



1. Classical MD to reproduce HMW

- A previous MD study showed hyper mobility in translational self-diffusion coefficient (Dtr) near the oxygen atom only in urea solution (not in tetra methyl urea), although the system size was small, water model was poor, and the rotational motion was not investigated(Tovchigrechko '99)
- Here, we tried MD simulations exhaustively to elucidate dynamical properties of hydrating water molecules around many types of solutes.





Calcul sev	ated self-diffu erely depnd o	ision coefficients,Dtr n the water model.	,
System		water model	Dtr
Water No.	267- 2050	SPC	3.83
Box length	20–40 Å	SPC/E	2.49
cutoff	8-12 Å	TIP3P	5.19
simulation	1-20 ns	Experiment	2.30
temperature	298.15 K	$SPC/E(bond = 1 \rightarrow 0.905)$	2.63
density	1.0 g cm-3	$SPC(charge \rightarrow SPC/E)$	3.21
SHAKE 🖉 a	19	TIP3P (charge \rightarrow SPC/E)	4.45
NTV			
NTP		$TIP3P(vdw \rightarrow SPC/E)$	5.40
	7	TIP3P (bond \rightarrow SPC/E)	2.57







Coordination number, Nc, and hydrogen bond number, Nh of water molecules in the bulk and the first layer plotted against the solute net charge. In HMW region, 4.6 •••••nc−1 •••••nh−1 both the Nh and PO4 type Nc of the 1st layer4.4 — nc-b solute - nh-b is smaller than 42 bulk Nc bulk ATP hydrolysis Nc 1st Nh bulk 2nd lay 3.2 Nh 1st lav -4 -5 -3 -1 0 Solute Net Charge (e.u) 2 3 solute Qs:



- Shape of solute molecule was important, that is, no HMW was observed without LJ potential on H or O atom.=> No HMW for alkali and halogen ions.
- Effect of charge distribution is negligible in CH4,NH3 type solute, but not negligible in PO4 type solute.
- The reason of the hyper mobility was explained with the lower coordination number (density) and hydrogen bond network than bulk water.

Summary of classical MD calculations 2

MD for amino acids as solute

- · No HM Water was observed
- *τ* rot was effected by each chemical group but Dtr was not =>Due to cooperative motion of water around solute
- MD for proteins (pepsin, 1f32, and lysozyme, 6lyz)
- · Mw and ASA almost same, net charge largely
- different
- No HM Water
- No difference for τ rot and Dtr

Model or parameters used in this MD study was not enough => Improvement is needed!



Previous Quantum Chemical Calculations

* Previous Car-Parrinello MD : alkali ions (Li⁺,Na⁺,K⁺) with 62 water molecules (T.Ikeda, M.Boero, K.Terakura,'07)
Water molecules around K⁺ ion :Compared with bulk water Water dipole(∝polarization) ↓ Mobility ↑

But..still problems

Water molecules around Na+ ion also the same result Absolute value of Dtr was much smaller than experiment Results are only alkali ions.

Therefore,

we tried more calculation conditions (system size, basis set function, model chemistry) and more solutes such as halogen ions and phosphate ions

KeyWord	Metho	d
HF	Hartre	e-Fock(HF)Self-Consistent Field (SCF)calculation
B3LYP	Becke correla	3 (B3)-parameter functional + Lee, Yang, Parr tion functional (LYP) DFT calculation
Basis set	Atoms	Content
6-311G	H-Kr	Pople's valence tripe-zeta
CEP-121G	H-Rn	valencetriple-zeta Effective-CorePotential (ECP) Stevens/Basch/Krauss ECP triple-split basis set
Polarizable	Continuun	n Model (PCM) solvation method : $\varepsilon = 78.2$
Mulliken &	NBO an	alysis method for charge assignment
M. P. N	/cGrath ar	nd L. Radom, J. Chem. Phys. 94, 511 (1991)
W. Ste	vens, H. B	asch, and J. Krauss, J. Chem. Phys. 81, 6026 (1984)
http://s	www.hno.c	a in/hit/adution/gaugaian halp/m hasia acta htm









Summary of QC calculations

- * Except for Li⁺ ion, electric dipole (polarization) of surrounding water decrease (Mobility increase) ⇔K+, I-, Br- OK, but inconsistent with Na⁺ ion
- * Size dependence (number of water) was small
- Model Chemistry (HF, MP2,B3LYP) and basis set dependence was small and not esential.
 Natural Bond Orbital analysis (NBO) also
- * Natural Bond Orbital analysis (NBO) also showed the same tendency as Mulliken charge analysis and showed much smaller dependence for the calculation conditions.
- * We could also obtained charge parameters of phosphate ions, which are applicable to classical MD simulations.

For more investigation

At present, we are calculating

- MD and QC for Poly phospates (HxP3O10, HxP2O7) with counter ions.
- Hydrogen bond analysis in detail

Starting

- Model improvement for MD
- MD for ATP=>ADP+Pi reaction.
- MD with enzyme protein such as ATPase.
- Analysis of protein surface group effect on the hydration water dynamics.

Acknowledgement

Mr. Morishita, Mr. Komatani (Ritsumeikan Univ.)

This study is partly supported by MEXT. "Development of calculation methods of solvation dynamics and application to ATP hydrolysis" is a research thema in A01 group of "Water as a key player in ATP energy transduction"

http://www.material.tohoku.ac.jp/atpwater 水を主役としたATPエネルギー変換(科研費:新学術領域研究)