 | 0.3201 | 648 | 0.5046 | 0.307 | 0.3555 | 1373 |
| 0.1851 | 0.263 | 0.3209 | 974 | 0.5985 | 0.309 | 0.3570 | 1304 |
| 0.2970 | 0.279 | 0.3339 | 1233 | 0.7984 | 0.369 | 0.3987 | 869 |
| 0.4024 | 0.290 | 0.3426 | 1354 | 0.9216 | 0.638 | 0.5341 | 396 |

TABLE 3

Parameters a_i of best fitting equation for (x, y) at 298.15 K, standard deviations S and chromatographic response factors k determined by the least-squares procedure

| Component i | Solvent | a_1 | a_2 | S | k^a |
|---------------|-------------|-------|--------|--------|---------------|
| Ethanol | C_6H_{12} | 2.218 | -0.196 | 0.013 | 0.56 (0.55) |
| A_{112} | C_6H_{12} | 0.171 | -0.013 | 0.001 | 0.47 (0.44) |
| A_{112} | C_7H_{16} | 0.067 | -0.030 | 0.002 | 0.36 (0.32) |
| D_1 | C_7H_{16} | 0.290 | -0.006 | -0.016 | 0.33 (0.31) |
| D_2 | C_7H_{16} | 0.275 | -0.016 | 0.009 | 0.019 (0.018) |
| D_3 | C_7H_{16} | 0.237 | -0.035 | 0.007 | 0.008 (0.007) |

^a Values in parentheses are the experimental k values (eqn. 2).

values of the Redlich-Kister equation ($i, j = 1, 2; i \neq j$) [18]

$$\ln \gamma_i = \left[a_0 - 3(-1)^j a_1 + 5a_2 \right] x_j^2 + 4(-1)^j \times \left[a_1 - 4(-1)^j a_2 \right] x_j^3 + 12a_2 x_j^4 \quad (6)$$

which was found convenient for representing the activity coefficients in eqn. (4).

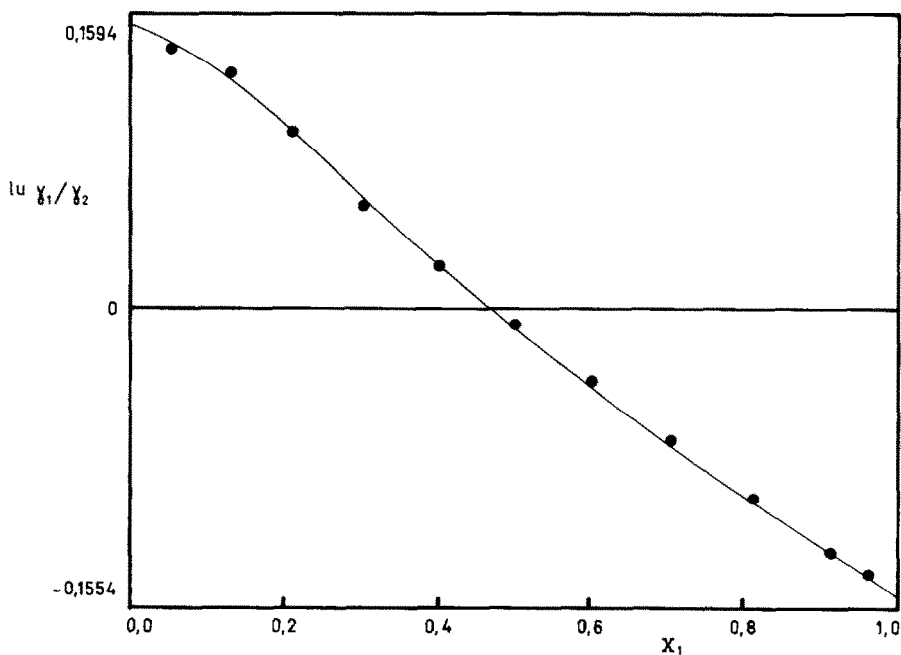


Fig. 2. Plot of $\ln(\gamma_1/\gamma_2)$ versus x_1 for dimethylethylamine, (A_{112})(1)+cyclohexane(2) mixtures at 298.15 K; points, experimental results; full lines, calculated from eqn. (6) with parameters from Table 3.

