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STRUCTURE, PROPERTIES

Effect of Change in the Physical Properties of Water at Its Peculiar Temperature Points on the Dielectric Behavior of Sodium Polyacrylate

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Abstract—The behavior of sodium polyacrylate is studied via broadband dielectric spectroscopy. The non-Debye response in the frequency range 0.1 Hz–1.0 MHz, the non-Markovian dispersion in the infralow-frequency range, and the anomalies of dielectric permittivity and ac conductivity near "peculiar" temperatures of water (20, 35, 50, and 75°C) are ascertained experimentally. These facts make it possible to assign sodium polyacrylate to disordered media, in which the temperature behavior of dielectric parameters is described by the Kohlrausch–Williams–Watts relaxation function.

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INTRODUCTION

The study of the response of relaxation characteristics and structures of objects to external stimuli (temperature, fields) is a traditional method of materials science in physics, chemistry, molecular biology, and corresponding directions in applied science.

The relaxation of dielectric properties provides a way to easily gain information about the interrelationship between individual structural elements from their response to external stimuli [1].

One of the common problems concerns determining the role of water, hydroxyl groups, or hydrogen bonds in reactions in condensed media. It is known that the manifestation of the effect of some properties of water depends on its percentage in the polymer and the method of preparing samples, which determines the conditions of sorption of water molecules from the environment and the conditions of existence of these molecules in voids of the sample and regions adjoining electrodes. The specific state of the sample controls the temperature dependence and specific features of its dielectric response.

There are many materials for which conductivity and dielectric properties may be described by the Kohlrausch–Williams–Watts relaxation function, the so-called "stretched exponent" [2–7]. This effect is advantageously used to study electric properties in weakly structured media: glasses, polyelectrolytes, biopolymers, and semiconductors.

The dielectric properties of crystallohydrates containing hydrogen bonds in weak electrical fields were investigated via broadband dielectric spectroscopy (0.1 Hz–1.0 MHz) [8–12]. The collected experimental data made it possible to formulate a number of common parameters of these objects: proton multiposition hopping conductivity, the non-Debye relaxation spectrum, and low-frequency linear dispersion. In addition, a sequence of temperatures typical for anomalies of the dielectric response (20 ± 5, 35 ± 5, 50 ± 5, and 75 ± 5°C) was established in the abovementioned experiments. In our opinion, this circumstance may be explained by the presence of OH···O bonds with lengths of 2.6–2.9 Å, because crystals containing hydrogen bonds of exactly these lengths were studied in [8–12]. One of the possible mechanisms governing the influence of hydrogen bonds on change in the properties of compounds may be the redistribution of protons over energy levels in the two-minimum potential [13].

The goal of this study is to investigate the dielectric properties of polyelectrolyte sodium polyacrylate.

Polyelectrolytes belong to an important class of polymers providing a wide range of technological applications in a fantastically broad range of spheres from materials science to biophysics. Polyelectrolytes, such as sodium polyacrylate, have found wide use as glues, dispersing agents, wetting agents, and additives to various coatings. Owing to their ability to absorb water, polyacrylates are employed as absorbents of water, for example, as diaper fillers, fire-retardant gels, etc. Moreover, a considerable interest in the fundamental understanding of the behavior of such charged macromolecules arises because of their simi-

