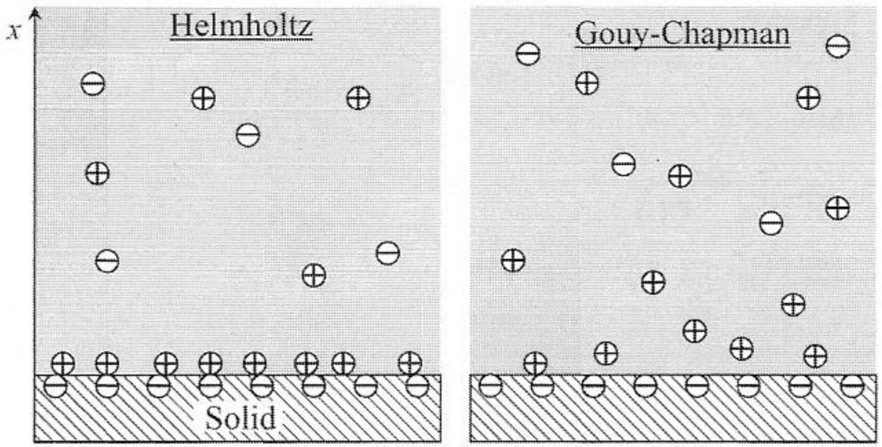
Charge inversion in diffusive double layer :
experimental and theoretical approach

SEOK, SANGJUN

Diffusive double layer – on the 1:1 salt (Z=1)

Diffusive double layer model :



What is the potential distribution in the solution??

Poisson-Boltzmann theory

Poisson equation

$$\nabla^2\varphi = \frac{\partial^2\varphi}{\partial x^2}+\frac{\partial^2\varphi}{\partial y^2}+\frac{\partial^2\varphi}{\partial z^2} = -\frac{\rho}{\varepsilon\varepsilon_0}$$

$$\rho = e(c^+ - c^-) = c_0 e\cdot\left(e^{-\frac{e\varphi(x,y,z)}{k_B T}} - e^{\frac{e\varphi(x,y,z)}{k_B T}}\right)$$

$$\varphi = \varphi_0\cdot e^{-\kappa x}$$

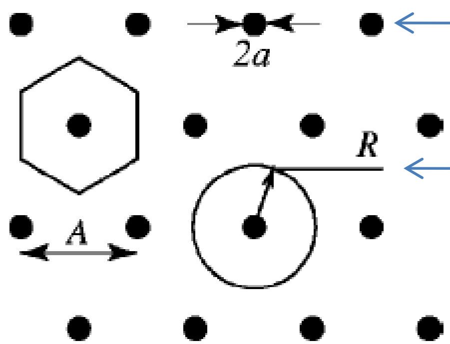
$$\kappa = \sqrt{\frac{2c_0e^2}{\varepsilon\varepsilon_0 k_B T}}$$

Debye length

$$\lambda_D = \kappa^{-1}$$

H. Butt, K. Graf, M Kapple, physics and chemistry of interface, WILEY-VCH (2006)

Diffusive double layer– Z=2,3,4…



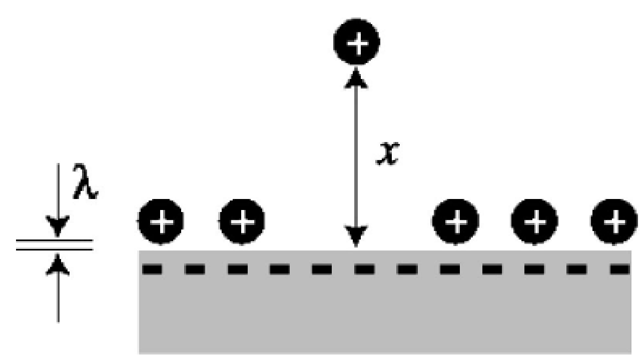
Positive Z-ion on a uniform background of negative surface charge