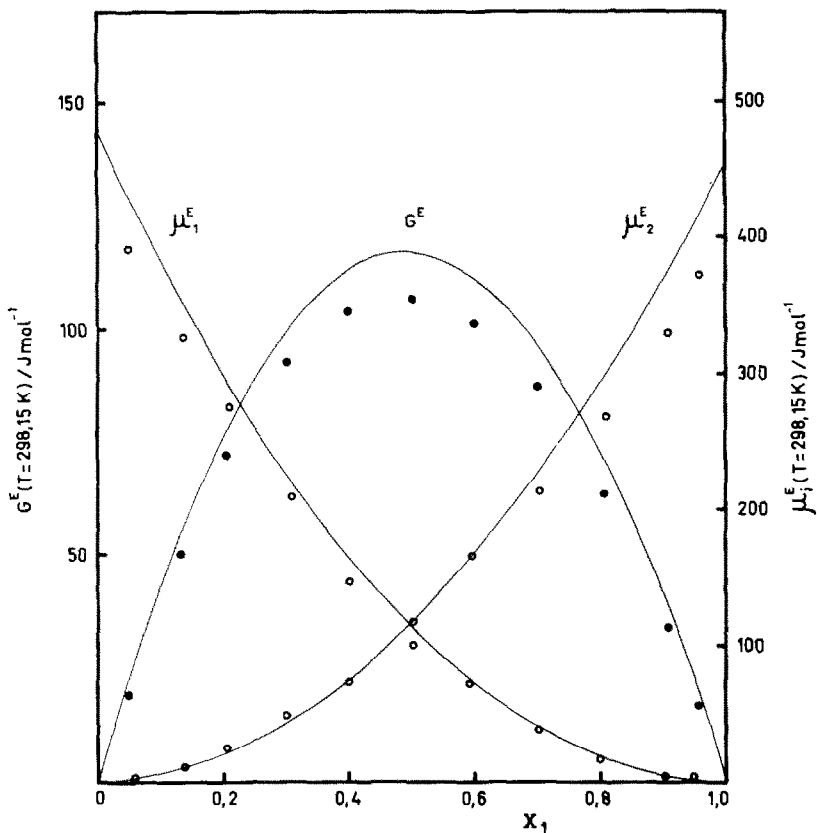


Fig. 3. Comparison of theory with experiment for molar Gibbs energy G^E and the partial molar excess Gibbs energies μ_i^E at 298.15 K, of dimethylethylamine(1)+cyclohexane(2) mixtures versus x_1 , the mole fraction of amine. Full lines, predicted values; points, smoothed values obtained by reduction of direct experimental $x-y$ values.

This table also lists the values of k obtained from the fitting as well as the standard deviation for the representation of $\ln(\gamma_1/\gamma_2)$.

In Fig. 2 the plot of y_1 and $\ln(\gamma_1/\gamma_2)$ is shown for the system dimethylethylamine + cyclohexane.

In Figs. 3 and 4 the behaviour of the excess molar Gibbs energy G^E for all the systems investigated is illustrated. The G^E curves were computed from the coefficients a_i in eqn. (6) through the equation

$$\frac{G^E}{RT} = x_1 x_2 \sum_{i=0}^{i=N} a_i (x_2 - x_1)^i \quad (7)$$

All mixtures exhibit positive deviations and the G^E curves are slightly asymmetric.

