Dielectric Relaxation of Water in Hydration Shells of Ions†

Andrey Lyashchenko* and Alexander Lileev

N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Science, Moscow, Russia

Microwave spectroscopy has been used to study the dielectric properties of aqueous electrolyte solutions over a wide range of concentrations, the frequency range (7 to 25 or 7 to 120) GHz, and the temperature range (283 to 313 or 288 to 308) K. The static dielectric permittivity, dielectric relaxation time, and activation enthalpy have been calculated for 46 binary systems. General relations between dielectric relaxation parameters and structural effects in aqueous salt solutions are considered. The increase in the order of complementary structural organization for water in the bulk and hydration shells of ions gives rise to the molecular-kinetic stabilization of water and to the structure-making effect. This explains the difference between dielectric relaxation characteristics for a wide variety of electrolyte solutions. We present systematic dielectric data for aqueous electrolytes with hydrophilic and hydrophobic hydration of cations and anions. The temperature effect is also examined. On the basis of this study, new criteria for the difference between hydrophilic and hydrophobic hydration of ions are suggested.

Introduction

New developments in dielectric relaxation spectroscopy (DRS) of aqueous electrolyte solutions combine the experimental investigations for a variety of systems within extended frequency, temperature, and concentration ranges,[1−5] computer simulations using the method of molecular dynamics,[6] and analytical models over the entire range of orientation polarization.[7,8] On the other hand, a molecular-level understanding of this problem has not been attained to date, and the choice of model relaxation functions for wide-band dielectric spectra (ε', ε'') of aqueous electrolyte solutions is difficult.

The complex dielectric permittivity ε^* is given by the expression $\varepsilon^* = \varepsilon' - i\varepsilon''$, where ε' and ε'' are the high-frequency dielectric permittivity and loss, respectively. Different relaxation models are described in detail in the works of Barthel and co-workers.[2,3] The analysis is carried out using empirical dielectric functions that are sufficiently good for a quantitative description of relaxation processes. For asymmetric bands over a wide frequency range, the function with several Debye processes or the Havriliak−Negami equation is used:

$$\varepsilon^* = \frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\tau\omega^{1-\alpha})^\beta} \qquad (1)$$

where ε_s and ε_∞ are the low- and high-frequency limits of the dielectric permittivity, respectively, τ is the relaxation time, α is the parameter for a symmetric distribution of relaxation times ($1 > \alpha \geq 0$), and β is the parameter for an asymmetric distribution of relaxation times. In some cases, the parameters take the values $\beta \approx 1$, $\alpha = 0$, and we can use the Debye relaxation model ($\tau = \tau_d$).

Ion−ion or water−ion pairs and clusters could contribute to the total polarization of a system. On the other hand, the ranges of the main mode of dielectric permittivity for such ion−water forms is separated on the frequency scale from that of water molecules in the hydration shells.[2,3,9] In the neighborhood of the maximum of dielectric losses for water, the variations in dielectric properties can be related to the changes in water caused by hydration processes. Thus, in the first approximation, no relaxation modes for ionic or ion−water pairs need to be taken into account. For such cases, a so-called spectroscopic "dielectric window", in which only water molecules in the bulk and/or the hydration shells of ions relax, can be specified over the frequency range (7 to 25 or 7 to 120) GHz. A major goal of this study is to compare the relaxation changes for water in electrolyte solutions of different types.

Experimental and Computational Methods

The dielectric permittivities for the 46 aqueous electrolyte solutions were measured over the frequency range (7 to 25 or 7 to 120) GHz and over the temperature interval (283 to 313 or 288 to 308) K.[9−25] Our earlier and new results are reported in this paper. For the frequency range (7 to 25) GHz (centimeter wavelengths), we used the method of a thin cylindrical rod in a waveguide.[26] The apparatus is presented schematically in Figure 1. A description of the experimental apparatus and measurement procedure are given elsewhere.[11,27] The relative uncertainties in the measurements of ε' and ε'' are ± (1.0 to 1.5) % and ± (2.0 to 2.5) %, respectively (depending on the frequency, temperature, and salt concentration).

At present it is still impossible to determine ε' and ε'' values over the entire frequency range using any specific single experimental setup. Therefore, in the high-frequency region (higher than 80 GHz) we used a quasi-optical method involving measurement of the absorption (K) and reflection (R) coefficients. The complex dielectric permittivity ε^* is related to the K and R values through the following equations:

$$K = \frac{2\omega}{c}\,\mathrm{Im}\sqrt{\varepsilon^*} \qquad (2)$$

$$R = \left|\frac{\sqrt{\varepsilon^*} - 1}{\sqrt{\varepsilon^*} + 1}\right|^2 \qquad (3)$$

where Im denotes the imaginary part of a complex number and c is the light velocity.

[†] Part of the "Josef M. G. Barthel Festschrift".

* Corresponding author. E-mail: aklyas@mail.ru.

10.1021/je900961m

To measure the coefficients K and R in the (80 to 120) GHz (millimeter wavelength) region, a special apparatus was designed.[9,10,28] The complex dielectric permittivity was then derived from the power absorption and reflection coefficients (see eqs 2 and 3) numerically. In this quasi-optical method, the real part of the permittivity, ε', was measured with a relative uncertainty of ± (7 to 8) %, and that of the imaginary part, ε'', was ± (5 to 6) %.

There exist some specific difficulties in the description of experimental dielectric spectra for electrolyte solutions. The first of these is connected with the high electric conductivity of such systems. The dielectric dipole losses in the microwave range are determined as $\varepsilon_d'' = \varepsilon'' - \varepsilon_i''$, where ε_i'' represents the ionic losses. The ionic losses are calculated as $\varepsilon_i'' = 2\sigma/\omega$, where σ is the low-frequency conductivity. To take into consideration ionic losses, the values of the specific conductivity σ for the investigated solutions are required. The conductivity was measured in a U-shaped glass cell with smooth platinum electrodes using the digital bridge E7-8 at a frequency of 1 kHz. The cell was calibrated using a standard 1 M KCl solution and thermostatted using a U-8 thermostat with an uncertainty of ± 0.05 K. The low-frequency conductivity was measured for 46 electrolyte systems over the specified temperature range. The calculations of the contribution of the ionic conductivity to the imaginary part ε'' of the dielectric permittivity by the above-mentioned standard approach were performed using low-frequency specific conductivity data for the examined electrolyte solutions measured over the frequency range up to 120 GHz. It should be noted that the contribution of ionic losses to the ε'' value is significant even at such high frequencies. A comparison of the ε_i'' and ε_d'' values in the centimeter range is presented in Figure 2. It is seen that the ε_i'' value can be as high as 50% of the ε'' value. The effect of temperature on the value of ε_i'' and its increase at lower frequencies (decimeter wavelength range) should also be noted.

