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CALORIMETRIC STUDY OF MOLECULAR INTERACTIONS IN MIXTURES OF SUBSTANCES CONTAINING CARBONYL AND DIALKYLAMINO GROUPS

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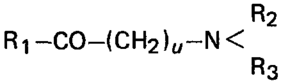
A Tian—Calvet type calorimeter has been used to determine molar excess enthalpies at 298.15 K as a function of concentration for mixtures of *N,N*-dialkylated aminoketones or amides + n-heptane. These data are examined on the basis of a quasi-chemical theory using group-surface interactions. The occurrence of the "hetero-proximity effect" between –CO– and –N < groups is suggested by the variation of the interchange parameters.

Group contribution methods [1] are currently used for the prediction of thermodynamic properties of organic mixtures of importance in the design of industrial processes. Previous investigations have shown that well-founded group contribution models may also give valuable information as to the structure of, and molecular interactions in, liquid mixtures of organic compounds.

One of the basic assumptions in group contribution theories, independently of the particular method used, is that each group is situated in a well-defined intramolecular environment. A change in the nearest environment of a given group usually produces a perturbation of the force field around the group and, consequently, a modification of the interaction energies. For example, the steric effect exerted by the chain length of the adjacent alkyl groups (R–) is aliphatic aldehydes [4] (–CHO group), ketones (–CO– group) [5] or tertiary amines (–N< group) [6, 7] is one among the many intramolecular factors which alter the values of the interchange energy coefficients.

In polyfunctional molecules the proximity of two identical or different groups in a given molecule usually has a quite strong influence on the interchange parameters. This "proximity effect" has previously been demonstrated for molecules containing the following pairs of identical group ("homoproximity"): –O– . . . –O– [8], –S– . . . –S– [9], Cl– . . . –Cl [10] and >N– . . . –N< [11].

The present work is a preliminary study of the intermolecular interactions between –CO– and –N< groups and of the intramolecular "heteroproximity" effect in molecules of the type



$$R_1\text{–CO–}(CH_2)_u\text{–N}\begin{matrix} R_2 \\ < \\ R_3 \end{matrix} \qquad (u = 0, 1, 2, \ldots)$$

The substances are *N,N*-dialkylated aminoketones ($u \geqslant 1$) or amides ($u = 0$).

The input data are usually the molar excess Gibbs energies, G^E, and the molar excess enthalpies, H^E, obtained from liquid–vapor equilibrium and calorimetric measurements.

The equations relating the experimental data to the interchange energy coefficients, $C_{st,1}$ (Gibbs energy) and $C_{st,2}$ (enthalpy), were essentially the same as used previously [4–7]. These equations correspond to the group-surface interaction version of the Guggenheim–Barker quasi-lattice model of liquid mixtures [2], in the Disquac extension [1]. The systems were regarded as possessing three types of surfaces: type *a* (CH_3– or –CH_2– groups), type *k* (–CO– group), and type *n* (>N– group). The (*a*, *k*) contacts were treated in the quasi-chemical approximation with a coordination number $Z_{ak} = 10$ [5]. The (*a*, *n*) contacts were treated in the random mixing approximation, $Z_{an} = \infty$ [6, 7].

The present study suggests that the random mixing approximation fits best to the (*k*, *n*) contact, $Z_{kn} = \infty$. The interchange coefficients $C_{ak,1}$, $C_{ak,2}$, $C_{an,1}$ and $C_{an,2}$ were the same as found in the ketone + alkane [5] and tertiary amine + alkane mixtures [6, 7]. For the estimation of coefficients $C_{kn,1}$ and $C_{kn,2}$ we need G^E and H^E data for alkanone + *N,N*-dialkylmethylamine mixtures:

$$\begin{aligned} &CH_3(CH_2)_{s-1}\text{–CO–}(CH_2)_{t-1}CH_3 + \\ &\quad + CH_3(CH_2)_{m-1}\text{–N}(CH_3)\text{–}(CH_2)_{n-1}CH_3 \end{aligned} \qquad \text{(A)}$$

For such mixtures of almost linear molecules the steric effect is relatively small [5–7] and, obviously, there is no proximity effect, since the –CO– and –N< groups belong to two different molecules.

The simplest class of mixtures for study of the Co . . . N heteroproximity effect is:

$$CH_3\text{–CO–}(CH_2)_u\text{–N}(CH_3)_2 + CH_3(CH_2)_{m-2}CH_3 \qquad \text{(B)}$$

No experimental G^E and H^E data could be found in the literature for any representative of these two classes, except H^E for *N,N*-dimethylethanamide ($u = 0$) + heptane [12].