In Table 4 the values of the activity coefficients at infinite dilution γ_i^∞ , obtained from the parameters of the fitting to eqn. (6), are reported

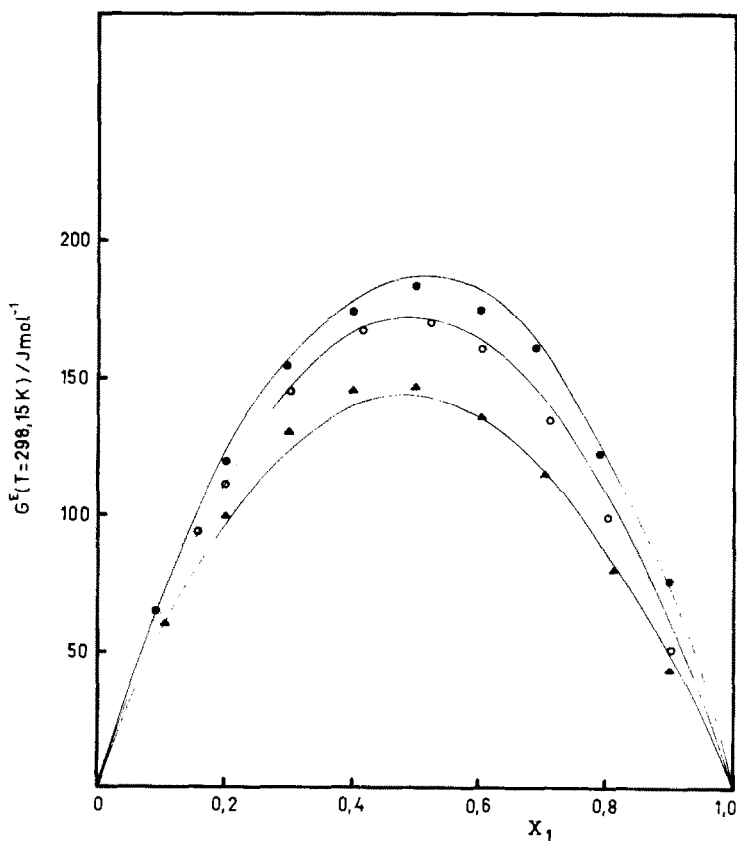


Fig. 4. Comparison of theory with experiment for molar Gibbs energy G^E (at 298.15 K) of tetramethylalkane-diamine (D_u)(1) + n -heptane(2) mixtures versus x_1 , the mole fraction of diamine. Full lines, predicted values; points, smoothed values obtained by reduction of direct experimental x - y values: ●, tetramethylmethane-diamine; ○, tetramethyl-1,2-ethanediamine; ▲, tetramethyl-1,3-propanediamine.

TABLE 4

Activity coefficients at infinite dilution γ_i^∞ evaluated from eqn. (5) with parameters from Table 3. Comparison with values calculated using the coefficients $C_{un,1}$ from Table 7

| System | $\ln \gamma_1^\infty$ | | $\ln \gamma_2^\infty$ | |
|-----------------------|-----------------------|-------|-----------------------|-------|
| | Exp. | Calc. | Exp. | Calc. |
| $A_{112} + C_6H_{12}$ | 1.2 | 1.2 | 1.2 | 1.2 |
| $A_{112} + C_7H_{16}$ | 1.1 | 1.1 | 1.1 | 1.1 |
| $D_1 + C_7H_{16}$ | 1.3 | 1.4 | 1.3 | 1.4 |
| $D_2 + C_7H_{16}$ | 1.4 | 1.3 | 1.2 | 1.3 |
| $D_3 + C_7H_{16}$ | 1.3 | 1.3 | 1.2 | 1.2 |

compared with the values calculated from theory using the parameters of Table 7.

DISCUSSION

Correlation of excess properties with molecular structure

Molar excess enthalpies H^E have been determined previously [1–3] as a function of concentration at atmospheric pressure and 298.15 K for all binary mixtures studied in the present work. From the smoothed calorimetric H^E values which are all positive, and from the G^E values given by eqn. (7), molar excess entropies S^E were calculated and found to be systematically positive. The positive values of G^E , H^E and S^E suggest that the unfavourable mixing of tertiary amines and diamines with heptane or cyclohexane is to be attributed exclusively to enthalpic effects, which exceed the favourable entropic effect. A sort of correlation between the structure and thermodynamic excess properties of alkylamine or diamine systems is shown in Fig. 5 where H^E , G^E and $-TS^E$ for equimolar mixtures are

