THE THERMODYNAMIC INTERACTION OF N-METHYLLACTAMS WITH CYCLOHEXANE AND METHANOL

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Received January 14, 1991
Accepted April 19, 1991

The study deals with the dependence of thermodynamic interaction of the N-methylamide group in N-methyllactams with the acid hydrogen atom of methanol on the size of the lactam ring. The heats of mixing of N-methyl-4-butanelactam, N-methyl-6-hexanelactam, N-methyl-7-heptanelactam and N-methyl-8-octanelactam with methanol and cyclohexane were measured, and the data thus obtained were treated in terms of Barker's quasichemical theory. In a series of N-methyllactam–cyclohexane systems the mixing is endothermic, and the heats of mixing decrease with increasing size of the lactam ring. On the contrary, the mixing of N-methyllactams with methanol proceeds exothermically: first, the heats of mixing decrease depending on the lactam ring size, but for N-methyl-8-octanelactam they are very close to values obtained for N-methyl-4-butanelactam. However, with increasing ring size the energy of interaction between the N-methylamide group and the acid hydrogen atom of methanol increases. Such apparent discrepancy may be explained, in particular, by an opposite effect of the interaction between this group and the alkyl hydrogen atom.

An important role in the preparation of polyamides by the polymerization of lactams is played by electronegativity of the individual lactams. In this study an attempt is made to arrange N-methyllactams with various ring sizes according to the interaction between their amide group and the protondonor OH group in methanol. For this purpose we measured the heats of mixing of N-methyllactams (ML*n*) of the general formula

$$\mathrm{CH_3\overline{N(CH_2)_{\mathit{n}-2}\text{-}CO}}$$

(*n* being the number of ring forming atoms) with methanol and with cyclohexane. The following compounds were taken for comparison: N-methyl-4-butanelactam (ML5, N-methyl-2-pyrrolidone), N-methyl-6-hexanelactam (ML7, N-methyl-ε-caprolactam), N-methyl-7-heptanelactam (ML8), and N-methyl-8-octanelactam (ML9).

The heats of mixing thus determined were treated along with the published activity data in terms of Barker's theory[1,2], which interprets changes in the thermodynamic quantities of mixing as a sum of contributions of pair interactions between various atoms or groups. Mixing of methyllactam with a protondonor is accompanied by the formation of hydrogen bonds (exothermic process) and a simultaneous decrease in the frequency of dipole interactions between methylated amido groups (endothermic process). The energy parameters of the latter process were calculated from the heats of mixing of methyllactams with cyclohexane. By using these values, parameters of the interaction between the amide group of the lactam and the acid hydrogen atom in methanol were estimated. Due to side interactions, these parameters cannot be determined unequivocally, yet they make possible a comparison between members of the lactam series.

EXPERIMENTAL

Materials

N-Methyllactams were synthetized in the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences and purified so that purity was higher than 99·9%. Cyclohexane was an A.R. product of Reanal (Budapest), purity again higher than 99·9%, as proved by UV spectra and gas chromatographic measurements. Methanol was an A.R. product of Lachema Brno and was purified by distillation with CaH_2.

Calorimetry

The heats of mixing were measured with a Calvet microcalorimeter, a standard model made by Setaram, Lyon, France, sensitivity 0·2 μW. The data were digitalized by means of an A/D convertor, 4 1/2 digit range. To the weighed amount of the first component, a second component was gradually added with a mechanical burette Metrohm E 427 (Switzerland), 5 cm^3 in volume, reproducibility $\pm 0{\cdot}001$ cm^3. During data treatment using a Wang 2200/C calculator, an approximate correction for the vapour phase and mechanical stirring was also made.

RESULTS

The measured heats of mixing, ΔH^E, at 298·15 K were correlated using the Redlich and Kister equation in the form

$$\Delta H^E = x(1 - x)\sum_{i=0}^{m} A_i(2x - 1)^i \,, \qquad (1)$$

where $x = x_A$ is the mole fraction of N-methyllactam. The values of constants in this series thus obtained are summarized in Table I.