Since $Z_{kn} = \infty$, a knowledge of G^E is not mandatory for the estimation of $C_{kn,2}$. We decided, therefore, to measure H^E for two mixtures of class *A*, viz. 2-propanane ($s = t = 1$) + *N,N*-dimethylethylamine ($m = 1$, $n = 2$) or + *N,N*-diethylmethylamine ($m = n = 2$) and for three mixtures of class *B*, viz. for aminoketones ($u = 3,1$) and *N,N*-dimethylethanamide ($u = 0$) + heptane ($m = 7$). Since dimethylethanamide +

heptane is only partly miscible, we have also determined the liquide–liquid equilibrium (LLE) curve.

Experimental

Calorimetric measurement

The excess enthalpies, H^E, were measured using a Tian–Calvet ("CRMT") type calorimeter which was manually tilted.

The batch mixing and the experimental procedure are reported in the literature [13]. The calorimeter was calibrated by the Joule effect and the calibration was repeated after each experiment. Check measurements on benzene + cyclohexane compared with the literature data [14] indicate that the precision of our results is 2%. All measurements were made at an average temperature of 298.15±0.10 K. Except for dimethylethanamide + heptane, the experimental values H^E_{exp} were fitted to the smoothing equation:

$$H^E_{\mathrm{sm}} = x_1 x_2 \sum_{i=0}^{N-1} a_1 (x_1 - x_2)^i \tag{1}$$

where x_i is the mole fraction of component 1 and $x_2 = 1 - x_1$. The values of the coefficients a_i and the standard deviation, σ,

$$\sigma(H^E) = \left[\frac{\sum (H^E_{\mathrm{sm}} - H^E_{\mathrm{exp}})^2}{N - n} \right]^{1/2} \tag{2}$$

where N is the number of experimental points and n the number of coefficients a_i, are reported in Table 1.

Liquid–liquid equilibrium measurements

The liquid–liquid equilibrium (LLE) for the mixture of dimethylethanamide + heptane was investigated in the temperature range 278.15–358.15 K, using a glass reactor equipped with a thermostated jacket and helicoidal stirring. The strirring speed was measured by means of a stroboscope; the contact between the two fluids was started in nitrogen and a fine dispersion of the two fluids was reached only at a strirring speed of 1600 r.p.m. After a contact time of about 30 min, the mixtures were allowed to decant so that the two phases could form; after drawing off an aliquot of each, homogenization was effected with known quantities of propanol and the composition was determined by gas-chromatography.

The instrument used was a Hewlett-Packard 5700 A equipped with a 2.0 m long column packed with Durapack.

Helium was used as the carrier gas and the column temperature was 473.15 K. Figure 1 shows the LLE curve for the dimethylethanamide + heptane system.

Table 1 Values of the coefficients a_i of Eq. (1) and standard deviation $\sigma(H^E)$, Eq. (2), of the experimental molar excess enthalpies H^E at 298.15 K

Component 1	Component 2	a	a_1	a_2	a_3	a_4	$\sigma(H^E)$
$CH_3CH_2N(CH_3)_2$	CH_3COCH_3	2754	1281	253	−325	621	3.5
$(CH_3CH_2)_2NCH_3$	CH_3COCH_3	3717	966	280	−10	−74	4.5
$(CH_3)_2NCOCH_3$	$CH_3(CH_2)_5CH_3$	(a)					
$(CH_3)_2NCH_2COCH_3$	$CH_3(CH_2)_5CH_3$	4642	−704	523	−1025	122	2.2
$(CH_3)_2N(CH_2)_3COCH_3$	$CH_3(CH_2)_5CH_3$	3127	−1101	370	−343	361	3.0

(a) Eq. (1) not applicable because of the presence of the miscibility gap.

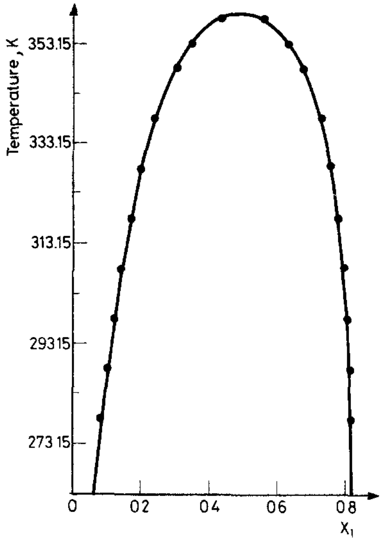


Fig. 1 Liquid-liquid equilibrium curve for the *N,N*-dimethylethanamide (1) + heptane (2)

Results and discussion

The H^E values for dimethylethanamide + heptane change linearly with the mole fraction x_1 over the range $x_1 = 0.2$ to 0.8 (see Fig. 2). This is due, as pointed out previously [12], to phase separation. The H^E curves of the two amine + ketone systems investigated can be described by the same value for the interchange enthalpy coefficient, $C_{kn,2} = 107$. The shape of the H^E curves *vs.* x_1 is quite well represented by the model for $Z_{kn} = \infty$ (Fig. 3).