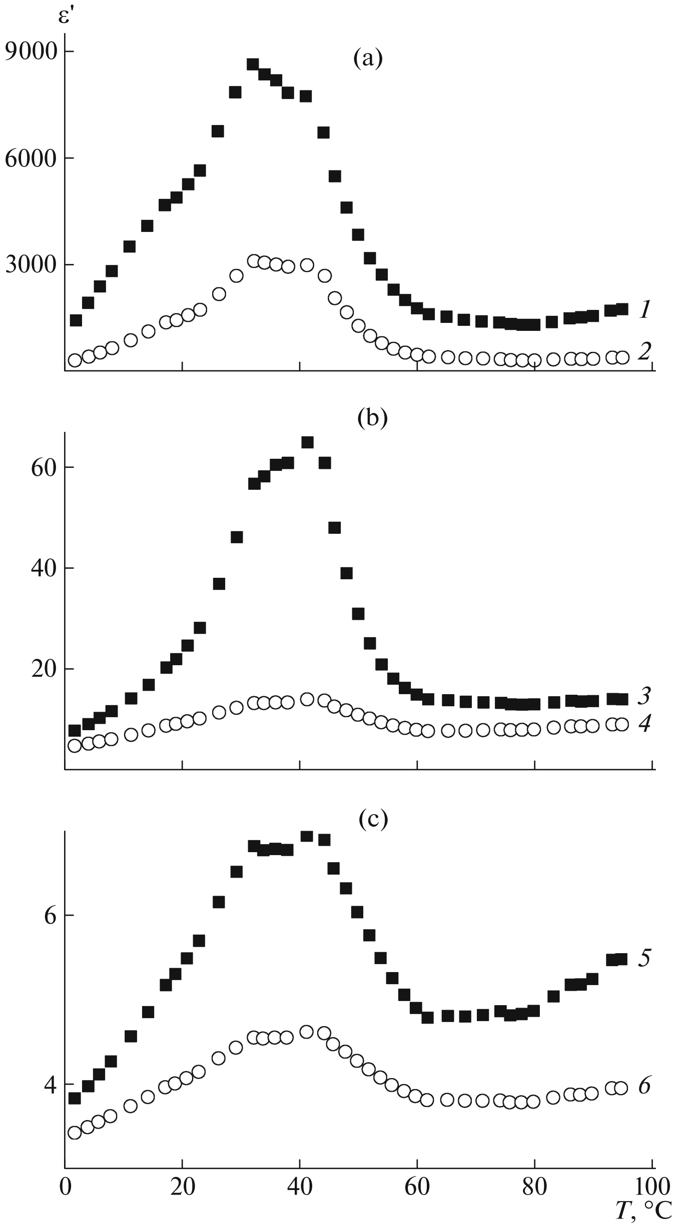

Fig. 1. Temperature dependences of dielectric permittivity ε' (T, f = const) of sodium polyacrylate at (a) low, (b) medium, and (c) high frequencies: f = (*1*) 0.1, (*2*) 1.36, (*3*) 1.13×10^3, (*4*) 12×10^3, (*5*) 123×10^3, and (*6*) 1.13×10^6.

larity to biopolymers. Electrostatic interactions have a strong effect on the structure and properties of polyelectrolytes.

With the use of various experimental methods (NMR spectroscopy, neutron and X-ray scattering, etc.), several forms of water (free, bound, nonfreezing) were found in polymers, and the interrelationship between the sorption behavior of water and the structures of polymers was considered [14]. At present, it is generally agreed that a monolayer of bound water occurs at most hydrophilic groups of macromolecules. Water associated with ionogenic groups of polymers cannot be removed during drying. Because the bound water of macromolecules is the water of hydration of their ionogenic groups, an analogy may be drawn with the water of crystallohydrates.

With consideration for the previous data [8–12], this study is aimed at the experimental verification of the above suggestion about the decisive role of hydrogen bonds and about the effect of adsorbed water at some of its temperature points on the dielectric characteristics of a hydrophilic polymer (sodium polyacrylate).

EXPERIMENTAL

Sodium polyacrylate (Fluka, $M_w = 18 \times 10^3$) was used as received. The samples were pellets with diameters of 14.5 mm and thicknesses of 1.96 mm pressed at room temperature from a powder obtained via thorough grinding of a solid sodium polyacrylate powder in a mortar. Neutral graphite electrodes were deposited on pellet surfaces.

Measurements were performed on a BDS Novocontrol Concept 40 broadband dielectric spectrometer in the frequency range 0.1 Hz–1.0 MHz and in the temperature range 2–95°C in the heating and cooling regimes with 10-min stabilization of temperature points. The interval 2–95°C covers the above-mentioned temperature anomalies of dielectric properties. The voltage of the measuring field was ~5 V/cm.

RESULTS AND DISCUSSION

Figures 1 and 2 show the measured temperature dependences of dielectric permittivity ε' and conductivity σ' at various frequencies. The dependences of ε' (T, f = const) demonstrate a well-defined blurred single peak with an axis at $T \sim 35$°C. Note that this blurred maximum corresponds to a peculiar temperature point of water of 35 ± 5°C.

The dependences of σ' (T, f = const) (Fig. 2) are characterized by a gain in conductivity with an increase in frequency and the presence of a maximum centered at $T \sim 35$°C.

Presentation of the same data in other coordinates σ' (f, T = const) (Fig. 3) makes it possible to find exponent s of power dependence $\sigma' \sim f^s$ for various frequency and temperature intervals: for $T < 35$°C, $s \sim 0.3$–0.6, and for $T > 54$°C, $s \sim 0.4$–0.52. These values of s unambiguously determine the mechanism of ac conductivity of sodium polyacrylate as hopping conductivity [15].