In the case of 1:1 and 1:2 electrolytes, long-lived hydrate complexes appear to be absent, so we can consider the case where the water molecules rotate separately. The molecules in the first hydration spheres of the ions can take part in the relaxation of the total dipole moment of the system, as was confirmed by the low values of the hydration numbers calculated using ε_s data. Correspondingly, over the range of dielectric dispersion for water, the frequency dependence of $\varepsilon_d'' = f(\varepsilon')$ can be represented by a Cole−Cole diagram with a small value of the relaxation time distribution parameter α:

$$\varepsilon(\omega) - \varepsilon_\infty = \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega{\tau_d}^{1-\alpha}} \tag{4}$$

Values of the static dielectric permittivity ε_s and the time for dielectric relaxation τ_d were obtained for aqueous electrolyte solutions using eq 4. The values of the static dielectric permittivity were found from such Cole−Cole diagrams by the circular extrapolation of ε' to zero frequency. Two slightly different calculation schemes were used for such calculations. In the first scheme, the value of the high-frequency limit ε_∞ was chosen to be the same as for pure water ($\varepsilon_\infty = 5$). The temperature and concentration dependence of ε_∞ was not taken into account because the variations of ε_s and τ_d with small variations of ε_∞ were also small and within the limits of experimental errors for ε_s and τ_d. In the second scheme, ε_∞ was allowed to vary. In this case, the calculations of ε_s and τ_d were carried out for data in the frequency range (7 to 120 or 7 to 25) GHz. Measurements at frequencies in the range (80 to 120) GHz enabled us to make more accurate estimates of the high-frequency limit of the dielectric permittivity ε_∞. We used a narrower frequency range of (7 to 25) GHz in other analyses, since the values of ε_∞ were found to be close.

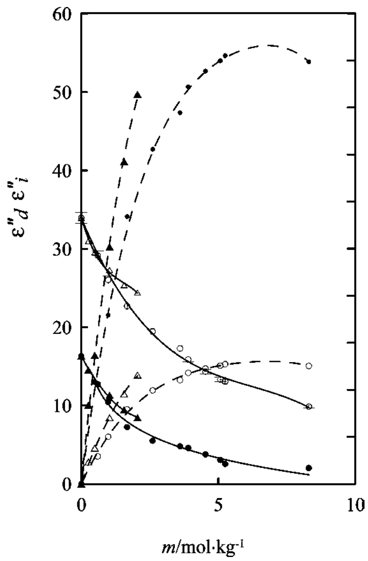

Figure 2. Composition dependence of dipole ε_d'' (solid lines) and ionic ε_i'' (dashed lines) losses in aqueous solutions of KNO_3 (△, 25 GHz; ▲, 7 GHz) and $LiNO_3$ (○, 25 GHz; ●, 7 GHz) at 313 K.

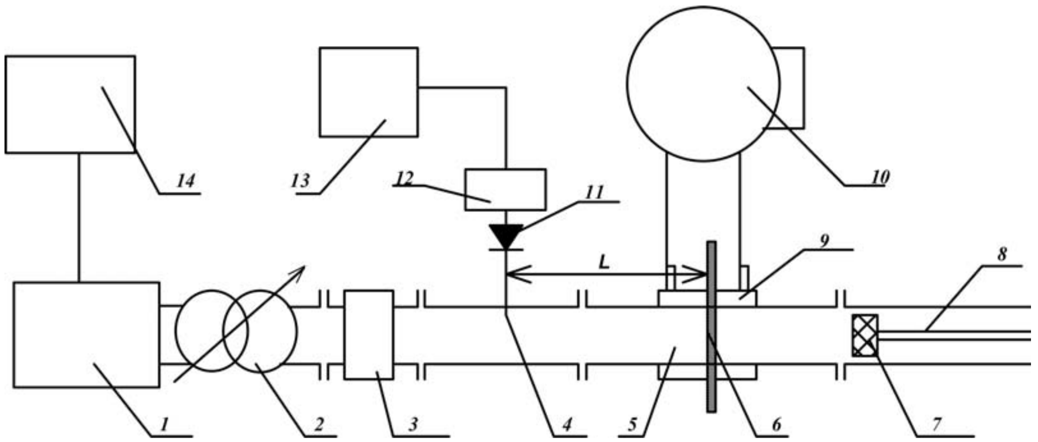

Figure 1. Schematic illustration of the apparatus for measurement of microwave dielectric permittivity at (7 to 25) GHz. Labeling key: 1, generator; 2, attenuator; 3, valve; 4, probes of a power takeoff; 5, waveguide; 6, sample; 7, cylinder pistons; 8, micrometer screws; 9, thermostat jacket; 10, thermostat; 11, detector; 12, filters of a very high frequency; 13, voltmeter, 14, frequency counter.

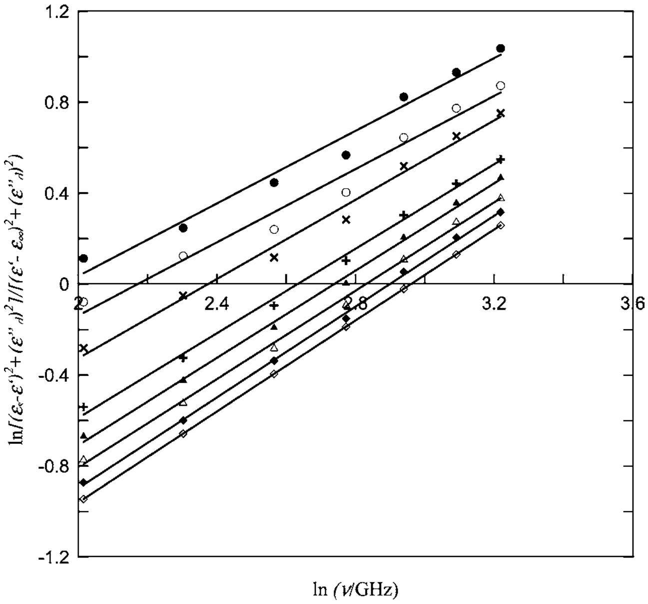

Figure 3. Frequency dependence of the function $f(\omega) = [(\varepsilon_s - \varepsilon')^2 + (\varepsilon_d'')^2]/[(\varepsilon' - \varepsilon_\infty)^2 + (\varepsilon_d'')^2]$ for aqueous diallylmethylammonium trifluoroacetate solutions at 298 K: ◇, water; ◆, 0.25 mol·L^{-1}; △, 0.50 mol·L^{-1}; ▲, 0.75 mol·L^{-1}; +, 1.0 mol·L^{-1}; ×, 1.5 mol·L^{-1}; ○, 2.0 mol·L^{-1}; ●, 2.5 mol·L^{-1}.

The values of dielectric relaxation time τ_d were found using a "graphical" representation of Cole−Cole diagrams. The frequency dependence of the function

$$f(\omega) = \frac{(\varepsilon_s - \varepsilon')^2 + (\varepsilon_d'')^2}{(\varepsilon' - \varepsilon_\infty)^2 + (\varepsilon_d'')^2}$$

becomes a straight line in logarithmic coordinates, and this line crosses the *x* axis at the point corresponding to $\omega_0 = 1/\tau_d$, where ω_0 is the circular frequency that corresponds to the maximum of ε_d''. An example of such a graphical representation of the dielectric relaxation time for aqueous diallylmethylammonium trifluoroacetate solutions at 298 K is given in Figure 3. The uncertainty in the determination of the dielectric relaxation times was ± (5 to 7) % and depended on the number of frequencies at which the measurements of dielectric permittivity were carried out and on their position relative to the dispersion maximum.