Application of Barker's Theory

Due to the strongly polar character of some groups, the assumption of random mixing in the systems under study was given up. In such cases theories based on the assumption of a quasichemical equilibrium appear to be useful. In this study Barker's theory has been used[1,2]. According to this theory, expressions for excess thermodynamic quantities were derived on the basis of a description of energy interactions between surface molecular groups. In this procedure, molecules are divided into segments, each of which occupies one site in the pseudolattice. Hence, in each application of Barker's theory to a real mixture one should make the following operations:

a) To choose the coordination number of the lattice, z.

b) To determine the number of the individual types of surface sites, m; relative surfaces of the i type in a molecule of component K, Q_i^K, must satisfy the condition

$$q_K z = \sum_{i=1}^{m} Q_i^K \qquad (2)$$

where $q_K z$ is the total number of surface sites in the molecule of component K. It is connected with the total number of segments, r_K, occupied in the lattice by the molecule of component K, by the following relations:

$$q_K z = r_K(z - 2) + 2 \qquad (3a)$$

for linear molecules, and

$$q_K z = r_K(z - 2) \qquad (3b)$$

for cyclic molecules.

TABLE I

Constants A_i (J/mol) of the Redlich and Kister series expansion (*1*) of heats of mixing ΔH^E for mixtures of N-methyllactams (ML*n*) with cyclohexane and methanol at 298·15 K. Symbol s denotes standard deviation of measurement of ΔH^E (in J/mol)

ML*n*	A_0	A_1	A_2	A_3	A_4	s
			Systems ML*n*(A)–cyclohexane (B)			
ML5	6 180	851	2 764	−2 560	—	13
ML7	4 943	−487	1 331	−1 378	—	21
ML8	4 744	−746	199	−1 955	2 556	15
ML9	4 519	−592	1 408	−1 732	—	15
			Systems ML*n*(A)–methanol (B)			
ML5	−2 634	78	79	269	—	4
ML7	−3 027	162	218	290	—	5·5
ML8	−3 419	474	242	−148	—	6·8
ML9	−2 527	227	12	642	—	13·9

c) To define energy relations between contacts by means of the Gibbs energies $F^{\mathrm{KL}}_{\mathrm{i,j}}$ and enthalpies $U^{\mathrm{KL}}_{\mathrm{i,j}}$ of contacts between the surface of type *i* in component K and the surface of type *j* in component L for all possible pair interactions in the system.

Let $N^{\mathrm{KL}}_{\mathrm{i,j}}$ be the number of contacts between surface sites of type *i* from molecule K and surface sites of type *j* from molecule L. If, now, $X^{\mathrm{K}}_{\mathrm{i}}$ is defined in terms of the equation

$$N^{\mathrm{KK}}_{\mathrm{i,i}} = (X^{\mathrm{K}}_{\mathrm{i}})^2\, N \tag{4a}$$

in which N is the total number of molecules, equations of the quasichemical equilibrium between contacts of various types can be written as

$$N^{\mathrm{KL}}_{\mathrm{i,j}} = 2\eta^{\mathrm{KL}}_{\mathrm{i,j}} X^{\mathrm{K}}_{\mathrm{i}} X^{\mathrm{L}}_{\mathrm{j}} N\,. \tag{4b}$$

By combining these equations with balance equations, a system of nonlinear equations is obtained for the quantities $X^{\mathrm{K}}_{\mathrm{i}}$, which for a binary mixture of components A, B can be written in the following matrix form[3,4]

$$\mathsf{LT}\boldsymbol{x} = \boldsymbol{b}\,, \tag{5a}$$

where

$$\mathsf{L} = \begin{bmatrix} X^{\mathrm{A}}_{1} \cdot & & & \\ & \cdot\, X^{\mathrm{A}}_{\mathrm{m_A}} & & \\ & & X^{\mathrm{B}}_{1} \cdot & \\ & & & \cdot\, X^{\mathrm{B}}_{\mathrm{m_B}} \end{bmatrix} \tag{5b}$$

is the diagonal matrix; matrix T is the matrix of the Boltzmann factors, $\eta^{\mathrm{KL}}_{\mathrm{i,j}} = \exp\left(-F^{\mathrm{KL}}_{\mathrm{i,j}}/(RT)\right)$, derived from the pair interaction Gibbs energies,