During estimation of characteristic parameters of the dielectric-relaxation process, the thermodynamically nonequilibrium state of the objects under study should be taken into account. In other words, time

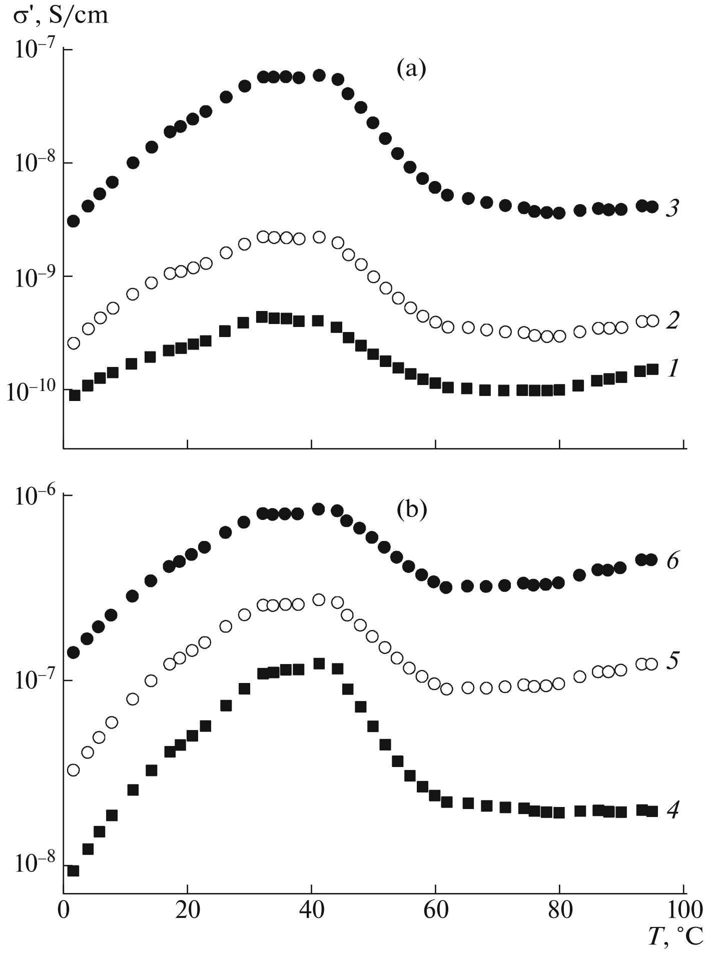

Fig. 2. Temperature dependences of conductivity σ' (T, f = const) of sodium polyacrylate at (a) low and (b) high frequencies: f = (*1*) 0.1, (*2*) 1.36, (*3*) 1.13×10^3, (*4*) 12×10^3, (*5*) 123×10^3, and (*6*) 1.13×10^6.

dependences of the measured values should be allowed. In this study, measurements were performed a month after sample preparation.

The temperature dynamics of the relaxation process during heating may be observed more vividly in Fig. 4, which shows, for various temperatures, the frequency dependences of dielectric modulus M'' (f, T = const), as estimated via the relationship:

$$M^* = M' + iM'' = \frac{1}{\varepsilon^*} = \frac{\varepsilon'}{(\varepsilon')^2 + (\varepsilon'')^2} + i\frac{\varepsilon''}{(\varepsilon')^2 + (\varepsilon'')^2}. \qquad (1)$$

Activation energies in various temperature intervals for two processes in approximation $\tau_{\max}(T)$ via the Boltzmann–Arrhenius law

Process	T, °C	Activation energy ΔU, eV
1	2–30	0.96 ± 0.05
1	78–95	0.53 ± 0.02
2	78–95	0.37 ± 0.03

The dynamics is ambiguous in the studied frequency range 10^3–10^5 Hz. As temperature increases from 2 to ~30°C, the maxima of M'' shift to high frequencies (Fig. 4a). The same shift in $M''(f)$ was observed for erbium and holmium formates [9, 13]. In the range 44–65°C, the maximum of M'' shifts to low frequencies (Fig. 4b, curve *6*). A further increase in temperature from 74 to 93°C leads to the stabilization of frequency maximum M'' with a weak tendency to increase (Fig. 4c). This behavior indicates a change in the dominant relaxation mechanisms. In the same temperature range, a shoulder suggesting the appearance of one more peak M'' (f) is clearly seen against the background of the main peak of M'' (f) in a lower frequency region (10^2–10^3 Hz).

Temperature variation in the relaxation time τ for each peak was determined via approximation of the

