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Experimental determination of rotational motion correlation times of choline iodide in aqueous solutions

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The influence of complexation on the molecular reorientation of choline iodide in dilute aqueous solutions was determined using the multiplet relaxation effect of ^{13}C nuclei.

Key words: multiplet relaxation effect, ^{13}C NMR spectroscopy, auto- and cross-correlation times, molecular reorientation, clathrate-like structures, choline iodide.

Ion mobility in aqueous solutions of electrolytes is studied by different computational[1] and experimental methods[2—6] based on measurements of compressibility, viscosity, dielectric losses, diamagnetic susceptibility of sonic speed, and diffusion. NMR spectroscopy is often used presently to study rotational diffusion correlation times of ions in aqueous solutions of electrolytes.[7—9] Chemical shifts and nuclear magnetic relaxation times are usually used as spectral parameters. Concentration- and temperature-induced changes in the spectral parameters allow one to conclude about ion mobility.

Two approaches are mainly used to study the dynamic properties of aqueous solutions using the nuclear magnetic relaxation method. The first approach is based on the determination of relaxation characteristics of protons of water and deuterons of heavy water for different concentrations of a dissolved salt and at different temperatures. Then, Samoilov´s model is used for aqueous solutions of salts to interpret the results obtained.[6] The second approach is based on the study of dynamic characteristics of polyatomic ions by magnetic relaxation.[10] The application of both approaches is exemplified in Refs 10 and 11.

The first approach was used[12] to study the hydration properties of tetraalkylammonium ions in heavy water using ^{2}D quadrupole relaxation. The authors concluded[12] that these solutions are specific due to high hydration numbers and a significant elongation of the correlation time τ_D owing to the structure-strengthening properties of tetraalkylammonium ions. The correlation time τ_D of water molecules in the free state is 8 ps, while the correlation time of these molecules in hydrate shells of the tetraethylammonium ions Et_4N^+ is 20 ps.[12] The correlation time of water molecules in the hydrate shells of Br^- is 5 ps, which indicates the structure-destruction properties of these ions. We used the second approach to study the dynamic characteristics of the ammonium ions.

Earlier,[13] the concentration dependences of the spin-lattice relaxation of protons of water and deuterons of heavy water were studied in strongly dilute solutions of the choline salts. The local maxima in the curves of these plots were explained[13] by the formation of clathrate-like structures in the solution. However, the dynamic characteristics of the ions were not studied. The temperature dependence of the spectral parameters of the ions was studied[14] by ^{13}C and ^{14}N NMR spectroscopy. At the same time, it should be taken into account that the knowledge of temperature dependences of these parameters in saturated aqueous solutions does not allow the correct determination of diffusion characteristics of ions in dilute solutions.

An analysis of published data indicate that molecular mobility in aqueous solutions was studied in numerous works using nuclear magnetic relaxation, although it is difficult to interpret experimental data. Since information obtained is very important, it seems reasonable to continue these studies.

The purpose of the present study is the experimental determination of the rotational motion correlation times of choline iodide using ^{13}C nuclear magnetic relaxation in aqueous solutions.

Choline iodide was chosen because of its possible participation in the formation of clathrate-like structures that has previously[15] been assumed. Moreover, choline iodide is characterized by the most pronounced concentration dependences of the relaxation characteristics of the ^{1}H and ^{2}D nuclei.[13]

Therefore, we studied the dynamic characteristics of systems forming clathrate-like structures and the rotation characteristics of choline iodide determined from the data on ^{13}C nuclear magnetic relaxation.

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Experimental

The relaxation characteristics of ^{13}C nuclei of choline iodide were measured on an FT-80A NMR spectrometer using the inversion—recovery method.[7,16]

The cross-correlation times τ'_{CH} were determined[17,18] using the known equation

$$\tau'_{CH} = 4\pi\int_0^\infty \left\langle Y_{20}(\theta_i(t))Y_{20}(\theta_j(0))\right\rangle dt, \qquad (1)$$

where Y_{20} is the spherical harmonic; θ_i and θ_j are the angles between the CH_i and CH_0 vectors, respectively, and magnetic field direction; and brackets imply averaging over an ensemble. For $i = j$, we obtain the expression for the autocorrelation (correlation) time τ_{CH} from formula (1).

The rotational autocorrelation times τ_{CH} for CH vectors were experimentally determined from a slope of the relaxation curves of the overall magnetization vector of the ^{13}C nuclei and the Overhauser coefficient η using the equation[16]

$$\tau_{CH} = 2W_C\eta r_{CH}{}^6/(\hbar^2\gamma_C\gamma_H{}^2N),$$

where W_C is the spin-relaxation rate of the ^{13}C nuclei for the CH_N group, $\hbar$ is Planck's constant, γ is the gyromagnetic ratio, r_{CH} is the distance between the H and C nuclei, η is the Overhauser coefficient, and N is the number of protons in the alkyl group ($N = 2, 3$).