$$\mathsf{T} = \left[\begin{array}{l} \eta^{\mathrm{AA}}_{1,1}, \;\ldots, \eta^{\mathrm{AA}}_{1,\mathrm{m_A}}, \eta^{\mathrm{AB}}_{1,1}, \;\ldots, \eta^{\mathrm{AB}}_{1,\mathrm{m_B}} \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \eta^{\mathrm{AA}}_{\mathrm{m_A},1}, \ldots, \eta^{\mathrm{AA}}_{\mathrm{m_A},\mathrm{m_A}}, \eta^{\mathrm{AB}}_{\mathrm{m_A},1}, \ldots, \eta^{\mathrm{AB}}_{\mathrm{m_A},\mathrm{m_B}} \\ \hdashline \eta^{\mathrm{BA}}_{1,1}, \;\ldots, \eta^{\mathrm{BA}}_{1,\mathrm{m_A}}, \eta^{\mathrm{BB}}_{1,1}, \;\ldots, \eta^{\mathrm{BB}}_{1,\mathrm{m_B}} \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \eta^{\mathrm{BA}}_{\mathrm{m_B},1}, \ldots, \eta^{\mathrm{BA}}_{\mathrm{m_B},\mathrm{m_A}}, \eta^{\mathrm{BB}}_{\mathrm{m_B},1}, \ldots, \eta^{\mathrm{BB}}_{\mathrm{m_B},\mathrm{m_B}} \end{array}\right] \tag{5c}$$

and $\boldsymbol{x}$, $\boldsymbol{b}$ are column vectors

$$\boldsymbol{x} = \begin{bmatrix} X^{\mathrm{A}}_{1} \\ \vdots \\ X^{\mathrm{A}}_{\mathrm{m_A}} \\ X^{\mathrm{B}}_{1} \\ \vdots \\ X^{\mathrm{B}}_{\mathrm{m_B}} \end{bmatrix} \quad \boldsymbol{b} = \begin{bmatrix} Q^{\mathrm{A}}_{1} x_{\mathrm{A}}/2 \\ \vdots \\ Q^{\mathrm{A}}_{\mathrm{m_A}} x_{\mathrm{A}}/2 \\ Q^{\mathrm{B}}_{1} x_{\mathrm{B}}/2 \\ \vdots \\ Q^{\mathrm{B}}_{\mathrm{m_B}} x_{\mathrm{B}}/2 \end{bmatrix} \tag{5d}$$

in which x_A, x_B are mole fractions of components A and B respectively, m_A, m_B are the numbers of types of surface sites in molecule A and B respectively.

Such system of equations can be easily solved numerically, by employing Newton's and Raphson's method, because, basically, this is a quadratic form in the unknown quantities X_i^K.

Finally, for the excess quantities of mixing in the binary mixture A–B it can be written:

$$\Delta G^E/(RT) = \sum_{K=A,B} x_K \{ \sum_{i=1}^{m_K} Q_i^K \ln [X_i/(x_K X_i^{K1})] + r_K (z/2 - 1) \ln (x_K/\phi_K) \} , \qquad (6)$$

where ϕ_K is the volume fraction of component K.

$$\Delta H^E = 2 \{ \sum_{i=1}^{m_A - 1} \sum_{j>i}^{m_A} (X_i^A X_j^A - x_A X_i^{A1} X_j^{A1}) \eta_{i,j}^{AA} U_{i,j}^{AA} +$$

$$+ \sum_{i=1}^{m_B - 1} \sum_{j>i}^{m_B} (X_i^B X_j^B - x_B X_i^{B1} X_j^{B1}) \eta_{i,j}^{BB} U_{i,j}^{BB} + \sum_{i=1}^{m_A} \sum_{j=1}^{m_B} X_i^A X_j^B \eta_{i,j}^{AB} U_{i,j}^{AB} \} , \qquad (7)$$

where X_i^{A1}, and X_i^{B1} denote the respective values of X_i^A and X_i^B, valid for the pure component A and B respectively.

In this study we employed a lattice with the coordination number $z = 4$. To describe all systems investigated by us, four types of surface sites are sufficient: methylene and methyl groups (R), amide group (Am), oxygen (O) and hydrogen (H) of the hydroxyl group (such division of the hydroxyl group has proved to be useful already in the investigation of interactions of other compounds with alcohols, and has been supported theoretically (cf. e.g. Smirnova[5])).

Geometrical parameters entering Barker's theory have been fixed in an approximate agreement with volume and surface contributions of the particular groups (cf. Bondi[6]) and rounded off so as to meet relations (3*a*,*b*). With N-methyllactams, the surface contribution of the methyl group bound onto N has been included in the surface of methylene groups. Values of the geometrical parameters of the components in the systems under study are summarized in Table II.

