Hydration thermodynamics of the proton and why establishing accurate values matters for aqueous chemistry

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U Cincinnati Chemistry
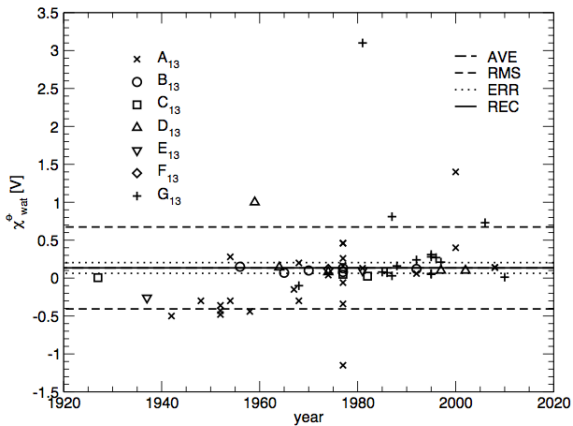
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ϕ_{np} history: Hünenberger and Reif

Single-ion hydration involves interfaces

$$\mu_X^{ex} = \mu_{X,b}^{ex} + q_X \phi_{np} = \mu_{X,int}^{ex} + q_X \phi_{sp} = -kT \ln\langle \exp(-\beta \Delta U) \rangle_0 \qquad (1)$$

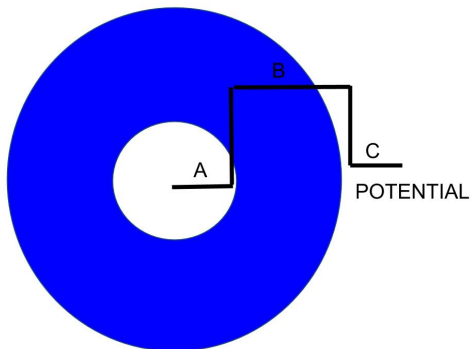What are ϕ_{np} and ϕ_{sp}?

AIR

WATER

Potential shifts

A to B is local potential ϕ_{lp}

B to C is surface or contact potential ϕ_{sp}

A to C is net potential or electrochemical surface potential ϕ_{np}

Goal:

- Determine ϕ_{np} by analysis of μ_X^{ex} and $\mu_{X,b}^{ex}$, not by direct direct calculation

- Get μ_X^{ex} by re-analysis of experimental data (no model). Proton value is -264.2 kcal/mol (shifted from previous Tissandier et al. value by 1.7).

- Get consistent $\mu_{X,b}^{ex}$ (-254.3 kcal/mol for proton) from multiple approaches (below)

- Comments on ϕ_{np}: 1) It is a free energy term with a mean and higher-order (odd) terms. 2) It should be a property of water only, that is a solvent contribution with no ion specificity. 3) Later we will see if we introduce ANY ions, the resulting ϕ_{np} is ion specific. Thus we should study one ion in a water droplet (200-500 waters are enough).

Steps to insert an ion (QCT):

$$\mu^{ex} = \mu_P^{ex}(\lambda) + \mu_{LR}^{ex}(\lambda) + \mu_{IS}^{ex}(\lambda) \tag{2}$$

Real FE = Cavity Formation + Long-Range FE + Inner-Shell FE

Stepwise Free Energies to Insert Ion

Dig Cavity   Insert Pt Chg   Convert to Ion   Relax Cavity
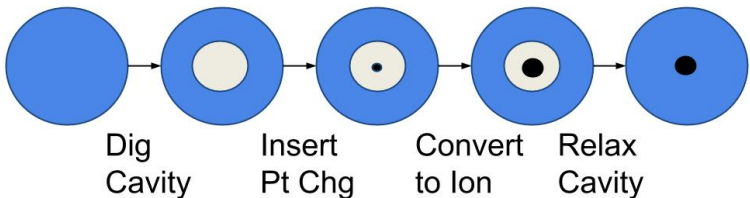
What is μ_X^{ex}?

- The 'real' chemical potential
- This is the free energy to take one ion from vapor into liquid, across the surface
- It thus includes interfacial potential effects
- Is this measurable? Yes, in principle from a combination of bulk thermodynamic and cluster data (see below)
- The sought quantity is only for one ion in a large drop of water (with no other ions present)

What are $\mu_{X,b}^{ex}$ and $\mu_{X,int}^{ex}$?

