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EXCESS PROPERTIES OF BINARY MIXTURES. SECONDARY AMINE + *n*-ALKANE SYSTEMS

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ABSTRACT

Excess enthalpies have been measured for secondary amine + *n*-alkane binary systems at 298.15 K. Two microcalorimetric techniques were used, one based on the measurement of integral enthalpies using a Calvet microcalorimeter, the other on the determination of partial excess enthalpies by continuous-flow conduction microcalorimetry with deconvolution of the calorimetric response. The results have been used to compare the application of two theories of functional group interactions, those of Kehiaian and Chao, to these systems.

INTRODUCTION

Microcalorimetry constitutes one of the most accurate methods known for the determination of the excess enthalpies of mixtures, which provide very precise information concerning the kinds of intermolecular interaction that occur in condensed phases. The present study investigates systems of the type di-*n*-propylamine + *n*-alkane (hexane, heptane, octane, nonane and decane). The excess molar enthalpy of the di-*n*-propylamine + *n*-octane system was found using a continuous-flow conduction microcalorimeter whose intrinsic response was deconvoluted from the output data. A classical Calvet microcalorimeter was used for the other systems.

The experimental results obtained have been interpreted in terms of molecular interactions within the systems and then used to compare two theoretical models on the basis of their predictions for these systems. Both models aim at cheap prediction of the properties of mixtures by using the concept of functional groups to which geometrical and energy interaction parameters are assigned. The models used were those of Kehiaian [1], which is a lattice theory, and a cell theory due to Chao [2].

EXPERIMENTAL METHODS

The Calvet microcalorimeter [3] used for most of the systems studied was calibrated electrically by the Joule effect. The accuracy of the calibration was tested by determining the excess enthalpies of the standard binary system, hexane + cyclohexane. The results differ by less than 1% from those of Marsh and Stokes [4]. The temperature of the microcalorimeter was kept constant to within ± 0.005 K and a mixing device [5] was used which permitted the work to be carried out at constant pressure.

The second technique used a continuous-flow conduction microcalorimeter with deconvolution of the instrument response [6]. The calibration, which was effected by using the excess enthalpy of the standard binary system, cyclohexane + benzene, was tested by studying the hexane–cyclohexane system. The results differed by less than 0.1% from those of Stokes and Marsh [7].

For the experimental determination of excess enthalpies, products supplied by Fluka (Buchs, Switzerland) were distilled to a purity of the order of 99.95% per mole as checked by comparing the results from measurements of refractive index, density and boiling point with published values [8]. All the molar quantities used were taken from the IUPAC tables of relative atomic weights [9].

All the experimental results obtained were fitted by a Redlich–Kister-type empirical equation [10], i.e.

$$H^{\mathrm{E}}_{\mathrm{exp}} = x(1-x) \sum_{i=0}^{n-1} A_i (2x-1)^i \qquad (1)$$

A statistical consistency test was used to determine the number of parameters A_i. Values of A_i are shown in Table 1 for each system studied.

TABLE 1

Values of the parameters occurring in the empirical curves fitted to the excess molar enthalpies

System		A_0	A_1	A_2	A_3	A_4
Component 1	Component 2	(J mole^{-1})	(J mole^{-1})	(J mole^{-1})	(J mole^{-1})	(J mole^{-1})
Di-*n*-propylamine +	*n*-hexane	1716	−110	−192	−299	528
Di-*n*-propylamine +	*n*-heptane	1824	−91	−41	−271	372
Di-*n*-propylamine +	*n*-octane	1890	−172	293	−186	
Di-*n*-propylamine +	*n*-nonane	1969	27	15	−157	374
Di-*n*-propylamine +	*n*-decane	2096	79	174	−52	

