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Direct Observation of Charge Inversion by Multivalent Ions as a Universal Electrostatic Phenomenon

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We have directly observed reversal of the polarity of charged surfaces in water upon the addition of trivalent and quadrivalent ions using atomic force microscopy. The bulk concentration of multivalent ions at which charge inversion reversibly occurs depends only very weakly on the chemical composition, surface structure, size, and lipophilicity of the ions, but is very sensitive to their valence. These results support the theoretical proposal that spatial correlations between ions are the driving mechanism behind charge inversion.

SEOK, SANGJUN

(i) Understanding screening due to mobile ions in liquid
(ii) Charge inversion due to strongly correlated liquid **(SCL)** on water
    - experimental probe & theory

For describing screening – SCL by multivalent on water
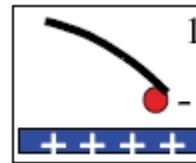
Negative Surface Charge (σ_s)
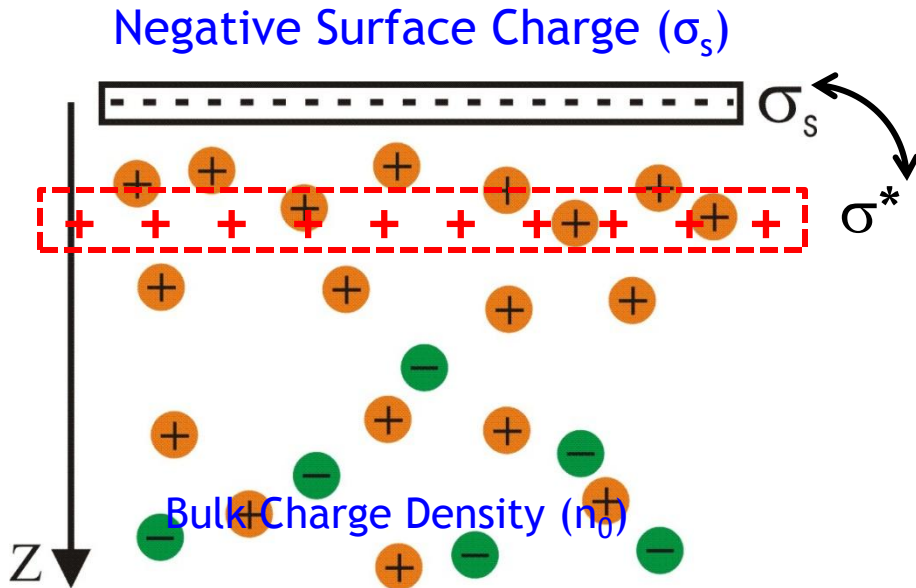
If multivalentions are overcompensated on negatively charged surface.

Surface charge inversion

Similarly.... Using the AFM, observed charge inversion in that paper

● Counterions (Cations)

● Coions (Anions)

(1) Consisting of ions confined by the surface. (i.e. Stern layer)
(2) A diffuse component described by the Poisson-Bolzmann (PB) equation that decays exponentially with distance far from the charged surface.

Experimental section

Using an atomic force microscope (AFM), measured the force between two oppositely charged surface.

Positively charged amine-terminated surface… made method omission.!!

Negatively charged surface were prepared silica spheres (10 μm dia.) with epoxy resin to AFM cantilevers.

AFM to yield force F on the silica bead versus the bead-surface separation d.

$$F = F_0 \exp(-d/\lambda), \qquad d > \lambda \qquad \text{Debye length } \lambda$$

