

Strength of ion-dipole interaction

> let us take typical interatomic separations

↳ bind polar polar molecules, align them

Water and ion, Na^+ , $a = 0.095 \text{ nm}$

↓
spherical molecule

$$W_{\text{max}} = W(r, \theta) =$$

point dipole: 1.85 D

$$\frac{-ze \cos \theta}{4\pi\epsilon_0 r^2} = 1.6 \cdot 10^{-19} \text{ J}$$

$$\stackrel{\sim}{=} 39 kT$$

or 96 kJ mol^{-1} at 300 K

4.2

$$\Gamma = \mu \cdot \delta_i = \frac{4}{3} \pi r^2 \cdot \delta_i$$

$$x_s \propto \exp(-\Gamma/kT)$$

or

$$\mu_I + RT \ln x = \mu_{II} + RT \ln x$$

⇒

$$W(r, \theta = 0^\circ) = - \frac{(1.602 \cdot 10^{-19})^2 (1.85 \cdot 3,336 \cdot 10^{-30})}{4\pi (8.854 \cdot 10^{-12}) ((0.095 + 0.14) \cdot 10^{-9} \text{ (m)})^2} \quad -\frac{q^2}{\epsilon}$$

↑
max.
I.A. energy

$$= 1.6 \cdot 10^{-19} \text{ J}$$

$$= 39 \text{ kT} \quad (\text{or } 96 \text{ kJ mol}^{-1}) \quad \text{at } 300 \text{ K}$$

experimentally found: 100 kJ mol^{-1} !!

$$\text{Li}^+ \sim 50 \text{ kT} \quad (125 \text{ kJ mol}^{-1}) \quad \text{exp: } 142 \text{ kJ mol}^{-1}$$

$a = 0.068 \text{ nm}$

$$\text{Mg}^{2+}, a = 0.065 \text{ nm}$$

$$100 \text{ kT}$$

c.f. Table 4.2

$$\text{Be}^{2+}, a = 0.03 \text{ nm}$$

$$150 \text{ kT}$$

strong attractive interaction between ions
and water!

- ionic nucleation of rain drops in thunder clouds

Ions in polar solvents

- in water: $\epsilon \approx 80$, reduced I.A. energies!
however: still exceeds kT

- in bulk water: not the process of bringing the ^{water} ~~ion~~ up to
an ion (since another water must be
removed!!)

however: orientation from $\cos \theta$ (in continuum approach!)

large separations: randomly oriented towards the ion

→ interaction energy = 0 since

$$\langle \cos \theta \rangle = 0$$

↘ Estimation of free energy change brought about by orienting the polar ~~dipoles~~ solvent molecules around the ions. reference state = randomly oriented dipoles

— ion-dipole IA energies: comparable to or greater than kT ; reflect the aligning effect of ions on surrounding water.

Strong ion dipole - interactions

- small, multivalent ions in highly polar solvents
- ⇒ favoring $\theta = 0^\circ$ near cations
- ⇒ $\theta = 180^\circ$ near anions

Li^+ , Mg^{2+} , Be^{2+} , Al^{3+} : orientationally bound water

4-6 H_2O molecules, do exchange with bulk water! (more slowly)

⇒ Hydrated radius: includes bound water

smaller ions: larger hydrated radii!

(from: viscosity, diffusion, compressibility, conductivity, solubility, spectroscopic properties...
However: rarely agree!)

However: insight into hydration by rotational correlation times: water: 10^{-11} s

~ life time of water/water bonds

first hydration shell: 10^{-11} s and ~~shorter~~ (to hours)

weak hydration / negative hydration: $N(CH_3)_4^+$, Cl^- , Br^- , I^- 10^{-11} s and shorter
also complexes: $[Hg(H_2O)_6]^{2+}$, and $[Be(H_2O)_4]^{2+}$, $(H_3O^+)(H_2O)_3$ etc.

rotation time

Solvation forces

-4-

- first hydration shell: most restricted in motion
 - 2nd free to rotate/exchange with bulk water
 - 3rd shell
- ⇒ 'solvation zone', significantly different solvent properties

→ effect on ϵ :

restricted mobility → lower ϵ
ice: higher ϵ } still not well understood

→ weakness of continuum models, molecular approach might help

overlap of two solvation zones → short range force arises, which cannot be treated in terms of continuum models

Water around ion $\neq 80$ → short range interaction due to Coulomb forces would be modified

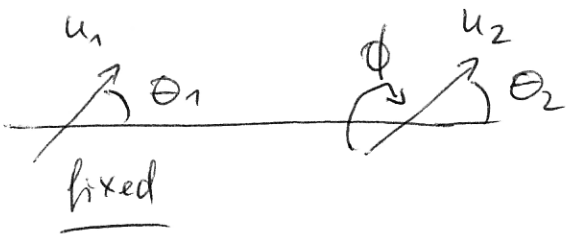
→ subtle effects, high residual activity

4.7.

Dipole - dipole interactions

- two polar molecules near each other → analogy to two magnets
- similar procedure to ~~charge~~ ^{con} - dipole IA yields

$$W(r, \theta_1, \theta_2, \phi) = \frac{u_1 u_2}{4\pi\epsilon\epsilon_0 r^3} (2 \cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\phi)$$



\Rightarrow max attraction: dipoles lying in line when

~~total~~
 (1) $w(r, 0, 0, \phi) = -2u_1u_2 / 4\pi\epsilon\epsilon_0 r^3$

(2) parallel:
 $= -u_1u_2 / 4\pi\epsilon\epsilon_0 r^3$

if $u = 1D$

$W(r_{...})$ in vacuum is ~~at~~ ^{equal} KT at $r = 0.36 \text{ nm}$ (1)
 and $r = 0.29 \text{ nm}$ (2)

$\frac{1}{2}$ order of molecule separations in liquids/solids
 \rightarrow dipole/dipole bond only very polar molecules

transparency 4.3:

- significant deviations from point dipole behavior even occur for $r < 3l$
- mostly align in parallel, due to anisotropy in shape and not in line (as one would expect for same r ...)
- weak interaction = (in vacuum smaller than KT at 0.35 nm for $u = 1D$)
 \Rightarrow ^{generally} not strong enough to result in alignment ~~in the liquid~~
 exceptions: water (small, large dipole moment)