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The dielectric relaxation in aqueous acetamide solutions

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Based on the studies of SHF dielectric properties of aqueous solutions of acetamide in the temperature range 283–318 K and frequency range 3–26 GHz the dielectric relaxation parameters of the solutions were determined, and it was shown that the relaxation process is associated with the collective structural changes in water–nonelectrolyte network of bonds, during which the influence of hydrophilic interactions of polar groups and the effects of hydrophobic hydration almost completely counterbalance each other.

Aqueous solutions of acetamide can be regarded as a typical example of a system in which a polyfunctional molecule has both polar and nonpolar groups. Manifestations of hydrophobic and (or) hydrophilic hydration in this case are mainly connected with the influence of CH_3CONH_2 molecules on the structure of water. It should be noted that the polar $CONH_2$ group tends to form hydrogen bonds with the water molecules, these H-bonds being stronger than the water–water bonds.[1] The available data on solutions of formamide and urea show that the structure breaking of the water in these solutions is due to the influence of $CONH_2$ groups on the H-bond network in water.[2–4] On the other hand, the presence of the nonpolar CH_3 group in the acetamide molecule should cause opposite effects (effect of the hydrophobic hydration of nonelectrolyte molecules). However, it is impossible to predict *a priori* the sign of resulting changes, because of the nonadditive joint influences of polar and nonpolar groups of molecules on the structure of water.[5–8] These influences can be different for nonelectrolyte molecules with different polar groups.

The structural changes of water occurring in solutions of acetamide have been studied using various structure-sensitive methods (viscosity, volume properties, *etc.*[9,10]). The SHF dielectric properties of acetamide solutions have also been investigated earlier.[11–13] However, the results of these studies were neither accurate enough nor complete enough. A dielectric spectrum for the frequency range of 1 MHz–40 GHz has been reported.[11] However, the data were obtained for only one concentration (1 mol dm^{-3}) and only one temperature, 298 K. Parameters of the dielectric relaxation of acetamide solutions in the temperature range 278–323 K were calculated from the data on ε' and ε'' obtained for two frequencies only.[12,13] Therefore, it seems the estimates of the time (τ) and activation enthalpy (H_ε^{++}) for the dielectric relaxation should be refined.

In the present study the SHF dielectric characteristics (ε' and ε'') of aqueous solutions of acetamide were studied at low nonelectrolyte concentrations and at 283–318 K. The measurements were conducted by the method of cylindrical rod in a waveguide[14] at 5–9 frequencies (7.0, 10.22, 13.0, 13.1, 16.0, 16.1, 23.5, 25.0, 26.0 GHz). The accuracy of the measurement of ε' and ε'' was ±1.5–2.0 and ±2.5–3.0%, respectively. Solutions for the study were prepared by the weight method from bidistilled water and acetamide of ‘chemically pure’ grades.

The resulting frequency dependences of ε' and ε'' were analysed using Cole-Cole relation:

$$\varepsilon\ (\omega) = \varepsilon\ + \frac{\varepsilon'_s - \varepsilon}{1 + (i\tau\omega)^{1-\alpha}} \tag{1}$$

where: ε^* is the complex dielectric permittivity, ω is circular frequency, ε'_s and ε are low- and high-frequency limits of the investigated region of dielectric permittivity dispersion, α is a parameter of distribution of relaxation times, τ is the most probable relaxation time. At limiting cases when $\alpha = 0$ equation (1) transforms to Debye relation. It was used at low acetamide concentrations. Examples of the Cole-Cole diagrams and frequency dependences of ε' and ε'' are given in Figure 1 and Figure 2. The calculated parameters of the relaxation process for solutions in the temperature range studied are given in Table 1. The τ values were found by the graphical method,[2,15] and the activation parameters H_ε^{++}, G_ε^{++} and S_ε^{++} were calculated using relations of the theory of absolute reaction rates.[16]

