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Thermodynamic Characteristics of Water–*N*-Methylpyrrolidone Mixtures and Intermolecular Interactions in Them

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Abstract — Thermodynamic characteristics of water–*N*-methylpyrrolidone mixtures in the range 298.15–338.15 K were calculated from the data obtained in our previous studies and by other authors. The specific and nonspecific terms of the total energy of intermolecular interaction were determined within the framework of a model approach using the internal pressure as a measure of nonspecific interactions in a liquid. The parameters obtained indicate that, with an increase in the *N*-methylpyrrolidone concentration, the three-dimensional network of hydrogen bonds in water undergoes transformations and is broken. For the solutions differ in the type of intercomponent association and structural organization the boundaries of concentration ranges were determined.

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The simplest cyclic amides with various extents of N-substitution are widely used in various branches of industry and in laboratory practice thanks to their very high thermal and chemical stability. Solutions based on these compounds have been extensively studied [1]. Of particular interest are pyrrolidone derivatives in which replacement of the NH proton by an alkyl group, leading to the loss of the proton-donor power, leads to structural changes in solutions. Despite a large number of published papers, the physicochemical properties of mixtures of water with pyrrolidone and its derivatives are insufficiently understood [1, 2]. At the same time, thermodynamic analysis of intermolecular interactions and structural changes in aqueous solutions of nonelectrolytes is still an urgent problem of solution chemistry [2, 3]. This paper continues our studies of thermodynamic properties of aqueous solutions of *N*-methylpyrrolidone. Previously we determined excess thermodynamic functions of this system (H^E, G^E, S^E) and estimated the parameters (ΔH, ΔG, ΔS) of formation of a heterocomponent hydrogen bond [4]. Among solvents of network structure, water has the most perfect hydrogen bond network [5]. *N*-Methylpyrrolidone is a typical aprotic polyfunctional nonelectrolyte capable of formation of strong hydrogen bond with water through the carbonyl oxygen atom, C=O···H–O. One of the main goals of this study was to reveal the effect exerted by *N*-methylpyrrolidone on the H-bond network of water using the thermodynamic characteristics calculated from our previous data and data obtained obtained by other authors.

Kartsev et al. [6, 7] demonstrated for a wide range of individual liquids and a series of aqueous solutions that the internal pressure p_{int} and its temperature coefficient are very sensitive to structural organization of the liquid. The quantity p_{int} characterizes the change in the internal energy U of a liquid in the course of its small isothermal expansion [3]; it can be calculated by Eq. (1):

$$p_{int} = (\partial U/\partial V)_T = T(\partial p/\partial T)_{V-p} \approx T\alpha/\beta_T, \qquad (1)$$

where V is the molar volume; α and β_T, coefficients of isobaric (cubic) expansion and isothermal compression, respectively. In this equation, the atmospheric pressure p can be neglected, because its contribution to p_{int} is less than 0.1% [3].

The internal pressures of *N*-methylpyrrolidone solutions, calculated for three temperatures by Eq. (1), are given in the table. The thermal expansion coefficients were calculated by Eq. (2) after approximation of the molar volumes [8] by polynomials of second degree in the temperature:

$$\alpha = 1/V(\partial V/\partial T)_p. \qquad (2)$$

The isothermal compressibility coefficients were calculated from Eq. (3):

$$\beta_T = 1/u^2\rho + \alpha^2 VT/C_p, \qquad (3)$$

where u is the ultrasound velocity; ρ, density; and C_p, heat capacity of the solutions. In the calculations we used data on $u(T)$ and $\rho(T)$ from [8] and on the heat

capacity from [9]. The isothermal compressibility of *N*-methylpyrrolidone calculated by this procedure, $537.8 \times 10–12$ Pa^{-1}, is in good agreement with the value calculated from data on its compressibility at 298.15 K [10].

From the data obtained, we calculated the temperature coefficients of the internal pressure $\Delta p_{int}/\Delta T$ in the system for ΔT = 40 K (Fig. 1). It is seen that, at $0 < X < 0.2$, the internal pressure of solutions increases with temperature, which is typical of systems with a three-dimensional network of H bonds [5]. Then the temperature coefficient of the internal pressure changes sign, becoming negative. This fact suggests that aqueous solutions of *N*-methylpyrrolidone are associated and the character of association changes with a decrease in the water content. The large negative values of S^E in the system support this assumption [4].

Figure 1 shows that, between the two concentration intervals in which the dependence of $\Delta p_{int}/\Delta T$ on X is approximately linear, there is a transition region in which the form of the function $(\Delta p_{int}/\Delta T) = f(X)$ changes most essentially. To reveal the character of the occurring changes, it is appropriate to present the function $(\Delta p_{int}/\Delta T) = f(X)$ in the coordinates $(1/X) \times (\Delta p_{int}/\Delta T) = f(X)$ (Fig. 2); this procedure makes the bends sharper [11]. Figure 2 shows that there is only a bend of the concentration dependence of $\Delta p_{int}/\Delta T$ in a relatively broad concentration range $0.07 < X < 0.35$.

