Ion-Specific Induced Charges at Aqueous Soft Interfaces

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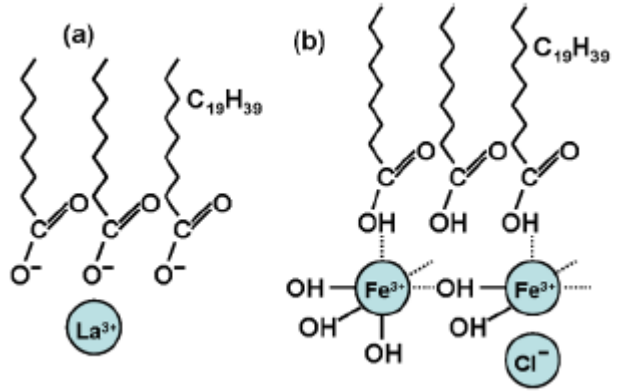
Ionic specificity effects, i.e., ions of the same valence leading to different macroscopic effects, are studied by considering a Langmuir monolayer of arachidic acid over a solution containing either Fe^{3+} or La^{3+}. We systematically vary *p*H levels as a way to control the interfacial surface charge and characterize the system by surface-sensitive x-ray scattering and spectroscopic techniques. We show that the critical surface pressure at the tilted (*L2*) to untilted (*LS*) transition is ionic specific and varies with *p*H. While the maximum density of surface bound La^{3+} per head group of arachidic acid is ~0.3, the amount necessary to neutralize the surface charge, for Fe^{3+} it is nearly 0.6 and it is accompanied with a significant accumulation of the coions Cl^- as revealed by surface x-ray spectroscopy. We account for the experimental observations by a statistical mechanical model including ion specificity.

maximum density (neutralize the surface charge)



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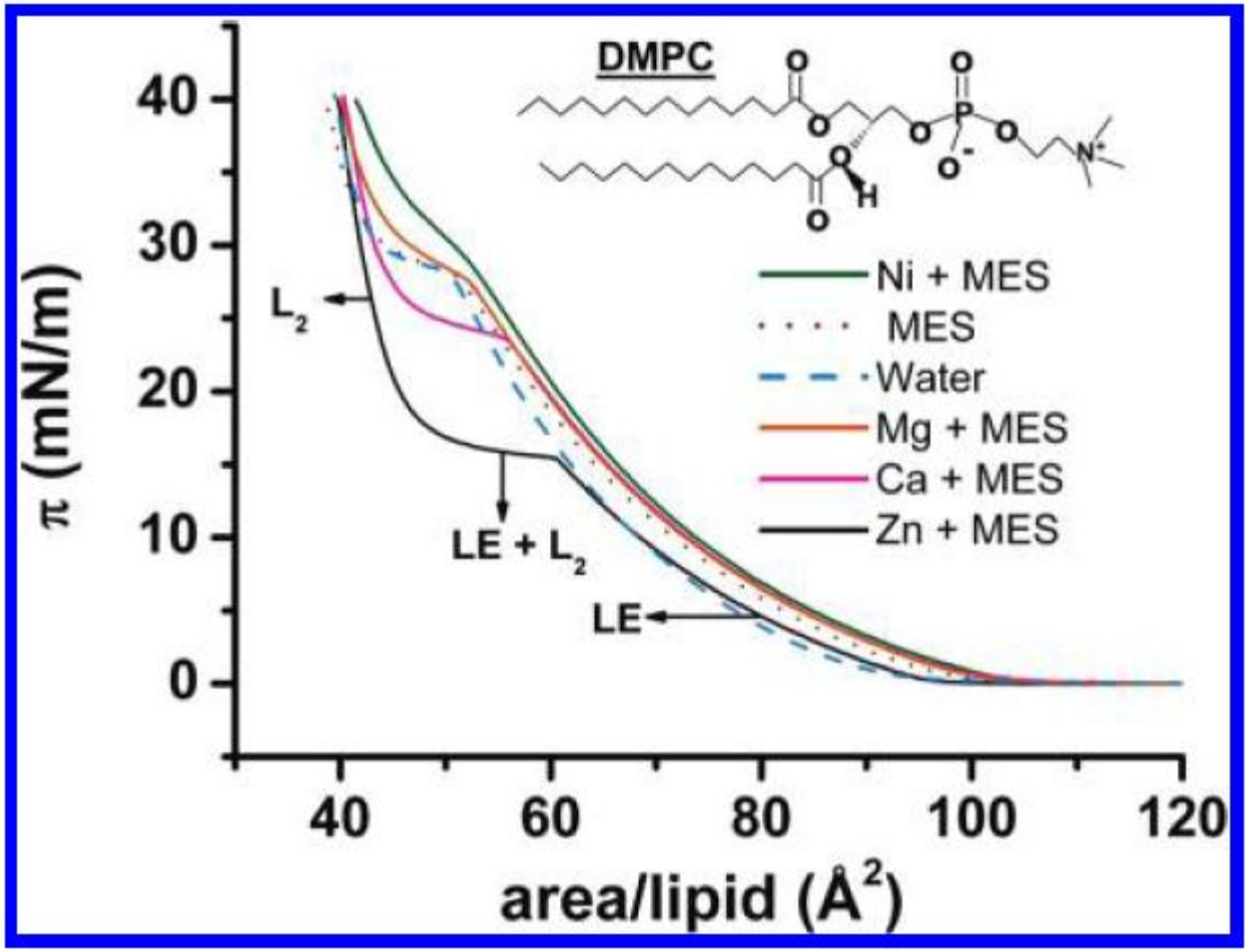
Motivation in that paper