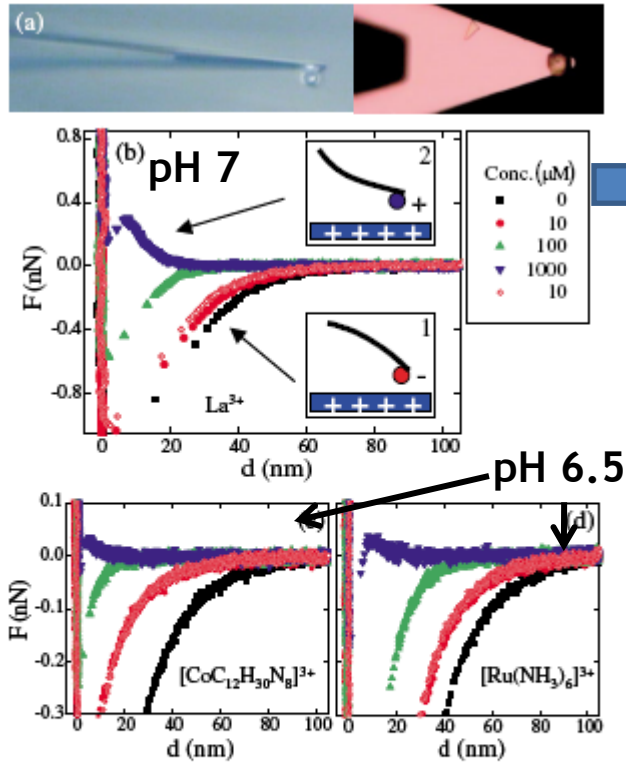Fit the value F_0 is renormalized surface by σ^*/σ_s

Cationic salt

FIG. 1 (color). (a) Optical microscope images of the side (left) and top (right) of a cantilever with a silica sphere. Force versus separation measurements in different concentrations of (b) $LaCl_3$, (c) $CoC_{12}H_{30}N_8Cl_3$, and (d) $Ru(NH_3)_6Cl_3$. The insets illustrate schematically the attractive (1) and repulsive (2) forces between the silica bead and the amine-terminated surface. The legend applies to all three graphs.
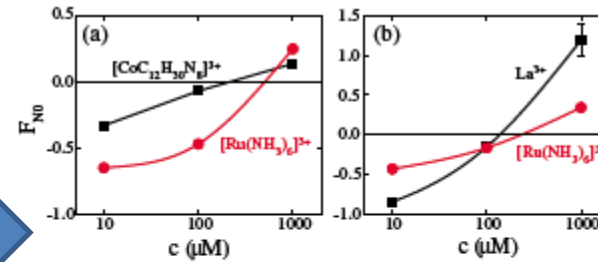
FIG. 2 (color online). Normalized force extrapolated to zero separation obtained from fits to Eq. (1), versus multivalent ion concentration c for (a) $CoC_{12}H_{30}N_8Cl_3$ (squares) and $Ru(NH_3)_6Cl_3$ (circles) and for (b) $LaCl_3$ (squares) and $Ru(NH_3)_6Cl_3$ (circles). In each case the data were obtained consecutively using the same silica bead. Lines are guides to the eye.

Anionic salt
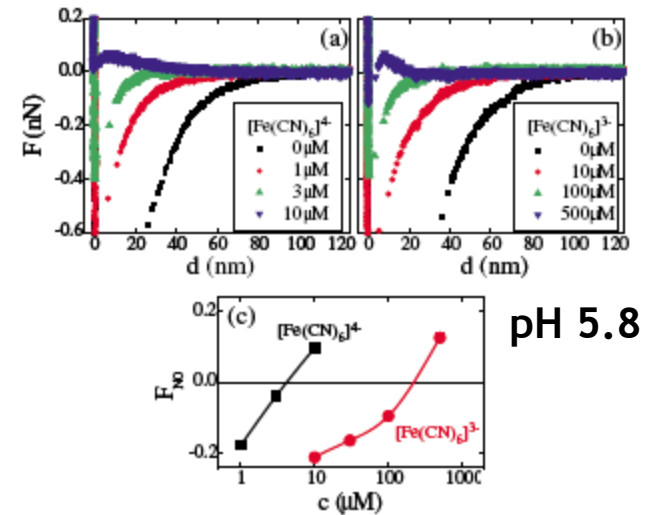
FIG. 3 (color). Force versus separation measurements in different concentrations of (a) $K_4Fe(CN)_6$ and (b) $K_3Fe(CN)_6$. (c) Normalized force at zero separation versus multivalent ion concentration c for $K_4Fe(CN)_6$ (squares) and $K_3Fe(CN)_6$ (circles). Lines are guides to the eye.

Summary

$[Ru(CN)_6]^{-4}$??

TABLE I. Summary of measurements in which the same surface was charge inverted by two different ions.