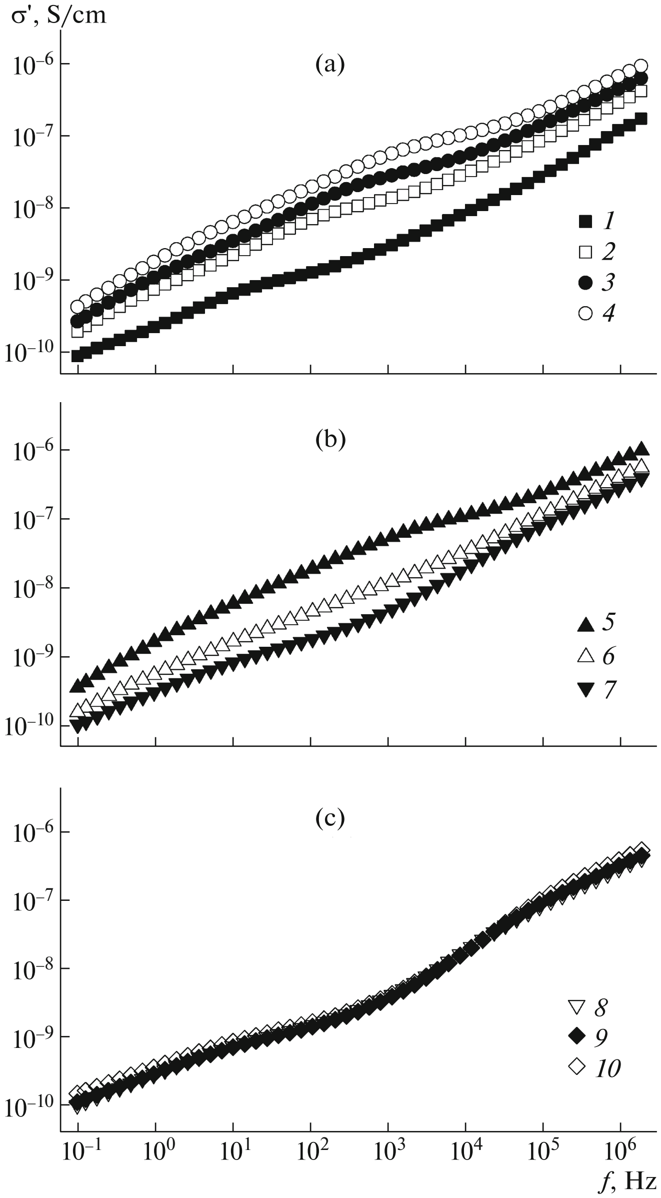

Fig. 3. Frequency dependences of conductivity σ' (*f*, $T =$ const) of sodium polyacrylate at various temperatures: $T =$ (*1*) 2, (*2*) 14, (*3*) 23, (*4*) 34, (*5*) 44, (*6*) 54, (*7*) 65, (*8*) 74, (*9*) 83, and (*10*) 93°C.

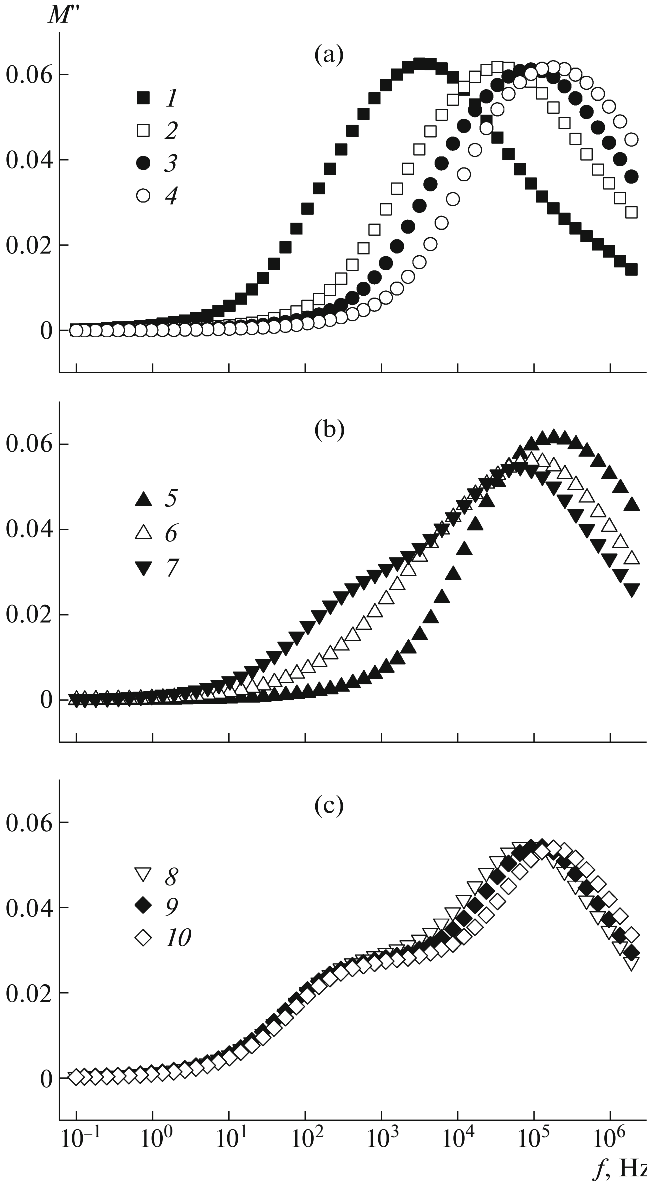

Fig. 4. Frequency dependences of the dielectric modulus *M*'' (*f*, $T =$ const) of sodium polyacrylate at various temperatures: $T =$ (*1*) 2, (*2*) 14, (*3*) 23, (*4*) 34, (*5*) 44, (*6*) 54, (*7*) 65, (*8*) 74, (*9*) 83, and (*10*) 93°C.

experimental data *M*'' (*f*) through the Havriliak–Negami formula [16]:

$$M^* = M_\infty - \frac{\Delta M}{[1 + (i\omega\tau_{\mathrm{HN}})^{\alpha}]^{\gamma}}, \tag{2}$$

where M_∞ is the dielectric modulus at the infinite frequency, $\Delta M = M_\infty - M_s$ is the intensity of relaxation, τ_{HN} is the time of relaxation, and α and γ are parameters reflecting deviation of the process from the Debye process (α characterizes the width of the relaxation-time spectrum, and γ characterizes the asymmetry of the relaxation-time spectrum). Errors in the determination of α, γ, Δ*M*, and τ did not exceed the values of the found parameters by more than 10–12%.