Determinations of the Parameters of Energy Interactions

In the application of Barker's theory to our systems, pair interactions between the groups R–Am, R–O, R–H, Am–O, O–H, and Am–H are characterized by the Gibbs energy (F) and enthalpy (U) values. Thus, the number of interaction parameters in the ML*n* (A)–methanol (B) system for the given *n* reaches 12. Parameters of the interaction R–Am have been obtained by treating the series of ML*n* (A)–cyclohexane (B) systems. In order to reduce the number of adjustable parameters in the data treatment of ML*n*–methanol systems, simplifying assumptions had to be introduced. Our procedure can be summarized as follows:

a) First, the ML*n*–cyclohexane systems were treated; their matrix of the Boltzmann factors has the form:

$$\mathsf{T} = \begin{bmatrix} 1, & \eta_{\mathrm{R,Am}}, & 1 \\ \eta_{\mathrm{R,Am}}, & 1, & \eta_{\mathrm{R,Am}} \\ 1, & \eta_{\mathrm{R,Am}}, & 1 \end{bmatrix} . \qquad (8)$$

The "ones" off the main diagonal express an assumption that the pair of alkyl hydrogen atoms has zero Gibbs energy of interaction, irrespective of the fact in which component of the mixture the atoms are situated. Since, however, no activity data at 298·15 K have so far been available for any of the systems considered in this study, two possibilities arise, namely: (i) by employing the reported ΔG^{E} values for the system ML7–cyclohexane measured at 313·15 K by Bittrich and Hradetzky[7], to recalculate $\eta_{\mathrm{R,Am}}$ thus obtained using enthalpy values to 298·15 K; (ii) to assume that the nonrandomness of mixing will not be reflected in the R–Am interaction, i.e. to put $\eta_{\mathrm{R,Am}} = 1(F_{\mathrm{R,Am}} = 0)$ and to adjust only a single parameter, i.e. $U_{\mathrm{R,Am}}$ so as to obtain the best possible fit with our own data on the heats of mixing. We favoured the latter of the two procedures, which gave us concentration dependences of the heats of mixing closer to the experimental curves, especially as regards the position of their maxima. The optimal $U_{\mathrm{R,Am}}$ values are summarized in Table III.

b) As no suitable activity data on systems of the n-alkane–methanol series at 298·15 K could be found, we decided to carry out a common adjustment of the remaining energy parameters using the experimental ΔG^{E} values for the ML7–

TABLE II

Geometrical parameters of Barker's theory for $z = 4$. Symbol r_{K} denotes the number of segments (lattice sites) occupied by a molecule of component K. Relative surface: q_{K} of one contact point, Q_{R} of hydrogens of methyl and methylene groups, Q_{Am} of the amide group, Q_{O} of the oxygen of the hydroxyl group, Q_{H} of the hydrogen of the hydroxyl group

Component	r_{K}	q_{K}	Q_{R}	Q_{Am}	Q_{O}	Q_{H}
Methanol	2	1·5	3	—	2	1
Cyclohexane	6	3	12	—	—	—
ML5	6	3	9	3	—	—
ML7	8	4	13	3	—	—
ML8	9	4·5	15	3	—	—
ML9	10	5	17	3	—	—

–methanol system at 313·15 K (cf. refs[7,8]). In such case the matrix of the Boltzmann factors $\eta_{i,j}$ has the form

$$T = \begin{bmatrix} 1, & \eta_{R,Am}, & 1, & \eta_{R,O}, & \eta_{R,H} \\ \eta_{R,Am}, & 1, & \eta_{R,Am}, & \eta_{Am,O}, & \eta_{Am,H} \\ 1, & \eta_{R,Am}, & 1, & \eta_{R,O}, & \eta_{R,H} \\ \eta_{R,O}, & \eta_{Am,O}, & \eta_{R,O}, & 1, & \eta_{O,H} \\ \eta_{R,H}, & \eta_{Am,H}, & \eta_{R,H}, & \eta_{O,H}, & 1 \end{bmatrix} . \tag{9}$$