The accuracy of τ_{CH} determination is 5—10 rel.%, depending on the choline iodide concentration. The rotational cross-correlation times $\tau'_{CH'}$ for the CH′ and CH″ vectors of the CH_N group were experimentally found from the initial relaxation rates of the outermost and central multiplet lines in the ^{13}C NMR spectrum using the equation[17]

$$\tau'_{CH} = 5/[N(N+1)]\cdot[r_{CH}{}^6/(\hbar^2\gamma_C{}^2\gamma_H{}^2)]\cdot(W_0 - W_i),$$

where W_0 and W_i are the initial relaxation rates of the outermost and central multiplet lines in the ^{13}C NMR spectrum (multiplet effect) of the CH_N group. The rotational correlation times τ_0 for the symmetry axis of the CH_3 group was calculated by the formula[18]

$$\tau_0 = 3(\tau_{CH} + 2\tau'_{CH}).$$

All measurements were carried out at 38±1 °C. Experimental results were analyzed using the TENZOR-2 program[7] based on the modified Kirkwood—Steel—Huntress (KSH) theory.[19,20] This theory relates components of the rotational diffusion tensor D_{xx}, D_{yy}, and D_{zz} to the second derivatives of the intermolecular interaction potential. Using the Langevin equation for rotational motion, the D_{xx} component of the rotational diffusion tensor can be written as follows:

$$D_{xx} = k_BT\sqrt{\pi/(2I_{xx})}\left\langle\partial^2U/\partial\theta_x^2\right\rangle^{-(1/2)},$$

where I_{xx} is the molecular moment of inertia relatively to the x axis, θ_x is the rotation angle relatively to the x axis, k_B is the Boltzmann constant, and brackets mean averaging. The potential (U) describing the interaction between solvent molecules s and atoms k of solute molecules has the form

$$U = \sum_{ks}V_{ks}(r_{ks}) = 4\varepsilon_{ks}\sum_{ks}[(\sigma_{ks}/r_{ks})^6 - (\sigma_{ks}/r_{ks})^{12}],$$

where ε_{ks} and σ_{ks} are the parameters of the Lennard-Johnes potential, and r_{ks} is the distance between the k-th atom of the substance molecule and the s-th solvent molecule.

The auto- and cross-correlation times of CH vector reorientation of the choline iodide molecules and ions were calculated by the TENZOR-2 program[7] using the effective interaction model.[21] The auto- and cross-correlation times of the CH vectors were calculated for all alkyl groups of choline.

To analyze the experimental results, we calculated the correlation characteristics of the CH vectors of all alkyl groups of choline iodide and its ion in the free and bound states using the TENZOR-2 program. The geometric parameters for the ion model have been published earlier.[22] The results of published works[14,23—25] were taken into account in the refinement of the conformational state of the molecule. To describe intermolecular interactions of choline iodide with water, we used the four-parameter effective center: σ_{eff}, ε_{eff}, m_{eff}, d_{eff} (effective interaction model).[25]

It is necessary to use the effective interaction model because of strong interactions between the choline iodide molecules and water molecules in an aqueous solution. The essence of the effective interaction model is the replacement of the OH group by an effective interaction center. The interaction parameters and position of this center reflect a possibility of binding of the water molecules by the OH group. The interaction potential of the effective center is a Lennard-Johnes one. For the formation of these structures, the main factor determining the arrangement of molecules is considered to be geometry, whereas the long-range electrostatic forces are, probably, secondary.[22,26,27]

Results and Discussion

The experimental concentration plots of the correlation times of the CH vectors of choline iodide molecules are presented in Fig. 1. It is seen that the correlation times of the CH vectors are minimum within a concentration range of 0.03—0.05 mol. fraction (molar fraction is the ratio of solute molecules to the total number of molecules, *i.e.*, the sum of molecules of the solute and solvent). In addition, note that the most significant change in the correlation times is observed for the CH vectors related to the methylene group $^bCH_2$, which is directly bonded to the N atom. The correlation times τ_{CH} of the CH vectors of the $^aCH_2$ group, which is bound to the O atom, change to a less extent than those of the above-discussed group. The lowest change is characteristic of τ_{CH} of the CH vectors of the CH_3 group. Thus, we can conclude that τ_{CH} of all the CH vectors decrease with a decrease in the choline iodide concentration, which indicates an increase in the freedom of molecular motion. This result does not contradict the classical concepts on molecular motion in solutions.

