Calculations of concentration dependences of chemical shifts for acrylamide in water—DMSO mixed solvent

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The lattice model of associated solutions was used to calculate the concentration dependences of the chemical shifts of ^{13}C magnetic nuclei in the acrylamide molecule in water—DMSO solvent. Each pair of bonds between the acrylamide group containing a magnetic nucleus and the neighboring solvent molecule was assumed to additively contribute to the change in the chemical shift of the nucleus in question. The new approach affords the same accuracy in describing the experimental data at any ratios of the solution components. It was shown that the chemical shifts and the excess heat of mixing of the water—DMSO binary solution can be simultaneously described using the same set of energy parameters of the model. The model makes it possible to employ experimental data on chemical shifts for studying intermolecular interactions in solutions.

Key words: water—DMSO solution, acrylamide, specific interactions, chemical shifts, lattice model of solution.

The formation of specific bonds results in changing the values of chemical shifts of magnetic nuclei in molecules depending on the solution composition.[1–3] Taking the acrylamide—water—dimethylsulfoxide (DMSO) system as an example, it has been established that the composition of water—DMSO mixed solvent has a strong effect on the chemical shifts of ^{13}C nuclei in acrylamide while the proton chemical shifts are little affected.[4–6]

Usually, the following relationships[1,7,8] are used to calculate the concentration dependences of chemical shifts of magnetic nuclei (m), $1 \le m \le f$ (f is the number of different magnetic nuclei in the molecule i) in the case of fast (in the NMR time scale) exchange between different states:

$$\delta^i(m)A_i = \Sigma_q n_q^i N_q^i \delta_q^i(m),\ A_i = \Sigma_q n_q^i N_q^i,\quad 0 \le q \le p, \qquad (1)$$

where n_q^i is the number of molecules i in the associate q, $1 \le q \le p$, and p is the number of different associates containing molecules i in solution; $q = 0$ corresponds to free molecules i; N_q^i is the number of species q; and A_i is the total number of molecules i in solution. As has been shown experimentally,[1,3] the $\delta_q^i(m)$ values remain unchanged while the number of different associates N_q^i is changed as the concentrations of the solution components change. The latter are usually calculated using the mass action law[3] strictly substantiated for ideal solutions.[9] Previously,[7,8] an experimental procedure for studying concentration dependences of chemical shifts for arbitrary ratios of the solution components was proposed; this procedure makes it possible to obtain $\delta_q^i(m)$ values without using the mass action law. This procedure is based on the hypothesis that the minimum possible number (p) of different associates is realized in solution and that linear portions of the concentration dependence $\delta^i(m)$ with a predominant contribution of one associate can be located.

Lattice models of associated solutions,[10] among which the Barker model[11] is the most widely used, provide another possibility to exclude the mass action law when calculating chemical shifts. In this work this model is used for calculating the concentration dependences of chemical shifts of the ^{13}C magnetic nuclei of acrylamide in the water—DMSO solution.

We will assume that the total volume of the s-component solution is divided into elementary volumes of the order of the size of the smallest component of the mixture. Large molecules are divided into several elements, and each of them occupies one lattice site. Let the molecules of the sort i ($1 \le i \le s$, s is the number of solution components) occupy m_i lattice site with the coordination number z. If Q_i is the number of nearest neighboring points for the type i molecule (for chain molecules, $Q_i = zm_i - 2m_i + 2$ [10]), then the surface of the molecule can be divided into Q_i parts (the so-called contacts) and it can be assumed that each of them has a specific energy of interaction with the neighboring contact of another molecule. For instance, if molecules i and j occupy neighboring points in such a way that contact k of molecule i is contiguous to contact n of molecule j, then the $\varepsilon_{ij}^{k,n}$ parameters are the average

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energies of interaction between these contacts (positive $\varepsilon_{i,j}^{k,n}$ correspond to attraction).

