

Hydration of Ions in Aqua-Solution: Concept of Affected Viscosity.

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Processes of hydration in aqueous solutions play an important role in many chemical reactions. Methods such as NMR, X-ray and neutron diffraction allowed to investigate its static and dynamic properties. However, some data obtained by these methods cannot be explained by the classical hydrodynamic concept. Thus the diffusion and rotation motion of hydrating water molecules were found to be depending on the kind of hydrated ion and not on the viscosity of the solvent [1]. This phenomenon may be explained from the concept of viscosity affected in the vicinity of the ion (micro-viscosity) which was used elsewhere [2]. The ion micro-viscosity $\tilde{\eta}_i$ ($\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$) is involved in the Stokes-Einstein law in its microscopic form:

$$u_i^0 = \frac{e|z_i|}{6\pi\tilde{\eta}_i r_i} \quad (1)$$

The ion micro-viscosity is defined as the viscosity of the water molecules in the first hydration shell of the ion. u_i^0 is the absolute ion mobility ($\text{m}^2 \text{V}^{-1}\text{s}^{-1}$), e the elementary charge ($1.6022\cdot 10^{-19}$ C), z_i the charge number of the ion, r_i the ionic radius (m).

The magnitude of $\tilde{\eta}_i$ against $\tilde{\eta}^0$, the viscosity of the water ($\tilde{\eta}^0 = 8.903\cdot 10^{-4}$ $\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$ at 298.1 K), reflects the effect of the ion on the structure of water.

The ion micro-viscosities $\tilde{\eta}_i$ calculated above using the known values of the absolute ion mobility are given in Figure 1 versus surface charge density $\sigma_i = |z_i|e/4\pi r_i^2$ ($\text{C}\cdot\text{m}^{-2}$). The $\tilde{\eta}_i$ decreases with increasing of σ , reaches some minimum value and begins to increase.

The number of water molecules leaving the hydration sphere over the period of time in which the outer bulk water shell is renewed, may be given as follows:

$$\Delta n = N(1 - e^{-\tau_{\text{H}_2\text{O}}/\tau_i}) \quad (2)$$

where N is number of water molecules in the first hydration shell at time zero, $\tau_{\text{H}_2\text{O}}$ and τ_i the correlation time of rotation process of water molecule in the bulk and hydration shell, respectively. The relative exchange rate of the water molecules between the hydration sphere and the bulk, $\Delta n/N$ may be expressed as a complicated exponential function of the surface charge density of the ion [2]. Since the rotation correlation time is proportional to the viscosity of the media by Debye relation, the micro-viscosity can be expressed as (solid line in Figure 1):

$$\frac{1}{\tilde{\eta}_i} = \frac{1}{\tilde{\eta}^0} \ln[1 - [e^{-4\pi\sigma_i} (e^{-\sigma_i} (e^{p\sigma_i} - e^{q\sigma_i}) + e^{q\sigma_i} - 1)]] \quad (3)$$

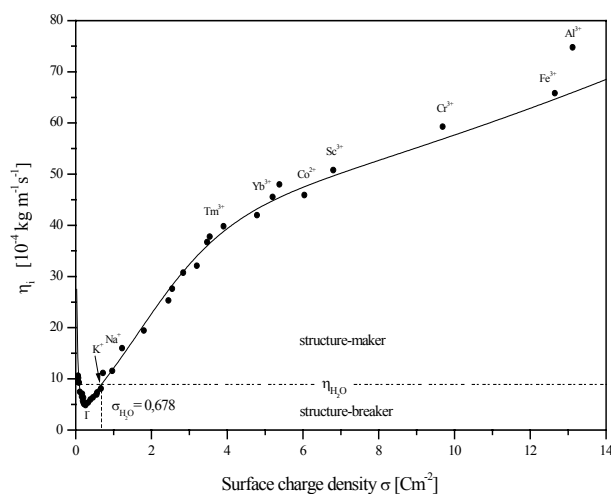
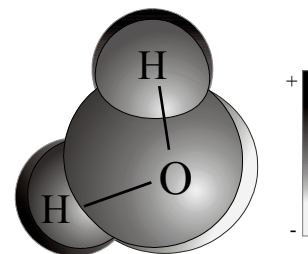


Figure 1. The ion micro-viscosity versus the surface charge density of the ions. The solid line corresponds to Eq. (3).

where $p = 11.65$ ($\text{m}^2 \text{C}^{-1}$), $q = 12.52$ ($\text{m}^2 \text{C}^{-1}$) and $\sigma_s = 0.24$ ($\text{C}\cdot\text{m}^{-2}$). The σ_s - value corresponds to the minimum of the $\tilde{\eta}_i$. It is obviously from Figure 1 that micro-viscosity is a result of several effects. Thus the ion micro-viscosity can be represented by two components (i) dependence on the size of the ion $\tilde{\eta}_i^g$ - *geometrical effect*; (ii) component of the ion-dipole interaction $\tilde{\eta}_i^e$ - *electrofriction*.

The two points corresponding to magnitude $\tilde{\eta}^0$ can be derived from Eq. (3) - $\sigma_1 = 0.095$ and $\sigma_2 = 0.678$ ($\text{C}\cdot\text{m}^{-2}$).

Some ions with these surface charge densities provide a micro-viscosity identical with that in the bulk. Due to the highly polarised structure of the water



molecules the

interaction in the bulk is affected mainly by Coulomb attraction. We propose the value $\sigma_2 = 0.678$ ($\text{C}\cdot\text{m}^{-2}$) as *surface charge density of the water molecule* in the places of the maximum concourse of the electron density (see Figure 2).

The application of this theory allows to solve the several important problems: (i) to estimate the behaviour of the hydration water molecule; (ii) to calculate the transport properties of the ions.

[1] By L. Endom, H. G. Hertz, B. Thül and M. D. Zeidler, Ber. Bunsenges. Phys. Chem., **71**, 1008 (1967). [2] E. Mauerhofer, F. Rösch, Phys. Chem. Chem. Phys., **5**, 117 (2002).