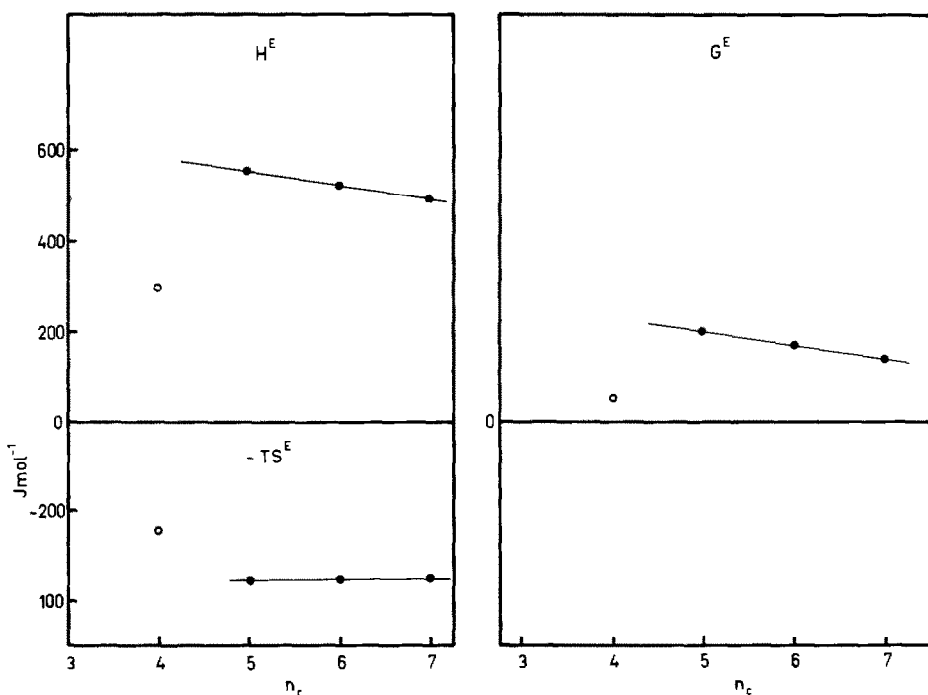


Fig. 5. Plots of H^E , $-TS^E$ and G^E against the number n_c of carbon atoms in the amine (A_{112}) or diamine (D_u)(1) + n -heptane(2); equimolar mixtures at 298.15 K: \circ , amine; \bullet , diamine.

plotted against the number of carbon atoms n_c . It is seen that both G^E and H^E decrease with n_c and increase with the number of nitrogen atoms. The opposite happens for $-TS^E$, the entropic contribution to free energy. The dependence of G^E on the molecular structure of amines and diamines is dominated by the enthalpic factor.

Analysis in terms of a pseudo-lattice group contribution model

The substitution of a CH_2 group in an n -alkane with a >N- atom influences the intermolecular forces as a result of two oppositely-acting effects, one weakening, due to smaller forces exerted by the N atoms compared with the CH_2 groups, and the other strengthening, due to the electrostatic interactions between the C–N bond dipoles. The latter being relatively weak, the amount of order in the liquid phase is rather small. Thus, tertiary amines or diamine + n -heptane or cyclohexane mixtures could be described fairly well by a pseudo-lattice group contribution model in the zero (random-mixing) approximation [7].

Three kinds of contact surface were distinguished on the molecules investigated in this work: a , aliphatic (CH_3 and CH_2); c , cyclohexane (C_6H_{12}); and n , nitrogen (N). The total relative contact surface, q_i , the total relative molecular volume r_i , and the surface fractions, α_{ia} , α_{ic} and α_{in} of a , c or n surfaces on a molecule of type i of all the molecular species were calculated additively from the increments given by Bondi [19], methane being taken as the standard segment [7], see Table 5. Table 6 lists these parameters for all the compounds referred to in this paper. In the random-mixing approximation, the molar excess Gibbs energy G^E is given by