Effective of divalent cations on phase behavior (π-A isotherms)



metal chloride (MCl_2)
150 mM & 10 mM MES, pH6

critical external pressure at the transition

$$\pi_c = \pi_c^0 + \delta\pi_c$$

binding sequence

$Zn^{2+} > Ca^{2+} > Mg^{2+} > Ni^{2+}$

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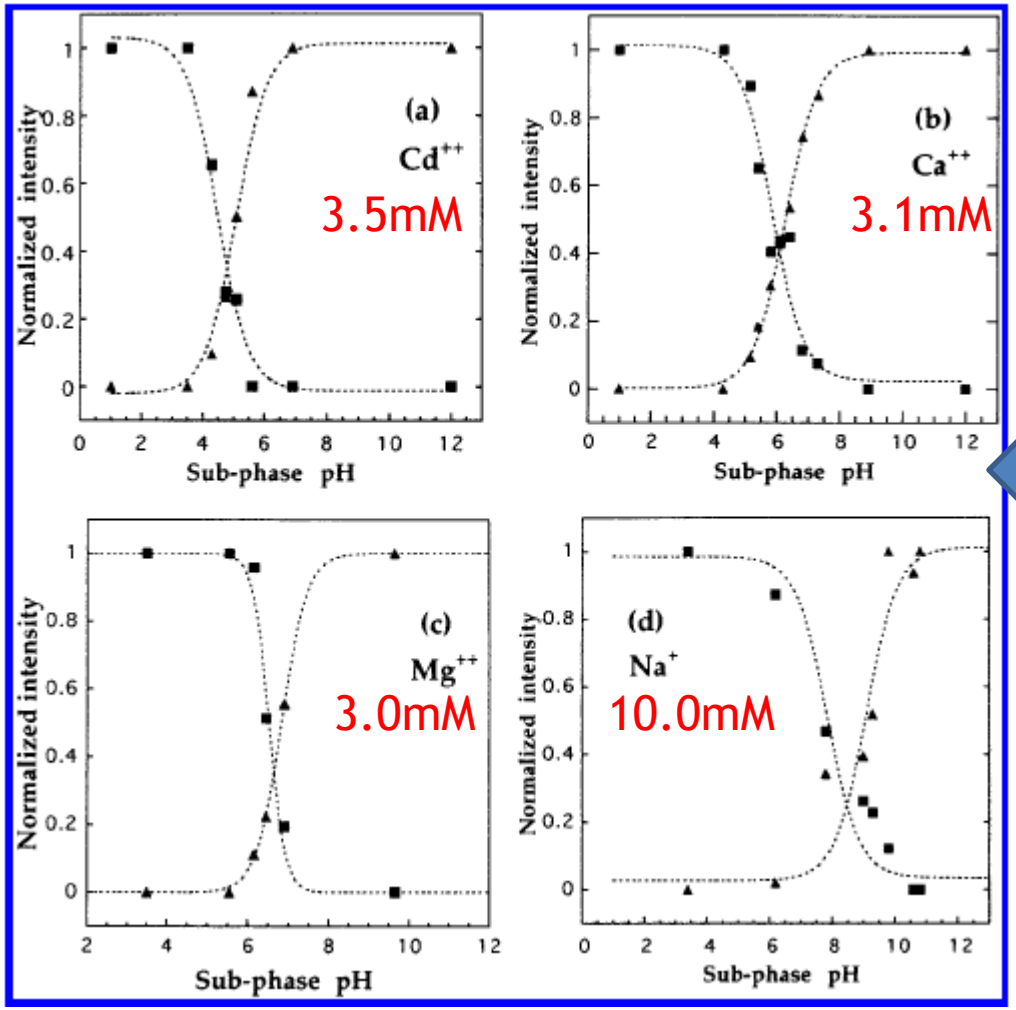
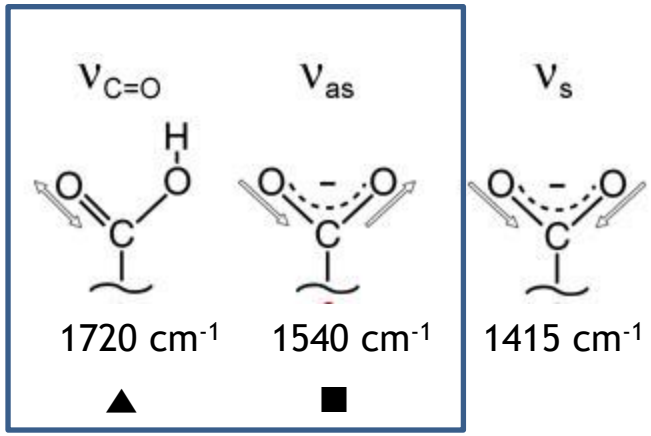
Effect of Cations on Arachidic acid Monolayers

To determine the subphase pH at which the half-neutralization of acid

PM-IRRAS **(Polarization-modulated Infrared reflection absorption spectroscopy)** intensity





Langmuir, **17**, 670 (2001)

