

## Determination of the proton hopping rate

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A non linear decrease of the absolute individual ion mobility (a.i.i.m.) of uni-, di- and trivalent ions at tracer scale has been observed for increasing proton concentrations of inert aqueous electrolyte mixtures of type  $\text{NaClO}_4/\text{HClO}_4$  ( $T=298.1$  K) in previous works [1,2].

According to the microscopic version of the Stokes law, this effect could be explained by an increase of the frictional forces exerted on the ion due to an excess of hydrated protons in the electrolyte bulk water. The non-negligible presence of hydrated proton with the limiting structures  $\text{H}_5\text{O}_2^+$  (Zundel cation [3]) or  $\text{H}_9\text{O}_4^+$  (Eigen cation [4]) could modify the dynamical (reorientation time) and structural properties (translational and orientational order) of the electrolyte bulk water [5]. This results in an increase of the reorientation time of water molecules in the hydration shell of the ion and, thus, in a lowering of the ion mobility.

The variation of the rotational reorientation time,  $\tau_{\text{H}_2\text{O}}$ , of electrolyte bulk water with the proton concentration as well as with the ionic strength of the electrolyte was deduced from the systematic analysis of the pH-dependence of the a.i.i.m. at tracer scale for 11 radio-ions of various charge [6].

As shown in Fig. 1, the dynamical properties of bulk water for  $\text{NaClO}_4$ -electrolytes are only affected by the presence of the ions composing the electrolyte since the proton concentration is very low ( $\text{pH} = 5 - 6$ ). In the case of  $\text{HClO}_4$ , the proton of the acid is directly transferred to a water molecule forming an hydrated proton and never comes back as the nearest neighbour of the perchlorate anion. The migration of the excess proton in water occurs via a process of structural diffusion (Grötthuss mechanism) in which charge transfer takes place through an interchange of covalent and hydrogen bonds [7]. As shown in Fig.1, the rotational reorientation time of bulk water for  $\text{HClO}_4$ -electrolytes increases strongly with increasing proton concentration and thus with the fraction of water molecules which exchanges protons per unit of time. The data were fitted using the following expression:

$$\tau_{\text{H}_2\text{O}} = \frac{\tau_{\text{H}_2\text{O}}^0}{1 - \tau_p / \tau_{\text{H}_2\text{O}}^0 \cdot (1 - \exp(-b[\text{H}^+]/[\text{H}_2\text{O}]))} \quad (1)$$

where  $\tau_{\text{H}_2\text{O}}^0 = 8.3$  ps [8] is the rotational reorientation time for pure water (Debye relaxation rate of water at 298.1 K),  $\tau_p$  the mean residence time of a proton with a given water molecule,  $[\text{H}_2\text{O}] = 55.5$  mol/L and  $b$  a constant. The result of the fit leads to a value for  $\tau_p$  of 1.44(18) ps ( $T = 298.1$  K). The inverse of this number corresponds to the rate constant for proton transfer between  $\text{H}_2\text{O}$  and  $\text{H}_5\text{O}_2^+$  or  $\text{H}_9\text{O}_4^+$ . The value found here is  $0.69(9)$  ps<sup>-1</sup> and compares well with:

- (1) the experimental value obtained from the NMR studies of proton transfer in water,  $0.67$  ps<sup>-1</sup> [9] and,
- (2) the proton hopping rates calculated by quantum molecular dynamic simulation,  $0.69$  ps<sup>-1</sup> for proton transfer in the Eigen cation and  $0.60$  ps<sup>-1</sup> for proton transfer in the Zundel cation [10].

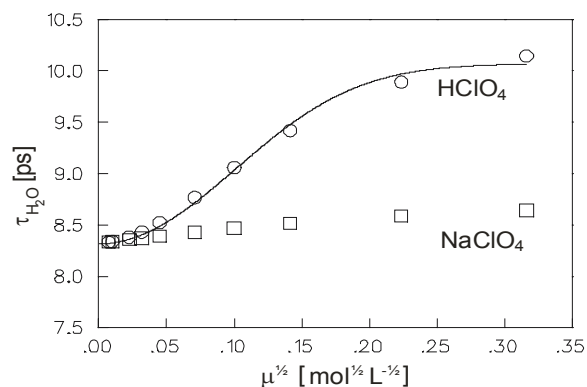


Fig.1. Dependence of  $\tau_{\text{H}_2\text{O}}$  with the ionic strength ( $\mu$ ) for  $\text{NaClO}_4$  and  $\text{HClO}_4$  electrolytes deduced from the experimentally observed a.i.i.m. of 11 various non-carrier-added radio-cations [1]. The solid line represents the fit of the data with Eq. (1).

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