Kartsev et al. [7] noted that the strongest structural changes in aqueous solutions of nonelectrolytes occur within the region of the bend in the concentration dependence of the temperature coefficient of the internal pressure; the composition corresponding to the end of this bend corresponds to the most stable water–nonelectrolyte associate. Indeed, in the system under consideration at X ~0.33 the functions $H^E(X)$ and $S^E(X)$ pass through an extremum, due to formation of the complexes $C_5H_9NO \cdot 2H_2O$ in the largest amount. The existence of these associates in solutions is confirmed in the majority of papers concerning physicochemical properties of this system [12] and also by computer simulation [13] and spectroscopy [14]. We showed previously that the heterocomponent hydrogen bond formed in the system (ΔH –18.3 kJ mol^{-1}, ΔS –41.9 J mol^{-1} K^{-1}) is appreciably stronger than water–water hydrogen bonds [4]. Computer simulation showed that the H-bond network of water is successively broken with an increase in the concentration of amides and in aqueous DMF is fully broken at X ~0.3 [15]. Presumably (Figs. 1, 2), the system under consideration passes through the percolation threshold already at X ~ 2, because of the larger molecular volume of *N*-methylpyrrolidone compared to DMF.

Internal pressure ($p_{int} \times 10^{-6}$, Pa) of aqueous solutions of *N*-methylpyrrolidone at various temperatures (X is the mole fraction of the amide)

X	298.15 K	308.15 K	318.15 K
0.0000	178	301	423
0.0100	216	334	447
0.0246	272	381	480
0.0359	315	415	504
0.0443	347	439	520
0.0632	415	489	553
0.0743	452	516	568
0.1004	528	568	603
0.1151	563	591	618
0.1258	584	606	626
0.1464	619	629	640
0.2480	679	669	655
0.3496	667	648	629
0.4507	635	613	593
0.4982	619	597	576
0.5466	603	580	560
0.6519	569	548	527
0.7535	541	519	494
0.8316	519	503	486
0.9478	499	485	469
1.0000	492	479	462

Available data on the internal pressure allow us to estimate the contribution of nonspecific interactions

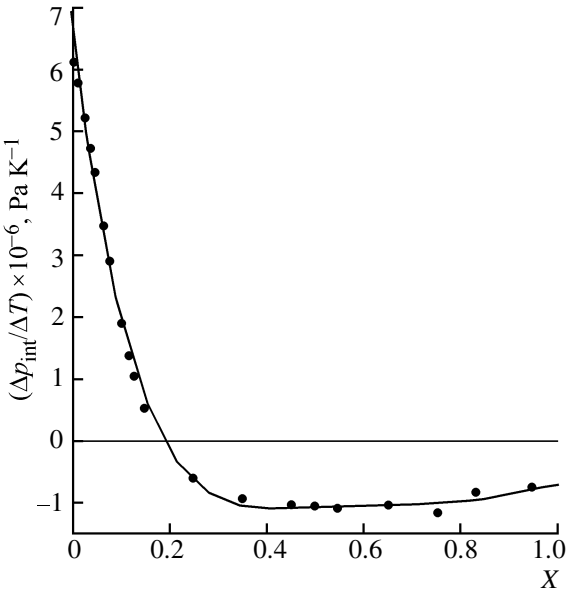

Fig. 1. Composition dependence of the temperature coefficient of the internal pressure of water–*N*-methylpyrrolidone mixtures in the range 298.15–338.15 K (here and hereinafter, X is the mole fraction of the amide).

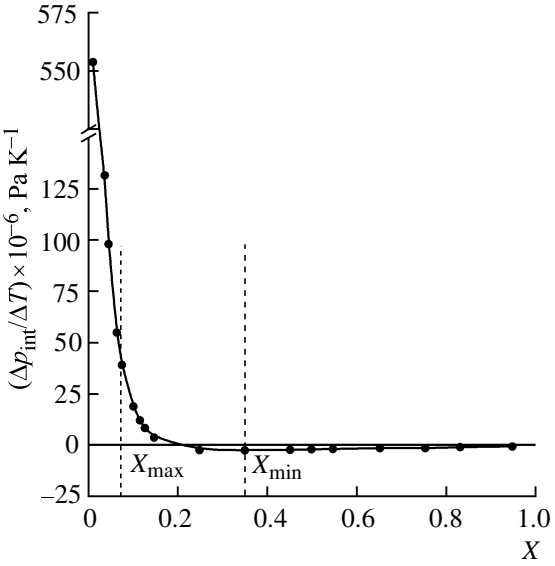

Fig. 2. Concentration dependence of the function $(1/X)(\Delta p_{int}/\Delta T)$ of water–*N*-methylpyrrolidone mixtures in the range 298.15–338.15 K.