$$\frac{G^E}{RT} = x_1 \ln \left(\frac{\phi_1}{x_1} \right) + x_2 \ln \left(\frac{\phi_2}{x_2} \right) + (q_1 x_1 + q_2 x_2) \xi_1 \xi_2 g_{12} \quad (8)$$

where

$$\phi_i = \frac{r_i x_i}{r_1 x_1 + r_2 x_2}$$

TABLE 5

Relative group increments for molecular volumes, $r_G = V_G/V_{\text{CH}_4}$, and areas, $q_G = A_G/A_{\text{CH}_4}$, calculated by Bondi's method [19] ($V_{\text{CH}_4} = 17.12 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ and $A_{\text{CH}_4} = 2.90 \times 10^5 \text{ m}^2 \text{ mol}^{-1}$)

| Group | r_G | q_G |
|--------------------|---------|---------|
| – CH_3 | 0.79848 | 0.73103 |
| – CH_2 – | 0.59755 | 0.46552 |
| c– CH_2 – | 0.58645 | 0.43277 |
| >N- | 0.25290 | 0.07932 |

TABLE 6

Volumes r_i , total surfaces q_i and molecular fractions α_{si} ($s = a, c, n$) of tertiary amines, diamines and solvents calculated from the group increments r_G and q_G given in Table 5

| Compound | r_i | q_i | α_{ai} | α_{ci} | α_{ni} |
|-------------------|--------|--------|---------------|---------------|---------------|
| A ₁₁₂ | 3.2459 | 2.7379 | 0.9710 | 0.0000 | 0.0290 |
| D ₁ | 4.2973 | 3.5482 | 0.9553 | 0.0000 | 0.0447 |
| D ₂ | 4.8948 | 4.0138 | 0.9605 | 0.0000 | 0.0395 |
| D ₃ | 5.4924 | 4.4793 | 0.9646 | 0.0000 | 0.0354 |
| <i>n</i> -Heptane | 4.5847 | 3.7897 | 1.0000 | 0.0000 | 0.0000 |
| Cyclohexane | 3.5187 | 2.5966 | 0.0000 | 1.0000 | 0.0000 |

and

$$\xi_i = \frac{q_i x_i}{q_1 x_1 + q_2 x_2}$$

are respectively the volume fraction and surface fraction of component i ; g_{12} is the molecular interchange Gibbs energy parameter, which depends on the molecular structure of components but not on the composition. For tertiary amines or diamine(1) + *n*-heptane(2) mixture, g_{12} is related to the group interchange parameter $C_{an,1}$ (the suffix 1 refers to the Gibbs energy property) as

$$g_{12} = \alpha_{n1}^2 \times C_{an,1} \quad (9)$$

For tertiary amines(1) + cyclohexane(2) mixtures, g_{12} is related to the group interchange parameters, $C_{an,1}$, $C_{cn,1}$, and $C_{ac,1}$, by

$$g_{12} = \alpha_{n1} C_{an,1} - \alpha_{n1} (C_{ac,1} + C_{an,1} - C_{cn,1}) + C_{ac,1} \quad (10)$$

TABLE 7

Interchange-Gibbs energy coefficients $C_{an,1}$ and $C_{cn,1}$ for diamine + *n*-heptane mixtures calculated from eqns. (7-9), using the smoothed experimental equimolar G^E data at 298.15 K^a

| u | $C_{an,1}$ | n^e | n^p | $C_{an,1}^0$ |
|----------|-----------------|-------|-------|-----------------|
| 0 | 36 | 2 | 0 | 38 |
| 1 | 42 | 1 | 2 | 43 |
| 2 | 46 | 1 | 1 | 47 |
| 3 | 48 | 1 | 1 | 49 |
| 4 | 50 | 1 | 1 | 51 |
| ∞ | 51 ^b | 1 | 1 | 52 ^c |

^a $C_{an,1}^0$ is the interchange-Gibbs energy coefficient corrected for steric effects by eqn. (13), using the specific values of n^c (see text).

^b Value calculated from eqn. (13) with $C_{an,1}^0 = 52$.

^c Value determined for trimethylamine + *n*-alkane mixtures [1].