The values of the static dielectric permittivity and relaxation time for a number of systems are in good agreement with data reported in the literature (NaCl and KCl solutions and others). The agreement between our data and literature values[2,4,5] for τ_d and ε_s is demonstrated in Figure 4. Several examples of the frequency dependence of ε' and ε_d'' and diagrams of $\varepsilon_d'' = f(\varepsilon')$ for NaCl solutions are shown in Figure 5. They were constructed using our own experimental data in the centimeter and millimeter frequency range along with literature data in the centimeter range (including data from Barthel et al.[2]). Examples of Cole−Cole diagrams for aqueous potassium fluoride solutions are shown in Figure 6. They also consist of our own experimental data[14] and data from Barthel et al.[2]

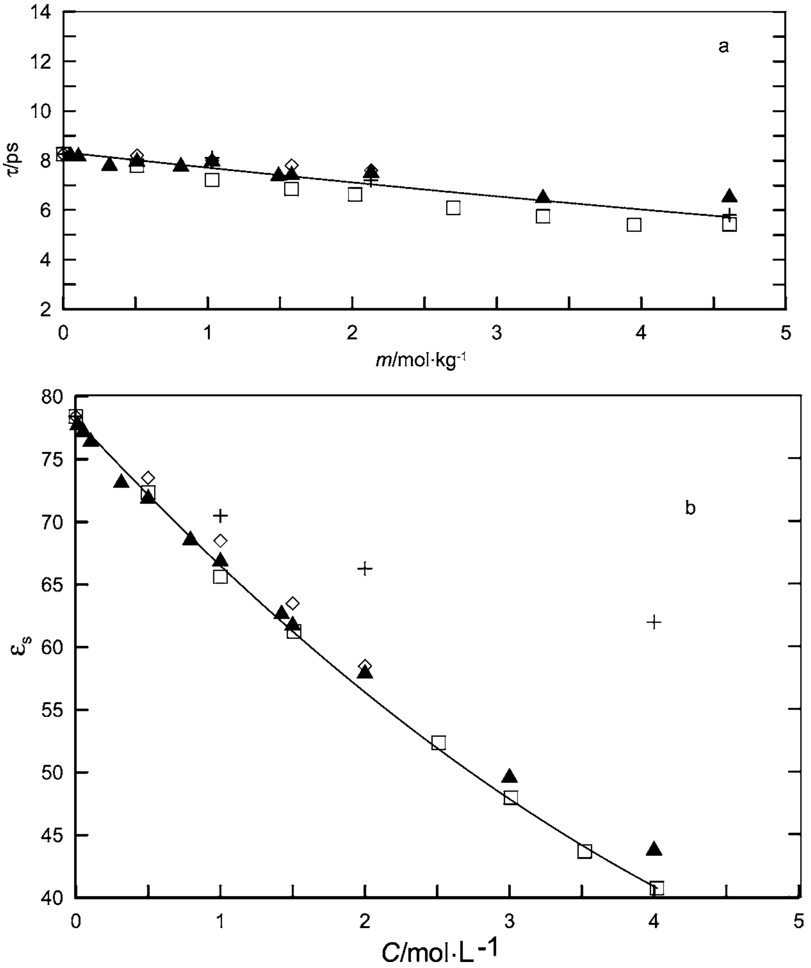

Figure 4. Composition dependence of (a) the dielectric relaxation time and (b) the static dielectric permittivity at 298 K for aqueous KCl solutions: □, our data; ▲, ref 2; ◇, ref 4; +, ref 5.

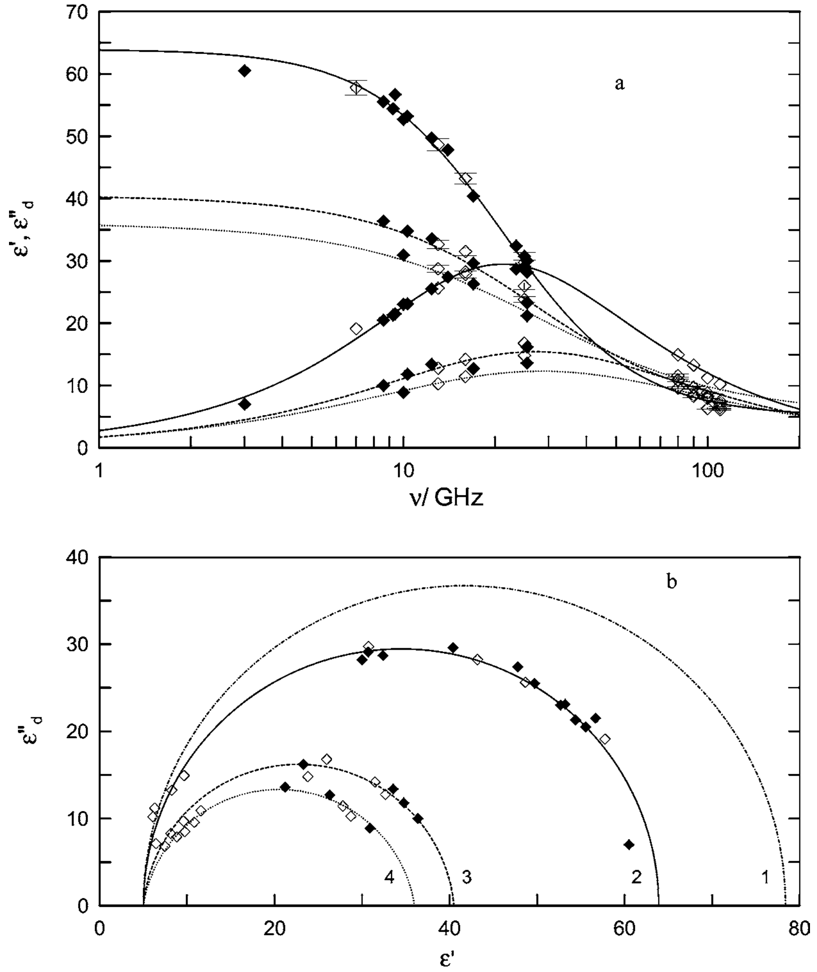

Figure 5. (a) Frequency dependence of ε' and ε_d''. (b) Cole−Cole diagrams for aqueous NaCl solutions at 298 K: ◇, our data; ◆, literature data.[2,4,5] Curve labels: 1, H_2O; 2, 1 mol·L^{-1}; 3, 4 mol·L^{-1}; 4, 5 mol·L^{-1}.

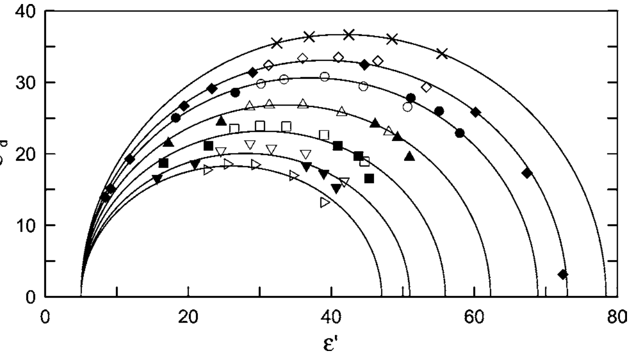

Figure 6. Cole−Cole diagrams for water and aqueous KF solutions at 298 K. Open symbols, our data;[14] solid symbols, literature data.[2] Symbols: ×, water; ◆/◇, 0.50 mol·kg^{-1}; ○/●, 1.00 mol·kg^{-1}; △/▲, 2.00 mol·kg^{-1}; □/■, 3.00 mol·kg^{-1}; ▽/▼, 4.00 mol·kg^{-1}; right-pointing triangles, 5.00 mol·kg^{-1}.

