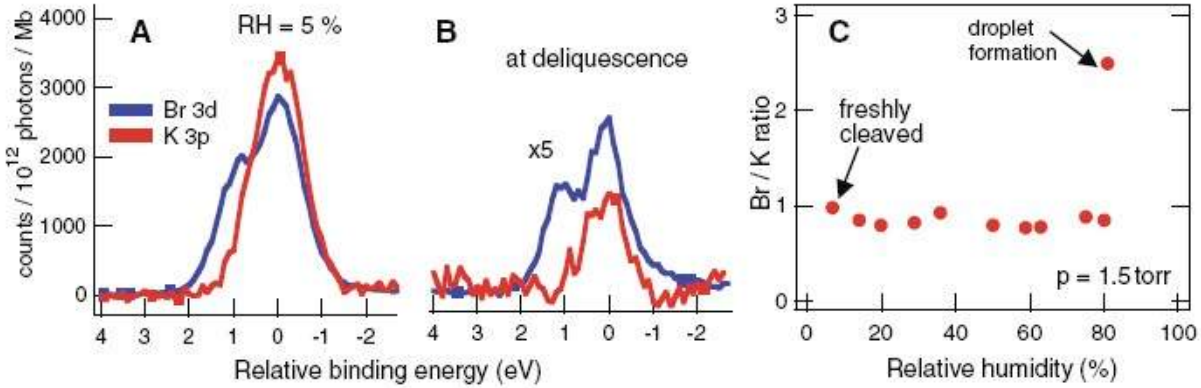
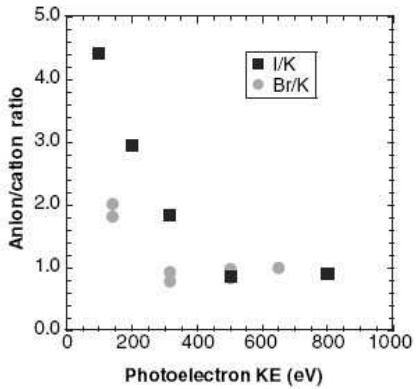
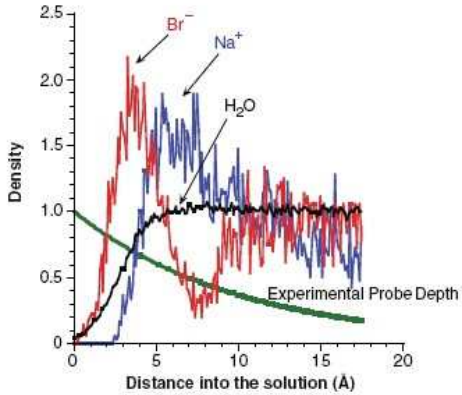
Surface excess of halide anion at charged surface

Science AAAS

Electron Spectroscopy of Aqueous Solution Interfaces Reveals Surface Enhancement of Halides
Sutapa Ghosal, *et al.*
Science **307**, 563 (2005);
DOI: 10.1126/science.1106525







From x-ray photoelectron spectroscopy

After aqueous droplet forming,
Anion / cation ratio is enhanced

Theoretical modification

PRL **102,** 147803 (2009) PHYSICAL REVIEW LETTERS week ending 10 APRIL 2009

Polarizable Ions at Interfaces

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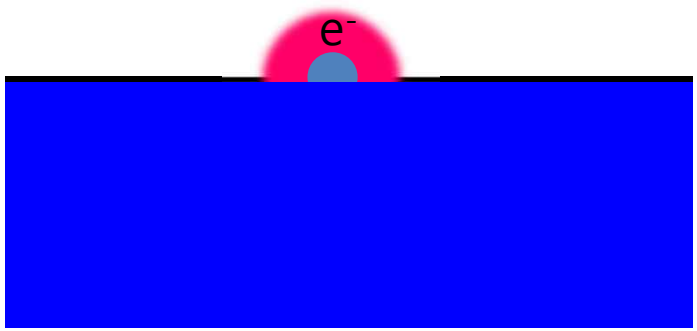
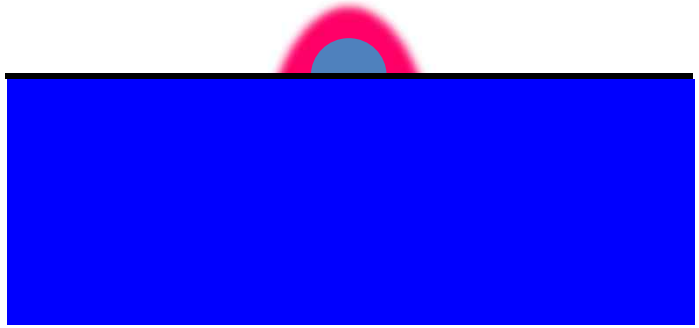
A nonperturbative theory is presented which allows us to calculate the solvation free energy of polarizable ions near water-vapor and water-oil interfaces. The theory predicts that larger halogen anions are adsorbed at the interface, while the alkali metal cations are repelled from it. The density profiles calculated theoretically are similar to those obtained using molecular dynamics simulations with polarizable force fields.