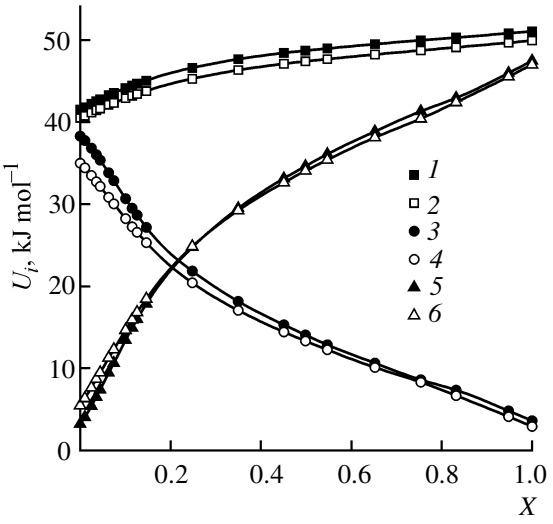

Fig. 3. (*1, 2*) Total energy of intermolecular interactions U_t in the water–*N*-methylpyrrolidone system and contributions (*3, 4*) U_{sp} and (*5, 6*) U_{nsp} at (*1, 3, 5*) 298.15 and (*2, 4, 6*) 318.15 K.

(using the model from [16] and taking the internal pressure as their measure) to the total intermolecular interaction in the system [Eq. (4)]:

$$U_{nsp} = p_{int}V \approx TV\alpha/\beta_T. \quad (4)$$

The validity of concept [16] is confirmed by the fact that, in nonpolar liquids in which there are only van der Walls interactions, the internal pressure is identical to cohesion ($p_{int} = D$). In nonelectrolytes associated by H bonds the cohesion is considerably higher, whereas p_{int} is of the same order as in hydrocarbons. It was shown in [16, 17] that, insofar as p_{int} mainly reflects the nonspecific interactions and D reflects the total spectrum of the interactions, the difference $D - p_{int}$ includes a contribution of hydrogen bonds to the iontermolecular interactions (per unit volume of liquid). Therefore, the total energy of intermolecular interactions in solution (U_t) as a sum of specific and nonspecific contributions [18] can be calculated by Eq. (5) [16]:

$$U_t = DV = \Delta H_v - RT = U_{sp} + U_{nsp}, \quad (5)$$

where ΔH_v is the enthalpy of vaporization of solutions, and R is the universal gas constant. The specific and nonspecific terms of the intermolecular interaction in water–*N*-methylpyrrolidone mixtures at 298.15 and 318.15 K, calculated using this approach, are plotted in Fig. 3. The enthalpies of vaporization of solutions were calculated by Eq. (6):

$$\Delta H_v = [(1 - X)\Delta H_{v1} + X\Sigma H_{v2}] - H^E, \quad (6)$$

where X is the mole fraction of *N*-methylpyrrolidone and ΔH_{v1} and ΔH_{v2} are the enthalpies of vaporization of water [19] and *N*-methylpyrrolidone [20], respectively. The enthalpies of mixing of the components (H^E) at 298.15 and 318.15 K were measured previously [4].

In mixtures of water with *N*-methylpyrrolidone, the temperature factor affects most strongly the specific interactions, which appreciably weaken with increasing temperature. As the mole fraction of the amide is increased to 0.35, the specific term decreases by ~20 kJ mol^{-1} at both temperatures. After that, the rate of variation of all the functions $U_i(X)$ decreases, and they become approximately linear. A decrease in the content of water, which is self-associated by hydrogen bonds, is accompanied by a decrease in U_{sp}, which is quite natural. It should be noted that the strongest deviations of U_{sp} from the additive values are observed in water-rich solutions (Fig. 3). Such a behavior of the $U_{sp}(X)$ function is most probably due to the fact that additions of the cyclic amide intensely break the water structure in this composition range.

It is known that in pure *N*-methylpyrrolidone (X 1.0) hydrogen bonds are absent, but there are strong dipole–dipole interactions [21]. The absolute value of their energy at 298.15 K, calculated within the framework of model [16], is ~5 kJ mol^{-1}, which amounts to ~10% of the total intermolecular interaction energy in

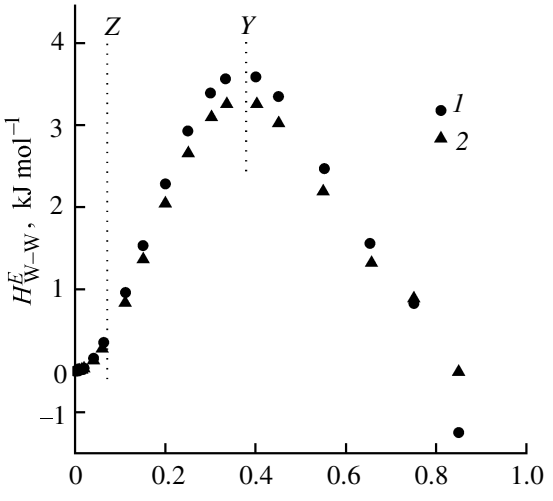

Fig. 4. Composition dependence of the enthalpy function of interaction H^E_{W-W} in water–*N*-methylpyrrolidone mixtures at (*1*) 298.15 and (*2*) 318.15 K.