Counterions can attract each other at small distance

For example, Z=3, and σ = 1.0 e/$\mathrm{nm}^2 \rightarrow \lambda$ = 0.08 nm^2

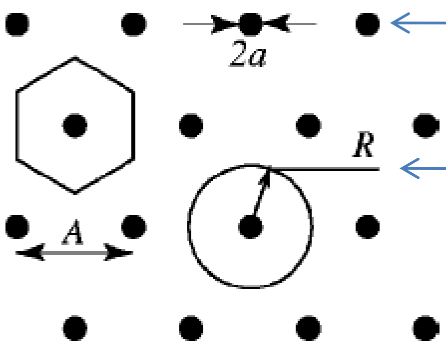
- The caounterions are located in surface
- The caounterions are strongly condensed in surface (repulsion)
- They formed 2-D strongly correlated liquid (SCL)
- Z-counterions generated hole in SCL

PB theory failed



Rev. Mod. Phys. 74, 329 (2002)

Diffusive double layer– Z=2,3,4…



Positive Z-ion on a uniform background of negative surface charge

Counterions can attract each other at small distance

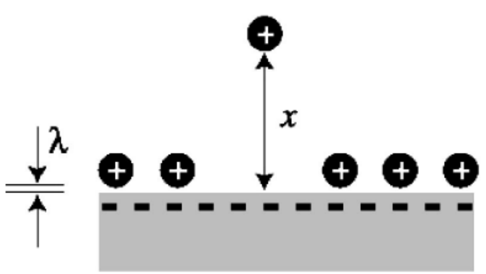
$n = \sigma / Ze$ 2D concentration of Z-ions

$\pi R^2 = 1/n$ The surface area per ion can be characterized by a radius

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

$\Gamma >> 1$ **S**trongly **C**orrelated **L**iquid (SCL)

For example, σ = 1.0 e/nm^2 , Γ=1.2, 3.5, 6.4, and 9,9 at Z=1, 2,3, and 4.



If counterion concentration is some more increased.

Counterions are attracted to a charged interface in excess of its own bare bare charge

Rev. Mod. Phys. 74, 329 (2002)

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Charge Inversion at High Ionic Strength Studied by Streaming Currents

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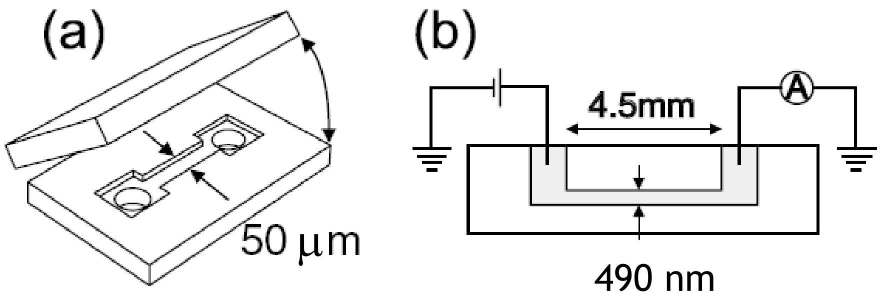
We report charge inversion, the sign reversal of the effective surface charge in the presence of multivalent counterions, for the biologically relevant regimes of divalent ions and mixtures of monovalent and multivalent ions. Using streaming currents, the pressure-driven transport of countercharges in the diffuse layer, we find that charge inversion occurs in rectangular silica nanochannels at high concentrations of divalent ions. Strong monovalent screening is found to cancel charge inversion, restoring the original surface charge polarity. An analytical model based on ion correlations successfully describes our

Experimental

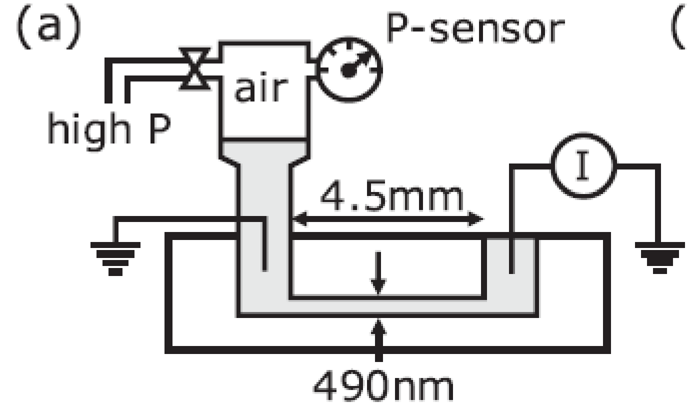
Streaming current (ionic current) that results from the pressure-driven transport of counterions in the diffusive double layer, were measured using Ag/AgCl electrodes.