The temperature dependences of relaxation time $\tau_{\max}(T)$ obtained via approximation are shown in Fig. 5 in Arrhenius coordinates, $\ln\tau_{\max}(10^3/T)$: Curve *1* corresponds to the main peak of *M*'' (*f*), and curve *2* corresponds to the low-frequency additional peak that appears only at high temperatures. The results of approximation of separate segments of curves *1* and *2* via the Boltzmann–Arrhenius equation $\tau_{\max} = \tau_0\exp(\Delta U/kT)$, where τ_0 is the pre-exponential factor

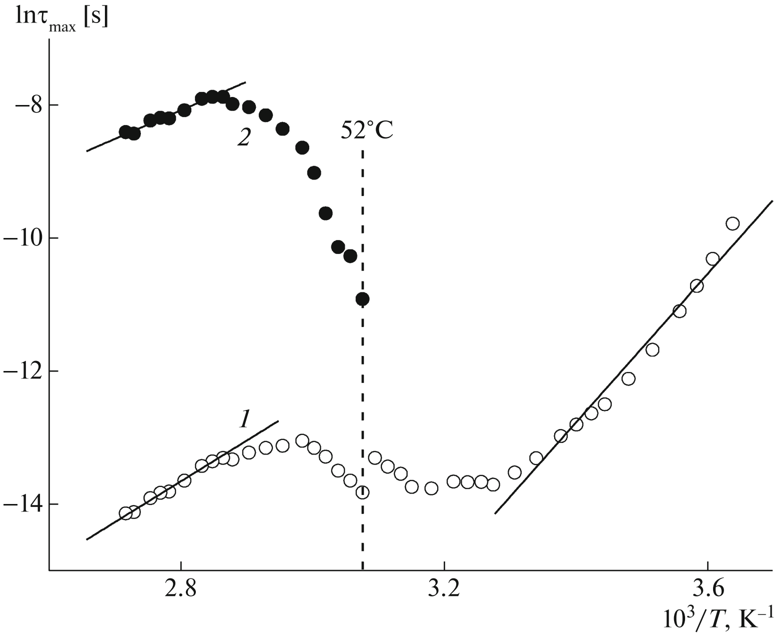

Fig. 5. Plot of τ_{max} vs. reciprocal temperature for sodium polyacrylate. Here and in Fig. 8, *1* is the main relaxation process, while *2* is the process appearing on dependences *M*'' (*f*) above 50°C.

(*c*), ΔU is the activation energy (eV), *k* is the Boltzmann constant, and *T* is temperature (K), are listed in the table.

Because the values of exponent *s* and activation energies for processes 1 and 2 correspond to the hopping ionic conductivity, it is most probable that sodium ions and protons serve as its carriers.

A decrease in the values of τ_{max} with an increase in temperature in the interval from 2 to 50°C (Fig. 5) is consistent with the behaviors of ε' (*T*) and σ' (*T*) (Figs. 1, 2).

As was mentioned, in our case, one more relaxation process appears above 40°C; it becomes distinct at frequencies $\sim 10^{-1}$–10^3 Hz. This process is not seen on dependences ε' (*T*) and σ' (*T*), a circumstance that is associated, as will be shown below, with widening of the relaxation-time spectrum. Figure 6 plots dependences of reduced dielectric modulus M''/M''_{max} on reduced frequency f/f_{max} which were calculated from the data presented in Fig. 4 for a number of temperatures. The same figure presents the Debye function for the sake of comparison. The width of the Debye curve is 1.14 at a height of 0.5 from the maximum at $f/f_{max} = 1$. For sodium polyacrylate, the width of the peak is ~3, as is vividly demonstrated by the non-Debye dielectric response. A similar phenomenon was observed for erbium and holmium formates and triglycerin selenate in a paraelectric phase [11, 12]. This behavior of compounds exhibiting the non-Debye spectra may be described by a set of certain systems with an intrinsic relaxation time for each system.