Surface	Probe	Supp. elect.	Ion(1)	Ion(2)	$c_0^{(1)}$ (μM)	$c_0^{(2)}$ (μM)	$c_0^{(high)}/c_0^{(low)}$
Chlorosilane	Silica bead	[19]	$[Fe(CN)_6]^{4-}$	$[Fe(CN)_6]^{3-}$	4	200	50
Chlorosilane	Silica bead	[19]	$[Fe(CN)_6]^{4-}$	$[Fe(CN)_6]^{3-}$	6	450	75
APTES	Silica bead	[20]	$[Fe(CN)_6]^{4-}$	$[Fe(CN)_6]^{3-}$	13	170	13
APTES	Silica bead	[20]	$[Ru(CN)_6]^{4-}$	$[Fe(CN)_6]^{4-}$	11	13	1.2
Silica bead	APTES	[20]	La^{3+}	$[Ru(NH_3)]^{3+}$	560	730	1.3
Silica bead	Poly-L-lysine	[17]	$[CoC_{12}H_{30}N_8]^{3+}$	La^{3+}	190	120	1.6
Silica bead	Poly-L-lysine	[17]	$[CoC_{12}H_{30}N_8]^{3+}$	La^{3+}	170	180	1.1
Silica bead	Chlorosilane	[17]	La^{3+}	$[Ru(NH_3)]^{3+}$	130	210	1.6
Silica bead	Chlorosilane	[18]	$[CoC_{12}H_{30}N_8]^{3+}$	$[Ru(NH_3)]^{3+}$	210	450	2.1
Poly-L-lysine	Silica bead	[20]	$[Ru(CN)_6]^{4-}$		22		

[17] The supporting electrolyte was a 1 mM HEPES (4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid) buffer, pH 7.0 ± 0.3 set by adding KOH.

[18] The supporting electrolyte was a mixture of 0.3 mM KOH and HCl with pH 6.5 ± 0.5.

[19] The supporting electrolyte was the same as [18] with pH 5.8 ± 0.3.

[20] The supporting electrolyte was a 0.1 mM MES (2-morpholinoethanesulfonic acid) buffer, pH 6.0 ± 0.3 set by adding KOH.

Compare to Shklovskii proposal theory in SCL.
In conclusion, charge inversion occurs depends only weakly on the chemical composition, surface structure, size, and lipophilicity of the ions, but is very sensitive to their valence.

$$c_0 = (\sigma_{bare}/2\pi Z) \exp\left[-\frac{\mu_c}{k_2 T}\right] \exp\left(\frac{\Delta\mu_0}{k_2 T}\right), \quad \mu_c \propto \sigma_{bare}^{1/2} \cdot Z^{3/2}$$

σ_{bare} : surface charge density, c_0 : charge inversion bulk concentration, μ_c : chemical potential of the SCL, $\Delta\mu_0$: standard energy of adsorption of an ions

σ_{bare} and $\Delta\mu_0$ are deduced $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ on the same surface

From rows 1 and 2 in table - σ_{bare} : +0.45 and +0.55 e/nm^2, $\Delta\mu_0$:-1.4kT and -0.1 kT
absolute μc are 9.4 kT and 10.6 kT for Z=4 and 5.8 kT and 6.5 kT for Z=3

From rows 3 in table - σ_{bare} : +0.2 e/nm^2, $\Delta\mu_0$: -3.0 kT
absolute μ_c is 5.8 kT and 3.5 kT for Z=4 and 3

Taking $\Delta\mu_0$ = 0 and c0 = 200 μM for $[CoC_{12}H_{30}N_8]^{3+-}$ screening silica gives σ_{bare} = -0.75 e/nm^2, consistent with commonly accepted vales.

Screening of a macroion by multivalent ions: Correlation-induced inversion of charge

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Screening of a strongly charged macroion by multivalent counterions is considered. It is shown that counterions form a strongly correlated liquid at the surface of the macroion. Cohesive energy of this liquid leads to additional attraction of counterions to the surface, which is absent in conventional solutions of the Poisson-Boltzmann equation. Away from the surface this attraction can be taken into account by a new boundary condition for the concentration of counterions near the surface. The Poisson-Boltzmann equation is solved with this boundary condition for a charged flat surface, a cylinder, and a sphere. In all three cases, screening is much stronger than in the conventional approach. At some critical exponentially small concentration of multivalent counterions in the solution, they totally neutralize the surface charge at small distances from the surface. At larger concentrations they invert the sign of the net macroion charge. The absolute value of the inverted charge density can be as large as 20% of the bare one. In particular, for a cylindrical macroion it is shown that for screening by multivalent counterions, predictions of the Onsager-Manning theory are quantitatively incorrect. The net charge density of the cylinder is smaller than their theory predicts and inverts the sign with a growing concentration of counterions. Moreover, the condensation loses its universality and the net charge linear density depends on the bare one. [S1063-651X(99)11311-4]

