

Transfer an ion from medium with  $\epsilon_1$

to medium with  $\epsilon_2$ ,  $\epsilon_1 < \epsilon_2$

$$\Delta \mu^i = \mu^i(\epsilon_2) - \mu^i(\epsilon_1)$$

$$\Delta \mu^i = - \frac{z^2 e^2}{8\pi \epsilon_0 a} \left( \frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right) [J]$$

$< 0$ , favorable!

$$= - \frac{28 z^2}{a} \left( \frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right) kT$$

per ion at 300K

$$\text{or } \Delta G = N_A \Delta \mu^i = - \frac{69 z^2}{a} \left[ \frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right] \text{ kJ mol}^{-1}$$

from gas ( $\epsilon=1$ ) to water ( $\epsilon=78$ ),  $a = 0.14 \text{ nm}$   
(ionic radius)  
per cations/anions

$$\Delta G = \frac{-2 \cdot 69}{0.14} \left( 1 - \frac{1}{78} \right) \approx -1000 \text{ kJ mol}^{-1}$$

$\Rightarrow$  formation of cavities in the medium:  
not included, however: small energies!

Solubility of ions in different solvents

8.5.06

- Why ~~do~~ salts dissociate in water (high lattice energy)

- ~~the~~ Coulomb interaction: reduced ~~due~~ due to  $\epsilon$  of the medium,

Coulomb law, however, not strictly valid at small (molecular) distances! (molecularity of the medium!)

⇒ continuum description breaks down, predicts the right trends & so!

simplest level: associated to dissociated state, conversion after Coulomb law, separation of  $\text{Na}^+ \text{Cl}^-$  from contact in a solvent medium

$$\Delta \mu^i \approx \frac{+e^2}{4\pi\epsilon\epsilon_0(a_+ + a_-)} \quad a_+, a_- : \text{ionic radii}$$

- Some fraction of the ion always dissociates due to entropy of dilution.  $X_s$ , concentration of saturated solution in equilibrium with the solid

$$X_s = \exp(-\Delta \mu^i / kT) \approx \exp\left(\frac{-e^2}{4\pi\epsilon\epsilon_0(a_+ + a_-)kT}\right)$$

$X_s$  = solubility in water (in the solid,  $X=1$ , (mole-fraction units)  $\downarrow$  when  $X=0 \downarrow \neq \dots$  see above)

Note in water:  $(a_+ + a_-) = 0.276 \text{ nm}$ ,  $\epsilon = 78$ ,  $T = 300 \text{ K}$

$$X_s \approx e^{-2.6} \approx 0.075, \quad \text{experimentally found: } 0.11 \frac{\text{mol}}{\text{mol}} \quad (36 \text{ g l}^{-1})$$

⇒ simplistic, but reflecting trends well:

$$\text{solubility} \sim e^{-\text{const}/\epsilon}$$

plot  $X_s$  vs  $1/\epsilon$ : straight line

⇒ table 3.2  
fig. 3.1

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= more strictly: difference in lattice energy of the ions in a lattice from that in solution.

→ splitting up in different stages I dissociation to gaseous ions  
II transfer to solvent

Two approaches: I: positive lattice energy

II: negative Born energies, transfer of ions to solvent of  $\epsilon$ , from  $\epsilon=1$

→ too large Born energies, larger than lattice energies  
correction of crystal lattice radii → increase  
to  $r_{cr}$  by 0.02 to 0.05 nm when in water  
(Hydration shells')

Born / Coulomb energy approach: right trend, not quantitatively reliable

→ ignore specific interactions between ions and solvent, 'solvent effect' particularly for water and for multivalent ions.

## ① Continuum and ② molecular theories

1) bulk properties hold right down to molecular dimensions

2) start at specific interactions, 'build up' system properties

① electrostatic theory: free energy density of an E field arising from a charge:  $\frac{1}{2} \epsilon_0 \epsilon E^2$

Born energy: integrating energy density over all space

$$\mu^i = \frac{1}{2} \epsilon \epsilon_0 \int E^2 dV = \frac{1}{2} \epsilon \epsilon_0 \int_a^{\infty} \frac{Q^2}{4\pi \epsilon \epsilon_0 r^2} 4\pi r^2 dr = \frac{Q^2}{8\pi \epsilon \epsilon_0 a}$$

→ electrostatic self energy: spread out around the ion

$\int_a^R$ , energy contained within a finite ~~sphere~~ <sup>sphere</sup> around the ion:

$$-\frac{Q^2}{8\pi\epsilon\epsilon_0} \left[ \frac{1}{a} - \frac{1}{R} \right]$$

0.1 nm radius ion: 50% of energy } contained in a sphere of 0.24 nm radius!  
90% " " } 1.0 nm radius!