THEORETICAL MODELS

Kehiaian's theory considers di-*n*-propylamine + *n*-alkane systems to be composed of two kinds of surface, type a ($-CH_3$ or $-CH_2-$ groups) and type n ($-NH-$ groups). The relative group increments for molecular volumes, r_G, and areas, q_G, are calculated by Bondi's method [11]. The molecular surface fractions, α_{ai} and α_{ni} are defined by

$$\alpha_{ai} = \frac{q_{ai}}{q_i} \quad \text{and} \quad \alpha_{ni} = \frac{q_{ni}}{q_i} \tag{2}$$

where q_{ai} and q_{ni} are the relative molecular areas of types a and n, and q_i is the total relative molecular area calculated additively from the relative group increments (Table 2). The surface fractions, α_a and α_n, of surfaces of types a and n in the mixture are given by

$$\alpha_a = \alpha_{a1}\xi_1 + \alpha_{a2}\xi_2 \quad \text{and} \quad \alpha_n = \alpha_{n1}\xi_1 + \alpha_{n2}\xi_2 \tag{3}$$

where

$$\xi_1 = \frac{q_1 x_1}{q_1 x_1 + q_2 x_2} \quad \text{and} \quad \xi_2 = \frac{q_2 x_2}{q_1 x_1 + q_2 x_2} \tag{4}$$

ξ_1 and ξ_2 represent the surface fractions of components 1 and 2 (x_1 and x_2 being the corresponding molar fractions).

The thermodynamical properties for a given temperature T are calculated from the exchange Gibbs energy, $g_{an}(T)$, and the coordination number, Z_{an}. The basic system of equations is

$$\begin{aligned} X_a(X_a + X_n\eta_{an}) &= \alpha_a \\ X_n(X_n + X_a\eta_{an}) &= \alpha_n \end{aligned} \tag{5}$$

where

$$\eta_{an} = \exp\left(\frac{-g_{an}}{Z_{an}RT}\right) \tag{6}$$

TABLE 2

Relative volumes, r_i, total surface areas, q_i, and molecular surface fractions, α_{ai} and α_{ni}, calculated from the relative group increments

	r_i	q_i	α_{ai}	α_{ni}
$CH_3-(CH_2)_4-CH_3$	3.9871	3.3241	1.0000	0.0000
$CH_3-(CH_2)_5-CH_3$	4.5847	3.7897	1.0000	0.0000
$CH_3-(CH_2)_6-CH_3$	5.18226	4.25518	1.0000	0.0000
$CH_3-(CH_2)_7-CH_3$	5.77981	4.72070	1.0000	0.0000
$CH_3-(CH_2)_8-CH_3$	6.37736	5.18622	1.0000	0.0000
$(CH_3-CH_2-CH_2)_2-NH$	4.45912	3.66552	0.90687	0.0000

The excess molar Gibbs energy, g^{E}, is given by

$$g^{\mathrm{E}} = RT\sum_{i} x_i \left[\ln\frac{\psi_i}{x_i} + Z_{\mathrm{an}} q_i \left(\alpha_{\mathrm{a}i} \ln\frac{X_{\mathrm{a}}\alpha_{\mathrm{a}i}}{X_{\mathrm{a}i}\alpha_{\mathrm{a}}} + \alpha_{\mathrm{n}i} \ln\frac{X_{\mathrm{n}}\alpha_{\mathrm{n}i}}{X_{\mathrm{n}i}\alpha_{\mathrm{n}}}.\right)\right] \tag{7}$$

where $X_{\mathrm{a}i}$ and $X_{\mathrm{n}i}$ are the solutions of eqn. (5) for $x_i = 1$.

The dependence of $g_{\mathrm{an}}(T)$ on the temperature is expressed by an equation with three constants, i.e.

$$\frac{g_{\mathrm{an}}(T)}{RT} = C_{1,\mathrm{an}} + C_{2,\mathrm{an}}\left(\frac{T_0}{T} - 1\right) + C_{3,\mathrm{an}}\left(\ln\frac{T_0}{T} - \frac{T_0}{T} + 1\right) \tag{8}$$

where $T_0 = 298.15$ K is the reference temperature. The exchange enthalpy, $h_{\mathrm{an}} = \mathrm{d}(g_{\mathrm{an}}/T)/\mathrm{d}(1/T)$, and the exchange heat capacity, $C_{p,\mathrm{an}} = \mathrm{d}h_{\mathrm{an}}/\mathrm{d}T$, are given by

$$\frac{h_{\mathrm{an}}(T)}{RT} = C_{2,\mathrm{an}}\left(\frac{T_0}{T}\right) - C_{3,\mathrm{an}}\left(\frac{T_0}{T} - 1\right) \tag{9}$$

and

$$\frac{C_{p,\mathrm{an}}}{R} = C_{3,\mathrm{an}} \tag{10}$$

The excess molar enthalpy, $H_{\mathrm{m}}^{\mathrm{E}}$, is given by

$$H_{\mathrm{m}}^{\mathrm{E}} = (q_1 x_1 + q_2 x_2)\{[X_{\mathrm{a}} X_{\mathrm{n}} - (\xi_1 X_{\mathrm{a}1} X_{\mathrm{n}1} + \xi_2 X_{\mathrm{a}2} X_{\mathrm{n}2})]\eta_{\mathrm{an}} h_{\mathrm{an}}\} \tag{11}$$

