HYDROXYL RADICAL IN HIGH TEMPERATURE WATER – MECHANISM OF TRANSPORT

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METHOD

- molecular dynamic simulation (NVE)
- flexible models of water and •OH radical
- simulation of solution and pure water
- simulation box of solution: 400 water molecules and one •OH radical
- simulation box of pure water: 400 water molecules

THERMODYNAMIC STATES

<table>
<thead>
<tr>
<th>TEMPERATURE, K</th>
<th>DENSITY, g cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.997</td>
</tr>
<tr>
<td>310</td>
<td>0.994</td>
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<tr>
<td>373</td>
<td>0.969</td>
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<td>473</td>
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<td>573</td>
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<td>653</td>
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<tr>
<td>673</td>
<td>0.375</td>
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<tr>
<td>673</td>
<td>0.167</td>
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</tbody>
</table>

THE PHASE DIAGRAM

- Liquid (compressed) water
- Supercritical water
- Solid
- Liquid
- Vapour
- Critical point
- Subcritical fluid
- Supercritical fluid

Temperature, K
Pressure, MPa
THE STRUCTURE OF WATER

THE HYDROGEN - BOND NETWORK

CLUSTER
net of molecules having at least one H-bond to other members

The continuous hydrogen – bond network.

RADIAL DISTRIBUTION FUNCTION $g_{OrOw}(r)$

The decreasing density

310 K

673 K
T=310 K, $\rho=0.994$ g cm$^{-3}$  

T=673 K, $\rho=0.167$ g cm$^{-3}$
RADIAL DISTRIBUTION FUNCTION OF WATER

LIQUID WATER

SUPERCritical WATER
ABOVE THE CRITICAL DENSITY LIQUID WATER
SUPERCritical WATER BELOW THE CRITICAL DENSITY – INHOMOGENEITY OF THE STRUCTURE

\[ g_{OwOw}(r) \]

- solution
- pure water
TWO HYDRATION MECHANISMS

• LOCALISATION IN CAVITIES EXISTING IN THE SOLVENT STRUCTURE - LIQUID WATER AND SUPERCRITICAL WATER ABOVE THE CRITICAL DENISTY

• SELF – TRAPPING - SUPERCRITICAL WATER BELOW THE CRITICAL DENSITY


SPECTRAL DENSITY OF THE STRETCHING VIBRATIONS OF •OH

DECOMPOSITION OF THE SPECTRAL DENSITY

BAND-COMPONENTS WERE ASSIGNED TO STRETCHING VIBRATIONS OF •OH RADICAL FORMING 0, 1, 2 OR 3 HYDROGEN BONDS WITH WATER MOLECULES
The position of band-components assigned to non-bonded OH radical is unaffected by thermodynamic conditions.

The shifts between band-components confirmed the hydration mechanism.
DEFINITION OF H - BONDS

$r_{OH} \leq 2.7 \text{ Å}$
$\alpha, \beta \leq 40^\circ$
$E \leq -6 \text{ kJ mol}^{-1}$

$r_{w_{OH}} \leq 2.5 \text{ Å}$
$\gamma \leq 30^\circ$
$E \leq -8 \text{ kJ mol}^{-1}$

MEAN NUMBER OF HYDROGEN BONDS, $n_{HB}$

decrease with the decreasing density (water)

non-monotonic dependence

(*OH radical)
SELF - DIFFUSION COEFFICIENT OF WATER
DIFFUSION COEFFICIENT OF •OH RADICAL

Green –Kubo relation

\[ D_{ACF}^{\text{ACF}} = \lim_{t \to \infty} \frac{1}{3} \int_0^t \langle \vec{v}(0) \cdot \vec{v}(t') \rangle \, dt' \]
SELF-DIFFUSION COEFFICIENT OF WATER

LIQUID WATER: $D^{\text{H}_2\text{O}}$
- similar for pure water and solution
- linear increase with the decreasing density
- good accordance with experiment

SUPERCritical WATER: $D^{\text{H}_2\text{O}}$
- good accordance with experiment

Above the critical density
- similar for pure water and solution

Below the critical density
- the significant increase

COMPARISON OF DIFFUSION AND SELF-DIFFUSION COEFFICIENT

\[ D, \text{ } 10^{-9} \text{ m}^2 \text{ s}^{-1} \]

- **OH RADICAL**
- **WATER**

\[ \text{temperature } T, \text{ K} \]

\[ \rho, \text{ g cm}^{-3} \]

- \( (T < 473 \text{ K}) \) and \( (\rho > 0.8 \text{ g cm}^{-3}) \)
- \( D^{\text{H}_2\text{O}} \) and \( D^{\cdot\text{OH}} \) are similar

- \( (T > 573 \text{ K}) \) and \( (\rho < 0.74 \text{ g cm}^{-3}) \)
- \( D^{\cdot\text{OH}} \) is lower than \( D^{\text{H}_2\text{O}} \)

\[ D^{\text{H}_2\text{O}} \text{ and } D^{\cdot\text{OH}} \text{ increase with the decreasing density and the increasing temperature} \]
COMPARISON OF DIFFUSION AND SELF-DIFFUSION COEFFICIENT – SUPERCritical WATER

- Above the critical density
  \( D_{\text{H}_2\text{O}} \) and \( D_{\cdot\text{OH}} \) increase with the decreasing density

- Below the critical density
  \( D_{\text{H}_2\text{O}} \) increases significantly
  \( D_{\cdot\text{OH}} \) does not change
DIFFUSION COEFFICIENT FOR
•OH RADICAL

Stokes - Einstein relation
\[ D = \frac{k_BT}{(\alpha \eta \pi r)} \]

the hydrodynamic radius \( r = 2.2 \text{ Å} \)
the parameter \( \alpha = 4 \)

\( D^{\text{\textbullet OH}} \) in liquid water

• the hydrodynamic radius should increase to 3.3 Å to match \( D^{\text{\textbullet OH}} \) calculated from simulation

\( D^{\text{\textbullet OH}} \) in supercritical water

• below the critical density Stokes – Einstein relation predicts about 40% higher value.
CONCLUSIONS

1. In liquid compressed water up to ~473 K, in the presence of the continuous H-bond network, $D^{\cdot OH}$ scales with temperature like $D^{H_2O}$.

2. Breakage of the continuous H-bond network causes lowering of $D^{\cdot OH}$ in relation to $D^{H_2O}$, as the number of hydrogen bonds formed by $\cdot OH$ radical increases.

3. In the low density limit above the critical temperature self-trapping of $\cdot OH$ radical—noticeably hinders its diffusion.
Thank you for your attention