TABLE 8

Molar excess Gibbs energies G^E (T ; $x_1 = 0.5$) of dimethylethylamine (A_{112}) or diamine (D_n)(1) + *n*-heptane or cyclohexane(2) mixtures. Comparison of direct experimental results (exp.) with values calculated (calc.) using the coefficient $C_{an,1}$ from Table 7

| Component 1 | Component 2 | G^E (T ; $x_1 = 0.5$) ^a (J mol ⁻¹) | |
|----------------|----------------|--|------|
| | | Calc. | Exp. |
| A_{112} | C_6H_{12} | 117 | 106 |
| | C_7H_{16} | 48 | 42 |
| D_1 | C_7H_{16} | 189 | 180 |
| D_2 | C_7H_{16} | 172 | 170 |
| D_3 | C_7H_{16} | 143 | 147 |

^a $T = 298.15$ K.

Over a limited temperature range, in which H^E may be regarded as independent of T , the interchange parameters g_{st} and h_{st} ($s, t = a, c, n$) are related by

$$g_{st} = C_{st,1} + C_{st,2} \left[\left(\frac{T_0}{T} \right) - 1 \right] \quad (11)$$

and

$$h_{st} = c_{st,2} \left(\frac{T_0}{T} \right) \quad (12)$$

where $C_{st,1}$ and $C_{st,2}$ are, respectively, the interchange Gibbs energy and the interchange enthalpy coefficients and $T_0 = 298.15$ K. By means of eqns. (8–10) we calculated G^E values over the whole composition range for all the investigated mixtures (Table 8).

Tertiary amines + alkane or cyclohexane

The interchange Gibbs energy coefficients $C_{an,1}$ and $C_{cn,1}$ calculated from the equimolar value of G^E using eqns. (8–10) are $C_{an,1} = 51$ and $C_{cn,1} = 52$. The shapes of the experimental G^E curves are well reproduced by the model (see Fig. 3). It appears that for 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. $C_{ac,1} = 0$.

The agreement for the G^E of dimethylethylamine + cyclohexane is quite satisfactory and shows that the G^E values of amine + cyclohexane systems can be calculated using the same alkyl group increments, $\sigma_{an,1}^R$, of alkanes systems, i.e. $\sigma_{an,1}^R = \sigma_{cn,1}^R$, by slightly increasing the coefficient of the base compound, $C_{cn,1}^0 = 53$.

Diamines + *n*-heptane

The behaviour of a given diamine with *n*-heptane resembles in every respect that of a monoamine [1] with the same solvent. The random-mixing approximation describes very well the shape of the G^E versus x_1 curves, indicating the weakness of orientational forces (Fig. 4).

To evaluate the N–N proximity effect we corrected the $C_{an,1}$ values, as determined for mixtures of diamines + *n*-alkanes free of Patterson effect contributions [20], using the alkyl-group increments $\sigma_{an,1}^R$ for monoamines [1]. Substitution of the numerical values of $\sigma_{an,1}^R$ into eqn. (1) yields

$$C_{an,1} = C_{an,1}^0 (1 - 0.024 n^e) \quad (13)$$

The values of n^e and n^p adopted for the diamines and the corrected coefficients $C_{an,1}^0$ are listed in Table 7.