Using this coefficient $C_{kn,2}$, along with the previously-determined coefficients for the (*ak*) and (*an*) contacts, we calculate H^E values for aminoketone or amide +

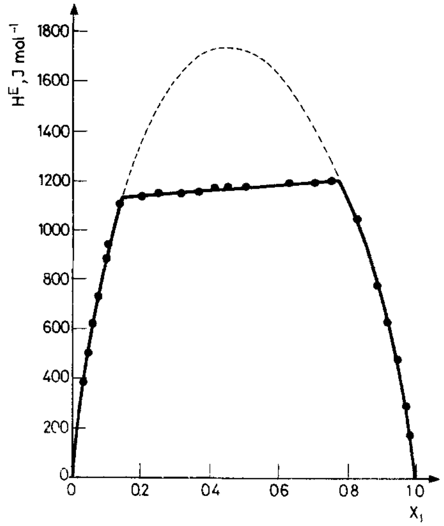


Fig. 2 Molar excess enthalpies, H^E, at 298.15 K of *N,N*-dimethylethanamide (1) + heptane (2) mixtures *vs.* x_1: ○ R. Tanaka [15], ● this work

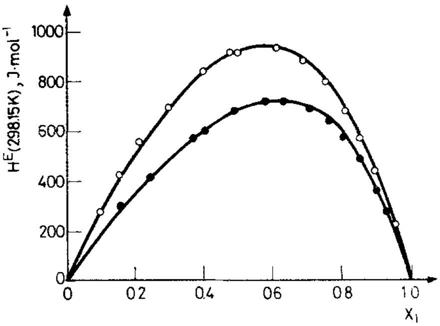


Fig. 3 Comparison of theory with experiment for the molar excess enthalpy H^E at 298.15 K of *N,N*-dialkylmethylamine (1) + 2-propanone (2) mixtures *vs.* x_1, full lines, predicted values; points, experimental H^E results: ○ *N,N*-diethylmethylamine, ● *N,N*-dimethylethylamine

heptane mixtures which larger than the experimental values (Fig. 4). This proves that the interactions between aminoketone molecules are weakened due to the proximity of the $-CO-$ and $-N<$ groups.

A priori, the heteroproximity effect modifies the interchange coefficients of all three types of contacts, (*ak*), (*an*) and (*kn*), but it is impossible at present to estimate the variations of each coefficient separately. Assuming, quite arbitrarily, that the coefficients corresponding to the (*ak*) and (*an*) contacts remain constant, we may calculate $C_{kn,2}$ as a function of u, the number of CH_2 groups between the $-CO-$ and the $-N<$ groups (Fig. 5). Surprisingly, instead of approaching the limiting value $C_{kn,2} = 107$, with increasing u, $C_{kn,2}$ increases in the range from $u = 0$ to $u = 3$. This

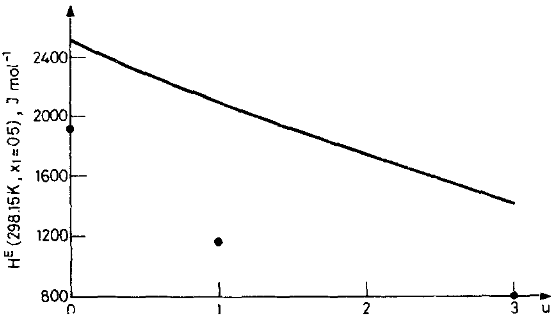


Fig. 4 Comparison of the theory with experiment for the molar excess enthalpy, H^E, at 298.15 K and $x_1 = 0.5$, of *N,N*-dialkylatedaminoketones or amides + heptane mixtures *vs.* *u*, the number of CH_2 groups between the $-CO-$ and $-N<$ groups. Full lines, predicted values; points, experimental results

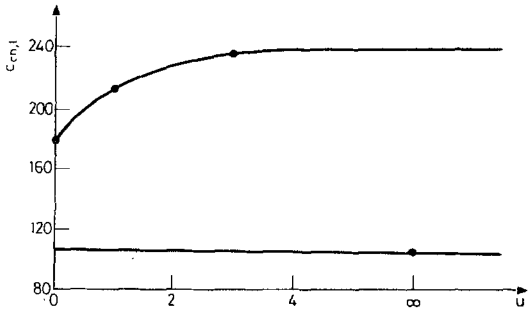
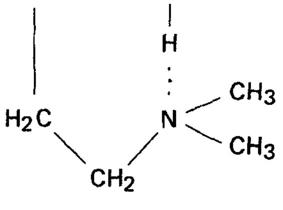