- The 'bulk' and 'intrinsic' chemical potentials
- The bulk free energy is a property of the ion deep in the solvent with no interfacial effects
- The intrinsic free energy includes an interfacial potential from nearby waters ϕ_{lp}
- Is $\mu_{X,b}^{ex}$ measurable? Not directly, theory/modeling can help (QCT)
- This is tantamount to dividing up interactions (like Coulomb) into parts
- *But we can infer an effective potential that may affect ions near the surface (pure solvent contribution to net potential)*
- Is $\mu_{X,int}^{ex}$ measurable? Yes in principle if we were able to measure ϕ_{sp} in a scattering experiment or otherwise (but this leaves 80 kcal/mol shifts floating around)

Guggenheim, JPC 33, 842 (1928) [and Gibbs (1899)]

"The electric potential difference between two points in different media can never be measured and has not yet been defined in terms of physical realities. It is therefore a conception which has no physical significance."

Yet (*surface or contact* potential)

$$\Delta\phi_{sp} = 4\pi \int_{-\infty}^{\infty} z\rho(z)dz = 4\pi \int_{-\infty}^{\infty} P_z(z)dz - 4\pi\Delta\mathrm{Tr}Q/3 \qquad (3)$$

Pratt, JPC 96, 25 (1992); $\Delta\phi_{cp} \approx +4$ V for water LV interface (Kathmann, Mundy, et al)! It is about -0.6 V for SPC/E water, however, a dramatic difference.

Ions and interfaces: thermodynamics

- Zhou/Stell/Friedman/Pratt fundamental relation: if two conducting phases in contact, the potential difference between them is determined by the *bulk* hydration free energies of the ions in each phase (one pair only here):

$$\text{real} = \text{bulk/intrinsic} + \text{surf potl}$$

$$\mu_X^{ex} = \mu_{X,b}^{ex} + q_X \phi_{np}^{tot} \tag{4}$$

$$\Delta\phi_{np}^{tot} = (\Delta\mu_{N,b}^{ex} - \Delta\mu_{P,b}^{ex})/2e \tag{5}$$

- This means the surface potential is an ion-specific quantity.
- Note $\Delta\phi_{np}^{tot}$ contains *both solvent and ion contributions*.
- There is a chicken/egg (interface/bulk) aspect to this formula: see Landau/Lifshitz vol. 8 "Galvanic cell" (echem cell emf)

Ions and interfaces

- It turns out solvent ϕ_{np} does have physical consequences
- These are: impact on ion distributions and water chemistry near the interface
- *We argue: this $\phi_{np}(solv)$ is the origin of OH^- excess near the water surface*

Single-ion hydration free energy

The potential distribution theorem (PDT) is

$$\mu_X^{ex} = -kT \ln \langle \exp\left(-\varepsilon_X / kT\right) \rangle_0 \qquad (6)$$

where $\varepsilon_X = U(W + X) - U(W) - U(X)$ involves all ion-water interactions. Insert vdW cavity first. Rewriting (mean-field plus fluctuations):
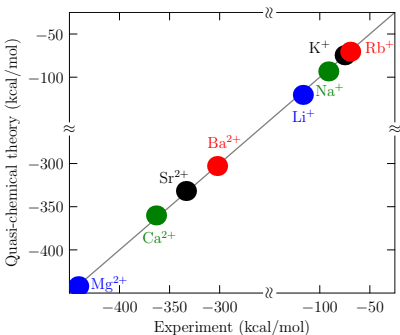
$$\mu_X^{ex,es} = \langle \varepsilon_{es} \rangle_{vdW} - kT \ln \langle \exp\left[-(\varepsilon_{es} - \langle \varepsilon_{es} \rangle_{vdW})\right]/kT \rangle_{vdW} \qquad (7)$$

where $\langle \varepsilon_{es} \rangle_{vdW} = q \langle \phi \rangle_{vdW} = q\phi_{np} = q(\phi_{lp} + \phi_{sp})$. The net potential is that at the center of a neutral cavity embedded deep inside a large water droplet. ($\phi_{sp} = 4$ V!) Then
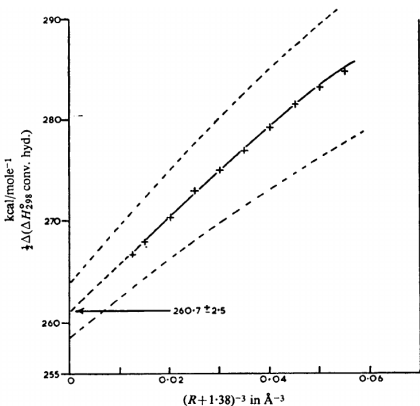
$$\mu_X^{ex} = \mu_{X,b}^{ex} + q\phi_{np} \qquad (8)$$

QCT (no ϕ_{np}) and Marcus: what is $\mu_{X,b}^{ex}$?