Another common feature of sodium polyacrylate, formates, and triglycine selenate is the linear dielectric dispersion of dependence ε'' (ε'), which, in the case of sodium polyacrylate, is observed at all temperatures from 2 to 95°C in the frequency range from 10^{-1} to 10^6 Hz (Fig. 7). Note that there is a marked difference in dielectric dispersions for temperatures above and below 50°C. The linear dispersion may be related to the hopping conductivity of H^+ and Na^+ ions over localized states.

Figure 8 shows the temperature dependences of exponents α(*T*) and γ(*T*) in relationship (2) for sodium polyacrylate that were obtained via approximation of the experimental data. As is seen, α(*T*) and γ(*T*) show anomalies in the vicinity of ~50°C. As in Fig. 5, the second relaxation process appears on curves α(*T*) and γ(*T*) above ~54°C. Parameter α(*T*) for processes 1 and 2 increases in the range 80–95°C, whereas γ(*T*) for process 1 remains practically the same in the same temperature range, while for process 2, γ(*T*) decreases as temperature is increased from 75 to 95°C (Fig. 8b). These phenomena probably are evidence for the cardinal rearrangement of the polymer. Regardless of the mechanism controlling the change in dielectric properties, region *T* ~ 50°C may be reliably regarded as critical.

The experimental study of relaxation processes in systems with various structural organization showed that the nonexponential character of relaxation is widespread [4–7, 17–20]. In these cases, conductivity curves are satisfactorily described by relationship σ' =

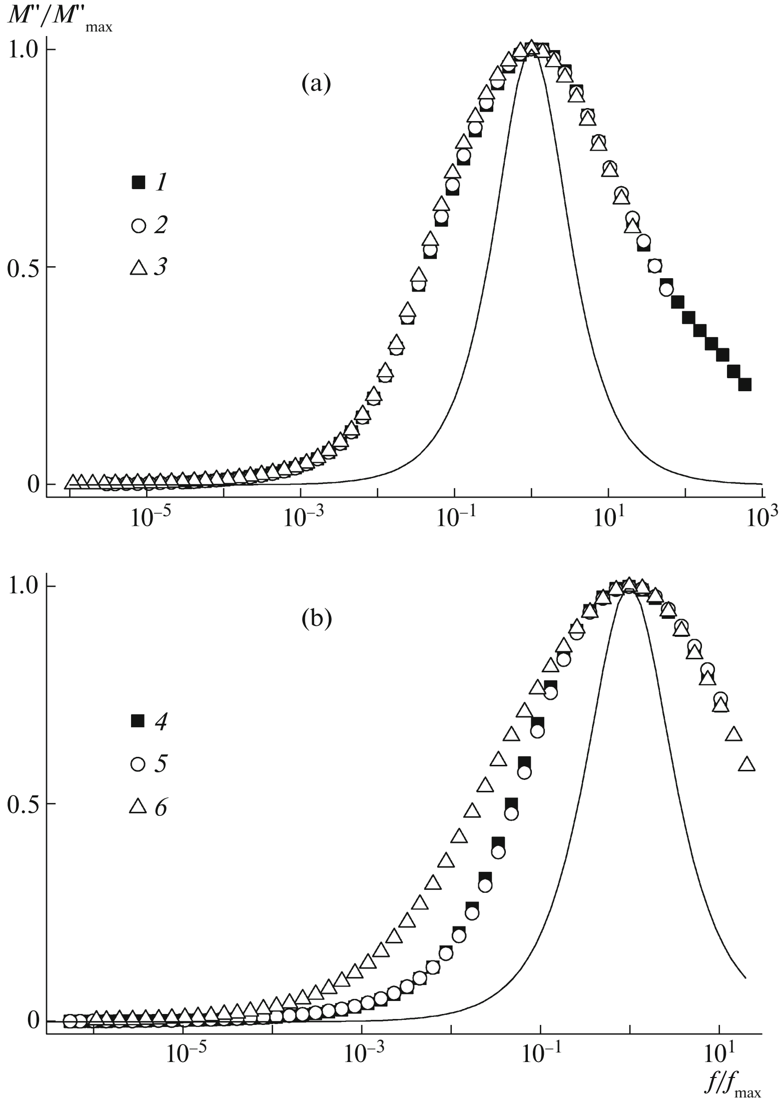

Fig. 6. Plot of reduced dielectric modulus M''/M''_{max} vs. reduced frequency f/f_{max} for sodium polyacrylate. The solid line refers to the Debye function. T = (*1*) 2, (*2*) 14, (*3*) 23, (*4*) 34, (*5*) 44, and (*6*) 54°C.

