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# Dielectric properties of aqueous hydrochloric acid solutions

**Alexander S. Lileev,* Dar'ya V. Loginova and Andrey K. Lyashchenko**

*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 954 1279; e-mail: lilaser@mail.ru*

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The structure-breaking effect of HCl molecules is established on the basis of the data on dielectric relaxation in aqueous solutions.

Proton hydration and electrical conductivity mechanism are of considerable interest in the physical chemistry of solutions and biochemistry.[1–4] Microwave dielectric spectroscopy is used for studying hydration in aqueous electrolyte solutions. It yields information on changes in the orientational mobility of water molecules under the influence of dissolved ions. The measurements of dielectric properties of HCl solutions, as well as the solutions of other strong acids, are complicated because of their high conductivity.[5–7] They are executed for low-concentration HCl solutions and at low temperatures, *i.e.*, in the cases when the conductivity of solutions is not very high. Hasted and co-workers[5,6] investigated 0.25 and 0.5 M HCl solutions at 298 K and 0.065–0.5 M solutions at 276 and 283 K for 3 and 10 cm wavelengths. Gerdes *et al.*[7] measured a 0.1 M solution at 298 K and 9.4 GHz.

In this work, we used the method of a cylindrical rod in a wave guide[8] for studying high-frequency dielectric permittivity ($\varepsilon'$) and losses ($\varepsilon''$). It allowed us to measure dielectrics with high losses. This method was modified for studying aqueous solutions. The experiments and calculations are described elsewhere.[9–11] The high-frequency complex permittivity of aqueous 0.25 to 2.0 M HC1 solutions was studied in the frequency range 7–25 GHz because it corresponds to a maximum of Debye's range of the dielectric permittivity dispersion in water and aqueous solutions of electrolytes. It allows us to determine most precisely the dielectric relaxation times, which characterise the orientation mobility of water molecules in an H-bond net.

The solutions of HC1 are highly conductive liquids; therefore, the measured dielectric losses contain an ionic component ($\varepsilon_i''$). The low-frequency specific conductivity ($\sigma$) of solutions was measured at 1 kHz for the calculation of $\varepsilon_i''$. The values of $\sigma$ are in good agreement with published data.[12,13] The ionic losses were calculated from the equation[14] $\varepsilon_i'' = \sigma/\varepsilon_0\omega$, where $\omega$ is the circular frequency, and $\varepsilon_0$ is the dielectric permittivity of a vacuum. The dipole component of dielectric losses was determined[15] as $\varepsilon_d'' = \varepsilon'' - \varepsilon_i''$.

The frequency dependence of $\varepsilon'$ and $\varepsilon_d''$ was analysed using the Cole–Cole relaxation model with the most probable relaxation time. In this case, complex dielectric permittivity is described by the equation[15]

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

which can be transformed to

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\frac{1 + (\omega\tau)^{1-\alpha}\sin\frac{\pi\alpha}{2}}{1 + 2(\omega\tau)^{1-\alpha}\sin\frac{\pi\alpha}{2} + (\omega\tau)^{2(1-\alpha)}},$$

$$\varepsilon_d'' = (\varepsilon_s - \varepsilon_\infty)\frac{(\omega\tau)^{1-\alpha}\cos\frac{\pi\alpha}{2}}{1 + 2(\omega\tau)^{1-\alpha}\sin\frac{\pi\alpha}{2} + (\omega\tau)^{2(1-\alpha)}},$$

where $\varepsilon_s$ is the static dielectric permittivity, $\varepsilon_\infty$ is the high-frequency limit of dielectric permittivity, $\omega$ is the circular frequency, $\tau$ is the relaxation time, $\alpha$ is a distribution parameter of relaxation times. The value of $\varepsilon_\infty$ for solutions was taken equal to 5 regardless of temperature and concentration. It was found previously that at small variations of $\varepsilon_\infty$ near 5 the changes of $\varepsilon_s$ and $\tau$ are also small.[9,16] These variations are within the limits of an error of definition of these parameters.

The static dielectric constant was found from Cole–Cole diagrams (Figure 1) by the circular extrapolation on zero frequency. Significant decrease of dielectric constant is observed

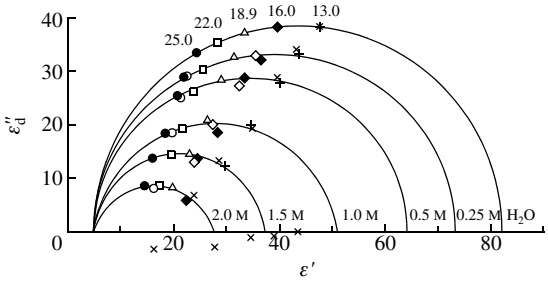


**Figure 1** Cole–Cole diagrams for water and HCl solutions at 288 K. Figures above the semicircles are frequencies (GHz).