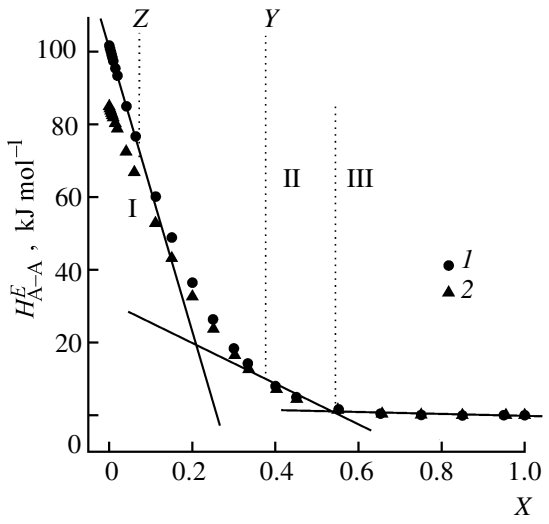

Fig. 5. Composition dependence of the enthalpy function of interaction H^E_{A-A} in water–*N*-methylpyrrolidone mixtures at (*1*) 298.15 and (*2*) 318.15 K.

this amide; the dipole–dipole interactions weaken with increasing temperature (Fig. 3). Available data on the structure and intermolecular interactions in cyclic amides and *N*-methylpyrrolidone are very limited [13, 21, 22]. The structure of the best studied N,N-disubstituted amide, DMF, is better understood. It has been reliably proved that the structure of liquid DMF can be described as a set of dimers with antiparallel arrangement of the molecules; these dimers are linked in linear chains [23]. We found that in DMF the contribution of strong dipole–dipole interactions at 298.15 K is ~9 kJ mol^{-1}, which amounts to more than 20% of the total intermolecular interaction energy in this amide [24]. This fact is in good agreement with the estimations made in [25] for DMF at 298.15 K and additionally confirms the adequacy of the approach suggested in [16]. A decrease in the contribution of strong dipole–dipole interactions in *N*-methylpyrrolidone by a factor of almost 2 relative to DMF is consistent with Bittrich and Kirsch's observations [26] that the content of dimers in amides decreases with an increase in the number or volume of alkyl substituents. The most probable cause of this trend is increased steric hindrance to formation of dipole–dipole dimers in *N*-methylpyrrolidone.

Koga [27] showed that the second derivatives of a number of thermodynamic functions can be used for analyzing changes in the structural state of aqueous solutions of nonelectrolytes. It is known that the partial molar excess enthalpy of ith component of a binary system (H^E_i) is identical to the enthalpy of its solution in a mixture of the corresponding composition, and this quantity can be estimated calorimetrically. However, it is impossible to determine experimentally the derivative of this quantity; the problem consists in determination of the partial derivative of the partial molar excess enthalpy of component i with respect to composition [Eq. (7)]:

$$H^E_{i-i} = (1 - X_i)(\partial H^E_i/\partial X_i). \quad (7)$$

In the physical sense, this quantity reflects the effect of an addition of ith component on H^E_i. Negative values of H^E_{i-i} indicate that addition of ith component makes its existence in the solution more preferable, or attractive (in enthalpy terms). Positive values of H^E_{i-i} indicate that the interaction of the component molecules is repulsive.

Figures 4 and 5 show the concentration dependences of the second derivatives of partial molar excess enthalpies of the components at two temperatures. An increase in the temperature does not affect the shape of the functions $H^E_{i-i}(X)$. The inflection points in the corresponding plots subdivide the whole concentration range into several sections. In accordance with Koga's approach [27], in the water–*N*-methylpyrrolidone system there are three concentration regions (I, II, III) and a transition region $Z < X < Y$.