In agreement with the preceding approximation $\eta_{R,Am} = 1$, a further simplification is introduced by putting also $\eta_{R,O}$, $\eta_{R,H}$ and $\eta_{Am,O}$ equal to unity. Furthermore, we were seeking optimal values of $\eta_{Am,H}$ for the series of chosen $\eta_{O,H}$ values so as to make the calculated concentration dependence $\Delta G^E(x_A)$ fit the experimental dependence as much as possible; this was tested by calculating the residual standard deviation s_G on an equidistant network of points for $x_A = 0{\cdot}1$; 0·2; ... 0·9. To recalculate the chosen $\eta_{O,H,298}$ values to those at 313 K, we used the Gibbs and Helmholtz equation, assuming that in the interval ⟨298 K, 313 K⟩ the enthalpy of interaction $U_{O,H}$ is constant and that, moreover, F/U at 298 K for the O–H interaction is 0·5.

When calculating the energy parameters $U_{i,j}$, we started from the concentration dependence of the heats of mixing $\Delta H(x_A)$ measured by us at 298 K in the ML*n*–methanol systems. The basic system was ML7–methanol, where the already determined $\eta_{O,H}$ and $\eta_{Am,H}$ could be employed. Furthermore, it was assumed for all systems in the series that $U_{Am,O} = 0$, while $U_{R,H} = U_{R,O} =$ const., which is positive and independent of the ring size of N-methyllactam. The $U_{R,Am}$ values were taken from the ML*n*–cyclohexane system having the same size of the lactam ring (*n*). Under these conditions, and assuming that $(F/U)_{O,H} = 0{\cdot}5$, F/U was adjusted for

TABLE III

Energy parameters of Barker's theory (for $z = 4$, and at $\eta_{R,Am} = 1$) for systems N-methyllactam (A)–cyclohexane (B): $U_{R,Am}$ is the interaction enthalpy of hydrogen of groups R with the amide group (Am), s_H is the standard deviation of ΔH^E values

Component A	$U_{R,Am}$ J/mol	s_H J/mol
ML5	8 765	106·98
ML7	10 624	51·84
ML8	12 195	69·03
ML9	13 860	47·70

the Am–H interaction so as to reach an optimal agreement between the theoretical dependence of $\Delta H^E(x_A)$ and the experimental one for the ML7–methanol system. The $(F/U)_{\mathrm{Am,H}}$ value thus obtained was then used also in other systems in the series, in which only the $U_{\mathrm{Am,H}}$ value was adjusted.

Agreement between the theory and experiment was evaluated using the sum of standard deviations s_H of the ΔH^E dependences for the individual systems. In this respect, $\eta_{\mathrm{O,H,298}} = 30$ and $U_{\mathrm{R,H}} = U_{\mathrm{R,O}} = 3\,000$ J/mol was the best choice.

TABLE IV

Energy parameters of Barker's theory for systems N-methyllactam (A)–methanol (B). For all systems $\eta_{\mathrm{R,Am}} = \eta_{\mathrm{R,O}} = \eta_{\mathrm{R,H}} = \eta_{\mathrm{Am,O}} = 1$; $U_{\mathrm{R,Am}}$ values for the given N-methyllactam are taken from Table III. For O–H contacts is assumed, moreover, that $(F/U)_{\mathrm{O,H}} = 0{\cdot}5$. Symbols: $\eta_{\mathrm{Am,H}}$ is the Boltzmann factor based on the free energy of contact of the group Am with the hydrogen atom of the hydroxyl group in methanol ($\eta_{\mathrm{Am,H}} = \exp(-F_{\mathrm{Am,H}}/(RT))$), $F_{\mathrm{Am,H}}$ is the Gibbs energy of contact Am–H, $U_{\mathrm{Am,H}}$ is the enthalpy of contact Am–H, s_G is the standard deviation of ΔG^E values, s_H is the standard deviation of ΔH^E values