Let $N_{i,j}^{k,n}$ be the total number of cases when contact k of component i is immediately contiguous to contact n of component j. Since all lattice sites are assumed to be occupied by the solution components, then $N_{i,j}^{k,n}$ are mutually related by the following relationship: $2N_{i,i}^{k,k} + \Sigma_{j,n}N_{i,j}^{k,n} = N_i$, where N_i is the number of the molecules of component i in solution. Let us assume that Q_i contacts of molecule i can be grouped to form σ_i classes and that Q_i^k is the number of contacts in class k of molecule i, $\Sigma_k Q_i^k = Q_i$, $1 \le k \le \sigma_i$. (All contacts of the same class are energetically equivalent.) Then, the normalizing relations for the contact pairs take the form

$$\theta_{i,j}^{k,n} = (1 + \Delta_{i,j}^{k,n})N_{i,j}^{k,n}/M,$$

$$M = \Sigma_{i,k}Q_i^k N_i,\quad \Sigma_{i,k}\Sigma_{j,n}\theta_{i,j}^{k,n} = 1,\quad \Sigma_{j,n}\theta_{i,j}^{k,n} = \theta_i^k,$$

$$\Sigma_{i,k}\theta_i^k = 1,\quad \theta_i^k = x_i\xi_i^k,\quad \xi_i^k = Q_i^k/\Sigma_{j,n}x_jQ_j^n,$$

$$\Sigma_i x_i = 1,\quad 1 \le i,j \le s,\quad 1 \le k \le \sigma_i,\quad 1 \le n \le \sigma_j, \qquad (2)$$

where $\Delta_{i,j}^{k,n} = 1$ if $i = j$ and $k = n$ (otherwise $\Delta_{i,j}^{k,n} = 0$); M is the doubled number of pairs of contacts; $x_i = N_i/\Sigma_l N_l$ is the mole fraction of component i; the function $\theta_{i,j}^{k,n}$ is the probability of the formation of a pair of contacts between contact k of molecule i and contact n of molecule j; and θ_i^k is the probability for the randomly chosen contact to be a type k contact of molecule i. We also used the function $t_{i,j}^{k,n} = \theta_{i,j}^{k,n}/\theta_i^k$, which is the conditional probability for contact n of molecule j be contiguous to contact k of molecule i; $\Sigma_{j,n}t_{i,j}^{k,n} = 1$.

The equilibrium probabilities of the formation of pairs of contacts between different molecules are related by the following relationship:[11]

$$\theta_{i,i}^{k,k}\theta_{j,j}^{n,n} = (\theta_{i,j}^{k,n})^2\exp\beta(\varepsilon_{i,i}^{k,k} + \varepsilon_{j,j}^{n,n} - 2\varepsilon_{i,j}^{k,n}),$$
$$\beta = 1/kT. \qquad (3)$$

Equation (3) is a generalization of the quasi-chemical approximation for spherically symmetric one-site species[10,12] for certain pairs of contacts of neighboring molecules of arbitrary size. (Formally, a random distribution of the contacts over the surface of the molecule in question is implied.) The following system of equations for equilibrium distribution of contact pairs can be obtained from expressions (2) taking into account relationship (3):

$$x_i\xi_i^k = u_i^k\Sigma_{j,n}u_j^n\exp(\beta\varepsilon_{i,j}^{k,n}),$$

$$u_i^k = [\theta_{i,i}^{k,k}\exp(-\beta\varepsilon_{i,i}^{k,k})]^{1/2}. \qquad (4)$$

Here u_i are variables; the concentrations of the components (x_i), the structural model of the solution (ξ_i), and the intermolecular interactions between the contacts ($\varepsilon_{i,j}^{k,n}$) are assumed to be known. The system of equations (4) makes it possible to calculate all equilibrium characteristics of the solution; we used this system to describe the dependences of chemical shifts of the ^{13}C magnetic nuclei of acrylamide on the water—DMSO solvent composition and the excess heat of mixing of binary water—DMSO solution, which is determined from the following equation:[11]

$$H = \Sigma_{i,k}\Sigma_{j,n}\theta_{i,j}^{k,n}\varepsilon_{i,j}^{k,n} - \Sigma_i H_i x_i,\quad H_i = \Sigma_k\Sigma_n\theta_{i,i}^{k,n}\varepsilon_{i,i}^{k,n}, \qquad (5)$$

where H_i is the enthalpy of the pure component i; the $\theta_{i,i}^{k,n}$ values for each i are determined from reduced systems (4) in which $x_i = 1$.