Koga [28] and Mancera et al. [29] found that, in composition region I ($0 < X < Z$), in the vicinity of alkyl substituents of an aprotic nonelectrolyte, the water H-bond network, as a rule, becomes stronger,

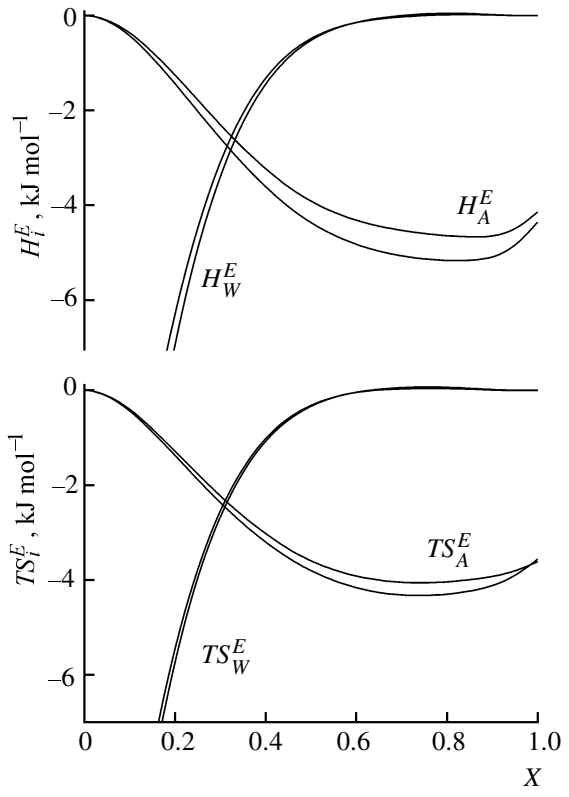

Fig. 6. Composition dependence of the excess partial molar enthalpies H_i^E and entropies TS_i^E of the components of the water–*N*-methylpyrrolidone temperatures at 298.15 (lower curves) and 318.15 K (upper curves).

whereas in the vicinity of polar groups it is broken. The results of dielectric relaxation studies of dilute aqueous solutions of dimethylacetamide [30] and polyvinylpyrrolidone [31] (compounds structurally related to *N*-methylpyrrolidone) suggest that, in the system under consideration, the effect of hydrophobic hydration of the nonpolar groups on the initial H-bond network in the solution will also prevail over the effect of hydrophilic hydration. This is confirmed by the results of simulation of aqueous solutions of *N*-methylpyrrolidone [13]. According to [2], on addition of a nonelectrolyte to pure water in a relatively narrow concentration range $0 < X < X^*$, the perturbing effect of the solute molecules on the properties of water is weak. The upper boundary X^* of this concentration range corresponds to the minima of the excess partial molar volumes of the nonelectrolyte. In the system under consideration, the minimum of the partial molar volume of *N*-methylpyrrolidone is observed at X 0.08 [8, 32, 33]. The upper boundary of region I of solutions in the water–*N*-methylpyrrolidone system (Fig. 5), in accordance with Koga's approach [27], is X ~0.07, which coincides with the onset of the bend in the concentration dependence of the internal pressure (Fig. 2). All these facts indicate that even such a large molecule as *N*-methylpyrrolidone in a certain concentration range exerts only a weak effect on the structure of water.

The broadest region of compositions in the system under consideration is region III (amide-rich solutions) covering the range $0.55 < X < 1$ (Fig. 5). Figure 6 shows that the quantities H_A^E and TS_A^E in this range are close to zero, and the functions $H_W^E(X)$ and $TS_W^E(X)$ vary insignificantly and are small and negative. Therefore, the quantities H_{A-A}^E are also virtually zero, indicating that the state of the amide molecules in this range is similar to their state in pure *N*-methylpyrrolidone. If there were free OH groups in this composition range, addition of the cyclic amide whould be accompanied by an exo effect [34]. On the other hand, in this composition range water dissolves with the same exothermic effect as in the pure organic solvent (Fig. 6). All these facts, and also the spectroscopic data [14], indicate that in composition region III water is mainly dispersed to separate molecules and is involved in heteroassociation with the amide present in excess. With a decrease in the amide concentration, the amount of the heteroassociates $2C_5H_9NO \cdot H_2O$ starts do decrease, with a simultaneous increase in the fraction of the complexes $C_5H_9NO \cdot H_2O$ [4, 14].

In composition region II ($0.4 < X < 0.55$), the functions $H_A^E(X)$ and $TS_A^E(X)$ are negative and increase in the absolute value, whereas the absolute values of the corresponding functions of water decrease (Fig. 6). This fact suggests the existence of free OH groups of water molecules, which can form not only heteroassociates but also clusters consisting exclusively of water. Such a possibility is, in particular, indicated in a study of the water–dimethylacetamide system [35]. The integral and differential characteristics of this system are close to those obtained for the water–*N*-methylpyrrolidone system. Also, in region II the interaction between *N*-methylpyrrolidone molecules becomes less preferable than in the pure amide (Fig. 5).

Between regions I and II there is a transition region $Z < X < Y$ in which the concentration dependence of $\Delta p_{int}/\Delta T$ has a bend (Fig. 2) and water undergoes the most significant structural changes. After passing through the percolation threshold (at X ~0.2), water clusters appear in the solution, which is accompanied by formation of the complexes $C_5H_9NO \cdot H_2O$ along with $C_5H_9NO \cdot 2H_2O$ [4, 14].