The values of the coefficients $C_{1,\mathrm{an}}$, $C_{2,\mathrm{an}}$ and $C_{3,\mathrm{an}}$ calculated from experimental data for excess Gibbs energies and excess enthalpies are shown in Table 3.

Chao's method considers the same kinds of surface as Kehiaian's. The number of contacts made by a group is given by

$$Q_i = \frac{ZA_i}{A_{\mathrm{s}}} \tag{12}$$

where $Z = 10$, A_i is the surface area of the group as calculated by Bondi's method [11] and A_{s} is the surface area of a standard group. The excess enthalpy of liquids at low pressure is given by

$$H^{\mathrm{E}} = U_{\mathrm{conf}} - \Sigma_A x_A U_{A_0\mathrm{conf}} \tag{13}$$

TABLE 3

Exchange energy coefficients for amine–alkane surfaces

$C_{1,\mathrm{an}} = g_{\mathrm{an}}^{\circ}/RT_0$; $C_{2,\mathrm{an}} = h_{\mathrm{an}}^{\circ}/RT_0$; $C_{3,\mathrm{an}} = C_{p,\mathrm{an}}/R$; $T_0 = 298.15$ K; coordination number, $Z = 8$.

Interaction	$C_{1,\mathrm{an}}$	$C_{2,\mathrm{an}}$	$C_{3,\mathrm{an}}$
(an)$^{\mathrm{q\,c}}$	5414	10397	

where the subscript A_0 indicates that the quantity refers to the pure liquid, and $U_{\text{conf.}}$ is the configurational energy, which for liquids at low pressure is given by

$$\frac{U_{\text{conf.}}}{NKT} = -\sum_{i \geqslant j}\sum \frac{N_{ij}}{NKT}\left\{\frac{\epsilon_{ij}}{\tilde{v}} \exp\left(\frac{\kappa}{\tilde{v}}\right) + \sigma'_{ij}\right\} \tag{14}$$

where ϵ_{ij} is the pairwise interaction energy; $\tilde{v} = V/V^*$ is the reduced volume (V being the volume of the liquid and V^* that of the hard core); κ is a constant equal to 0.7; and N_{ij} is the number of pairs in the mixture in question. This number is given by the equations

$$\frac{N_{ij}^2}{N_{ii}N_{jj}} = 4 \exp\left(-\frac{2\omega_{ij}}{KT}\right) \tag{15}$$

and

$$2N_{ii} + \sum_{j(\neq 1)} N_{ij} = Q_i n_i N \tag{16}$$

where the exchange energy $\omega_{ij} = \phi_{ij} - (\phi_{ii} + \phi_{jj})/2$. The chemical association energy varies with temperature according to the equation

$$\frac{\sigma}{T} = \frac{\sigma_0}{T_0} + \sigma'\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{17}$$

TABLE 4

Properties of methyl, methylene and amine groups according to Chao's functional group method [2]

a_i expresses the dependence of V^* on T.

Group	V^* (cm^3 mole^{-1})	a_i (K)	c_i	ϵ_{ii} (J mole^{-1})	Q_i
CH_2–	13.46	23.7	0.338	2515	6.71
–CH_2–	10.25	23.7	0.93	2515	4.27
–NH–	8.08	25	0.344	6607	3.132

Group	$\Delta\epsilon = \epsilon_{ij} + \frac{\epsilon_{ii} + \epsilon_{jj}}{2}$ (J mole^{-1})
CH_3–	678
–CH_2–	678
–NH–	0

Group	σ_0 (J mole^{-1})	σ_0' (J mole^{-1})
–NH–	4774	2380

where T_0 is the reference temperature, 298.15 K. Table 4 shows the characteristic parameters for each functional group as calculated from experimental data for molar volumes, energies of vaporization and excess enthalpies at different temperatures.