In the model (2—4), the pair contacts are basic concepts, whereas in the theory of associative equilibria those are the types of associates (see formula (1)). It should be noted that relationship (1) contains no explicit indication of functional groups of the molecules forming the associate and it is implied that only one structure of the associate is formed at fixed number of molecules i. This is inadequate if associates can be formed from several functional groups, since in this case the associates can have different structures. Therefore, the sum over different associate structures at q = const should be introduced into Eq. (1).

On the other hand, the model (2—4) takes into account all possible contacts of neighboring molecules; therefore any structural distinctions of the associates of fixed composition can be accounted for. In the Barker model, the probability of associate formation is expressed through the product of averaged proportion of contact pairs as $x_i\Pi_k(\xi_i^k t_{i,j}^{k,n})$ (the index k runs through all classes of contacts of molecule i); here the sort of molecule j and the type of its contact n are unambiguously related to the kind of the associate q under consideration. As a result, in the Barker model the observed chemical shift $\delta^i(m)$ is represented as the sum over $\Delta\delta_{i,j}^{k,n}(m)$ contributions from neighboring contact k of molecule i and contact n of molecule j instead of the sum over $\delta_q^i(m)$ contributions of associates as was done in Eq. (1). Let us accept that each associative bond produces a local perturbation and that the redistribution of the electron density results in an additive change, *i.e.*, $\delta_q^i(m) = \Sigma_{j,n}\Delta\delta_{i,j}^{k,n}$. Then we can write instead of Eq. (1):

$$\delta^i(m) = \Sigma_k\Sigma_{j,n}\,\Delta\delta_{i,j}^{k,n}(m)t_{i,j}^{k,n}, \qquad (6)$$

where the k index enumerates fragments of molecule i, responsible for the change in the chemical shift of the nucleus m because of the formation of associative bonds, and the j and n indices in the second sum run through all components and classes of the contacts in solution.

To describe the concentration dependences of chemical shifts of the ^{13}C magnetic nuclei of acrylamide in the water—DMSO solution,[4—6] the lattice structure of the solution with $z = 4$ was specified. (This number accounts best for directionality of the inner bonds in molecules of all solution components among the simplest three-dimensional lattice structures with z = 4, 6, 8, and 12.) Taking into account the relationships between molar volumes of the molecules, we postulate that the water molecule (sort A) occupies 1 lattice site

($m_A = 1$), the DMSO molecule (sort B) occupies 3 lattice sites ($m_B = 3$), and the acrylamide molecule (sort M) occupies 4 lattice sites ($m_M = 4$). The isolation of contacts should be associated with specific molecular structure. To simulate the dipole structure of water molecule ($\sigma_A = 2$, $Q_A = 4$), two types of contacts were taken into account, *viz.*, contacts of hydrogen atoms ($Q_A{}^1 = z/2$) and those of oxygen atom ($Q_A{}^2 = z/2$). Three types of contacts were taken into account for DMSO molecules ($\sigma_B = 3$, $Q_B = 8$), *viz.*, the first and the second on the S=O group and the third on the CH_3 group; $Q_B{}^1 = Q_B{}^2 = (z - 2)/2$, $Q_B{}^3 = 2(z - 1)$, since the CH_3 group and O and S atoms differ appreciably in their chemical properties. (This representation takes into account the character of local charge distribution in the molecules, though the molecules themselves are electroneutral.)