PACS number(s): 61.20.Qg, 77.84.Jd, 61.25.Hq

Poisson Boltzmann equation - PBE

$$\nabla^2 \Psi = -\frac{4\pi e}{D} \sum Z_i N_{0i} \exp\left(-\frac{Z_i e \Psi}{k_B T}\right) \qquad \text{PBE}$$

$$N(x) = N_0 \exp\left(-Ze\Psi \Big/ k_B T\right) \to 0 \text{ at } x \to \infty \qquad \text{Counterion concentration}$$

$$N(x) = \frac{1}{2\pi l}\frac{1}{(\lambda + x)^2} \qquad \text{Gouy-Chapman form}$$

$$\lambda = Ze/(2\pi l\sigma) \qquad \text{Gouy-Chapman length}$$
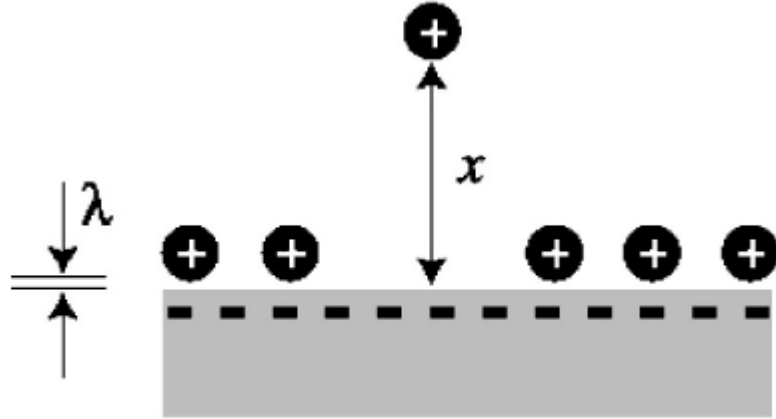
$$l = Z^2 l_B$$

$$l_B = e^2/(Dk_B T) \to 0.7 \text{ nm} \qquad \text{Bjerrum length}$$

e.g. Z=3 and σ=1.0 e/nm^2, λ=0.08 nm

Ions are located in the first molecular layer at the surface. i.e. they condense at the surface of a macroion.

At Z $\geq$ 2, repulsion between multivalent counterions condensed at the surface is so strong that they form a two dimensional strong correlated liquid in which the short order of counterions is similar to that of a Wigner crystal.

Surface Correlation Effect

FIG. 6. The origin of attraction of a new positive Z-ion to the already neutralized surface. Z-ions are shown by solid circles. The new Z-ion creates its negative correlation hole. cell and its simplified version as a disk with radius R are shown.

More strongly bound to the surface than in the PBE

The 2-dimensional concentration of Z-ions

This phenomenon can be understood as the attraction of a Z-valent counterion to its correlation hole in SCL

$n = \sigma / Ze$

The surface area per ion can be characterized a radius R

$$R = (\pi n)^{-\frac{1}{2}} = (Ze / \pi \sigma)^{\frac{1}{2}}$$

Γ Is the Coulomb coupling constant

$$\frac{R}{\lambda} = 2\Gamma, \ \Gamma = \frac{Z^2 e^2 / DR}{k_B T}$$

PBE becomes valid $\rightarrow x \gg l/4 \gg \lambda$ and the characteristic scale of the PBE solution $\rightarrow \Lambda \gg l/4$

e.g. monovalent ions, Z=1, $\rightarrow \Gamma \sim 1$ weakly coupled

Z=3 and σ=1.0 e/nm2 $\rightarrow \Gamma$ = 6.4, λ ~ 0.1 nm, and R ~ 1.0 nm strongly coupled

Thus SCL together with the intermediate boundary layer, $\lambda < x < l/4$ from the point of view of PBE, provide only a new boundary condition $N(x)=N(0)$ at x=0.

At finite $N(\infty)$, $N(x)=N(0) \rightarrow$ positive charge Z density of SCL compensates -σ.