RESULTS

Figures 1–6 show the experimental results together with the curves fitted. All the processes investigated may be seen to be endothermic, which means that the rupture of hydrogen bonds formed by the amine group predominates over the formation of other interactions in the mixture. The excess enthalpies increase with the length of the alkane chain, which can be interpreted as reflecting the increasing cost of breaking alkane–alkane interactions, whose energy rises linearly with the size of the molecule. The maxima of the curves lie somewhat towards the lower concentrations of amine, which can be explained by supposing that the addition of a small quantity of di-*n*-propylamine to an "inert" liquid breaks all hydrogen bonds, whereas unbroken bonds probably remain in mixtures rich in alcohol.

The predictions of Kehiaian's theoretical model are in excellent agreement with the experimental results, the largest discrepancy being no more than 3%. This shows the reliability for the parameters calculated and the coordi-

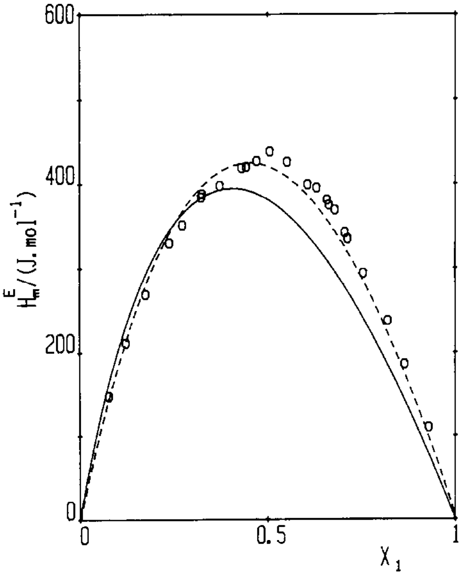


Fig. 1. Excess molar enthalpy, H_m^E, at 298.15 K for the system di-*n*-propylamine(1)+ *n*-hexane (2). 0, Experimental values, - - - - - -, theoretical curve as predicted by Kehiaian's model; ————, theoretical curve as predicted by Chao's model.

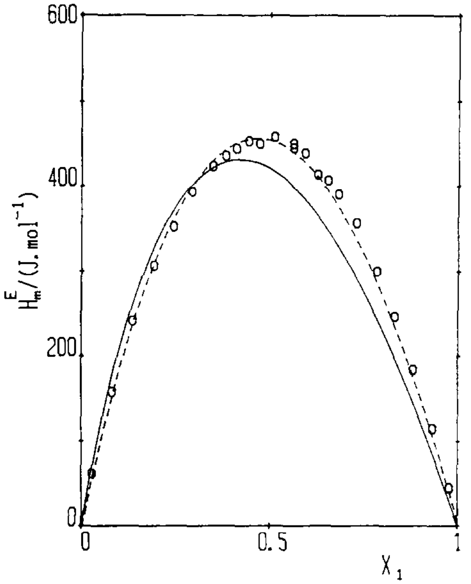


Fig. 2. Excess molar enthalpy, H_m^E, at 298.15 K for the system di-*n*-propylamine (1)+ *n*-heptane (2). 0, Experimental values; ------, theoretical curve as predicted by Kehiaian's model; ————, theoretical curve as predicted by Chao's model.