Results and Discussion

The problem of structural-kinetic states of water in the hydration shells of ions has been a subject of interest to many researchers. The above-mentioned frequency ranges correspond to the peak of dielectric losses for water and aqueous solutions, allowing us to examine the effect of dissolved salts on the structure and dynamics of water. The changes in the values of τ_d reflect the molecular-kinetic stabilization or destabilization of the H-bond network of water in the solutions. The activation parameters for dielectric relaxation processes were calculated using Eyring's theory of the absolute velocity of reactions. The enthalpy of activation was calculated for the temperature ranges (288 to 308 or 283 to 313) K using the equation

$$\Delta H_\varepsilon^\ddagger = R\frac{\mathrm{d}\ln\tau}{\mathrm{d}(1/T)} - RT \tag{5}$$

The changes in the $\Delta H_\varepsilon^\ddagger$ and $\Delta S_\varepsilon^\ddagger$ values reflect a degree of bonding strength as well as the structure-making or structure-breaking effect. Our attention is paid to the changes in τ_d and $\Delta H_\varepsilon^\ddagger$ over a range of ions with different ion−water interactions, strengths of H bonds, charges, geometrical forms, sizes or volumes, and functional groups for both cations and anions. Overall, 46 water−electrolyte systems were compared. They are listed in Table 1 and include aqueous solutions of fluorides, chlorides, nitrates, sulfates, formates, acetates, and propionates of alkali metal and ammonium ions as well as solutions of tetralkylammonium (TAA) and tetraallylammonium salts. The initial slopes of plots of τ_d versus concentration at 298 K are given in this table. It should be noted that these values are only first approximations because they are related to the particular relaxation model and the concentration range of the measurements. The sign of changes in $\Delta H_\varepsilon^\ddagger$ relative to pure water are also given in Table 1.

Hydrophilic Hydration of Ions. This section discusses the cations and anions without or with a small number of nonpolar groups. In most such cases for 1:1 electrolytes, the following inequalilties are maintained: $\tau_d(\text{solution}) - \tau_d(H_2O) < 0$ (298 K) and $\Delta H_\varepsilon^\ddagger(\text{solution}) < \Delta H_\varepsilon^\ddagger(H_2O)$. We can see the typical

Table 1. Initial Slopes of Plots of the Dielectric Relaxation Parameter τ_d versus Molality at 298 K and Signs of $\Delta(\Delta H_\varepsilon^\ddagger) = \Delta H_\varepsilon^\ddagger(\text{solution}) - \Delta H_\varepsilon^\ddagger(H_2O)$ for Aqueous Electrolyte Solutions Measured over the Given Molality (*m*) and Temperature (*T*) Ranges at Frequencies from (7 to 25) GHz or (7 to 120) GHz

electrolyte	*m* mol·kg^{-1}	*T* K	dτ_d/d*m* s·kg·mol^{-1}	$\Delta(\Delta H_\varepsilon^\ddagger)$
NaCl[a]	0.5 to 5.0	283 to 313	−0.75	<0
CsCl	1.05 to 4.57	288 to 308	−1.0	<0
KCl[a]	0.5 to 4	283 to 313	−0.91	<0
LiCl[a]	0.94 to 14.5	288 to 308	−0.66	<0
$CsNO_3$	0.28 to 0.75	283 to 313	<0	<0
κNO_3	0.27 to 2.03	283 to 313	<0	<0
$NaNO_3$	0.52 to 9.99	283 to 313	−0.36	<0
$LiNO_3$	0.60 to 8.30	283 to 313	−0.28	<0
CsF	0.5 to 6	288 to 308	−0.16	<0
KF	0.5 to 5	288 to 308	−0.35	<0
KH_2PO_4	0.25 to 1.4	288 to 308	0.08	≈0
NH_4Cl	0.25 to 2	278 to 323	<0	<0
NH_4F	0.51 to 13.7	288 to 308	0.15	≈0
NH_4SCN	0.25 to 2.0	288 to 308	−0.48	<0
$NH_4SO_3NH_2$	0.25 to 2.15	288 to 308	−0.34	<0
NH_4ClO_4	0.25 to 1.65	288 to 308	−0.83	<0
NH_4NO_3	0.25 to 3.7	288 to 308	− 0.63	<0
NH_4BF_4	0.25 to 1.7	288 to 308	−0.47	<0
$(NH_4)_2SO_4$	0.13 to 2.3	283 to 313	−0.28	<0
NH_4HSO_4	0.25 to 2	288 to 308	<0	<0
$NH_4H_2PO_4$	0.5 to 2.0	288 to 308	0.46	≤0
$(NH_4)_3PO4$	0.26 to 1.42	288 to 308	1.18	≤0
HCl	0.25 to 2[b]	288 to 308	−1.04[c]	<0
KOH	0.5 to 3[b]	288 to 308	−0.38[c]	<0
Li_2SO_4	0.22 to 2.77	298	−0.10	<0
Na_2SO_4	0.205 to 1.29	283 to 313	−0.5	<0
K_2SO_4	0.11 to 0.44	283 to 313	−0.49	<0
Cs_2SO_4	0.24 to 4.27	283 to 313	−0.5	<0
$(NH_2)_3CCl$	0.15 to 3.7	278 to 323	−0.65	<0
$(NH_2)_3CNO_3$	0.2 to 0.8	288 to 308	−0.88	<0
$(NH_2)_2NHCH_3CNO_3$	0.15 to 1.15	288 to 308	−0.22	<0
$[(NH_2)_3C]_2CO_3$	0.3 to 2.2	288 to 308	0.46	<0
CHOOK	0.70 to 8.88	288 to 308	−0.22	<0
CHOOCs	1.42 to 4.69	288 to 308	−0.12	<0
C_2H_5COOK	0.5 to 4.5	288 to 308	1.06	>0
C_2H_5COOCs	0.5 to 5	288 to 308	1.06	>0
$(CH_3)_3CCOOK$	0.25 to 1	288 to 308	1.23	>0
$(CH_3)_4NCl$	0.25 to 1	278 to 323	>0	<0
$(C_4H_9)_4NCl$	0.25 to 1	278 to 323	3.86	>0
$CF_3COOCH_3(C_3H_5)_2NH$	0.25 to 2.5[b]	288 to 308	3.81[c]	>0
$CF_3COO(C_3H_5)_2NH_2$	0.25 to 2.5[b]	288 to 308	2.91[c]	>0
$(CH_3)_2(C_3H_5)_2NCl$	0.25 to 2.5[b]	288 to 308	0.91[c]	>0
$HCOO(C_4H_9)_4N$	0.40 to 4[b]	288 to 308	5.19[c]	>0
$CH_3COO(C_4H_9)_4N$	0.42 to 4.69	288 to 308	6.91	>0
$C_2H_5COO(C_4H_9)_4N$	0.38 to 3.74	288 to 308	8.10	>0
$C_4H_9COO(C_4H_9)_4N$	0.33 to 4.15	288 to 308	12.4	>0

[a] Frequency range was (7 to 120) GHz. [b] Concentration is given in mol·L^{-1}. [c] Slope is given in s·L·mol^{-1}.

dependence of τ_d with the radius of the cation, but in some cases there is a different order (the examples are the KF and CsF solutions[14]). In the case of alkali metal nitrate systems, the variations in τ_d for solutions of the same concentration with different cations are small.[12] The changes in τ_d with concentration are more pronounced at lower temperatures [(283 or 288) K].

The differences over the range of anions with different structures was investigated for ammonium salts.[15] The values of τ_d and $\Delta H_\varepsilon^\ddagger$ were calculated, and the changes in τ_d and $\Delta H_\varepsilon^\ddagger$ for a number of anions with different H-bond strengths, geometrical forms and sizes ($F^- < SCN^- < NO_3^- < BF_4^-$, ClO_4^-, $SO_3NH_2^-$, HSO_4^-), charges ($HSO_4^- < SO_4^{2-}$), functional groups (SO_4^{2-}, $SO_3NH_2^-$, HSO_4^-) are considered. At the same time, the difference of these changes in the dependence of τ_d and $\Delta H_\varepsilon^\ddagger$ is not very large. It is shown that ammonium salts [NH_4NO_3, NH_4BF_4, NH_4ClO_4, $NH_4SO_3NH_2$, NH_4HSO_4, $(NH_4)_2SO_4$, NH_4SCN] have a structure-breaking effect on water.