Nanochanels (fused-silica)

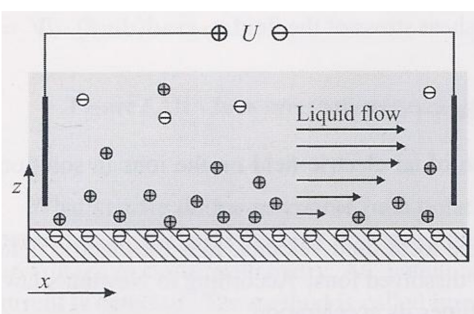


Phys. Rev. Lett. 93, 031901 (2004)

Microfluidics



Electro-osmosis



If we apply an electric field parallel to the surface the liquid begins to move.

The charged surface causes an increase in the concentration of counterions in the close to the surface.

H. Butt, K. Graf, M Kapple, physics and chemistry of interface, WILEY-VCH (2006)

Experimental

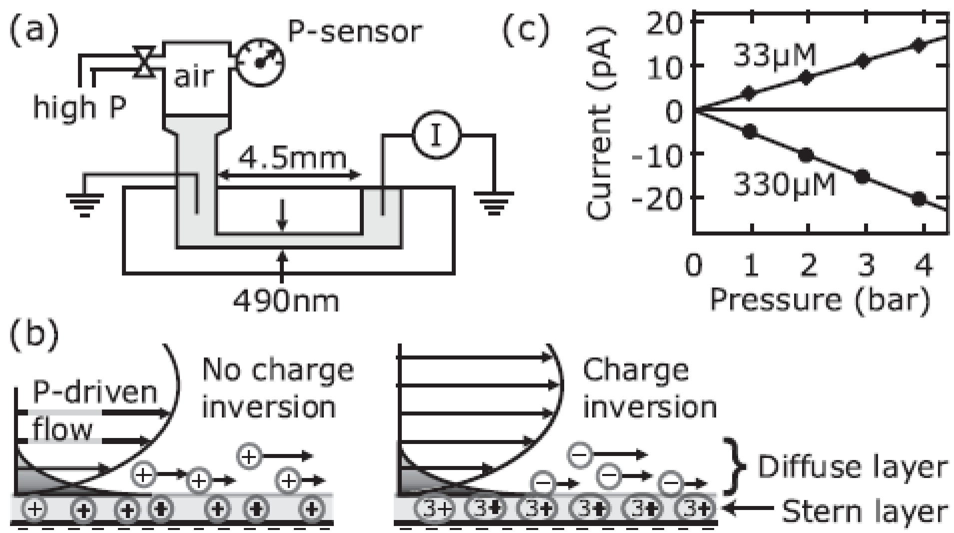


FIG. 1. (a) Side view of the nanochannel, including the pressure and electrical connections. (b) Schematic illustration of the origin of the streaming current and the effect of charge inversion for $Z = 3$. (c) Streaming current as function of applied pressure at low and high concentrations of trivalent CoSep ions. Solid lines are linear fits.

Inverted surface
(depending on applied pressure)

Positive ionic species:
CoSep ($CoC_{12}H_{30}N_8{}^{3+}$),
Ca^{2+}, Mg^{2+},
K+
Negative ionic species:
Cl^-

Buffer solution: (pH=7.5)
HEPES [4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid]
In deionized water