To reduce the number of adjustable parameters $\varepsilon \quad \varepsilon^{H_2O} = 5$ is assumed just for other solutions,[2–4,15] because the deflections of ε are not really important in the calculation of τ. The ε'_s value is also included in relation (1). The values of static dielectric permittivity ε_s measured at a low frequency are often regarded as the low-frequency limit of the investigated region of dispersion ($\varepsilon_s = \varepsilon'_s$). For acetamide solutions, data on ε_s at 298 K have been reported.[9] When values ε_s are used in calculations, it is assumed that in the solutions there are no additional lower-frequency regions of dispersion, related directly to the movement of the solute molecules or their hydration complexes. Thus, the relaxation model and the particular magnitudes of parameters in the calculation already include some implicit suggestions on the nature of molecular relaxation process. To calculate τ values without using ε_s requires additional analysis. The optimum relaxation model depends on the available frequency range. Therefore, the calculation at 298 K using formula (1) was performed for four different sets of data: (*1*) using our experimental data for frequencies of 7–26 GHz; (*2*) using both the present and some earlier data for frequencies 3, 9.4 and 14 GHz;[12,13] (*3*) and (*4*) the same calculations using ε_s from published low-frequency data.[9]

The values of dielectric relaxation time remain approximately the same to each variant of calculations. This can be seen from Table 1 and Figure 2, in which frequency dependences ε' and ε'', calculated for $\varepsilon'_s = \varepsilon_s$ and without using the values ε_s are presented. This confirms the assumption that no low-frequency relaxation processes are manifested in the considered dielectric spectrum of solutions (within the accuracy

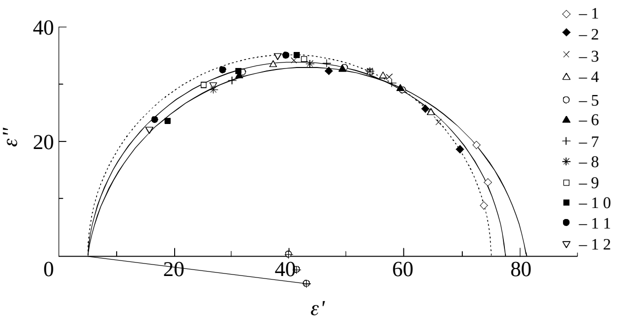

Figure 1 The Cole-Cole diagrams for water (dotted line), 5 (*a*) and 15 (*b*) mol% acetamide solutions at 308 K. Frequencies: 1 – 3 GHz, 2 – 7 GHz, 3 – 9.4 GHz, 4 – 10.22 GHz, 5 – 13 GHz, 6 – 13.1 GHz, 7 – 14 GHz, 8 – 16 GHz, 9 – 16.1 GHz, 10 – 23.5 GHz, 11 – 25 GHz; 12 – 26 GHz.

Table 1 Parameters of dipole relaxation process for aqueous acetamide solutions.[a]

C/mol%	τ/ps					α					G_ε^{++} 298 K/ kJ mol^{-1}	H_ε^{++} 298 K– 308 K/ kJ mol^{-1}	S_ε^{++} 298 K/ J mol^{-1} degree	τ/ps^c	
	283 K^b	288 K	298 K	308 K	318 K^b	283 K^b	288 K	298 K	308 K	318 K^b				298 K	308 K
0	12.8	11.0	8.25 (8.25)	6.45	5.2	0.00	0.00	0.00	0.00	0.00	9.75	17.2	25.0	8.25 (8.25)	6.45
1	13.8	11.9	8.91 (8.8)	6.9	5.4	0.01	0.01	0.00	0.01	0.00	9.9	17.5	25.4	8.9 (8.8)	6.9
3	16.2	14.0	10.2 (10.1)	8.1	6.3	0.03	0.03	0.01	0.04	0.03	10.3	17.6	24.8	10.3 (10.5)	8.2
5	19.2	16.1	11.7 (11.8)	9.5	7.4	0.05	0.05	0.02	0.07	0.05	10.6	16.9	21.2	11.9 (12.2)	9.5
7	21.1	18.7	13.4 (13.8)	11.1	8.7	0.06	0.07	0.03	0.08	0.06	10.9	16.9	19.8	13.3 (13.8)	11.0
10	25.0	24.0	16.9 (17.8)	12.5	10.4	0.07	0.10	0.07	0.07	0.06	11.5	21.5	33.5	16.9 (17.4)	12.8
15	38.9	32.4	23.0 (26.2)	17.5	14.4	0.09	0.11	0.09	0.10	0.08	12.3	20.4	27.1	23.0 (24.1)	17.6
20^d	50.0	44.1	34.2	20.3	17.9										24.5