JCP **140**, 224507 (2014) shows QCT has little or no ϕ_{np}. Mean deviation of QCT from Marcus is -2.3 kcal/mol. $\mu_{H^+,b}^{ex} = -254.3$ kcal/mol

Marcus method (Halliwell and Nyburg)

Conventional enthalpy difference of like-sized ions vs. $1/R^3$
A *quadrupole* model (from Buckingham)
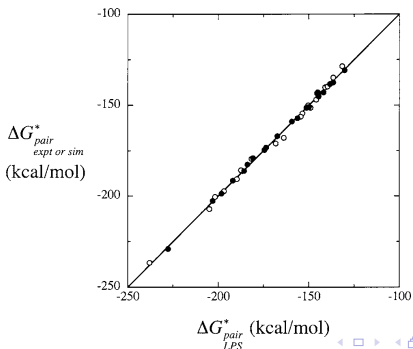
The potential at the cavity center

Mundy, et al. (quadrupole assumes central role)

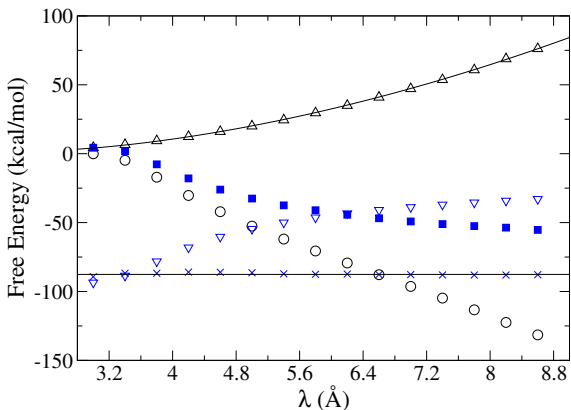| Model	R_C	μ	Θ	Ω	μ_z	$\Phi^{HW'}$	Φ^{HW}
SPC/E	2	-47	-134	-204	-260	-140	-147
	4	-237	-195	-90	-260	-262	-259
	6	-297	-167	-35	-260	-239	-251
TIP5P	2	-35	-20	-59	-103	-16	-14
	4	-72	-40	-24	-103	-33	-35
	6	-104	-32	-8	-103	-41	-42

What is ϕ_{np}?

Ashbaugh and Asthagiri (building on Latimer, Pitzer, Slansky) $\rightarrow$ -9.9 kcal/mol-e (-0.43 V). Single-ion values agree with Marcus. ($\delta_+ > \delta_-$ suggests anions more strongly hydrated than cations).

$$\mu^{ex}(\text{pair}) = -\frac{q^2}{2}\left(1 - \frac{1}{\epsilon}\right)\left(\frac{1}{r_+ + \delta_+} + \frac{1}{r_- + \delta_-}\right) + 2\lambda \qquad (9)$$
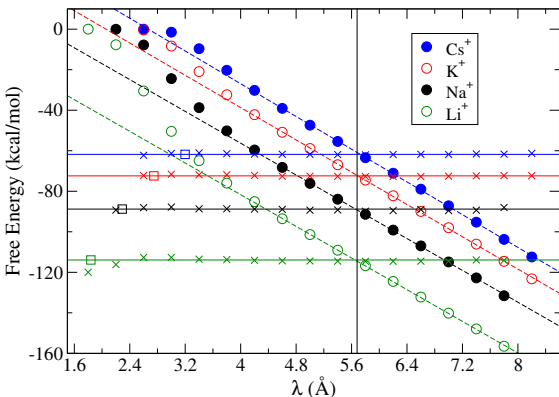

$\Delta G^*_{pair_{expt\ or\ sim}}$ (kcal/mol)