The role of particular constituents of intermolecular interaction in structure formation in solutions attracts much researchers' attention [2, 3]. Among different approaches suggested, the Kirkwood–Buff theory [36]

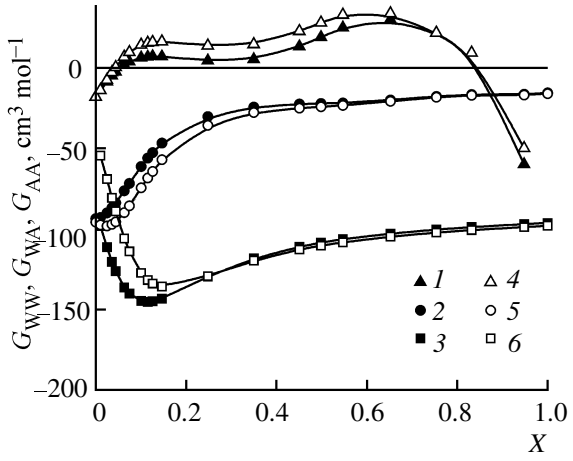

Fig. 7. Composition dependence of the Kirkwood–Buff integrals (*1, 4*) G_{WW}, (*2, 5*) G_{WA}, and (*3, 6*) G_{AA} in the water–*N*-methylpyrrolidone system at (*1–3*) 298.15 and (*4–6*) 318.15 K.

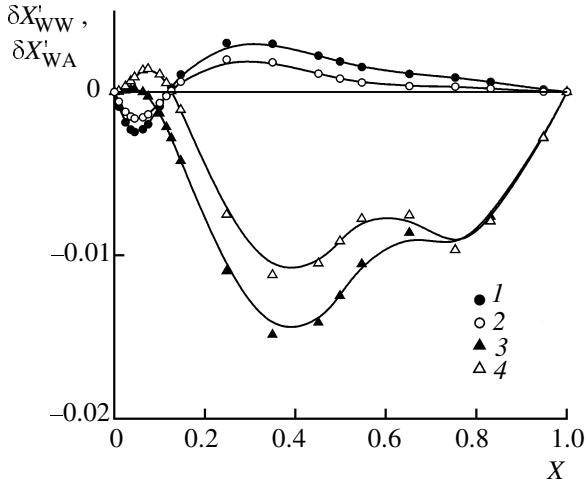

Fig. 8. Preferential solvation parameters (*1, 2*) $\delta X'_{WA}$ and (*3, 4*) $\delta X'_{WW}$ in the water–*N*-methylpyrrolidone system at (*1, 3*) 298.15 and (*2, 4*) 318.15 K.

[Eq. (8)] has been widely used in the past decades:

$$G_{ij} = \int_0^\infty (g_{ij} - 1)4\pi r^2 dr, \quad (8)$$

where g_{ij} is the function of radial distribution of molecule i around the central molecule j. Several algorithms were suggested for calculating the Kirkwood–Buff integrals, allowing the concentration dependences of G_{ij} to be obtained not only from Eq. (8), but also from experimental thermodynamic data [2, 3]. For the water–*N*-methylpyrrolidone system, we calculated these quantities (Fig. 7) from relationships (9–11) [37]:

$$G_{WA} = RT(\beta_T - V_W V_A/D), \quad (9)$$

$$G_{WW} = RT\{\beta_T + [X/(1 - X)](V_A^2/VD)\} - V/(1 - X), \quad (10)$$

$$G_{AA} = RT\{\beta_T + [(1 - X)/X](V_W^2/VD)\} - V/X, \quad (11)$$

where V is the molar volume of the mixture; V_W and V_A, partial molar volumes of water and amide [8]. The values of D were determined by Eq. (12) using data from [4]:

$$D = RT + X(1 - X)(\partial^2 G^E/\partial X^2)_{T,p}. \quad (12)$$

The integrals G_{ij} allow estimation of preferential solvation parameters [expressions (13), (14)] describing the difference between the local concentration of water (superscript L) around both components of the system and the molar concentration of water in the bulk of the solution:

$$\delta X_{WW} = X^L_{WW} - X_W, \quad (13)$$

$$\delta X_{WA} = X^L_{WA} - X_W. \quad (14)$$

Ben-Naim [38] suggested the relationships from which it is possible to calculate the quantities δX_{WW} and δX_{WA} characterizing the preferential solvation of water with water and of the amide with water. Matteoli [39] showed that an ideal reference system should be used for adequate estimation of these parameters. In this study we calculated the preferential solvation parameters (Fig. 8) by relationships (15) and (16):

$$\delta X'_{WW} = X(1 - X)(\Delta G_{WW} - \Delta G_{WA})/[(1 - X)\Delta G_{WW} + X\Delta G_{WA} + V_{cor\,W}], \quad (15)$$

$$\delta X'_{WA} = X(1 - X)(\Delta G_{WA} - \Delta G_{AA})/[(1 - X)\Delta G_{WA} + X\Delta G_{AA} + V_{cor\,A}]. \quad (16)$$