Results – Z=3

Charge inversion concentration c_0 to be 75~100 μM

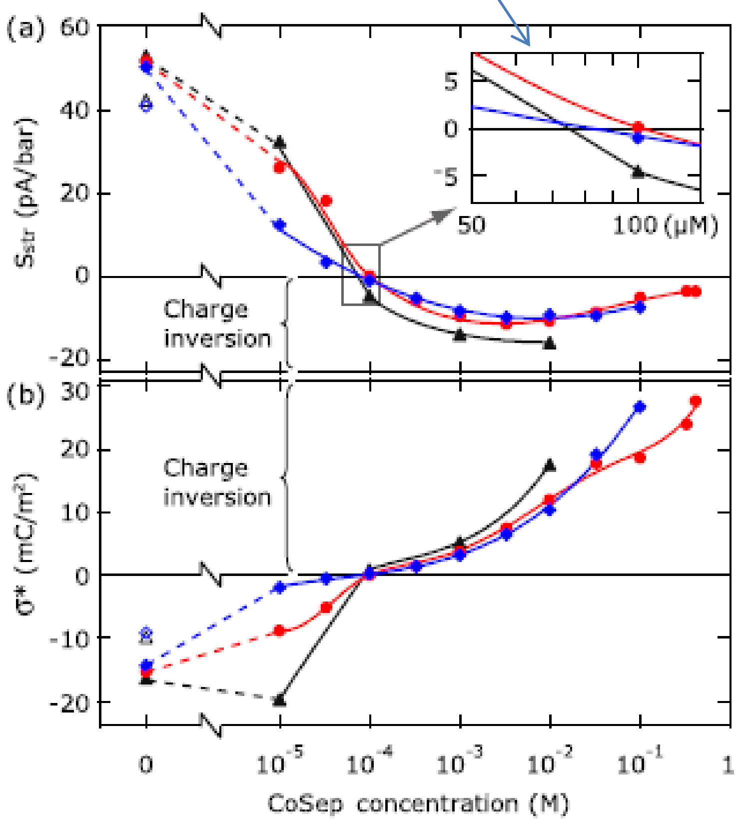


FIG. 2 (color online). (a) Three independent measurements of the streaming conductance S_{str} as function of the CoSep concentration. The lines are guides to the eye. The open symbols indicate that S_{str} regains positive values after each sweep from low to high concentration, although some hysteresis occurs. The inset highlights the charge inversion concentration region. (b) The effective surface charge σ^* as function of the CoSep concentration, converted from S_{str} as explained in the text.

Surface charge density

$$\sigma^* = \sigma_b + nZe$$

bare silica charge density

number density of Z ions

Predicts c_0 from Rev. Mod. Phys. 74, 329 (2002)

$$c_0 = \left|\frac{\sigma_b}{2 r_{ion} Ze}\right| \exp\left(\frac{\mu_c}{kT}\right)$$

$c_0 \rightarrow$ 170 ~ 300 μM (σ_b ~ -120 mC/m^2, Γ = 5.7)