$\Delta G^*_{pair_{LPS}}$ (kcal/mol)

QCT length scales (Cl⁻ ion):

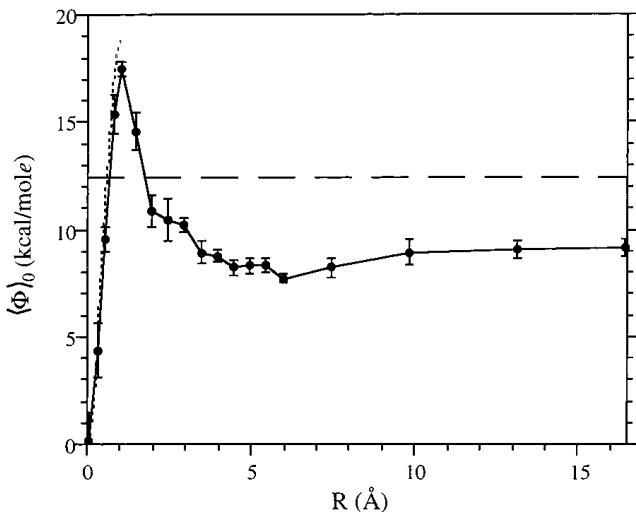## Universal length scale for monatomic ion hydration:

At crossing point $\mu_P^{ex}(\lambda) = -\mu_{LR}^{ex}(\lambda)$ (Born)

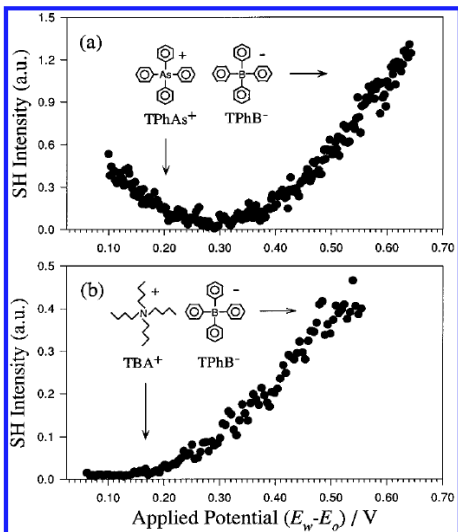Implies a similar quantum simulation $\rightarrow \mu_{X,b}^{ex}$

Ashbaugh local potential (Classical SPC, PBC, 2000):
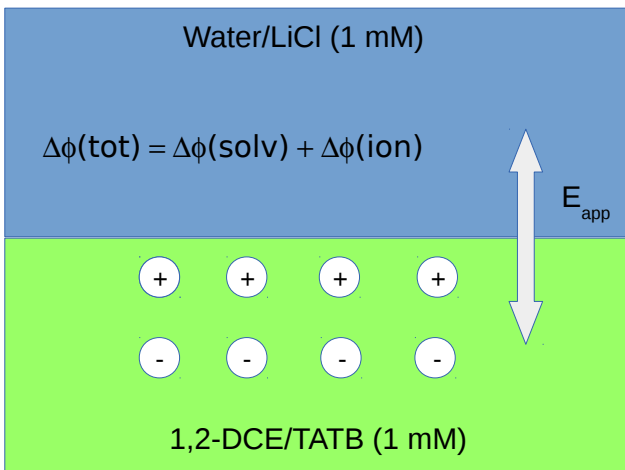
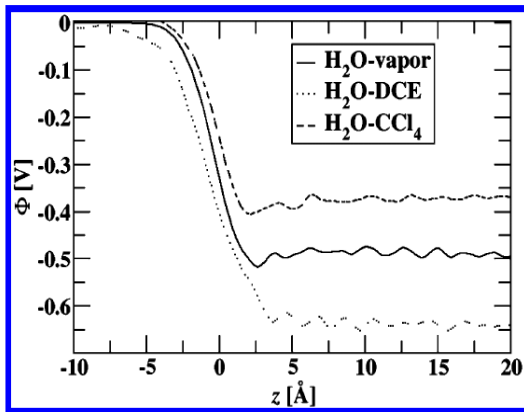Having a look at the behavior of ϕ_{np}:

Conboy and Richmond: SHG on TATB at water/1,2-DCE

Conboy and Richmond

E_{app} of ≈ 0.44 V $\rightarrow$ charge balance

Water/LiCl (1 mM)