-  $\epsilon$  of the medium must be equal to bulk value at ~ 0.1 nm distance! bulk value of  $\epsilon$  must be attained in the first shell of solvent molecules!

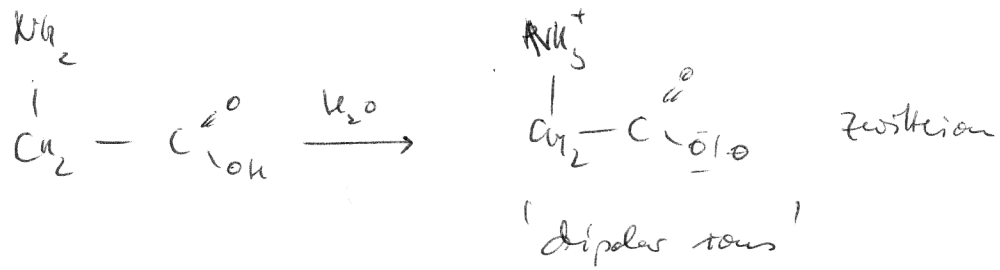
- Coulomb interaction can be derived from change in the electric field ~~and~~ energy when two charges are brought together. Even reduced Coulomb interaction strength if there is no solvent between the ionic pair. (long range electrostatic interaction). → provides insight why strong ionic bonds can be broken!

- more realistic molecular resolution: computer simulation which model each individual molecule

# Interactions involving polar molecules

- polar molecules, not only with net charge but also with electric dipole, as in  $\overset{\delta+}{\text{H}}-\overset{\delta-}{\text{Cl}}$ .

Dipoles depend on environment; glycine in water, e.g.



Dipole moment, definition  $\mu = ql$

$l$  = distance between two charges  $+q, -q$

if  $q = \pm e, l = 0.1 \text{ nm}$   $\mu = 1.602 \cdot 10^{-19} \cdot 10^{-10} \text{ Cm}$   
 $= 1.602 \cdot 10^{-29} \text{ Cm} = 4.8 \text{ D}$

unit:  $1 \text{ D} = 3.336 \cdot 10^{-30} \text{ Cm}$

Permanent dipoles:

- not in atoms, only in asymmetric molecules
- in isolated molecules: from the asymmetric displacements of electrons along covalent bonds
- > characteristic dipoles for covalent bonds, useful for estimation of molecular dipoles: vectorial summation of bond moments

e.g.  $\text{H}_2\text{O}$ :  $\begin{array}{c} \text{H} \\ \diagup \theta \\ \text{O} - \text{H} \end{array} \theta = 104.5^\circ$   $\mu_{\text{H}_2\text{O}} = 2 \cos\left(\frac{1}{2}\theta\right) \mu_{\text{OH}} =$   
 $2 \cos(52.25^\circ) \cdot 1.51 \text{ D} =$   
 $1.85 \text{ D}$

## 4.2. Dipole self energy

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$\mu^i$ : electrostatic self energy analogous to the Born self energy of an ion

$\hat{=}$  sum of the two Born energies for each charge

- Coulomb energy of bringing the two charges together to form the dipole

Calculation: two ions of radius a brought into contact to form a hypothetical dipolar molecule, length  $\hat{=}$  sum of the radii:  $l = 2a$

$$\mu^i = \frac{1}{4\pi\epsilon\epsilon_0} \left[ \frac{q^2}{2a} + \frac{q^2}{2a} - \frac{q^2}{r} \right] = \frac{q^2}{8\pi\epsilon\epsilon_0 a} \quad \text{with } \begin{matrix} u = lq \\ l = r = 2a \end{matrix}$$

see above!  $\leftarrow$   $\uparrow$   $= l = 2a$   $= \frac{u^2}{4\pi\epsilon\epsilon_0 l^3}$