[a] Calculations of τ, H_ε^{++}, G_ε^{++} and S_ε^{++} are carried out on data at 9 frequencies (7, 10.22, 13, 13.1, 16, 16.1, 23.5, 25, and 26 GHz); values τ, calculated using the literature data ε_s, are given in parentheses. [b] Calculations of τ using the results of measurements on 5 frequencies: 10.22, 13.1, 16.1, 23.5 and 26.0 GHz. [c] Calculations of τ using the results of measurements on 9 frequencies and earlier data at 9.4 and 14[12] and 3 GHz.[13] [d] Tentative values obtained by means of data averaging τ of present work and ref. 12.

of the experiment). On the other hand, it is clear that ε_s can barely be calculated precisely from the SHF dielectric data, when they are present only in the high-frequency region of the spectrum and at a limited number of frequencies. If the measurements at lower frequencies (3 GHz) are taken into account, the ε_s values for 10–15 mol% solutions differ from the published data by 3–5%, whereas without using this frequency, they differ by 3–15%.

Figure 3 presents the temperature dependences of τ plotted using both our and the earlier data.[12] When the acetamide concentration is increased, these dependences become more pronounced. The data[12] for concentrated solutions at 283 K are probably insufficiently exact. There are no published data for ε_s in this temperature range, therefore we used the τ values obtained for the first set of data (Table 1) to calculation of the activation parameters H_ε^{++}, G_ε^{++} and S_ε^{++}, which reflect the changes in the degree of bonding (average energy of bonds) and in the degree of structurisation of the system. In the first approximation, the dependence of $\ln\tau$ on $1/T$ is linear in the temperature range 283–328 K for all the solutions considered. Accordingly, the calculated H_ε^{++} and S_ε values, refer to the single process of relaxation of the water–non electrolyte H-bond net, which incorporates both water and acetamide molecules. Very weak (or nearly absent within the accuracy of experiment) dependence of τ/η on the concentration also confirms this. It is the same at various temperatures, confirming the absence of manifestations of different relaxation processes (processes with the different nature of temperature changes) and similarity of structural relaxation processes reflecting in these properties.

As can be seen from Table 1, at low concentrations of acetamide, the H_ε^{++} and S_ε^{++} values change only slightly at transition from water to a solution (up to 7 mol%). In typical cases of hydrophobic hydration of nonelectrolyte molecules values of enthalpy and entropy of dielectric relaxation processes are increased at transition from water to solution.[18] Usually at hydrophilic hydration of polyfunctional molecules the decrease of these parameters is observed.[2–4]

The variations of the H_ε^{++} values were compared with the data on the other structure-sensitive properties of solutions. The H_η values calculated on the basis of our own measurements of viscosity at 288–308 K[10] increase slightly (or do not change) at transition from water to solution (these changes are on the verge of the accuracy of the measurements).

The obtained H_ε^{++} and H_η values show that the breaking influence of polar or stabilizing influence of nonpolar groups of molecules on the water structure are not observed. This is also indicated by the dependence of the apparent molar volume (V_2) on the concentration of acetamide, calculated from our own experimental data on the density of solutions.[10] It is known[17] that in the presence of hydrophobic hydration of molecules of nonelectrolytes at low nonelectrolyte concentrations, the V_2 value decreases. The concentration dependence of V_2 passes through a minimum. In the case of hydrophilic hydration, V_2 slightly increases with an increase in the concentration of a