PBE fail at large Z

At $N(\infty) > N(0)$, it becomes even lager than σ, so that the total charge of the surface become positive.

A new boundary condition for the PBE

The condition of equilibrium between SCL at $x=0$ and the gaslike phase layer between $l/4 \ll x \ll \Lambda$ is

$$\mu(n) + Ze\Psi(0) = \mu(N) + Ze\Psi(x) + U(x)$$

Hydration energy at the surface   chemical potential of SCL

$$\mu(n,T) = -k_B T \ln(n_w/n) + \mu_s + \mu_c(n,T)$$

Hydration energy at the bulk

$$\mu(N) = -k_B T \ln(N_w/N) + \mu_b$$

$U(x)$ Correlation energy of attraction to the hole

For *N(x)* dose not depend on *x* and equals

$$N(0) = \frac{n}{w} \exp\left(-\frac{|\mu_c(n,T)|}{k_B T}\right) \qquad w = (n_w/N_w)\exp[(\mu_b - \mu_s)/k_B T)]$$

Due to the large value of $|\mu_c(n,T)|$, the concentration $N(0)$ can be very small. For example, at $\sigma = 1.0 \ e/\mathrm{nm}^{-2}$ and $Z = 2$, 3, and 4, at which $\Gamma = 3.5$, 6.4, and 9.9, according to Eq. (9) one gets $|\mu_c(n,T)|/k_B T = 4.5$, 8.8, and 14.3, respectively. This gives $N(0) = 30$ mM, 0.3 mM, and 0.8 μM for $Z = 2$, 3, and 4 (1 M $= 6 \times 10^{26} \ \mathrm{m}^{-3}$). It is clear now

Planer Geometry

$$N(x) = \frac{1}{2\pi l} \frac{1}{(\Lambda + x)^2} \quad (x \gg l/4)$$ The renormalized Gouy-Chapman length, lambda

$$\Lambda = [2\pi l N(0)]^{-1/2} = \sqrt{\frac{w}{2\pi n l}} \exp\left(\frac{|\mu_c(n,T)|}{k_B T}\right)$$

e.g. at σ=1.0 e/nm^{-2} Λ ~ 1.8, 12.3, 1.66 nm at Z=2,3,4 compared with l/4=0.7, 1.6, 2.8 nm

One finds the total surface charge density located at distance x<l/4 is

$$\sigma^* = -\sqrt{N(0)/(2\pi l_B)} = -\sigma(\lambda/\Lambda)$$

e.g. for σ=1.0 e/nm^{-2} , one obtain that σ*=7x10$^{-2}\sigma$, 7x10^{-3} σ, 4x10^{-4} σ at Z=2,3,4

One finds compared these results with from l/4 to ∞

$$\sigma^* = 2Ze/\pi l^2$$

e.g. σ*=5x10^{-2}, 2x10^{-2} nm^{-2} at Z=3,4

These values of σ* are much lager than intermediate region. Thus, binding to the surface is strongly enhanced by correlation effects.

Planer Geometry

Here, we imported by Debye-Hückel screening radius.

$$\phi(r) = \frac{Q}{Dr} e^{-r/r_s} \qquad r_s = \left(\frac{k_B TD}{8\pi N_1 e^2}\right)^{1/2}$$

Debye-Hückel screening leads to exponential decay of the potential around a pointlike charge Q.

If N(∞)>>N(0), negative charges dominate at x<<r. We try to PBE approach.

$$N(x) = N(\infty)\exp(-Ze\Psi / k_B T)$$

$$N_-(x) = N_-(\infty)\exp(e\Psi / k_B T) \longrightarrow N_-(0) = ZN_-(\infty)[N(\infty)/N(0)]^{1/Z}$$

Similar to...

$$N_-(x) = \frac{1}{2\pi l_B} \frac{1}{(\Lambda_- + x)^2}$$

$$\Lambda_- = [2\pi l_B N_-(0)]^{-\frac{1}{2}}$$

To compensate for the bulk negative charge, the positive surface charge density of SCL becomes lager than σ, so that the net surface charge density, σ*, becomes positive!!

$$\sigma^* = e\sqrt{\frac{N_-(0)}{2\pi l_B}} = \frac{e}{2\pi l_B \Lambda_-}$$