$\Delta\phi(\text{tot}) = \Delta\phi(\text{solv}) + \Delta\phi(\text{ion})$

E_{app}

+   +   +   +

-    -   -   -

1,2-DCE/TATB (1 mM)

Wick and Dang: contact potential (not $\Delta\phi_{np}$)

Fundmental interfacial electrostatics relation

- Partitioning:

$$K = \exp\left(-\sum \Delta\mu^{ex}_{X,b}/kT\right) \tag{10}$$

- Single ions:

$$\frac{\rho_X(W)}{\rho_X(O)} = \exp\left[-\left(\Delta\mu^{ex}_{X,b} + q_X\Delta\phi_{np}\right)/kT\right] \tag{11}$$

- Charge balance in organic phase

$$\sum_{\text{pairs}} c_{\text{pr}}\left(\frac{1}{1 + \eta_{\text{pr}}(P)/x} - \frac{1}{1 + \eta_{\text{pr}}(N)x}\right) = 0 \tag{12}$$
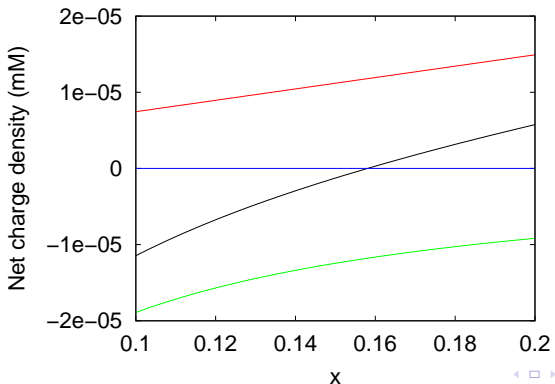
$\eta_X = \exp(-\Delta\mu^{ex}_{X,b}/kT)$; $x = \exp(\Delta\phi_{np}/kT)$

Solving for $\Delta\phi_{np}$: CsCl/TATB case (Li$^+$ not avail)

Red (CsCl), Green (TATB), Black (Total); $\Delta\phi_{np} = -0.05$ V
Should be smaller magnitude for Li$^+$: ChemComm 50, 1015 (2014)
$\Delta\phi_{np} = 0$ V for only TATB; $\Delta\phi_{np} = \Delta\phi_{np}(solv) + \Delta\phi_{np}(ion)$

Outline of the CPA: Pollard/Beck, JCP, 2014a

Real proton free energy (all ion pairs, cation$\rightarrow$anion difference):

$$\frac{1}{2}\Delta\mu_X^{ex,con} - \frac{1}{2}\Delta\mu_X^{ex} = \mu_{\mathrm{H}^+}^{ex} = \mu_{\mathrm{H}^+,b}^{ex} + \phi_{np} \tag{13}$$

As a limit (our calculations):

$$\frac{1}{2}\Delta\mu_X^{ex,con} - \frac{1}{2}\lim_{n\to\infty}\Delta\mu_{X,n}^{ex} = \mu_{\mathrm{H}^+}^{ex} \tag{14}$$

CPA makes an extra-thermo assumption for second term on left, uses clusters up to $n=6$, and locates point where $\Delta\mu_{X,n}^{ex} = 0$. Revision: consider

$$\frac{1}{2}\Delta\mu_X^{ex,con} = \frac{1}{2}\left(\frac{\Delta\mu_X^{ex}}{\Delta\mu_{X,n}^{ex}}\right)\Delta\mu_{X,n}^{ex} + \mu_{\mathrm{H}^+}^{ex} \tag{15}$$

Concerns about slope near the x origin?