In relationships (15) and (16) we used the quantities $\Delta G_{ij} = G_{ij} - G_{ii}^{dj}$ in which the values of G_{ii}^{dj} were calculated at $G^E = V^E = 0$ [39] and the correlative volumes of the components (V_{cor}) were calculated by the same procedure as in [37].

Figure 8 shows that an increase in the temperature exerts a stronger effect on the preferential solvation of water with water $\delta X'_{WW}$ and affects $\delta X'_{WA}$ to a lesser extent. The calculated characteristics of preferential solvation supplement the set of thermodynamic parameters of the water–*N*-methylpyrrolidone system obtained above using the approaches suggested in [7, 27]. At a low concentration of the amide in solution and T 298.15 K, the parameter $\delta X'_{WW}$ is close to

zero. The negative values of $\delta X'_{WA}$ and positive values of $\delta X'_{AA}$ ($\delta X'_{AA} = -\delta X'_{WA}$) are indicative of hydrophobic interaction between the amide molecules, due to the presence of alkyl substituents. This composition region is followed by a broad region in which the water structure is broken ($\delta X'_{WW} < 0$, minimum at $X \sim 4$) and water preferentially solvates *N*-methylpyrrolidone ($\delta X'_{WA} > 0$, maximum at $X \sim 0.3$). At $X \sim 0.8$, $\delta X'_{WA} \sim 0$ (Fig. 8). On the whole, the preferential solvation in the water–*N*-methylpyrrolidone system is relatively weakly pronounced compared to aqueous solutions of nonelectrolytes with stronger hydrophobic properties [3].

Thus, analysis of the thermodynamic characteristics of aqueous solutions of *N*-methylpyrrolidone in the range 298.15–338.15 K indicates that in the examined system there are three composition regions with the prevalent type of structural organization and an intermediate region $0.07 < X < 0.4$. In the narrow range $0 < X < 0.07$, *N*-methylpyrrolidone only weakly affects the structure of water and forms heteroassociates $C_5H_9NO \cdot 2H_2O$, and hydrophobic interaction between amide molecules is observed. With a further increase in the *N*-methylpyrrolidone concentration, the three-dimensional network of hydrogen bonds of water is perturbed and finally fully broken at $X \sim 0.2$. At $X \sim 0.33$, the composition dependences of $H^E(X)$ and $S^E(X)$ pass through a minimum, which is caused by formation of the maximal amount of the heteroassociates $C_5H_9NO \cdot 2H_2O$. A sharp decrease in the specific contribution and an increase in the nonspecific contribution to the total energy of intermolecular interaction at $X < 0.35$ additionally confirm the fact that in this range the structure of water undergoes the most dramatic changes. In the range $0.4 < X < 0.55$, most probably, homoassociates of both components and heteroassociates of various compositions are present simultaneously. In the widest range of amide-rich compositions, $0.55 < X < 1$, water is predominantly dispersed to monomeric molecules and is incorporated in heteroassociates $2C_5H_9NO \cdot H_2O$ and $C_5H_9NO \cdot H_2O$.

