Glasslike behavior in aqueous electrolyte solutions

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When salts are added to water, generally the viscosity increases, suggesting that the ions increase the strength of the water's hydrogen-bond network. However, infrared pump-probe measurements on electrolyte solutions have found that ions have no influence on the rotational dynamics of water molecules, implying no enhancement or breakdown of the hydrogen-bond network. Here, we report optical Kerr effect and dielectric relaxation spectroscopic measurements, which have enabled us to separate the effects of rotational and transitional motions of the water molecules. These data show that electrolyte solutions behave like a supercooled liquid approaching a glass transition in which rotational and translational molecular motions are decoupled. It is now possible to understand previously conflicting viscosity data, nuclear magnetic resonance relaxation, and ultrafast infrared spectroscopy in a single unified picture. © 2008 American Institute of Physics.

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- **viscosities of electrolyte solution $\propto$ concentration**

  low concentration range (up to ~ 0.5 M)

  $$\text{Jones–Dole equation,} \quad \eta / \eta_0 = 1 + Ac^{1/2} + Bc$$

  η : shear viscosity, η_0 : viscosity of water, c : salt concentration

- **viscosities of electrolyte solution $\propto$ diffusive orientation relaxation**

  $$\text{Stokes–Einstein–Debye equation } t_2 = V \eta / k_B T$$

  molecular volume V, diffusive rotational relaxation time t_2

But,

Infrared pump-probe experiments
- -> water, aqueous solution ($Mg(ClO_4)_2$, $NaClO_4$, Na_2SO_4)
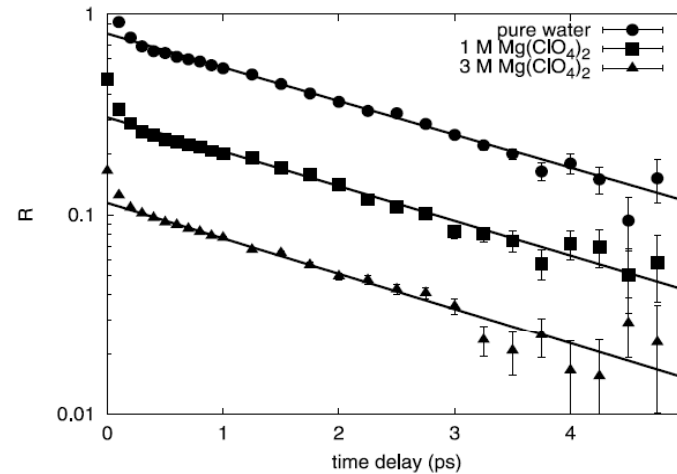- -> diffusive orientation relaxation time value of 2.5±0.1ps at all concentration

NMR
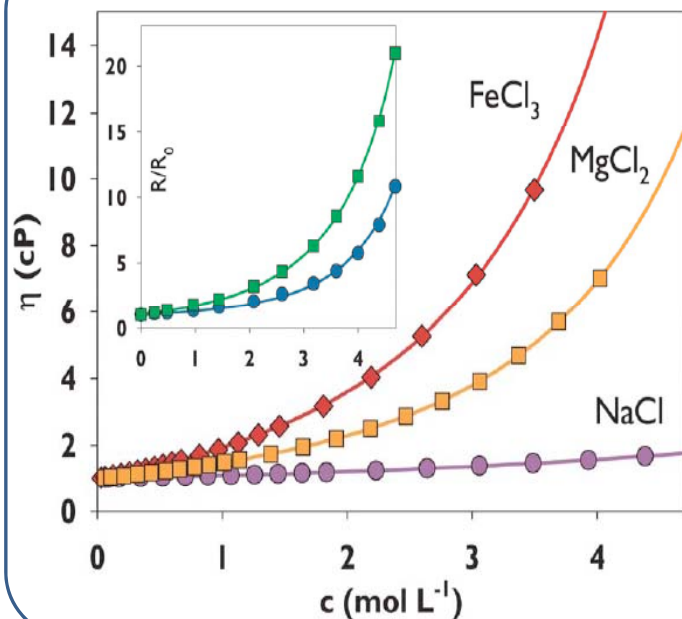- -> concentration $\propto$ viscosity

Infrared pump-probe experiments

Negligible Effect of Ions on the Hydrogen-Bond Structure in Liquid Water

Anne Willem Omta, *et al.*
Science **301**, 347 (2003);

Fig. 2. Logarithmic plot of the anisotropy parameter R as a function of time delay for different concentrations of $Mg(ClO_4)_2$ dissolved in H_2O with 4% HDO. The OD stretch vibration is pumped and probed at 4 μm (0 → 1 transition). For each solution, the orientational correlation time of the bulk water molecules is 2.5 ± 0.1 ps. The very fast decay during the first few hundreds of femtoseconds after the pump excitation is caused by a coherent artifact. The data have been fitted mono-exponentially in the delay range between 0.5 and 5 ps and are shifted vertically with respect to each other for clarity.