Outline of the CPA

CPA says:

$$\frac{\Delta\mu_X^{ex}}{\Delta\mu_{X,n}^{ex}} \approx \frac{\mu_N^{ex} + \mu_P^{ex}}{\mu_{N,n}^{ex} + \mu_{P,n}^{ex}} \qquad (16)$$

and

$$\Delta\mu_{X,n}^{ex} \approx 0 \rightarrow \Delta\mu_X^{ex} \approx 0 \qquad (17)$$

These both seem to be 'extreme' assumptions, yet the results are pretty close to results derived below. Original CPA says: -265.9 kcal/mol (free energy), -274.9 kcal/mol (enthalpy), and -30 cal/mol-K (entropy). We choose to use the data directly and stay away from the *x* origin. *Looks similar but quite different!* (Donald and Williams, 2010)
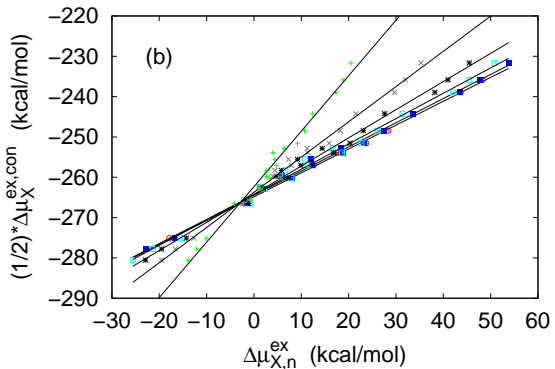
Bulk conventional and cluster data: all ions $n = 1 - 6$

Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, H_3O^+, NH_4^+, $CH_3NH_3^+$, F^-, Cl^-, Br^-, I^-, OH^-, HS^-, CN^-, HCO_2^-, $CH_3CO_2^-$, NO_3^-, and ClO_3^-
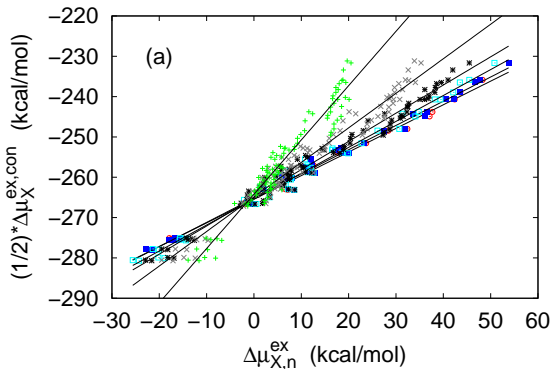
Bulk conventional and cluster data: alkali halides

Slope at $n = 6$ is about 0.59; large n limit is 0.5 (Pollard/Beck, JCP, 2014b)

| Proton thermodynamic data					
n	$\mu_{H^+}^{ex}$	$h_{H^+}^{ex}$	$s_{H^+}^{ex}$	$\mu_{H^+}^{ex}$	$h_{H^+}^{ex}$	$s_{H^+}^{ex}$
	Full range			Positive range		
All ions						
1	-264.2 ± 0.4	-272.0 ± 0.6		-263.6 ± 1.4	-271.2 ± 1.6	
2	-264.9 ± 0.3	-273.0 ± 0.6		-264.6 ± 0.6	-271.4 ± 1.1	
3	-265.1 ± 0.2	-273.7 ± 0.6		-264.9 ± 0.4	-272.3 ± 1.1	
4	-265.4 ± 0.2	-273.9 ± 0.5	-28.3	-265.3 ± 0.5	-272.5 ± 1.0	-24.0
5	-265.2 ± 0.3	-274.8 ± 0.5	-32.0	-265.3 ± 0.5	-273.9 ± 1.0	-28.7
6	-265.5 ± 0.3	-275.3 ± 0.9	-32.7	-265.9 ± 0.5	-275.1 ± 1.7	-30.7
Alkali halide ions						
1	-262.3 ± 0.4	-270.7 ± 0.4		-264.0 ± 1.5	-270.2 ± 0.9	
2	-263.7 ± 0.3	-272.7 ± 0.3		-263.9 ± 0.7	-271.8 ± 0.7	
3	-264.2 ± 0.3	-273.2 ± 0.5		-263.6 ± 0.7	-271.5 ± 0.9	
4	-264.3 ± 0.3	-273.1 ± 0.5	-29.3	-263.6 ± 0.6	-271.4 ± 0.9	-26.0
5	-264.5 ± 0.3	-273.2 ± 0.6	-29.0	-264.1 ± 0.5	-271.4 ± 1.0	-24.3
6	-264.8 ± 0.2	-273.6 ± 1.2	-29.3	-264.9 ± 0.4	-271.9 ± 2.2	-23.3

Implications

- Our large-cluster calculations using AMOEBA model and MP2 calculations agree very well with the lower right corner of the above table: alkali halides over limited x range.