Experimental

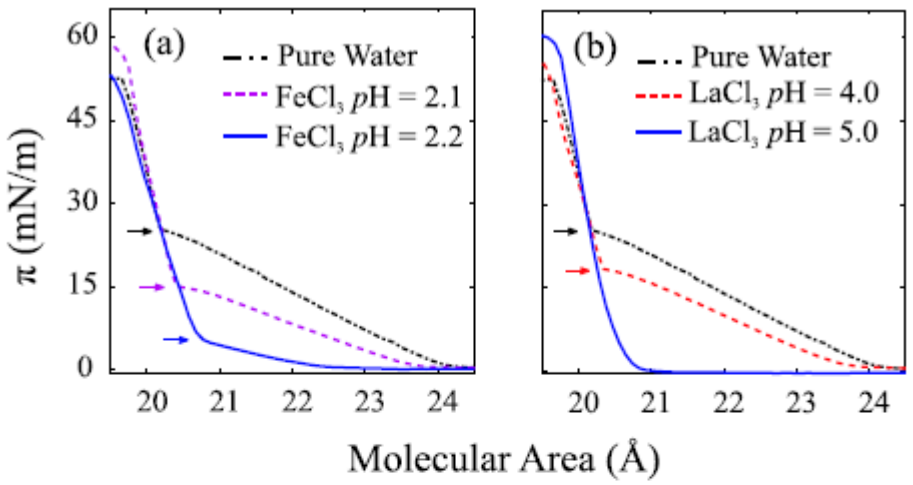
Langmuir monolayer

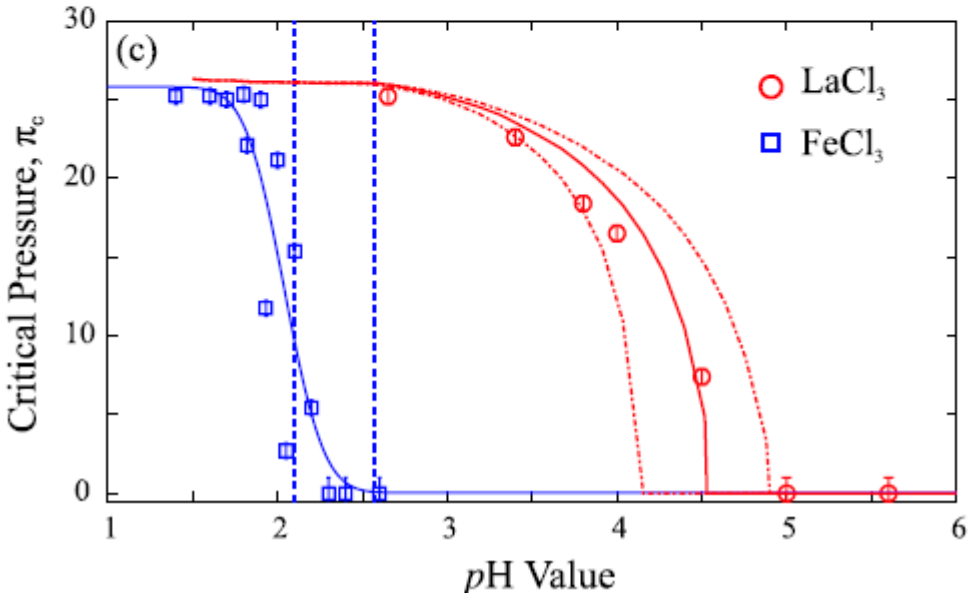
- Arachidic acid ($C_{20}H_{40}O_2$)
- Ion bulk concentration (1mM) – $FeCl_3$ and $LaCl_3$
- Buffer soultion - HCl

X-ray scattering

- APS, 8.0 Kev ; λ = 1.5498 Å
- fluorescence

Result – π-A isotherms



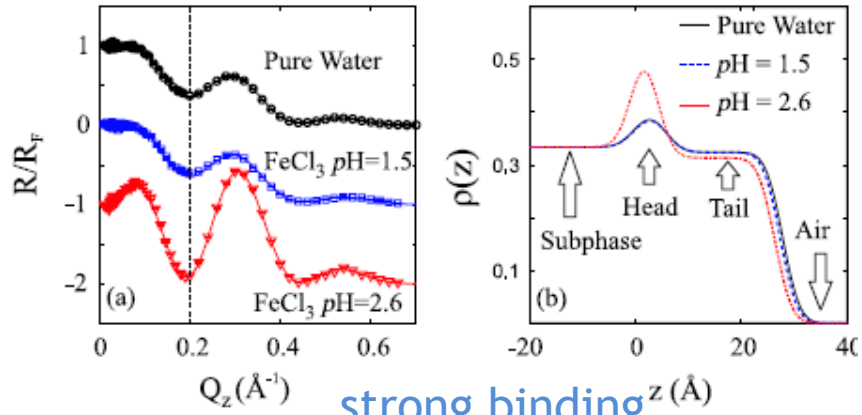


$$\delta\pi_c = \frac{\varepsilon_r}{4\pi}\int_0^\infty dz\left(\frac{d\Phi}{dz}\right)^2 - k_B T f_{DC}\gamma(f_b)\frac{l_B}{A_c^{3/2}}$$