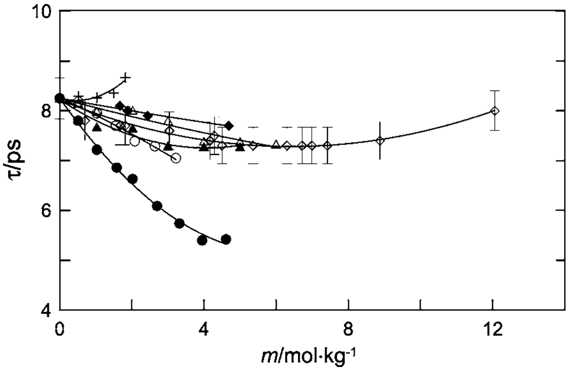

Figure 7. Composition dependence of the dielectric relaxation time for aqueous solutions with hydrophilic hydration at 298 K: +, KH_2PO_4; ◆, CsCHOO; △, CsF; ◇, KCHOO; ▲, KF; ○, KOH; ●, KCl.

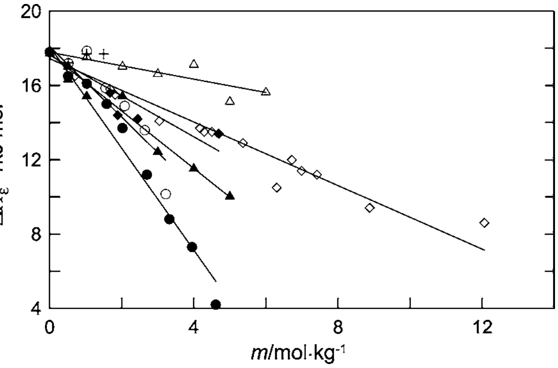

Figure 8. Composition dependence of the activation enthalpy of dielectric relaxation for aqueous solutions with hydrophilic hydration: +, KH_2PO_4; △, CsF; ◆, CsCHOO; ◇, KCHOO; ▲, KF; ○, KOH; ●, KCl.

The exception is NH_4F solutions. At lower concentrations $\tau_d(\text{solution}) \geq \tau_d(H_2O)$ and $\Delta H_\varepsilon^\ddagger(\text{solution}) \approx \Delta H_\varepsilon\ddagger\ (H_2O)$. The typical changes of τ_d and $\Delta H_\varepsilon^\ddagger$ for aqueous electrolyte solutions with hydrophilic ion hydration are given in Figures 7 and 8. $\tau_d(\text{solution}) > \tau_d(H_2O)$ occurs only in the cases of KH_2PO_4 and Gu_2CO_3 (Figure 9).

The question arises about the possibility of molecular-kinetic stabilization of water and the structure-making effect in the case of hydrophilic hydration. A large group of crystalline hydrates with a large number of water molecules are built from tetrahedral water frameworks. A good example of this type of arrangement is provided by the series of clathrate hydrates with F^-, $CH_3CO_2^-$, CO_3^{2-}, HPO_4^{2-} and other anions in the H-bond framework of the crystalline structure. There are the solid compounds based on the ice structure ($NH_4F \cdot H_2O$, $NH_3 \cdot H_2O$, potassium ethylviologen hexacyanometallates[29]). It should be noted that there exist solid solutions of NH_4F in water-ice.[30] This is determined by the peculiarities of the ion structures. NH_4^+ and F^- can form four tetrahedral H bonds with water molecules without the disruption of a lattice and the breaking of hydrogen bonds. Thus, there is a possibility of water stabilization in liquid electrolyte systems. We believe that the increase in the τ_d value for the solutions of NH_4F, Gu_2CO_3, NH_4HPO_4, $(NH_4)_3PO_4$, and KH_2PO_4 may be caused by this stabilization. Examples of such changes are shown in Figures 7, 9, and 10. The same sign of τ_d changes is seen in the case of hydrophobic hydration. However, there is a difference between hydrophilic and hydrophobic hydrations of ions in the case of variations in $\Delta H_\varepsilon^\ddagger$ values (Table 1).

Hydrophobic Hydration of Ions. The phenomenon of hydrophobic hydration is related to the stabilization of the H-bond network near nonpolar groups of molecules or ions and to the ordering of the tetrahedral structure of water. The dielectric

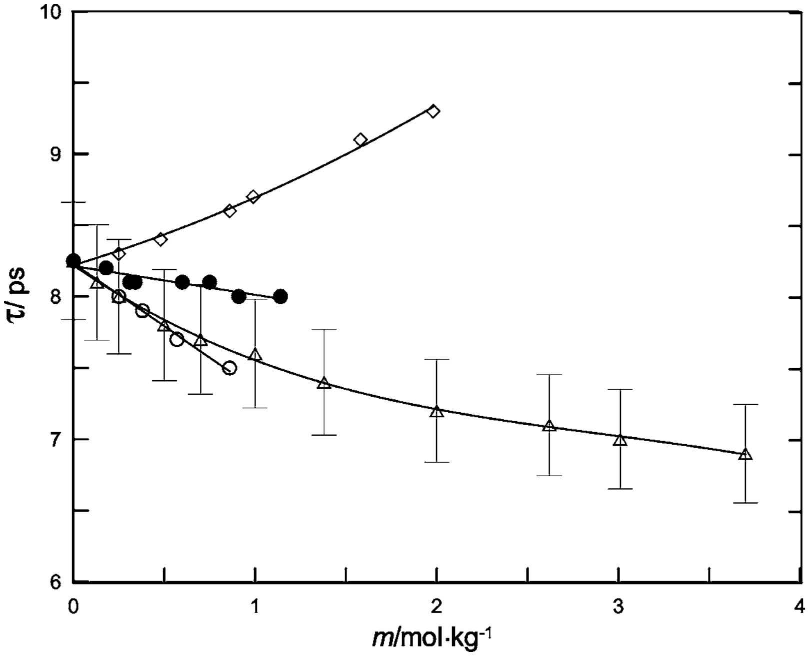

Figure 9. Composition dependence of the dielectric relaxation time for aqueous solutions of guanidinium salts at 298 K: ○, $GuNO_3$; △, GuCl; ●, CH_3GuNO_3; ◇, Gu_2CO_3 [Gu = $(NH_2)_3C^+$].

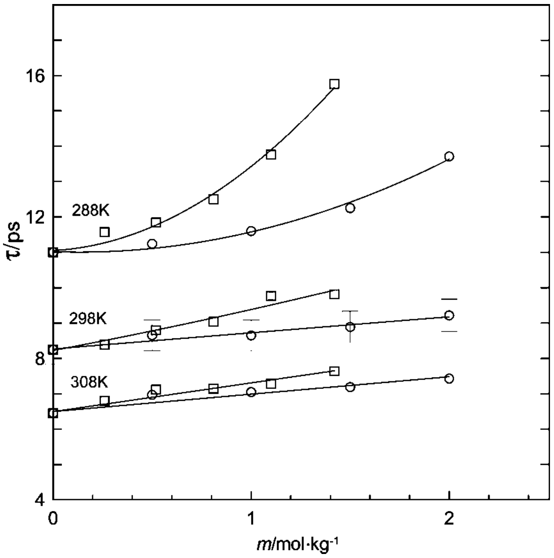

Figure 10. Composition dependence of the dielectric relaxation time for aqueous solutions at different temperatures: □, ammonium orthophosphate; ○, ammonium dihydrophosphate.

relaxation parameters over a temperature range are useful for studying the hydrophobic hydration in both nonelectrolyte[27,28,31] and electrolyte[21−25] aqueous solutions. While the hydrophobic hydration of cations over a *temperature* range was probed previously,[21,22] the hydrophobic hydration of anions has remained an open question to date. In the present work and refs 17, 20, and 25, the effect of the hydrophobic hydration of anions was investigated using, for example, solutions of alkaline-metal acetates, propionates, and trimethylacetate.