- (Expt)Average of $n = 4 - 6$ values: -264.2 kcal/mol, -271.6 kcal/mol, and -24.5 cal/mol-K-e vs. -265.9, -274.9, -30 CPA above.

- (Calc)(NaF and RbI): -264.7 kcal/mol, -271.9 kcal/mol, and -24.0 cal/mol-K-e. (n up to 242).

- We conclude mCPA yields "real" hydration quantities.

- Implies the temperature derivative of the surface potential is ≈ 0:

$$s_X^{ex} = s_{X,b}^{ex} - q_X \left(\frac{\partial \phi_{np}}{\partial T} \right)_P \tag{18}$$
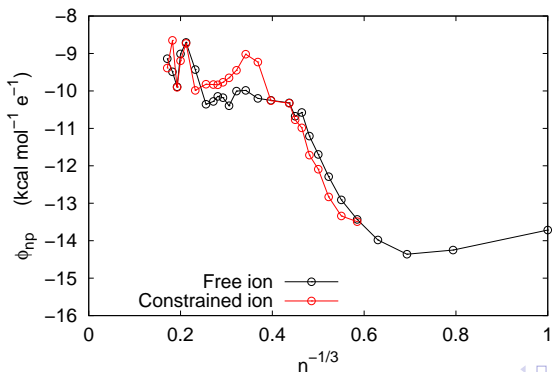
Enthapy shift vs. size: Free

Majority of shift by $n = 10$; NaF case, MP2 and AMOEBA
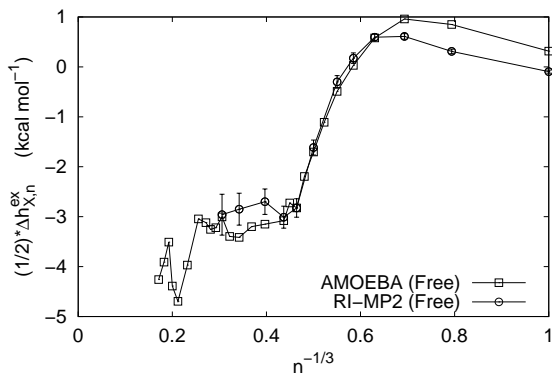
Net potential vs. size: CoM and Free

Free energy data in JCP 140, 224507 (2014) yield similar result

$$\phi_{np} = \frac{\Delta h_{X,b}^{ex}}{2} + T\left(\frac{\partial \phi_{np}}{\partial T}\right)_P - \frac{\Delta h_X^{ex}}{2} = \frac{\Delta \mu_{X,b}^{ex}}{2} - \frac{\Delta \mu_X^{ex}}{2} \qquad (19)$$

Remarks:

- *Any* partitioning of the real chemical potential involves a model and is not unique.
- We considered 3 alternatives and got the same answer from each, -0.4 V.
- This potential has an important contribution from water quadrupoles near the ion, suggesting a long-ranged effect $(1/z)$.
- This potential is the electrochemical surface potential, but relation to nonlinear spectroscopy, etc.?
- An essential feature is to understand the length scales for the decay of the net potential, and relate those to each experimental probe.

Net 'ionic' charge entering 'pure' water

$$Q(z) = \int_\infty^z \rho(z) dz \tag{20}$$

One possible scenario:

Net charge entering water: H+ and OH-
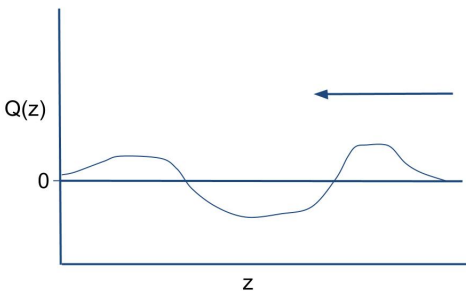
Closing:

- If this (solvent) potential exists it will alter charge distributions and change water chemistry: provides rationalization for negative ζ potential for bubbles and oil drops.

- Impact on electrochemistry, nano-science, energy storage, biological membranes.

- The derived value agrees with experiment: distribution of hydrophobic ions near the water/DCE interface and isoelectric point in droplet/bubble electrophoresis (Beattie, JPCB, 2009) and electrospray experiments (Colussi et al., PNAS, 2012)

- The pK_a of water shifts by $\approx 3 - 4$ units!