**Table 1** Dielectric parameters of aqueous HCl solutions.

| M/mol dm$^{-3}$ | $\tau$/ps | | | | $\alpha$ | | | | $\varepsilon_s$ | | | | | $\Delta H_\varepsilon^{++\,a}$/ kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 278 K | 288 K | 298 K | 308 K | 278 K | 288 K | 298 K | 308 K | 278 K | 288 K | 298 K | 308 K | 323 K | |
| 0 | 15.0 | 11.0 | 8.25 | 6.45 | 0.00 | 0.00 | 0.00 | 0.00 | 86.9 | 82.1 | 78.4 | 74.9 | 69.9 | 17.2 |
| 0.25 | 14.4 | 10.8 | 8.0 | 6.2 | 0.00 | 0.02 | 0.02 | 0.03 | 75.7 | 73.3 | 70.7 | 67.8 | 46.2$^b$ | 18.0 |
| 0.5 | 13.4 | 10.4 | 7.9 | 6.1 | 0.00 | 0.04 | 0.08 | 0.06 | 69.5 | 64.3 | 65.0 | 60.1 | 59.9$^b$ | 16.9 |
| 1.0 | 11.8 | 9.4 | 7.2 | 5.7 | 0.12 | 0.12 | 0.17 | 0.11 | 55.9 | 50.8 | 51.4 | 47.3 | — | 16.1 |
| 1.5 | — | 8.1 | 6.5 | 6.0$^b$ | — | 0.11 | 0.15 | — | — | 37.2 | 39.8 | 42.0$^b$ | — | 8.0 |
| 2.0 | 9.1$^b$ | 6.8 | 6.3 | 5.5 | — | 0.28 | 0.24 | 0.38 | 27.5$^b$ | 27.6 | 30.2 | 30.1 | — | 6.03 |

$^a$The values of $\Delta H_\varepsilon^{++}$ were calculated for 288–308 K. $^b$Approximate values.

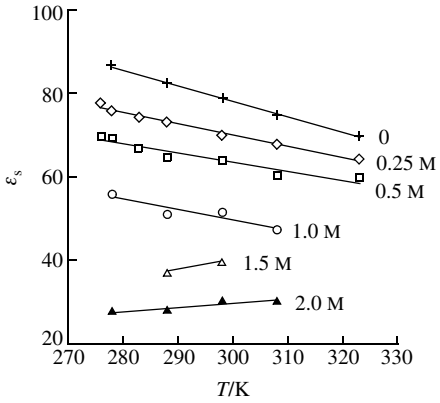


**Figure 2** The temperature dependence of dielectric constants for water and HCl solutions (data at 276 and 283 K were taken from ref. 6).

for all solutions at increasing HCl concentration. The temperature dependence of dielectric constant for water and aqueous HC1 solutions is shown in Figure 2. The dielectric constant in the dilute solutions decreases with temperature, as well as in pure water. For the concentrated solutions, the temperature coefficient of $\varepsilon_s$ became equal to zero or, possibly, changed its sign. A similar effect was observed in others highly concentrated aqueous electrolyte solutions.[11,17]

Using the polarization scheme of complex water dielectrics developed by Hasted,[15] the effective numbers of 'frozen' water molecules near the ions were found taking into account the volumes of ions. The hydration numbers are equal to 10–12 water molecules per HCl molecule. As the ion $Cl^-$ is weakly hydrated, it is possible to assume that the main part of 'frozen' water molecules relates to the ions $H^+$. Modern models of proton hydration[1–4] assume that the ion $H^+$ located between water molecules forms the hydration complex $H_5O_2^+$ or $H_9O_4^+$. The number of 'frozen' water molecules determined in this

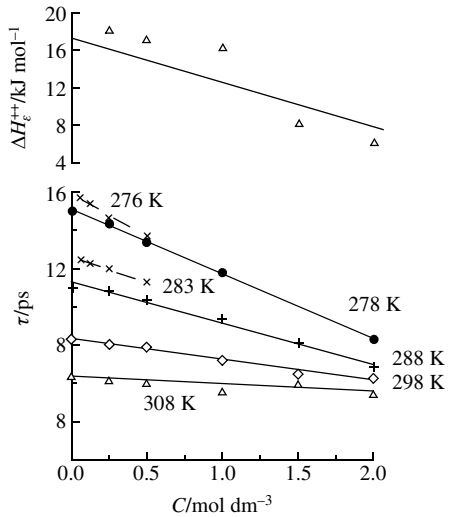


**Figure 3** Dependences of relaxation time and activation enthalpy on HCl concentration (data at 276 and 283 K were taken from ref. 6).

work is larger than the coordination number of a proton in these models. Thus, the proton forms the second hydration sphere.

The dielectric relaxation times ($\tau$) were determined graphically from the Cole–Cole equation. The function

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

in logarithmic coordinates represents a straight line crossing the $x$ axis at $\omega_0 = 1/\tau$. The activation enthalpies of dielectric relaxation ($\Delta H_\varepsilon^{\neq}$) were calculated from the temperature dependence of relaxation time $\tau$ using the Eyring theory of absolute reaction rates (Table 1).

The values of $\tau$ characterise the mobility of water molecules in the H-bond net. They decrease for aqueous HCl solutions in comparison with pure water at all temperatures (Figure 3). It denotes on the increase of water molecule mobility in solutions under the action of ions. The changes of $\tau$ are more at low temperatures where the water structure is destroyed by thermal motion to a lesser degree. The decrease of $\Delta H_\varepsilon^{++}$ shows that HCl addition yields breaking effect on a water structure in solutions. It is more significant than that in KCl solutions. Thus, hydrochloric acid is one of the strongest structure breakers among other electrolytes with hydrophilic hydration.

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