<sup>roughly</sup>  $\hat{=}$  of same magnitude as of ~~the~~ individual ion

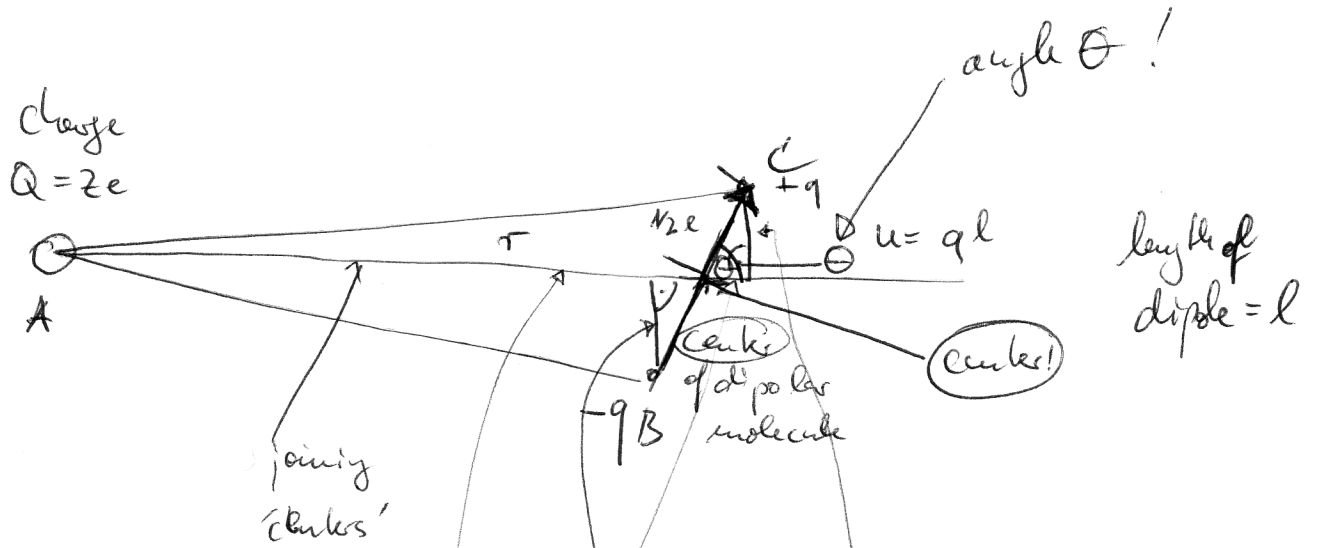
- same dependence on permittivity/dielectric constant of medium

- solubility of polar molecules should change in the same sense ~~so~~ <sup>with</sup> varied solvent  $\epsilon$  as for ions, generally true, but dipole can change with solvent,

~~and can~~ due to size (larger than ions): can have non-electrostatic contributions (v.d. Waals self energy)

# Ion dipole interactions

- second <sup>order</sup> electrostatic pair interaction, e.g.  $\text{Na}^+$  and  $\text{H}_2\text{O}$



total interaction energy: sum of ~~total~~ Coulomb energies of  $Q$  with  $-q$  at  $B$  and  $+q$  at  $C$ :

$$w(r) = -\frac{Qq}{4\pi\epsilon_0} \left[ \frac{1}{AB} - \frac{1}{AC} \right]$$

$$AB = \left( \left( r - \frac{1}{2} l \cos \theta \right)^2 + \left( \frac{1}{2} l \sin \theta \right)^2 \right)^{1/2}$$

$$AC = \left( \left( r + \frac{1}{2} l \cos \theta \right)^2 + \left( \frac{1}{2} l \sin \theta \right)^2 \right)^{1/2}$$

at  $r > l$ :  $AB \approx r - \frac{1}{2} l \cos \theta$  | point-dipole-approximations  
 $AC \approx r + \frac{1}{2} l \cos \theta$

$$\hookrightarrow w(r) = w(r, \theta) = -\frac{Qq}{4\pi\epsilon_0} \left[ \frac{1}{r - \frac{1}{2} l \cos \theta} - \frac{1}{r + \frac{1}{2} l \cos \theta} \right]$$

$$W(r, \theta) = \frac{-Qq}{4\pi\epsilon\epsilon_0} \left[ \frac{l \cos \theta}{r^2 - \frac{1}{4} l^2 \cos^2 \theta} \right] = \frac{-Qu \cos \theta}{4\pi\epsilon_0 \epsilon r^2} = \frac{-ze \cos \theta}{4\pi\epsilon\epsilon_0 r^2}$$

$\approx 0?$   
 $r \gg l$

in a medium!

Electric field of charge acting on the dipole:

$$E(r) = Q / 4\pi\epsilon\epsilon_0 r^2, \text{ therefore:}$$

$$W(r, \theta) = -u E(r) \cos \theta$$

IA with a cation: Max. attraction if dipole points away  
at  $\theta = 0^\circ$

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max repulsion:  $\theta = 180^\circ$

fig. 4.2

variation of the energy,  
dashed curve: point dipole approximation,  
accurate down to small separations!!

only  $r < 2l$ , deviation visible

However: greater dipole lengths (7-10 Å ions),  
interaction too small if calculated after point-  
dipole approximation.  $\rightarrow$  separate Coulombic contributions  
calculated

### Interaction strength

ion - water in vacuum:

$r_{\text{water}} = 0.14 \text{ nm}$ , point dipole 1.85 D (oversimplification!)

$\text{Na}^+ z = 1, a = 0.095 \text{ nm}$