Component A	$\eta_{\mathrm{Am,H}}$	$F_{\mathrm{Am,H}}$	$U_{\mathrm{Am,H}}$	s_G	s_H
$\eta_{\mathrm{O,H}} = 30$; $U_{\mathrm{R,H}} = U_{\mathrm{R,O}} = 3\,000$ J/mol; $(F/U)_{\mathrm{Am,H}} = 0{\cdot}5703$					
ML5	30·74	−8 491·8	−14 890	—	28·06
ML7	27·91	−8 252·3	−14 470	70·99	9·84
ML8	25·93	−8 069·7	−14 150	—	13·10
ML9	21·08	−7 556·5	−13 250	—	30·05
$\eta_{\mathrm{O,H}} = 50$; $U_{\mathrm{R,H}} = U_{\mathrm{R,O}} = 3\,000$ J/mol; $(F/U)_{\mathrm{Am,H}} = 0{\cdot}5824$					
ML5	55·95	−9 976·5	−17 130	—	34·44
ML7	47·36	−9 563·0	−16 420	69·37	13·02
ML8	42·41	−9 289·3	−15 950	—	12·16
ML9	32·90	−8 660·3	−14 870	—	27·60
$\eta_{\mathrm{O,H}} = 30$; $U_{\mathrm{R,H}} = U_{\mathrm{R,O}} = 5\,500$ J/mol; $(F/U)_{\mathrm{Am,H}} = 0{\cdot}4952$					
ML5	29·67	−8 403·5	−16 970	—	25·44
ML7	29·25	−8 368·9	−16 900	70·99	8·48
ML8	28·11	−8 269·8	−16 700	—	24·85
ML9	24·00	−7 878·6	−15 910	—	54·85
$\eta_{\mathrm{O,H}} = 50$; $U_{\mathrm{R,H}} = U_{\mathrm{R,O}} = 5\,500$ J/mol; $(F/U)_{\mathrm{Am,H}} = 0{\cdot}5163$					
ML5	53·75	−9 876·8	−19 130	—	31·82
ML7	49·56	−9 675·5	−18 740	69·37	8·05
ML8	45·98	−9 489·6	−18 380	—	19·01
ML9	40·50	−9 174·7	−17 770	—	48·80

The optimal parameters are given in the first part of Table IV. For the sake of comparison, the not too poor results obtained for other combinations of the $\eta_{O,H}$ values (30 or 50) and $U_{R,O} = U_{R,H}$ (3 000 or 5 500 J/mol) are also presented here. The order of members in the lactam series with respect to the magnitude of the interaction parameters is the same for all four sets of parameters. The difference between the parameters for ML8 and ML9 is always greater than for the other

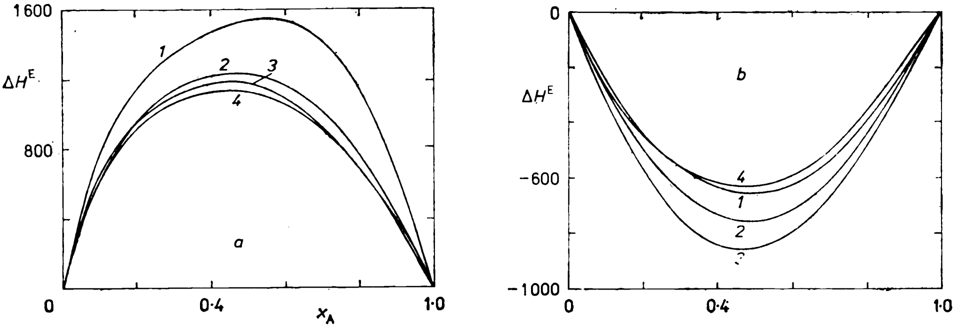

FIG. 1

Dependence of the heat of mixing, ΔH^E(J/mol), on the mole fraction of N-methyllactam, x_A, for mixtures *a* N-methyllactam (ML*n*)–cyclohexane and *b* ML*n*–methanol. Curves smoothed according to Eq. (*1*) with coefficients A_i according to Table I: *1* ML5, *2* ML7, *3* ML8, *4* ML9