Fig. 5 Interchange-enthalpy coefficient $C_{kn,2}$ for contact *kn* (*k* carbonyl surface, *n* nitrogen surface) for *N,N*-diaklylatedaminoketones or amides + heptane mixtures *vs.* *u*, the number of CH_2 groups between the $-CO-$ and $-N<$ groups; $C_{kn,2}$ ($u = \infty$) is the value of $C_{kn,2}$ for dialkylmethylamide + 2-propanone mixtures

suggests an anomalous decrease of the intermolecular aminometone interaction when the $-CO-$ and $-N<$ groups are separated by one to three $-CH_2-$ groups. We may except, of course, that at larger distances the proximity effect will disappear, i.e. $C_{kn,2} \rightarrow 107$. A plausible explanation for this anomalous behaviour could be the formation of cyclic amino-enols, stabilized by intramolecular H-bonding, e.g.



This is evidence indeed that proton acceptors, such as tertiary amines, shift the keto–enol equilibrium towards the formation of enols [3].

References

1 H. V. Kehiaian, Proc. Third Int. Conf. on Fluid Properties and Phase Equilibria for Chemical Process Design, Callaway Gardens, Georgia, USA, 1983 (in press).

2 H. V. Kehiaian, J.-P. E. Grolier and G. C. Benson, J. Chim. Phys., 75 (1978) 1031.

3 E. Hajós-Szikszay and F. Ratkovics, Symposium on Thermodynamics of Liquid Mixtures (Abstract), Veszprém, Hungary, 1983, p. 53.

4 I. Ferino, B. Marongiu, V. Solinas, S. Torrazza and H. V. Kehiaian, Fluid Phase Eq., 12 (1983) 125.

5 H. V. Kehiaian, J.-P. E. Grolier, M. R. Kechavarz, G. C. Benson, O. Kiyohara and Y. P. Handa, Fluid Phase Eq., 7 (1981) 95.

6 I. Ferino, B. Marongiu, V. Solinas, S. Torrazza and H. V. Kehiaian, Fluid Phase Eq., 9 (1982) 49.

7 I. Ferino, B. Marongiu, V. Solinas, S. Torrazza and H. V. Kehiaian, Fluid Phase Eq., 9 (1982) 213.

8 R. J. Meyer, J. V. Metzger, C. Kehiaian and H. V. Kehiaian, Thermochim. Acta, 38 (1980) 197.

9 Z. Ferhad-Hamida, R. Phillippe, J. C. Merlin and H. V. Kehiaian, J. Chim. Phys., 77 (1980) 445.

10 C. Polo, C. Gutierrez-Cosa, M. R. Kechavarz and H. V. Kehiaian, Ber. Bunsenges. Phys. Chem., 84 (1980) 525.

11 I. Ferino, B. Marongiu, V. Solinas, S. Torrazza and H. V. Kehiaian, Fluid Phase Eq., 11 (1983) 1.

12 M. Oba, S. Murakami and R. Fujishiro, J. Chem. Thermodyn., 9 (1977) 407.

13 D. Bares, M. Soulié and J. Metzger, J. Chim. Phys., 70 (1973) 1531.

14 K. N. Marsh, Int. DATA Ser., Ser. A, Sel. Data Mixtures, (1980) 100.

15 R. Tanaka, S. Murahami and R. Fujishiro, J. Chem. Thermodyn., 6 (1974) 209.

Zusammenfassung — Ein Kalorimeter vom Tian—Calvet-Typ wurde zur Bestimmung der molaren Überschußenthalpie von Mischungen von *n*-Heptan mit *N*,*N*-dialkylierten Aminoketonen bzw. Amiden bei 298.15 K in Abhängigkeit von der Konzentration verwendet. Die erhaltenen Daten wurden nach der quasi-chemischen Theorie unter Verwendung von Wechselwirkungen zwischen Gruppen und Überfläche ausgewertet. Das Auftreten des "hetero-proximity"-Effektes zwischen —CO— und —N<-Gruppen wird durch Veränderung der Austauschparameter angezeigt.

Резюме — Калориметр типа Тиан—Кальве был использован для определения молльных избыточных энтальпий при температуре 298.15 K в зависимости от концентрации смесей *N*,*N*-диалкилированных аминокетонов или амидов и н-гентана. Полученные данные исследованы на основе квази-химической теории, используя взаимодействия типа группа — поверхность. Предложен "эффект гетероблизости" между —CO— и —N< группами путем изменения взаимообменных параметров.