The values of the dielectric relaxation time of these solutions increase in comparison with water at all investigated temperatures (Table 1). The example of the concentration dependence of τ_d at 298 K is presented in Figure 11. The changes in τ_d for solutions with hydrophilic hydration (KCl, KCHOO) are also given in Figure 11 for comparison. The values of $\Delta H_{\varepsilon}^{\ddagger}$ increase with the concentration of salt (Figure 12). At the same time, the values of $\Delta H\varepsilon^{\ddagger}$ for potassium formate and chloride solutions decrease in comparison with water. The same difference in $\Delta H_{\varepsilon}^{\ddagger}$ is observed in the cases of cesium propionate and formate solutions. Thus, the dielectric relaxation characteristics of solutions with the same cation change in a different manner in relation to pure water. The change in the sign of the concentration dependence of $\Delta H_{\varepsilon}^{\ddagger}$ occurs near the transition from the potassium formate to the potassium propionate solutions. The above-mentioned anions have identical polar groups but different nonpolar parts. Therefore, the changes in τ_d and $\Delta H\varepsilon^{\ddagger}$ are determined by the action of nonpolar groups of ions. Thus, the structure-making effect primarily results from hydrophobic hydration of such anions. Similar but more pronounced changes are observed in the concentration dependence of τ_d and $\Delta H_{\varepsilon}^{\ddagger}$ with hydrophobic hydration of cations and anions.

The studies of complex permittivity and low-frequency conductivity of aqueous tetrabutylammonium carboxylate solutions were carried out over the frequency range (13 to 25) GHz. The measurements were performed using a wide range of concentrations and a temperature interval of (288 to 308) K.[23] The dielectric relaxation time and activation enthalpy were computed. We found growth in both of these parameters in aqueous tetrabutylammonium carboxylate solutions in comparison with pure water. The concentration dependence of τ_d and $\Delta H_{\varepsilon}^{\ddagger}$ indicates a substantial structure-making effect of both cations and anions. The dependence of τ_d on the number of nonpolar groups in the anion is found to follow the series tetrabutylammonium formate < acetate < propionate < valerate, as illustrated in Figure 13. Thus, the hydrophobic hydration of different anions is presented.

The molecular-kinetic properties of water in aqueous solutions have been investigated and classified at the transition from hydrophilic hydration of both the cation and anion (the potassium formate and chloride solutions) to hydrophobic hydration of the anion and hydrophilic hydration of the cation (the potassium acetate, propionate, and trimethylacetate solutions) to hydrophobic hydration of the cation and hydrophilic hydration of the anion (the TBA chloride and formate solutions) and finally to hydrophobic hydration of both the anion and cation

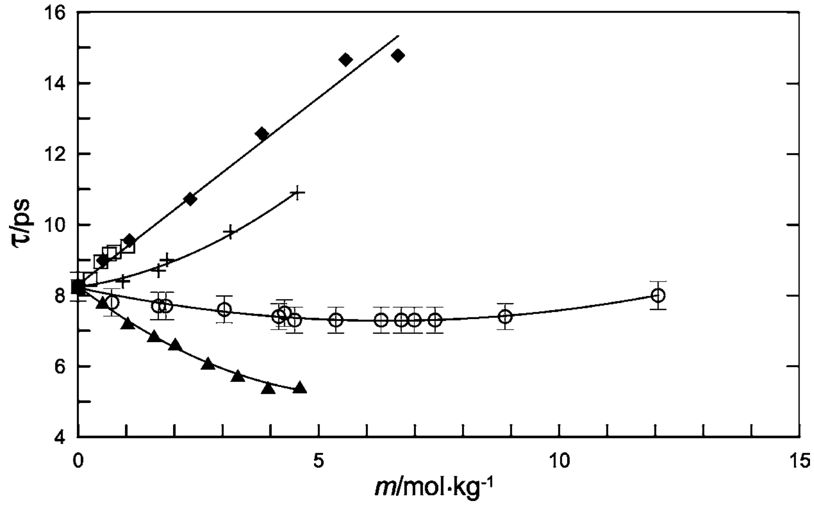

Figure 11. Composition dependence of the dielectric relaxation time for aqueous solutions of carboxylates at 298 K: □, $C(CH_3)_3COOK$; ◆, C_2H_5COOK; +, CH_3COOK; ○, CHOOK; ▲, KCl.

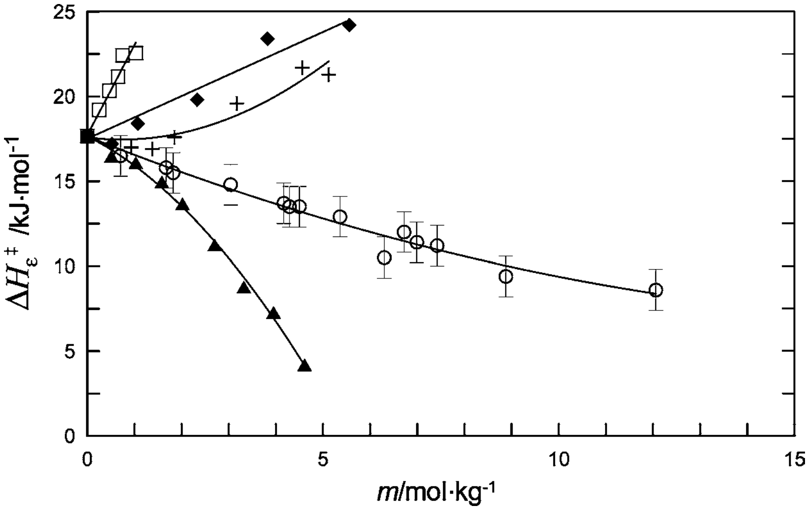

Figure 12. Composition dependence of the activation enthalpy of dielectric relaxation for aqueous solutions of carboxylates: □, $C(CH_3)_3COOK$; ◆, C_2H_5COOK; +, CH_3COOK; ○, CHOOK; ▲, KCl.

(the TBA acetate, propionate, and valerate solutions). In this sequence of investigated systems, the TBA valerate results in the strongest stabilization of the H-bond network of water. In this case, the values of τ_d for the concentrated solutions are three times larger than those for pure water (Figure 13).

