Glasslike Behaviour in Aqueous Electrolyte Solutions

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Why study salt solutions...?!

Surfaces of proteins and active sites of proteins are charged → changes water structure → affects reaction rates

Do ions alter the water’s hydrogen-bond network? Does it become more or less ice like?
Standard picture

Viscosity described by Jones-Dole:

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc$$

Jones-Dole $B$ coefficient is often used to classify ions as either structure makers (kosmotropes) or breakers (chaotropes).

They are supposed to strengthen or weaken hydrogen-bond network

Viscosity related to (diffusive) rotational relaxation by Stokes-Einstein-Debye (SED):

$$t_2 = \frac{g_2 V \eta}{k_B T}$$
Ultrafast pump-probe says: no

According to Laage & Hynes (PNAS 104, 11167 (2007)), the slow fraction represent exceptionally “slow waters”

In fact, rotational diffusion next to Cl\(^-\) is faster: 0.8×
NMR & viscosity say: yes

NMR relaxation from fluctuating electric-field gradients

\[ R \propto \chi^2 \tau_c \]

\[ \text{Fluctuations slow down with concentration} \]

(\text{Struis, JPC 93, 7943 (1989)})

Viscosity increase scales with surface charge density ion
NMA: glasslike behaviour

Contains the peptide linkage and is thought to form hydrogen-bonded chains in the liquid phase.

300 K
NMA on multiple timescales

\[ S(\omega) = \frac{A_D}{1 - i\omega \tau_D} \quad \text{Debye (\(\alpha\) relaxation)} \]

\[ + \frac{A_{CC}}{1 - (i\omega \tau_{CC})^{\beta_{CC}}} \quad \text{Cole-Cole (\(\beta\) relaxation)} \]
Super-cooled water fits KWW
\((\text{Righini, Nature 428, 296 (2004)})\)

Water fits to Cole-Cole \(\rightarrow\) Is this \(\beta\)-relaxation?

\(\tau_2 = 0.61\,\text{ps}, \beta = 0.86\)

Timescale for H-bond breaking
Dielectric relaxation

Dielectric data water at 25º C

At room temperature fits Debye curve with:
\[ \tau_1 = 8.38 \text{ ps} \]

Thus:
\[ \frac{\tau_1}{3} = 2.8 \text{ ps} \]

Compare with:
\[ \tau_2 = 0.61 \text{ ps} \]
Water: the ideal probe

Dipole moment large $\Rightarrow$
- **DRS** sensitive to molecular rotations

Polarisability very isotropic $\Rightarrow$
- **OKE** sensitive to “translations”

$$\langle \hat{\mu}(o) \hat{\mu}(t) \rangle \rightarrow \text{rotations}$$

$$\langle \hat{\alpha}(o) \hat{\alpha}(t) \rangle \rightarrow \text{translations}$$
OKE on electrolyte solutions

OKE fit to Cole-Cole
DRS fit to Cole-Cole

OKE was performed on aqueous NaCl and MgCl$_2$ solutions
DRS on MgCl$_2$ solutions
$t_2$ increases with concentration

$\beta$ decreases with concentration

Electrolyte solutions are more inhomogeneous
DRS on solutions

$t_{1/3}$ is constant with concentration

Dielectric constant drops $\rightarrow$ more water molecules immobilised

Thus, rotations remain constant while translation slow down with concentration
Vogel-Fulcher-Tammann behaviour

Angell has shown that salts increase the glass transition temperature of water. This follows VFT equation as a function of temperature

Under isothermal conditions we use:

$$\eta / \eta_0 = 1 + A \left\{ e^{B(x-x_0)} - e^B \right\}$$

where $x_0$ is the glass-transition (jamming) concentration.
VFT fits

VFT fit to viscosity: $x_0 = 12.0$ M, $B = 3.4$

VFT fit to NMR: $B = 4.5/4.1$

VFT fit to OKE: $B = 0.5$

CHEMISTRY

Does Saltwater Wobble?

When ionic salts dissolve in water, the resultant solution tends to become more viscous than the pure liquid. This observation can be broadly understood based on a picture in which the web of hydrogen bonds holding the water molecules together rigidifies around solvated ions. However, the molecular details appear much more complicated, because time-resolved vibrational spectroscopy has suggested that most individual water molecules

http://bcp.phys.strath.ac.uk/ucp/

Invited speakers:
Robin Hochstrasser
(Cornell University, Ithaca, NY)

Casey Hynes
(INL, Ames, IA)

Charles Schmuttenmaer
(Yale University, New Haven, CT)

Majed Chergui
(ESPCI, Paris, France)

Mischa Bonn
(AMOLF, Amsterdam)

Peter Hamm
(University of Zurich)

Thomas Elsaesser
(Max Born Institute, Berlin)