Somewhat lower value from measured value

Can be explained

More negative σ_b ~ -150 mC/m^2, Γ = 6.7

Results – Z=2 and Z = 1 with various concentration CoSep

Charge inversion concentration c_0 to be 350 (Mg^{2+}) and 400 (Ca^{2+}) mM

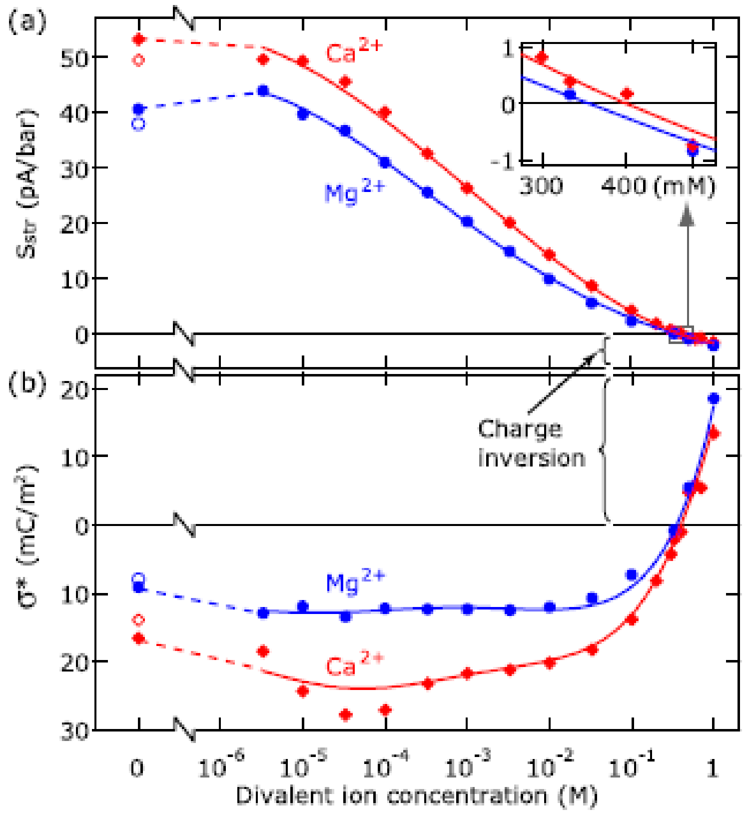


FIG. 3 (color online). Divalent ion concentration dependence of (a) the streaming conductance S_{str} and (b) the effective surface charge σ^*. Lines are guides to the eye; open symbols indicate measurements after each sweep from low to high concentration. The inset highlights the charge inversion concentration region.

Predicts c_0 from Rev. Mod. Phys. 74, 329 (2002)

$c_0 \rightarrow$ 47 mM (σ_b ~ -150 mC/m², Γ = 3.5)

No longer valid for Z = 2

Results – Z = 1 with various concentration CoSep

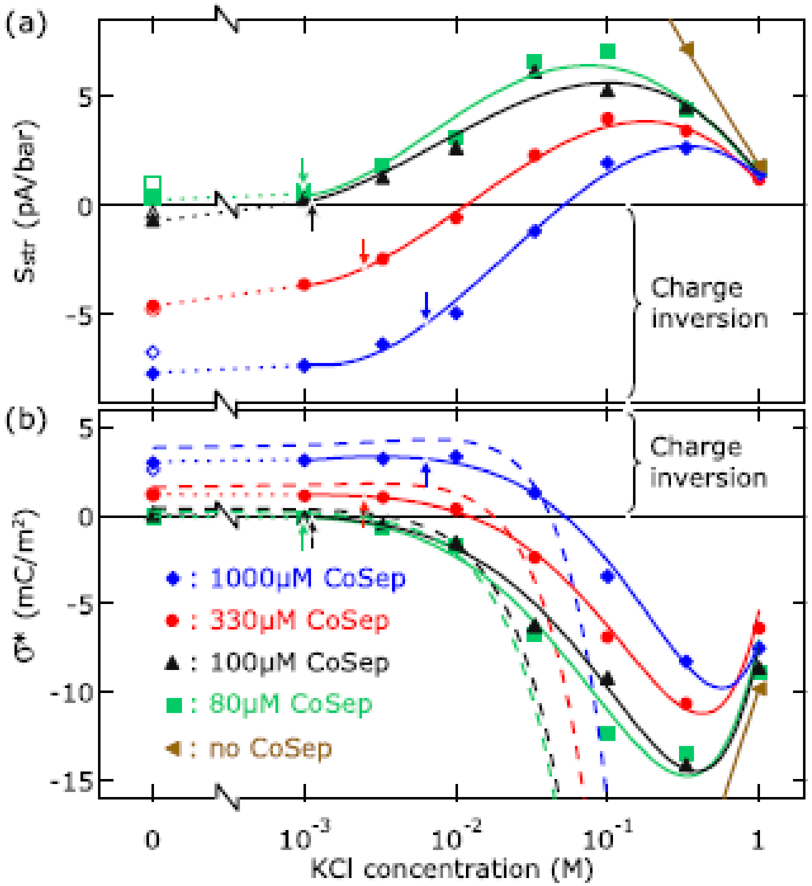


FIG. 4 (color online). Effect of screening on charge inversion by trivalent ions. The streaming conductance S_{str} (a) and the effective surface charge σ^* (b) are plotted as a function of KCl concentration for various CoSep concentrations. Solid lines are guides to the eye, while dashed lines are model curves for parameters $\sigma_b = -150\,\text{mC/m}^2$, $r_{ion} = 445\,\text{pm}$, and $\Delta\mu^0 = +0.8kT$. Open symbols indicate measurements after the completion of each data set. Arrows show where the KCl contribution to the screening length equals that of the buffer and CoSep ions.