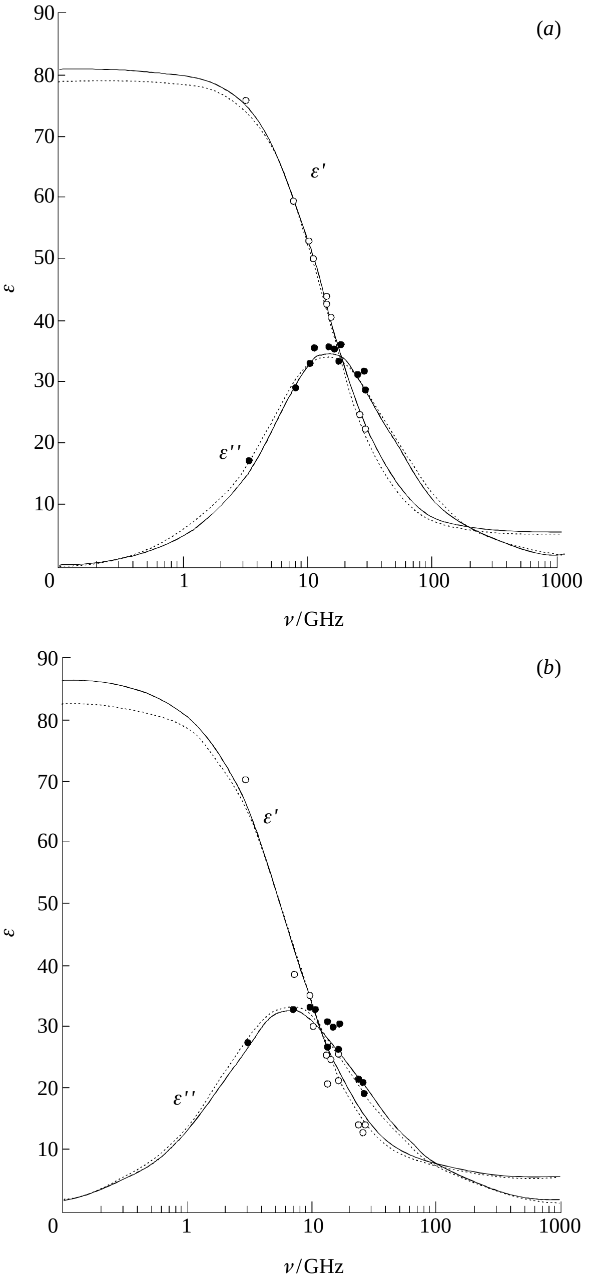

Figure 2 Frequency dependences of real (ε') and imaginary (ε') parts of complex dielectric permittivity for 5 (*a*) and 15 (*b*) mol% acetamide solutions at 298 K. Solid lines – calculation using Cole-Cole equations obtained parameters of relaxation and literature values ε_s, dotted lines – the same disregarding ε_s.

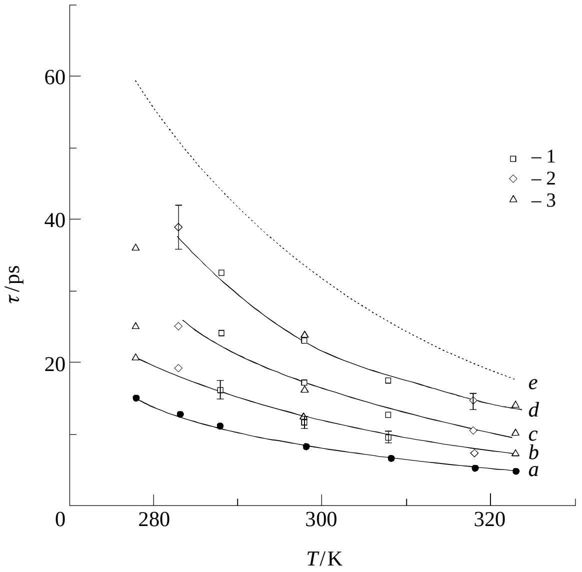

Figure 3 The temperature dependences of relaxation time for water (*a*), 5 (*b*), 10 (*c*), 15 (*d*) and 20 (*e*) mol% acetamide solutions. 1 – calculation of τ using the results of measurements on 9 frequencies, 2 – calculation of τ using the data for 5 frequencies (10.22, 13.1, 16.0, 23.5 and 26.0 GHz), 3 – literature data.[12] Curve for 20 mol% acetamide – tentative values obtained by means of averaging of data of present work and ref. 12.

nonelectrolyte. For acetamide solutions V_2 hardly depends on the concentration. Thus, the changes of V_2 in acetamide solutions confirm the results obtained from H_ε^{++} about the nature of the influence of acetamide on the structure of water.

Therefore, among the various possible cases of the influence of nonelectrolyte molecules on the initial H-bond network in solution, acetamide solutions provide an interesting example, where structural effects of hydrophilic and hydrophobic hydration having opposite signs counterbalance each other regarding their manifestation in structure-sensitive properties.

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