The experiment on studying the concentration dependences of chemical shifts was carried out for low acrylamide concentrations (sort M); therefore, the solvent was considered as a binary solution and the contacts between neighboring acrylamide molecules were neglected. The description of chemical shifts was performed for the carbon atoms in CH_2 and CO groups. Since no experimental data for different temperatures were available, it was assumed for simplicity that the contributions to the chemical shift from the acrylamide contacts with different parts of the same solvent molecule are equal (*i.e.*, the averaged effect of the neighboring molecule on the states of magnetic nuclei was taken into account). In this case Eq. (6) takes the form:

$$\delta_M{}^m(x) = \Sigma_{i=A,B}\delta_M{}^m(x_i = 1)t_{Mi}{}^m(x_i),$$

$$t_{Mi}{}^m(x_i) = \Sigma_n t_{Mi}{}^{m,n}(x_i), \qquad (7)$$

where $\delta_M{}^m(x_i = 1)$ is the value of chemical shift in pure solvent i, which can be taken from experimental data at $x_i = 1$, and $i = A,B$. The function $t_{Mi}{}^{m,n}$ is defined from normalization and quasi-chemical approximation as

$$t_{Mi}{}^{m,k} = u_i{}^k\exp(\beta\varepsilon_{\mu i}{}^k)/\Sigma_{j=A,B}\Sigma_{n\in j}u_j{}^n\exp(\beta\varepsilon_{Mi}{}^{m,n}).$$

Usually, the existence of specific interactions suggests that there are certain interactions of atoms or functional groups whose contributions to the energetics of the system are much larger than those of other interactions that are considered to be close to zero. There is a large number of unknown parameters in the Barker model (due to the large number of the types of pair contacts); therefore, in practice, only parameters of the most substantial interactions are taken as nonzero parameters.[10,11] Application of the model to calculating the excess heats of mixing of the binary water—DMSO solution makes it possible to obtain a satisfactory description of experimental data[13] (Fig. 1) for different sets of interaction parameters. Curve *1* corresponds to the case where the parameters of interactions of water molecules, DMSO molecules, and other molecules are commensurable and equal to 20.2 kJ mol^{-1}. Such a value is typical of the estimates of the hydrogen bond energy. (The bonds mentioned above determine the major specific interactions in the system.) Curve *2* corresponds to a somewhat higher energy of the bond between water molecules and to a somewhat lower energy of the bond between the OS groups in DMSO molecules (the energy of the OH—OS bond is close to that for curve *1*). Going to more complex models of intermolecular interactions improves the agreement with experimental data. The parameters of lateral interaction obtained from data on excess heat of mixing were fixed and used for calculating the concentration dependences of chemical shifts. In this case, the parameters of the interaction between the CH_2 and CO functional groups of acrylamide and the solvent components were varied. With the first set of parameters, typical curves qualitatively describing the situation at low (for CO) or high water content (for CH_2) are obtained (see curves *1* in Figs. 2 and 3). The more complex model (variant 2) gives a satisfactory description of experimental data (see curves *2* in Figs. 2 and 3). The negative values of the energy parameters of contact pairs indicate that the formation of such pairs is unlikely.