$\Phi(z)$: electric potential
A_c : molecular area
f_{dc} : fraction of carboxyl group (charged)
f_b : fraction of headgroups with a bound trivalent
γ : electrostatic correlations among the all the charged species
l_B : Bjerrum length

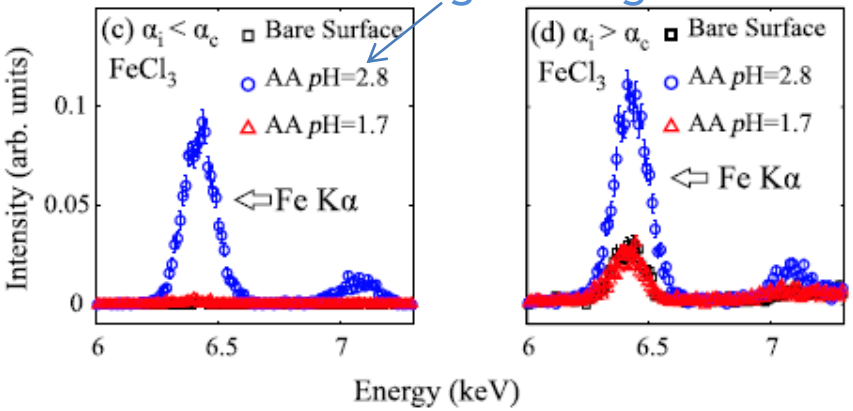
$$l_B = \frac{e^2}{\varepsilon_r k_B T} \approx 0.7nm$$