viscosity and NMR   on salt concentration

FIG. 1. (Color online) Dependence of viscosity and NMR relaxation rate on salt concentration. Points: Viscosities (Ref. 8) of aqueous solutions of NaCl (○), $MgCl_2$ (□), and $FeCl_3$ (△). Lines: Fits to Eq. (2) with $c_0/M = 12.7$ (NaCl), 12.0 ($MgCl_2$), and 11.9 ($FeCl_3$) and $Q = 0.6$, 3.4, and 3.9, respectively. (Inset) Points: NMR quadrupolar relaxation rates of $^{25}Mg^{2+}$ (○) and $^{35}Cl^-$ (□) in aqueous $MgCl_2$ solutions normalized to the rate extrapolated to pure water (Ref. 9) Lines: Fits to Eq. (2) with $c_0 = 12M$ (fixed) and the $Q = 4.5$ (Mg^{2+}) and 4.1 (Cl^-).

$$\eta/\eta_0 = 1 + P\{e^{Qc_0/(c_0-c)} - e^Q\}$$

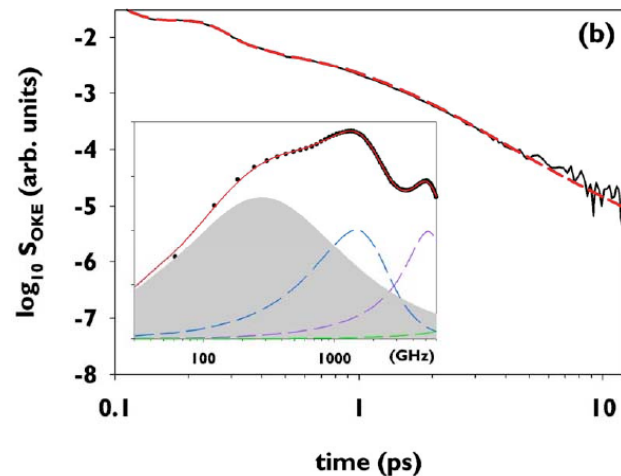(inset)Debye-Stokes-Einstein model, $R/R_0 = \eta/\eta_0$

◆ Pure water
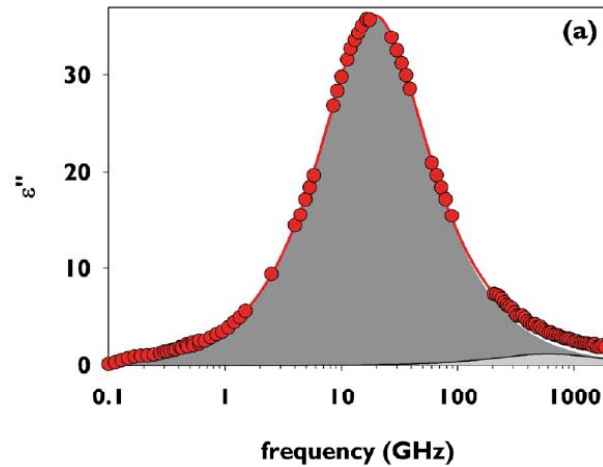
- DR spectrum of room-temperature water
- Dielectric loss spectrum $\varepsilon'''(\nu)$
- single Debye function $(1-iwt_1)^{-1}$

relaxation water molecular (dark gray) :
$t_1 = 8.38ps$ up to ~100GHz
intermolecular vibration (light gray) :
$t_1' = 0.3ps$

- relaxation of water measured by time-domain OKE spectroscopy
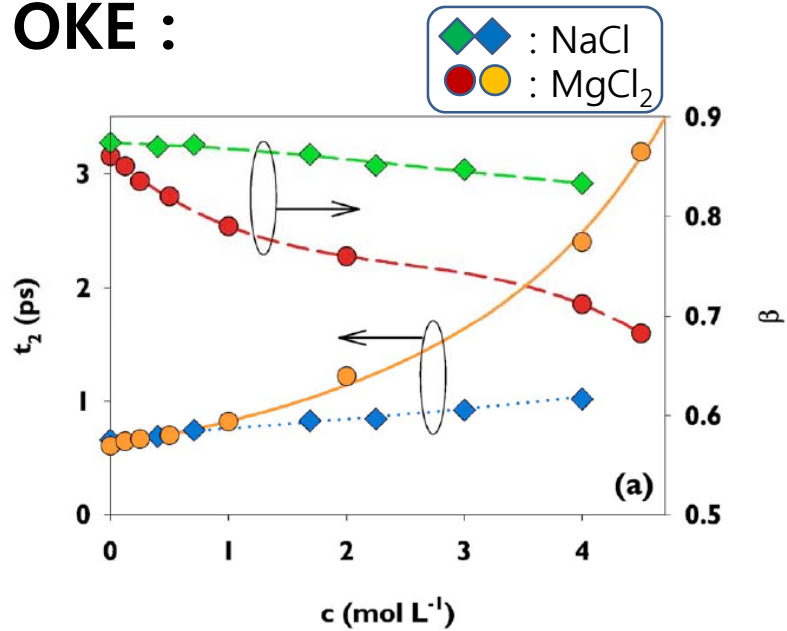- Cole-Cole function $[1-(iwt_2)^\beta]^{-1}$