$\sigma_0\exp\{-(t/\tau_0)^\beta\}$, where τ_0 is the characteristic time for the macroscopic process corresponding to the specific mechanism of molecular motion and β is the parameter of width of the dielectric-relaxation-time distribution. In accordance with [6, 21], the universal pattern of the frequency dependence of ac conductivity consists in that the transfer of charge carriers is determined by the polymer structure rather than by the conductivity mechanism. With consideration for the power character of the frequency dependence of conductivity $\sigma' \sim f^s$ [20], $\beta = 1 - s$ in accordance with [5, 6]. For conductivity in semiconductors at 20°C, β = 0.52–0.54 [17]; for dielectric properties [5, 6], β = 0.6–0.7. In accordance with the results of this study, for sodium polyacrylate, $\beta \sim 0.4$–0.7 at temperatures below 35°C and $\beta \sim 0.48$–0.6 at temperatures above 54°C. These values of β provide evidence for the non-Debye type of spectrum, as is typical for disordered systems. These values of β suggest that a whole set of components of the Debye relaxation corresponding to the Kohlrausch–Williams–Watts law occurs in the system. For sodium polyacrylate, the non-Debye relaxation spectrum is observed (Fig. 6), as follows from the frequency dependences of dielectric modulus M'' and relaxation times τ at various temperatures.

As temperature increases, conductivity σ' grows at all frequencies.

The abnormal behavior of properties in ranges ~35 ± 5, 50 ± 5, and 75 ± 5°C makes itself evident at various frequencies on plots $\varepsilon'(T)$ (Fig. 1) and $\sigma'(T)$ (Fig. 2) and $\alpha(T)$ and $\gamma(T)$ (Fig. 8).

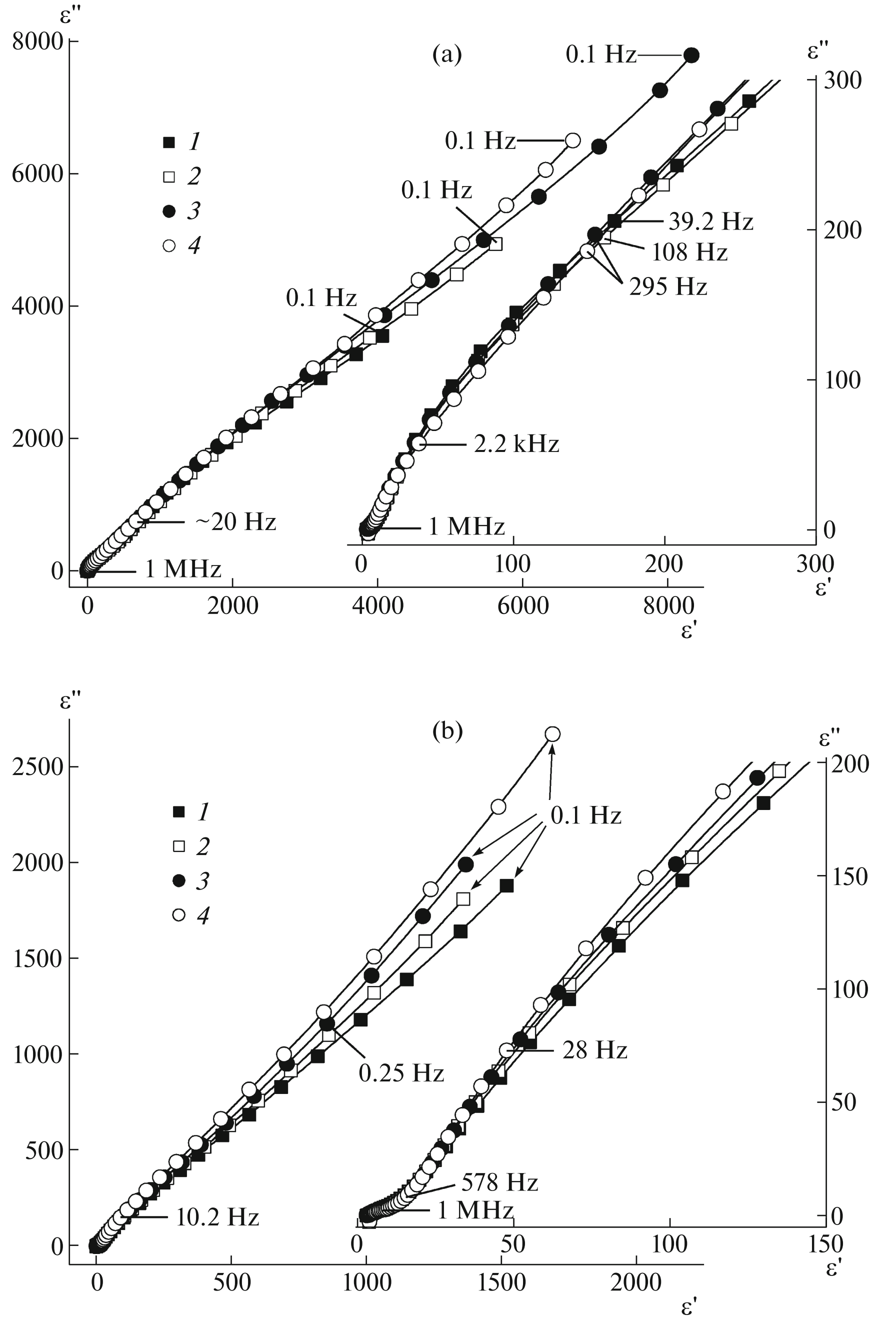

Fig. 7. Plots ε'' (ε') for sodium polyacrylate at infralow frequencies and (a) $T < 50$°C, i.e., T = (*1*) 14, (*2*) 23, (*3*) 34, and (*4*) 44°C, and (b) T > 50°C, i.e., T = (*1*) 65, (*2*) 74, (*3*) 83, and (*4*) 93°C. The inserts show high-frequency regions.