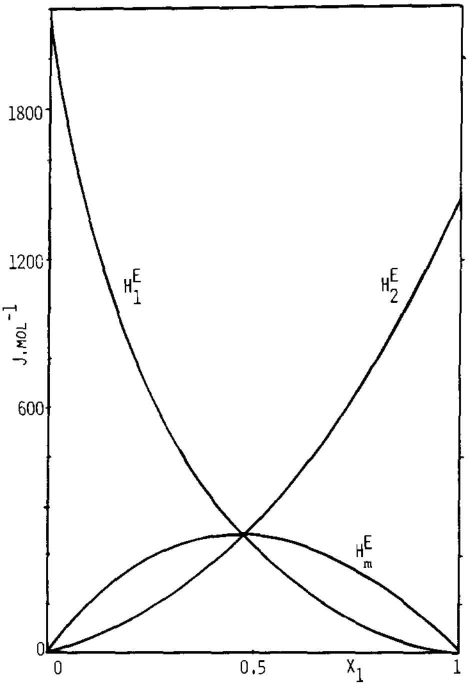
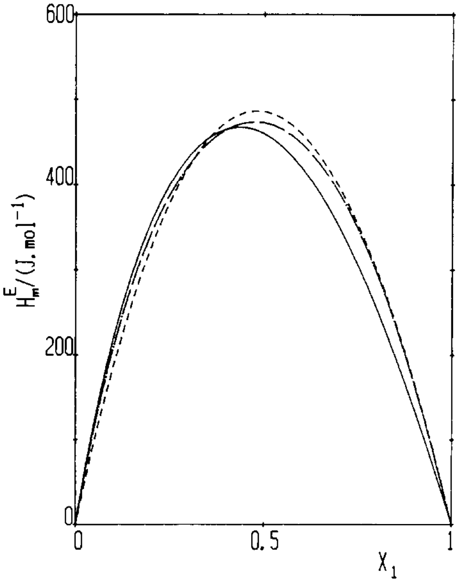


Fig. 3. Excess molar enthalpy, H_m^E, and partial molar heats of mixing, H_1^E and H_2^E, at 298.15 K for the system di-*n*-propylamine (1)+ *n*-octane (2).



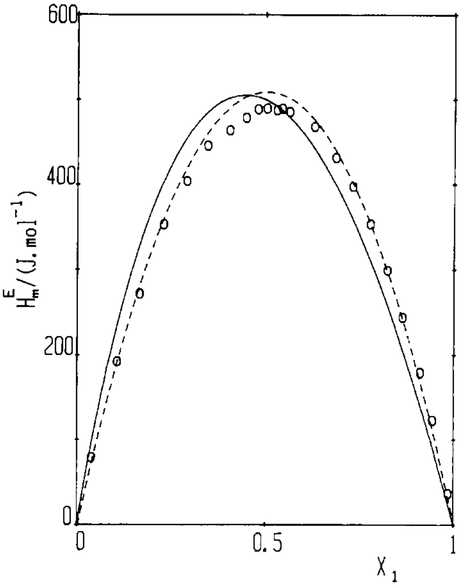


Fig. 4. Excess molar enthalpy, H^E_m, at 298.15 K for the system di-*n*-propylamine (1)+ *n*-octane (2). ·—·—·, Experimental curve; ------, theoretical curve as predicted by Kehiaian's model; ————, theoretical curve as predicted by Chao's model.

Fig. 5. Excess molar enthalpy, H^E_m, at 298.15 K for the system di-*n*-propylamine (1)+ *n*-nonane (2). 0, Experimental values; ------, theoretical curve as predicted by Kehiaian's model; ————, theoretical curve as predicted by Chao's model.

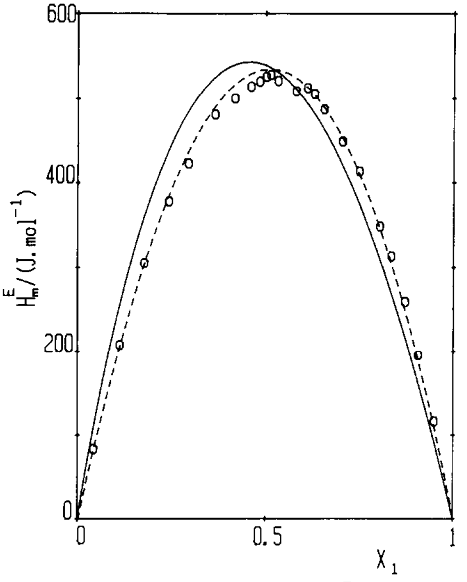


Fig. 6. Excess molar enthalpy, H^E_m, at 298.15 K for the system di-*n*-propylamine (1)+ *n*-decane (2). 0, Experimental values; ------, theoretical curve as predicted by Kehiaian's model; ————, theoretical curve as predicted by Chao's model.

nation number $Z = 8$ [12] for this kind of system. Chao's method, though correctly predicting the increase in excess enthalpy curves which are of the same general shape as the experimental curves, differs from them, especially for short alkane chains, to give an error of the order of 9%. It must therefore be concluded that although the results given by Chao's method are not totally incorrect, Kehiaian's method is a better model for the prediction of the excess enthalpies of secondary amine + *n*-alkane systems.

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