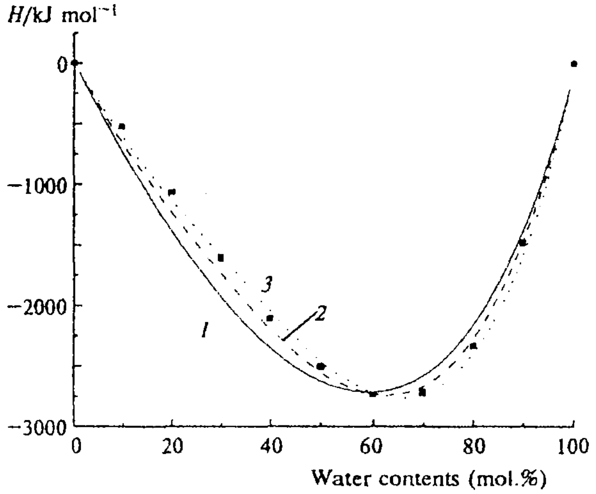

Fig. 1. The excess enthalpy of mixing of water—DMSO solution. The points are experimental data; the parameters of interaction (ε/kJ mol^{-1}) are: *1*, $\varepsilon_{OH-HO} = 20.2$; *2*, $\varepsilon_{OH-HO} = 22.4$, $\varepsilon_{OS-SO} = 10.7$, $\varepsilon_{OH-SO} = \varepsilon_{HO-OS} = 18.9$; and *3*, $\varepsilon_{OH-HO} = 22.4$, $\varepsilon_{OS-CH_3} = 10.7$, $\varepsilon_{OH-CH_3} = \varepsilon_{OS-CH_3} = 20.2$.

Generally, the solution of the problem of determining the energy parameters from experimental data is ambiguous. There is another complete set of parameters which also satisfactorily describes experimental data (see curves *3* in Figs. 1—3) but is physically meaningless. The non-physical character of the values of the parameters lies in the fact that the interactions between CH_3 groups prevail in DMSO molecules, whereas relatively inert CH_3 and CH_2 functional groups strongly interact with OH and OS groups. Thus, it is necessary to have control over the physical meaning of fitting parameters. To select the solutions found, additional experimental data should be used. They might be, *e.g.*, more detailed data of measurements of characteristics under study (the data in Figs. 2 and 3 are not numerous) and a larger number of different characteristics at different temperatures (here, only two equilibrium characteristics at the same temperature are taken). To estimate the parameters found, it is possible to use either known data on the atom-atom interactions (procedures for such estimations has been reported in the literature[14,15]) or quantum-chemical calculations. In the latter case, one more likely deals with correlations rather than with direct numerical comparison.

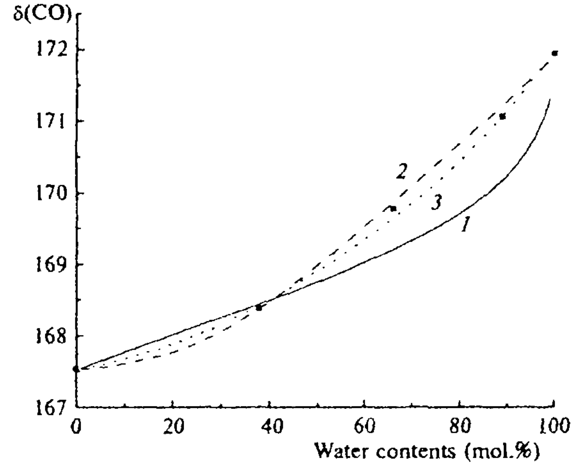

Fig. 2. The concentration dependence of the chemical shift of the carbon atom in the C=O group. The points are experimental data; the parameters of interaction between the C=O group and solvent contacts (ε/kJ mol^{-1}) are: *1*, $\varepsilon_{CO-OH} = \varepsilon_{CO-OS} = 10$; *2*, $\varepsilon_{CO-OH} = 10$, $\varepsilon_{CO-OS} = 9$, $\varepsilon_{CO-CH_3} = -10$; and *3*, $\varepsilon_{CO-OH} = 20.2$, $\varepsilon_{CO-OS} = 12.6$. For the parameters of interaction between the solvent molecules, see Fig. 1.