REFERENCES

1. Hradetzky, G., Hammerl, I., Kisan, W., Wehner, K., and Bittrich, H.J., *Data of Selective Solvents,* Berlin: Wissenschaften, 1989.
2. Belousov, V.P. and Panov, M.Y., *Thermodynamic Properties of Aqueous Solutions of Organic Substances,* Boca Raton: CRC, 1994.
3. Kessler, Yu.M. and Zaitsev, A.L., *Sol'vofobnye effekty* (Solvophobic Effects), Leningrad: Khimiya, 1989.
4. Zaichikov, A.M., Bushuev, Y.G., and Krestov, G.A., *J. Thermal. Anal.,* 1995, vol. 45, no. 4. p. 687.
5. Rodnikova, M.N., *Zh. Fiz. Khim.,* 1993, vol. 67, no. 2, p. 275.
6. Kartsev, V.N., Rodnikova, M.N., Bartel, I., and Shtykov, S.N., *Zh. Fiz. Khim.,* 2002, vol. 76, no. 6, p. 1016.
7. Kartsev, V.N., Rodnikova, M.N., Shtykov, S.N., and Bartel, I., *Zh. Fiz. Khim.,* 2003, vol. 77, no. 8, p. 1456.
8. George, J. and Sastry, V.N., *J. Chem. Eng. Data,* 2004, vol. 49, no. 2, p. 235.
9. Vasilev, V.A. and Novikov, A.N., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.,* 1989, vol. 32, no. 12, p. 53.
10. Uosaki, Y., Kitaura, S., Iwama, F., and Moriyoshi, T., *J. Chem. Thermodyn.,* 1991, vol. 23, no. 11, p. 1125.
11. Mikhailov, V.A. and Kirgintsev, A.N., *Zh. Fiz. Khim.,* 1962, vol. 36, no. 9, p. 2085.
12. Assarsson, P. and Eirich, F.R., *J. Phys. Chem.,* 1968, vol. 72, no. 8, p. 2710.
13. Carver, T.J., Drew, M.G.B., and Rodger, P.M., *Phys. Chem. Chem. Phys.,* 1999, vol. 1, no. 15, p. 1807.
14. Afanasenko, L.D., Yarym-Agaev, N.L., and Bilobrov, V.M., *Ukr. Khim. Zh.,* 1987, vol. 53, no. 2, p. 153.
15. Bushuev, Yu.G. and Korolev, V.P., *Kontsentrirovannye i nasyshchennye rastvory* (Concentrated and Saturated Solutions), Moscow: Nauka, 2002, p. 255.
16. Dack, M.R., *Aust. J. Chem.,* 1975, vol. 28, no. 8, p. 1643.
17. Holtzer, A. and Emerson, M.F., *J. Phys. Chem.,* 1969, vol. 73, no. 1, p. 26.
18. Durov, V.A., in *Rastvory neelektrolitov v zhidkostyakh* (Solutions of Nonelectrolytes in Liquids), Moscow: Nauka, 1989, p. 36.
19. Vargaftik, N.B., *Spravochnik po teplofizicheskim svoistvam gazov i zhidkostei* (Handbook on Thermal Properties of Gases and Liquids), Moscow: Nauka, 1972.
20. Marcus, Y., *Ion Solvation,* New York: Wiley, 1985.
21. Eastland, G.W., Rao, D.N.R., and Symons, M.C.R., *J. Chem. Soc., Faraday Trans. 1,* 1986, vol. 82, no. 10, p. 2833.
22. Langan, J.R. and Salmon, G.A., *J. Chem. Eng. Data,* 1987, vol. 32, no. 4, p. 420.
23. Bushuev, Yu.G. and Zaichikov, A.M., *Izv. Ross. Akad. Nauk, Ser. Khim.,* 1998, vol. 47, no. 1, p. 21.
24. Zaichikov, A.M. and Krest'yaninov, M.A., *Russ. J. Gen. Chem.,* 2004, vol. 74, no. 11, p. 1665.
25. Chalaris, M. and Samios, J., *J. Chem. Phys.,* 2000, vol. 112, no. 19, p. 8581.

26. Bittrich, H.J. and Kirsch, D., *Z. Phys. Chem. (Leipzig),* 1975, vol. 256, no. 5, p. 808.
27. Koga, Y., *J. Phys. Chem.,* 1996, vol. 100, no. 13, p. 5172.
28. Koga, Y., *Netsu Sokutei,* 2003, vol. 30, no. 2, p. 54.
29. Mancera, R.L., Chalaris, M., Refson, K., and Samios, J., *Phys. Chem. Chem. Phys.,* 2004, vol. 6, no. 1, p. 94.
30. Lyashchenko, A.K., Lileev, A.S., and Borina, A.F., *Zh. Fiz. Khim.,* 1998, vol. 72, no. 10, p. 1863.
31. Lyashchenko, A.K., Lileev, A.S., Palitskaya, T.A., and Ostroushko, A.A., *Zh. Fiz. Khim.,* 2001, vol. 75, no. 2, p. 250.
32. Davis, M.I., *Thermochim. Acta,* 1987, vol. 120, no. 1, p. 299.
33. Garcia, B., Alcalde, R., and Leal, J.M., *J. Phys. Chem. B,* 1997, vol. 101, no. 40, p. 7991.
34. Solomonov, B.N., Borisover, M.D., and Konovalova, L.K., *Zh. Obshch. Khim.,* 1986, vol. 56, no. 6, p. 1345.
35. Zaichikov, A.M. and Bushuev, Yu.G., *Zh. Fiz. Khim.,* 1995, vol. 69, no. 11, p. 1942.
36. Kirkwood, J.G. and Buff, F.P., *J. Chem. Phys.,* 1951, vol. 19, no. 6, p. 774.
37. Marcus, Y., *J. Chem. Soc., Faraday Trans. 1,* 1990, vol. 86, no. 12, p. 2215.
38. Ben-Naim, A., *Pure Appl. Chem.,* 1990, vol. 62, no. 1, p. 25.
39. Matteoli, E., *J. Phys. Chem. B,* 1997, vol. 101, no. 47, p. 9800.