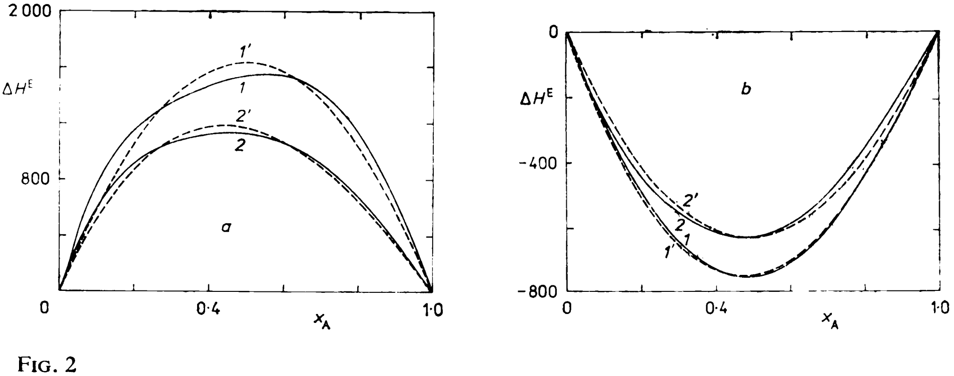

FIG. 2

Agreement between Barker's theory and experiment for dependences of the heat of mixing, ΔH^E(J/mol), on the mole fraction ot N-methyllactam, x_A, for mixtures *a* N-methyllactams. .(ML*n*)-cyclohexane and *b* ML*n*-methanol. Full curves represent smoothed experimental data, broken curves have been calculated using Barker's theory for $\eta_{R,Am} = 1$ and $U_{R,Am}$ according to Table III and for the remaining energetic parameters according to Table IV: *a* *1*,*1'* ML5, *2*,*2'* ML9, *b* *1*,*1'* ML7, *2*,*2'* ML9 neighbouring pairs in the series (although ML5 differs from ML7 by two carbon atoms).

DISCUSSION

As can be seen in Fig. 1*a*, all heats of mixing of N-methyllactams with cyclohexane are positive and decrease with increasing lactam ring size. The cause of this decrease should be sought in the decreasing concentration of the amide group and frequency of dipole interactions related to it. It can be seen in Table III that the calculated interaction energy values $U_{R,Am}$ increase from ML5 to ML9. Hence, the measured heats of mixing decrease more slowly than would be predicted by the theory used at $U_{R,Am}$ values independent of the ring size.

Figure 1*b* shows the heats of mixing of N-methyllactams with methanol. In this case the mixing is exothermic; first, on passing from ML5 to ML8, the heats of mixing decrease, but for ML9 ΔH^E thus obtained is very close to values for ML5. On the other hand, however, the interaction energy values $U_{Am,H}$ increase on passing from ML5 to ML9, and this increase becomes considerably faster between ML8 and ML9. The fact that the increase in energy $U_{Am,H}$ is not accompanied by an increase in ΔH^E on passing from ML5 to ML8 can in the first place be explained by an opposite effect of the group interaction R–Am.

It seems, therefore, that Barker's theory is suited for a description of the systems studied by us, as also illustrated by Fig. 2 showing systems for which, by using parameters from the first part of Table IV, both the best and the poorest representation of the experimental findings became feasible. For N-methyllactam–cyclohexane systems (cf. Fig. 2*a*) the fit was best for ML9 and poorest for ML5, while for systems N-methyllactam–methanol the best fit was observed with ML7 and the poorest, for ML9. Table IV suggests that for other, though close combinations of the energy parameters the pattern of standard deviations, s_H, is somewhat different, depending on the methyllactam ring size. Hence, for systems with methanol (Fig. 2*b*) it can only be stated, generally, that data for ML7 and ML8 are more adequately described than those for ML5 and ML9, which may be due to the fact that the $\eta_{Am,H}$ values were determined using the activity data just for the ML7–methanol system.

The authors are indebted to Dr Jan Šebenda for stimulating this study and for supplying samples of N-methyllactams.

REFERENCES

1. Barker J. A.: J. Chem. Phys. *20*, 794, 1526 (1952).
2. Barker J. A., Smith F.: J. Chem. Phys. *22*, 375 (1954).
3. Živný A., Biroš J., Obereigner B., Pouchlý J.: J. Chim. Phys. *72*, 379 (1975).
4. Biroš J., Živný A., Pouchlý J.: J. Chim. Phys. *72*, 385 (1975).
5. Smirnova N. A.: Pure Appl. Chem. *61*, 1115 (1989).

6. Bondi A. A.: *Physical Properties of Molecular Crystals, Liquids and Glasses.* Wiley, New York 1968.
7. Bittrich H.-J., Hradetzky G.: Z. Phys. Chem. (Leipzig) *270*, 451 (1989).
8. Hradetzky G., Bittrich H. J.: *Physicochemical Data of Selective Solvents.* Deutscher Verlag der Wissenschaften, Berlin 1988.

Translated by L. Kopecká.