CONCLUSIONS

The “polymer–water” combination is widely spread in living nature (plants, microbes, and animals) and in the abiotic environment (solutions, crystal hydrates, clays, etc.). These objects are very complex, and ascertainment of general features in their response to temperature and magnetic and electric fields is of fundamental interest.

With the use of one of the simplest hydrophilic polyelectrolytes, the sodium salt of poly(acrylic acid), which inevitably contains water molecules [22], hydroxide $(OH)^-$ and hydroxonium $(H_3O)^+$ ions, and more complex oxygen-hydrogen groups, anomalies of dielectric properties near “peculiar” points of water (35 ± 5, 50 ± 5, 75 ± 5°C) manifested themselves [23]. In the same temperature intervals, abnormal properties were observed for crystallohydrates [9–11], for-

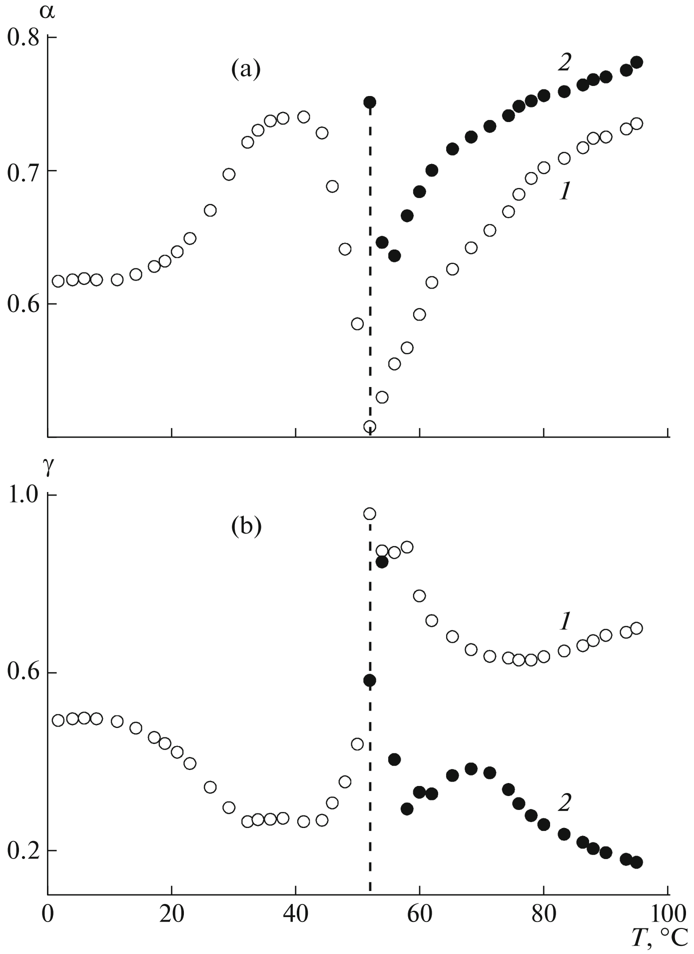

Fig. 8. Temperature dependences of exponents (a) α(*T*) and (b) γ(*T*) for sodium polyacrylate.

mates [8, 12], green leaves [24], polymers [2, 21, 25–28], and aqueous solutions [29, 30].

It is possible that, at these "peculiar" temperature points [23], the most active change in the polymer–water interaction occurs [21, 25–29].

In the study of the polymer–water interaction in the system (polymer, KCl–NaCl–H_2O) [31], the solvation-redundancy concept was developed to determine the mutual distribution of species of solution components; this concept may provide evidence for the main mechanism of this interaction. For the aqueous solution of HF, solvation redundancy Γ^+ (H_2O) has specific features in the temperature range from 25 to 55°C: Namely, Γ^+ increases in the interval from 25 to 35°C, remains constant in the range 35–50°C, and decreases at 50–55°C [30].

On the basis of the correlation between the temperature intervals of anomalies for hydrogen-containing objects and the ortho–para transitions of water at 4 ± 2, 35 ± 5, 50 ± 5, and 75 ± 5°C [32], it may be proposed that causes of temperature features of dielectric relaxation for the studied hydrophilic polyelectrolyte, the sodium salt of poly(acrylic acid), are of a fundamental and general character [33].

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