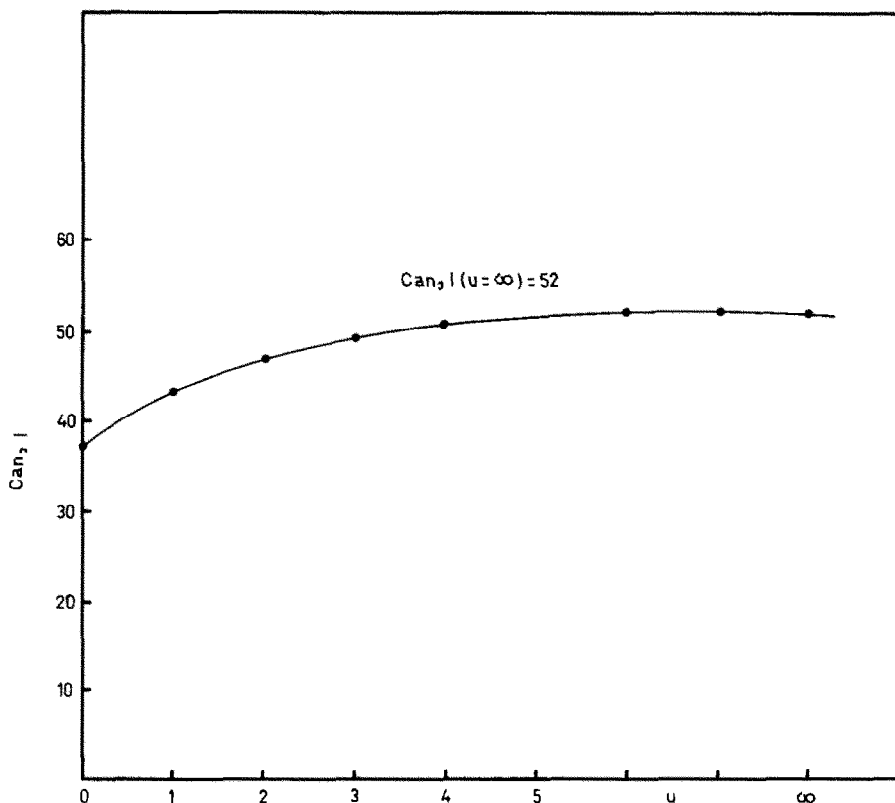


Fig. 6. Interchange Gibbs energy coefficient $C_{an,1}^0$ for contact an (a , aliphatic hydrocarbon surface; n , nitrogen surface) for tetramethylalkanediamine + alkane mixtures, $(\text{CH}_3)_2\text{N}-(\text{CH}_2)_u-\text{N}(\text{CH}_3)_2$, versus u , the number of CH_2 groups between the two nitrogen atoms: $C_{an,1}^0 (u = \infty)$ is the value of $C_{an,1}^0$ for trimethylamine + *n*-alkane mixtures [1].

Figure 6 represents the variation of $C_{an,1}^0$ as a function of u . As expected, $C_{an,1}^0$ increases with u and attains almost the limiting value $C_{an,1}^0 = 52$ for monoamines when $u = 4$. The N-N proximity effect is negative, i.e. the interchange coefficient decreases with decreasing N...N distance.

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LIST OF SYMBOLS

| | |
|------------|---|
| A | chromatographic peak area of vapour |
| B | second virial coefficient |
| C | interchange coefficient |
| C^0 | interchange coefficient of base compound |
| g | interchange Gibbs energy parameter |
| G | molar Gibbs energy |
| h | interchange enthalpy parameter |
| H | molar enthalpy |
| k | chromatographic response factor |
| n^R | number of C atoms in level R (e, ethyl; p, propyl; etc.) around $-N(CH_3)-$ group |
| P | vapour pressure |
| q | relative molecular area |
| r | relative molecular volume |
| R | gas constant ($8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$) |
| S | molar entropy |
| T | temperature (K) |
| T^0 | scaling temperature (298.15 K) |
| u | number of methylene groups, $-CH_2-$, between the two N atoms of a diamine |
| V | molar volume |
| x | molar fraction in liquid phase |
| y | molar fraction in vapour phase |
| α | molecular surface ratio |
| γ | activity coefficient |
| ξ | surface fraction |
| ϕ | volume fraction |
| σ^R | alkyl-group increment for level R (see n^R) |

Superscripts

| | |
|----------|---|
| E | excess properties |
| * | property of pure component |
| ∞ | property at infinite dilution ($x_i = 0$) |

Subscripts

| | |
|-----------|---|
| a, n, c | type of surface: a , aliphatic (CH_3, CH_2); c , cyclohexane (C_6H_{12}); n , nitrogen (N) |
| i | type of molecule (component) |
| l | order of interchange coefficient ($l = 1, 2$) |
| s | contact surface |

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