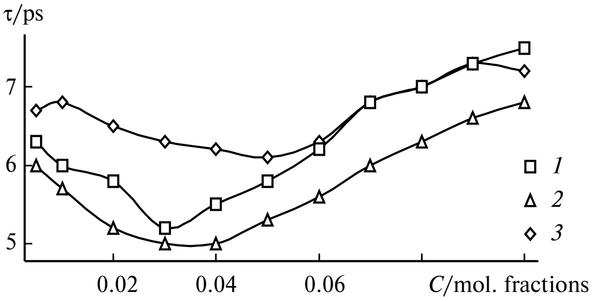

Fig. 1. Concentration plots of the correlation times τ_{CH} of choline iodide $HO^aCH_2{}^bCH_2N^+(^cCH_3)_3I^-$: $^aCH_2$ (*1*), $^bCH_2$ (*2*), and $^cCH_3$ (*3*).

According to published data,[12] the intramolecular reorientation of the CH vectors in a choline iodide molecule is the most inhibited for the methylene group $^bCH_2$, while the methyl group exhibits the least retardation. Therefore, according to the known regularities on contributions of different types of molecular motions to correlation times, we can assume that changes in the reorientation of choline iodide molecules, as a whole, have the strongest influence on the correlation times of the CH vectors of $^bCH_2$. The dependence found shows that the correlation time τ_{CH} of the CH vectors of the $^bCH_2$ group shortens with a decrease in the choline iodide concentration (see Fig. 1). Thus, according to our supposition, the reorientation time of the whole choline iodide molecule shortens with the concentration decrease.

The change in hydration numbers of choline iodide molecules and the formation of clathrate-like structures are shown[11] to be accompanied by a change in the slopes of the concentration plot of the relaxation rates. In our case, we also observe a change in the slope of the plot with a decrease in the choline iodide concentration. This result indicates in favor of clathrate formation in an aqueous solution of choline iodide.

In addition to the correlation times τ_{CH}, we determined the cross-correlation times τ'_{CH} from the relaxation measurements using the ^{13}C nuclear multiplet effect. The calculation of the anisotropy parameter ζ for the CH vectors of the $^bCH_2$ group ($\zeta = \tau'_{CH}/\tau_{CH}$) shows that the rotation of the choline iodide molecule at a concentration of 0.1 mol. fraction is anisotropic and becomes more isotropic with a decrease in the concentration (Table 1).

We calculated the correlation time of symmetry axis reorientation for the Me group (τ_0). It turned out that the correlation time τ_0 decreases with a decrease in the concentration, indicating an increase in the freedom of reorientation of choline iodide molecules. This conclusion agrees with the above-presented results.

The anisotropy parameter ξ of the alkyl groups of the ion was calculated using the theoretical values of the correlation characteristics (see Experimental). Then, based in the calculated data, we determined the anisotropy parameter ξ for the choline iodide molecule: $\xi(^aCH_2) = -0.19$, $\xi(^bCH_2) = -0.43$. This shows that isotropic rotation is typical of the molecular state of choline iodide. A comparison of the calculated and experimental ξ values suggests that the choline iodide molecules are in the dissociated state at a concentration of 0.1 mol. fraction. For this choline iodide concentration, rotation is anisotropic. According to the calculations, anisotropic rotation is characteristic precisely of the dissociated state of choline iodide. The calculation of τ_0 of the symmetry axis of the Me group of choline iodide, taking into account intermolecular interactions with water, showed that an increase in the degree of binding of choline iodide with water increases τ_0, which is consistent with experiment.

Table 1. Experimental correlation times of the symmetry axis of the methyl group (τ_0) and the anisotropy parameter (ξ) of the alkyl groups of choline iodide

Molar fraction of choline iodide in solution	ξ			τ_0*/ps, $^cCH_3$
	$^aCH_2$	$^bCH_2$	$^cCH_3$	
0.100	0.06	0.33	0.23	19.44
0.070	0.03	0.25	0.20	17.50
0.050	0.02	0.20	0.19	16.30
0.030	0.02	0.15	0.19	15.10
0.020	−0.02	0.10	14.05	0.17
0.005	−0.06	0.00	0.16	13.68

* For $^bCH_2$ the values were not determined, and for $^aCH_2$ τ_0 = 0.03 ps at a choline iodide concentration of 0.070 mol. fraction.

Thus, we can conclude that the parameters of molecular rotation anisotropy of choline iodide are sensitive, first, to the dissociation of its molecules into ions and, second, to structural rearrangements in solution (clathrate formation). The state of non-dissociated choline iodide molecules is characterized by anisotropic rotation, while isotropic motion is typical of the state of dissociated molecules.

The auto- and cross-correlation times of reorientation of the CH vectors of choline iodide molecules were measured by the method of ^{13}C nuclear magnetic relaxation and calculated in the framework of the modified KSH theory using the effective interaction model. This study made it possible to determine the parameters of anisotropy reorientation of choline iodide molecules in water and to show their dissociated state.

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