Result – x-ray studies

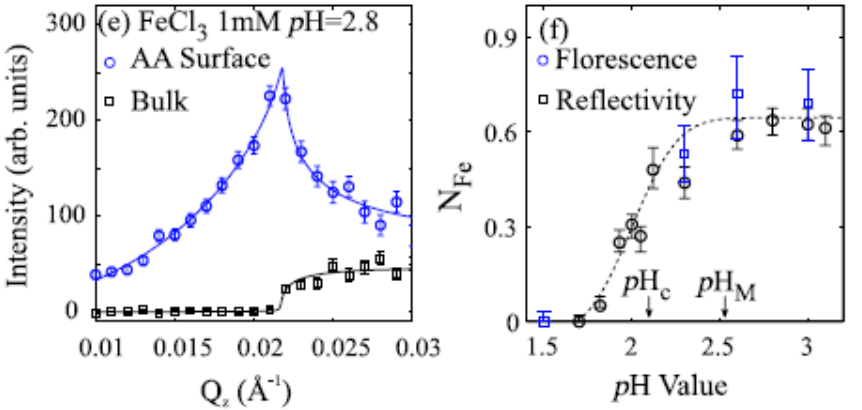


normalized x-ray

strong binding

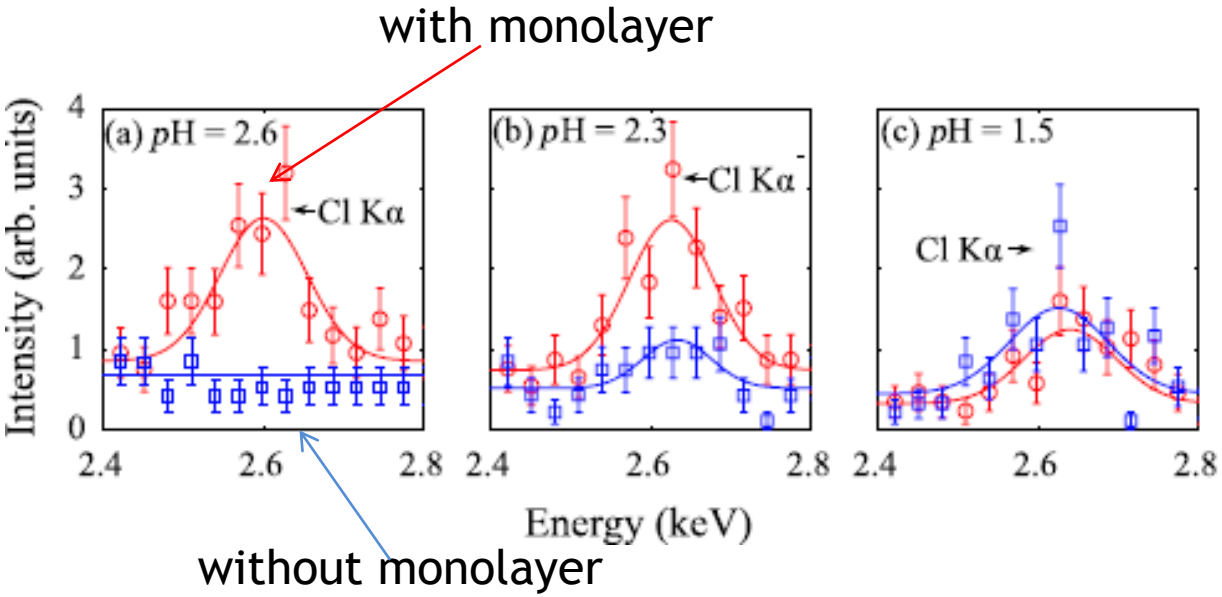


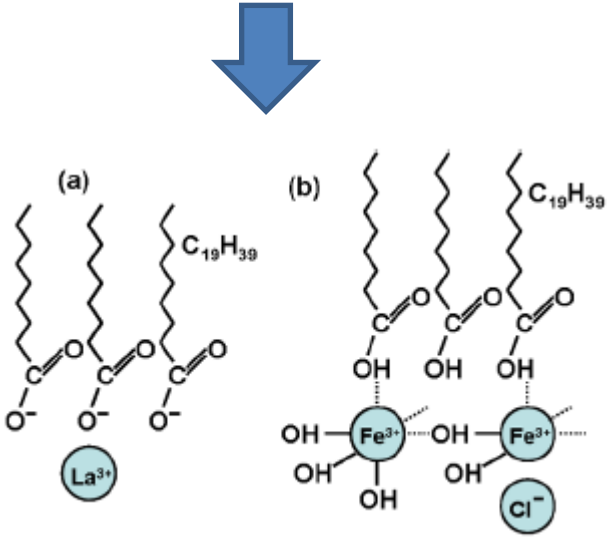
Fluorescence spectra in the energy range of the Fe K_α (~6.4 keV) and K_β (7.06 KeV)
α_c : critical angle for total reflection



(e) Integrated Fe emission line intensity over 6.3 ~ 6.6 keV with curve fit as function of Q_z
(f) pH dependence of iron accumulation at surface
cf. La^{3+} solution at pH values 1.5, 2.7, and yield 0,0, and 0.3 La^{3+} ions per AA

Result - Fluorescence spectra from the k_α emission lines of Cl (≈ 2.62 keV)





Result – Bulk complexes from stability constant

$$[T^{3+}][(OH)^-]^3 = K_{sp}$$ ← Solubility constant

$$[H^+][(OH)^-] = K_{pH}$$ ← hydrolysis constant

$$[T^{3+}(OH)^-] = K_1[T^{3+}][(OH)^-]$$

$$[T^{3+}(OH)_2^-] = K_2[T^{3+}][(OH)^-]^2$$

Binding constant

$$[H^+] - [H^+]_0 = 3(x_0 - [T^{3+}]) - 2[T^{3+}(OH)^-] - [T^{3+}(OH)_2^-] + [(OH)^-] - [(OH)^-]_0$$