In this context, the question of the existence of different cations with hydrophobic hydration arises. The aqueous solutions of allyl-substituted and alkyl-substituted ammonium salts have much in common. Any information on the hydration of allyl-substituted ammonium salts is absent in the literature. Therefore, it is interesting to find out how the differences in volume, form, number of nonpolar groups, etc., occur in the hydration of allyl-substituted ammonium ions in comparison to tetraalkylammonium salts. The features of their hydration were investigated for aqueous solutions of diallylammonium (DAA) and diallylmethylammonium (DAMA) trifluoroacetates and diallyldimethylammonium (DADMA) chloride, as an example. The complex dielectric permittivity for the series of solutions was obtained over the frequency range (13 to 25) GHz for a wide range of salt concentrations.[24] The measurements were performed in the temperature interval (288 to 308) K. The static relative permittivity and the parameters of the process of dielectric relaxation were calculated. The growth in the relaxation time τ_d in comparison with pure water is observed for all

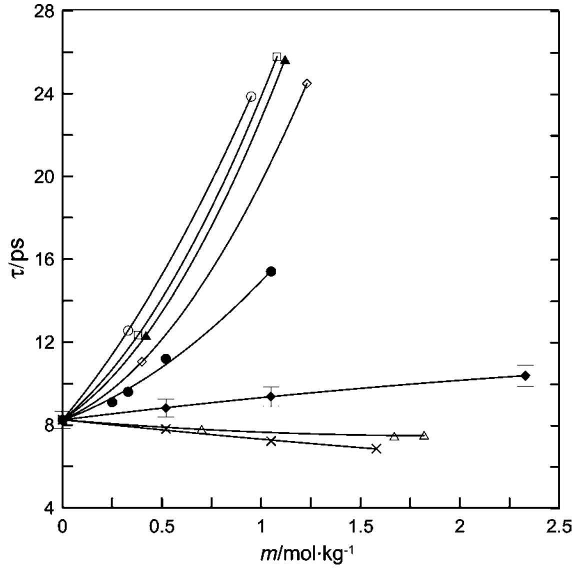

Figure 13. Composition dependence of the dielectric relaxation time for aqueous solutions with hydrophobic and hydrophilic hydration at 298 K: ○, TBA valerate; □, TBA propionate; ▲, TBA acetate; ◇, TBA formate; ●, TBA chloride; ◆, potassium propionate; △, potassium formate; ×, potassium chloride.

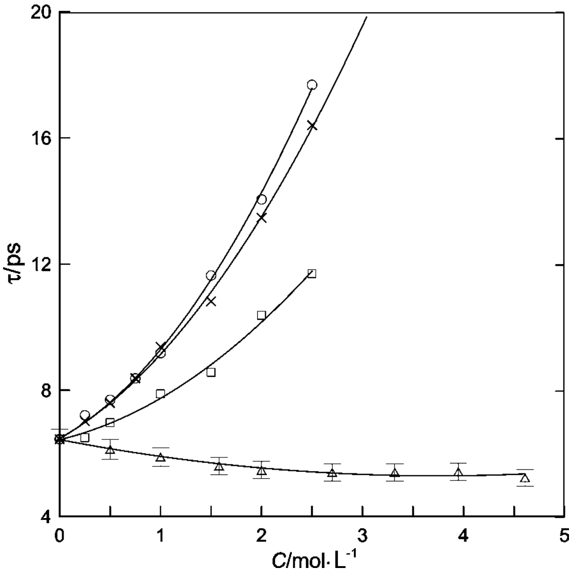

Figure 14. Concentration dependence of the dielectric relaxation time for aqueous solutions of allyl-substituted ammonium salts at 308 K: ○, DAMAFA; ×, DAAFA; □, DADMCl; △, potassium chloride.

of the examined solutions (see Table 1). This growth indicates a decrease in orientational mobility of the water molecules in the H-bond network upon the action of allyl-substituted ammonium ions, which points to the hydrophobic nature of the hydration of these ions. The example of the concentration dependence of τ_d at 308 K is presented in Figure 14. At 298 K, the values of τ_d increase according to the following series: KCl → H_2O → $(CH_3)_4NCl$ → DADMACl → $(C_4H_9)_4NCl$ and H_2O → DAAFA → DAMAFA. In the case of chloride solutions, the strongest effect is caused by the $(C_4H_9)_4N^+$ ion, as it has the largest hydrocarbon radicals. In the series of trifluoracetate solutions, the DAMA ion has a stronger effect than DAA, as it has one additional CH_3 group. The growth of τ_d for all of the considered allyl-substituted ammonium salt solutions indicates an effect on the mobility of water molecules in the tetrahedral H-bond network similar to that observed for alkyl-substituted ammonium salts.

DADMACl causes the least change in τ_d, though it has the larger number of nonpolar groups among the above-mentioned allyl-substituted ammonium salts. Probably, a stronger structure-breaking action of Cl^- ion becomes evident in this case. In the cases of DAAFA and DAMAFA solutions, we can see a stronger growth of τ_d values in comparison with the DADMACl solutions, so it can be assumed that hydrophobic hydration is manifested for diallylammonium and diallylmethylammonium ions. Our analysis of the temperature dependence of the dielectric relaxation time shows that values of $\Delta H_\varepsilon^\ddagger$ increase with increasing salt concentration (Table 1). The changes in $\Delta H_\varepsilon^\ddagger$ with concentration are similar to those for Bu_4NCl solutions,[22] and they have opposite sign for the KCl solutions.[13] Thus, it is possible to affirm the presence of structure-making effects for allyl-substituted ammonium ions as well as for the $(C_4H_9)_4N^+$ ion.

Conclusion

In the present paper, general relations between dielectric relaxation and structural effects of water in aqueous salt solutions have been suggested. This study includes an analysis of the effects of both hydrophobic and hydrophilic hydration for various cations and anions. The interpretation is given on the basis of our structural model for aqueous electrolyte solutions.[32,33] The model of hydration shells is based on the principle of complementary organization of the first coordination sphere of ions, the intermediate layer, and tetrahedral bulk water. The higher the degree of structural complementarity (in comparison with bulk water), the stronger is the molecular-kinetic stabilization and the structure-making effect. Structure-breaking effects are realized in the opposite case. These two variants can be inferred more or less directly from computer simulations of liquid solutions, analysis of the crystalline structures of clathrate and other salt hydrates, and geometrical models.[32] The different structural variations within hydration shells should be accompanied by some increase or decrease in the bonding strength, the orientation order, and the dynamics of water molecules. We find that for ions with hydrophobic hydration, there is a good complementary organization of hydration shells and bulk water. As a result, the following inequalities hold: $\tau_d(\text{solution}) > \tau_d(H_2O)$ and $\Delta H_\varepsilon^\ddagger(\text{solution}) > \Delta H_\varepsilon^\ddagger(H_2O)$. Thus, crystalline clathrate hydrates can be formed from such solutions.

In the case of hydrophilic hydration, there are possibly two different scenarios of changes for the structural geometrical parameters of water in the hydration shells of ions. These two scenarios determine the following relations:

$$(1) \qquad \tau_d(\text{solution}) < \tau_d(H_2O) \quad \text{and} \quad \Delta H_\varepsilon^\ddagger(\text{solution}) < \Delta H_\varepsilon^\ddagger(H_2O)$$

or

$$(2) \qquad \tau_d(\text{solution}) \geq \tau_d(H_2O) \quad \text{and} \quad \Delta H_\varepsilon^\ddagger(\text{solution}) \approx \Delta H_\varepsilon^\ddagger(H_2O)$$

As a result, new general criteria for hydrophilic and hydrophobic hydration of ions are suggested on the basis of the microwave dielectric measurements over the range of temperatures.

Supporting Information Available:

Experimental data on dielectric properties, relaxation time, and activation enthalpy of dielectric relaxation. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Barthel, J.; Krienke, H.; Kunz, W. *Physical Chemistry of Electrolyte Solutions: Modern Aspects*. Springer: New York, 1998; p 401.

(2) Barthel, J.; Buchner, R.; Munsterer, M. *Electrolyte Data Collection, Part 2: Dielectric Properties of Water and Aqueous Electrolyte Solutions*; Chemistry Data Series, Vol. XII, Part 2; Dechema: Frankfurt am Main, Germany, 1995; p 365.

(3) Barthel, J.; Buchner, R. Dielectric relaxation in solutions. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **2001**, *97*, 349–382.