$t_2 = 0.61$, $\beta = 0.86$

$t_2 = t_1/3$ (DR measures a correlation function of vectors while OKE measures one of tensors)

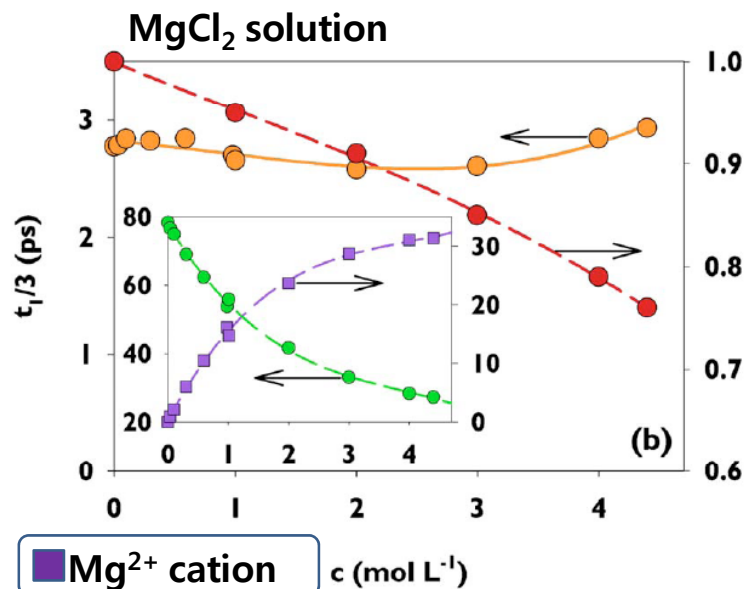**DR :** diffusive orientational relaxation of water molecule
OKE : interaction induced effects due to translational motion

OKE :

- Cole-Cole β exponent decreases with concentration
  : environment of the water molecules becomes increasingly inhomogeneous

DR :
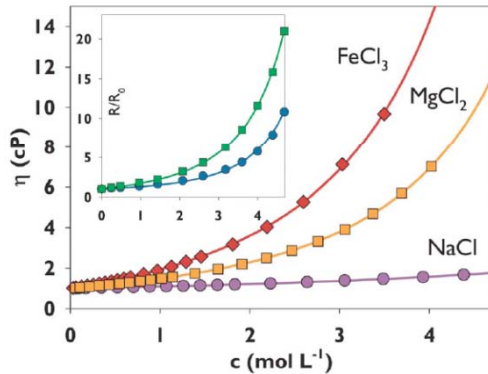

- $t_1/3$
  ~0.5M (slight decrease) : small inorganic ions
  ~3M slight increase

  ▸ **$t_1/3$ is essentially decoupled from solution viscosity fig1**

- **(inset)** y axis , ε_{cc} : static dielectric const.

$$\hat{\epsilon}(\nu) = \frac{\epsilon_{CC} - \epsilon_{\infty}}{1 + (i\,2\pi\nu\tau_{CC})^{1-\alpha}} + \epsilon_{\infty}$$

- glass transition of the pure water : ~135K
  (increases with the addition of salt or other solutes. ex) ~5M $MgCl_2$: 170K)

- C_0:glass transition concentration,   P , Q : empirical parameters

$$\eta/\eta_0 = 1 + P\{e^{Qc_0/(c_0-c)} - e^Q\}$$

	NaCl	MgCl2	FeCl3
C_0 glass transition concentration	12.7M	12M	11.9M
Q parameter	0.6	3.4	3.9

Molecular dynamics simulation	Na^+	Mg^{2+}	Fe^{3+}
Ⓐ Residence time	14ps~39ps	228ps~422ps	10^{-5}~10^{-3} s (ex)

Ⓐ water in the first hydrations shell of the cation

- inset :
- C_0 identical 12M
- Q parameter 4.5(Mg^{2+}), 4.1(Cl^-) , due to ion-ion interaction at the highest concentrations

- Fig3 (a)) shows Eq. (2) fit to the t_2 relaxation time parameter measured with OKE spectroscopy

$$\eta/\eta_0 = 1 + P\{e^{Qc_0/(c_0-c)} - e^Q\} \qquad \text{Eq2)}$$

- C_0 :12M , Q: small at 2.0
- relaxation same : fig1)
- OKE follows the same trend as the viscosity, NMR.
- Crucially, the three measurements are consistent with an essentially identical glass-transition concentration
- OKE spectroscopy in water sensitive to translational than rotational motion slowing down transitions and a complete arrest of the translational motion at the glass transition concentration

Fig 1)