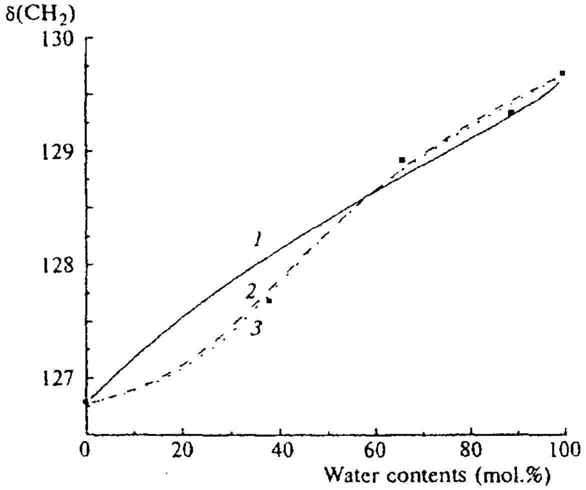

Fig. 3. The concentration dependence of the chemical shift of the carbon atom in the CH$_2$ group. The points are experimental data; the parameters of interaction between the CH$_2$ group and contacts of solvent molecules (ε/kJ mol^{-1}) are: *1*, $\varepsilon_{CH_2-OH} = \varepsilon_{CH_2-OS} = 15$; 2, $\varepsilon_{CH_2-OH} = 13$, $\varepsilon_{CH_2-OS} = 9.1$, $\varepsilon_{CH_2-CH_3} = -10$; and *3*, $\varepsilon_{CH_2-OH} = 15$, $\varepsilon_{CH_2-OS} = 10$, $\varepsilon_{CH_2-SO} = -6.3$, $\varepsilon_{CH_2-CH_3} = -5$. For the parameters of interaction between the solvent molecules, see. Fig. 1.

The correlation found between chemical shifts of ^{13}C magnetic nuclei in the C=O and C=C functional groups in the acrylamide molecule (Fig. 4) plays an important role in changing the reactivity of the double C=C bond with changing the solvent composition due to the electron density conjugation between the C=O and C=C groups.[4,5] Calculations of concentration dependences for the system in question using the known procedure[8,9] give a linear correlation between the chemical shifts of both carbon-containing groups (see Fig. 4, curve *1*). The use of the lattice model results in a good agreement with the experimental correlation (curve *2*). This model makes it possible to give a more accurate description of this correlation without describing the electron density conjugation between the C=O and C=C groups.

Thus, the approach proposed for analyzing the concentration dependences of the chemical shifts of magnetic nuclei in the components of associated solutions makes it possible to describe experimental data for all ranges of concentrations of the components with the same accuracy (in contrast to the equations of the mass action law which are only valid at low concentrations of associates) and can be used for the solutions of components with any ratios of molar volumes. The parameters of the lattice model have a clear physical meaning, *viz.*, they are the average values of the energies of interactions between neighboring functional groups and can be determined from independent experimental data (*e.g.*,

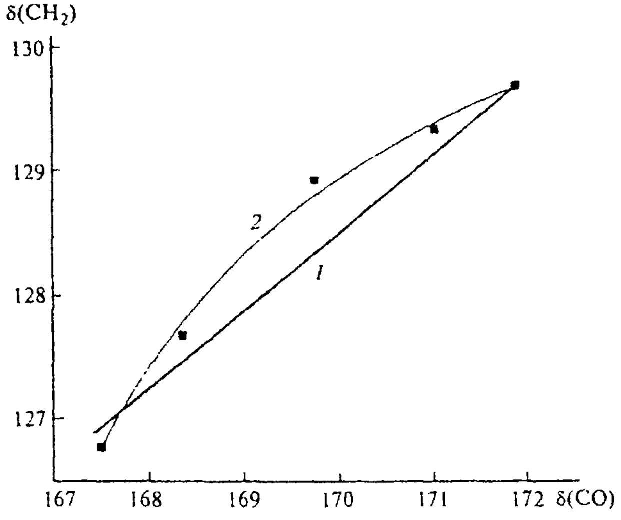

Fig. 4. Dependence of the chemical shift of the carbon atom in the CH$_2$ group on the chemical shift of the carbon atom in the C=O group; *1*, reference data;[8,9] *2*, parameters of curves *2* and *3* as in Figs. 1—3; the points are experimental data.

from data on the heats of mixing or vapor—liquid equilibrium). In principle, these parameters can be estimated using the potential functions of intermolecular interaction (for instance, the atom-atom potentials[14,15]) or quantum-chemical calculations. This approach makes possible to use experimental data on the concentration dependences of chemical shifts for obtaining information on intermolecular interactions in solutions as an alternative or complementary investigation technique.

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