(4) Hasted, J. *Aqueous Dielectrics*; Chapman & Hall: London, 1973; p 203.

(5) Harris, F. E.; O'Konski, C. T. Dielectric properties of aqueous ionic solutions at microwave frequencies. *J. Phys. Chem.* **1957**, *61*, 310–316.

(6) Schroder, C.; Hunger, J.; Stoppa, A.; Buchner, R.; Steinhauser, O. On the collective network of ionic liquid/water mixtures. II. Decomposition and interpretation of dielectric spectra. *J. Chem. Phys.* **2008**, *129*, 184501.

(7) Lyashchenko, A. K.; Lileev, A. S.; Zasetsky, A. Yu.; Novskova, T. A.; Gaiduk, V. I. Orientational relaxation in hydrogen bonded systems: aqueous solutions of electrolytes. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1985–1991.

(8) Lyashchenko, A. K.; Novskova, T. A.; Klemenkova, Z. S. The mechanism of the interaction of electromagnetic irradiation with aqueous NaCl solutions in orientation polarization frequency range. In *MM Waves of Low Intensivity in Biology and Medicine*; Institute of Radioengineering and Electronics, Russian Academy of Sciences: Moscow, 2009; pp 226−228.

(9) Lyashchenko, A. K.; Zasetsky, A. Yu. Complex dielectric permittivity and relaxation parameters of concentrated aqueous electrolyte solutions in millimeter and centimeter wavelength ranges. *J. Mol. Liq.* **1998**, *77*, 61–75.

(10) Zasetsky, A. Yu.; Lyashchenko, A. K. Quasi optical method of measurement of solution complex dielectric permittivity in millimeter waves and relaxation characteristics of solutions. VINITI deposited paper no. 2181-B99, July 6, 1999, p 62.

(11) Zasetsky, A. Y.; Lyashchenko, A. K.; Lileev, A. S. Dielectric-properties of NaCl aqueous-solutions in UHF-range. *Russ. J. Inorg. Chem.* **1994**, *39*, 990–996.

(12) Lileev, A. S.; Filimonova, Z. A.; Lyashchenko, A. K. Dielectric permittivity and relaxation in aqueous solutions of sulfates and nitrates of alkali metals in temperature range 288−313 K. *J. Mol. Liq.* **2003**, *103−104*, 299–308.

(13) Loginova, D. V.; Lileev, A. S.; Lyashchenko, A. K. Dielectric properties of aqueous potassium chloride solutions as a function of temperature. *Russ. J. Inorg. Chem.* **2002**, *47*, 1426–1433.

(14) Loginova, D. V.; Lileev, A. S.; Lyashchenko, A. K. Microwave dielectric properties of aqueous solutions of potassium and cesium fluorides. *Russ. J. Phys. Chem.* **2006**, *80*, 1626–1633.

(15) Lileev, A. S.; Lyashchenko, A. K. Dielectric properties of aqueous ammonium salt solutions. *J. Mol. Liq.* **2009**, *91*, 21–31.

(16) Lyashchenko, A. K.; Kokovina, G. V.; Lileev, A. S. Aqueous ammonium fluoride solutions − dielectric and structural parameters. *J. Struct. Chem.* **1987**, *28*, 709–713.

(17) Lyashchenko, A. K.; Loginova, D. V.; Lileev, A. S. Complex dielectric permittivity and relaxation of aqueous electrolyte solutions with hydrophobic and hydrophilic hydration. *Sci. Bull. Lodz Technical University* **2006**, *982*, 233–234.

(18) Lileev, A. S.; Loginova, D. V.; Lyashchenko, A. K. Dielectric properties of aqueous solutions of the hydrochloric acid. *Mendeleev Commun.* **2007**, *17*, 364–365.

(19) Lileev, A. S.; Lyashchenko, A. K.; Yastremsky, P. S. Dielectric-properties of guanidinium salt aqueous-solutions. *Russ. J. Phys. Chem.* **1986**, *60*, 535–537.

(20) Loginova, D. V.; Lileev, A. S.; Lyashchenko, A. K.; Kharkin, V. S. Hydrophobic hydration of the propionate ion. *Mendeleev Commun.* **2003**, *2*, 68–70.

(21) Yastremsky, P. S.; Kokovina, G. V.; Lyashchenko, A. K.; Samoylov, O. Ya.; Mirgorod, Yu. A. Hydration of tetraalkylammonium salts. *J. Struct. Chem.* **1975**, *16*, 921–925.

(22) Kokovina, G. V.; Lyashchenko, A. K; Yastremsky, P. S. Stabilization of the structure of D_2O by the tetrabutylammonium ion. *Zh. Struct. Khim.* **1983**, *24*, 121–124.

(23) Loginova, D. V.; Lileev, A. S.; Lyashchenko, A. K.; Aladko, L. S. The high frequency dielectric spectroscopy of the aqueous solutions of tetrabutylammonium carboxylates. *J. Non-Cryst. Solids* **2005**, *351*, 2882–2887.

(24) Lileev, A. S.; Loginova, D. V.; Lyashchenko, A. K.; Timofeeva, L. M.; Kleshcheva, N. A. The hydrophobic hydration in aqueous solutions of allyl-substituted ammonium salts. *J. Mol. Liq.* **2007**, *131−132*, 101–104.

(25) Lileev, A. S.; Loginova, D. V.; Lyashchenko, A. K. Structure-making effect of trimethylacetate-ion. *31st International Conference on Solution Chemistry*, Innsbruck, Austria, 2009; Rode, B. M., Randolf, B. R., Eds.; P-118.

(26) Le Bot, J. Metode de mesure de la constante dielectrique comptes rendus. *C. R. Acad. Sci.* **1953**, *236*, 469–470.

(27) Lyashchenko, A. K.; Lileev, A. S.; Kharkin, V. S.; Efremov, P. V. Complex permittivity and relaxation in aqueous solutions of methyl ethyl ketone. *Russ. J. Phys. Chem.* **2001**, *75*, 195–201.

(28) Lyashchenko, A. K.; Kharkin, V. S.; Lileev, A. S.; Efremov, P. V.; Zasetsky, A. Yu. Complex permittivity of low-concentration aqueous solutions of acetone. *Russ. J. Phys. Chem.* **2000**, *74*, 529–534.

(29) Ilyukhin, A. B.; Ketsko, V. A.; Kotov, V. Yu.; Lyashchenko, A. K. Icelike $(H_2O)_{12}$ fragment in the structure of potassium ethylviologen hexacyanometallates. *J. Struct. Chem.* **2002**, *43*, 977–979.

(30) Lyashchenko, A. K.; Malenkov, G. G. X-ray investigation of solid solutions of NH_4F in ice. *Zh. Struct. Khim.* **1969**, *10*, 724–725.

(31) Lyashchenko, A. K.; Novskova, T. A.; Lileev, A. S.; Kharkin, V. S. Dielectric relaxation of aqueous nonelectrolyte solutions (experimental, structural and molecular-kinetic aspects). *J. Mol. Liq.* **2001**, *93*, 29–33.

(32) Lyashchenko, A. K. Structure and structure-sensitive properties of aqueous solutions of electrolytes and nonelectrolytes. *Adv. Chem. Phys.* **1994**, *87*, 379–426.

(33) Lyashchenko, A. K. Concentration transition from water−electrolyte to electrolyte−water solvents and ionic clusters in solutions. *J. Mol. Liq.* **2001**, *91*, 21–31.

Received for review November 10, 2009. Accepted March 16, 2010. This work was supported by the RFBR, Projects 08-03-00095 and 09-03-00367.

JE900961M