DOI: 10.1103/PhysRevLett.102.147803 PACS numbers: 61.20.Qg, 05.20.−y, 82.45.Gj

(1) Electron Cloud is more flexible for larger halide ion. → Cost less electrostatic energy

Ex)





$$U_s(a) = \frac{q}{4\varepsilon_w a} + \frac{q}{4\varepsilon_0 a}$$

$$U_s(a) \sim \frac{q}{2\varepsilon_w a}$$

Theoretical modification

(2) Cavitation energy – Energy cost for breaking hydrogen bonding network.

$$U_{\text{cav}}(h) = \begin{cases} \nu a^3 & \text{for } h \geq 2a \\ \frac{1}{4}\nu a^3 (\frac{h}{a})^2 (3 - \frac{h}{a}) & \text{for } 0 < h < 2a \end{cases}. \qquad \nu \approx 0.3 k_B T / \text{Å}^3.$$

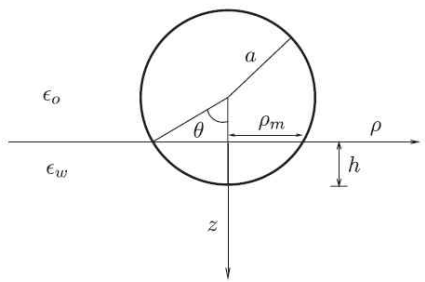


FIG. 1. Ion of radius a at an interface.

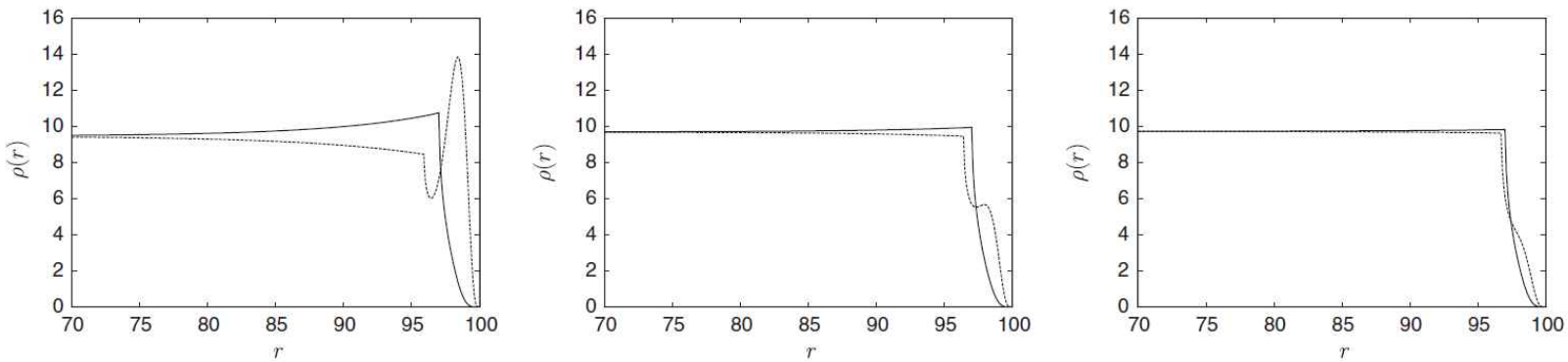
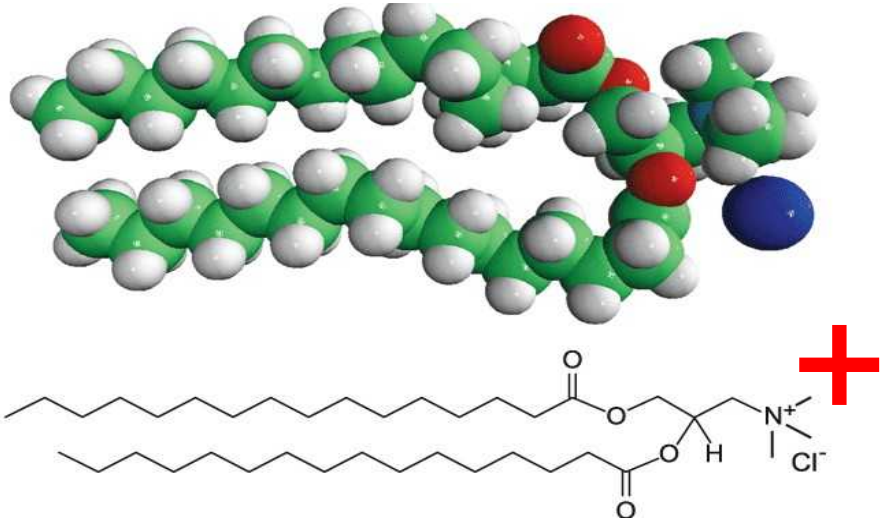


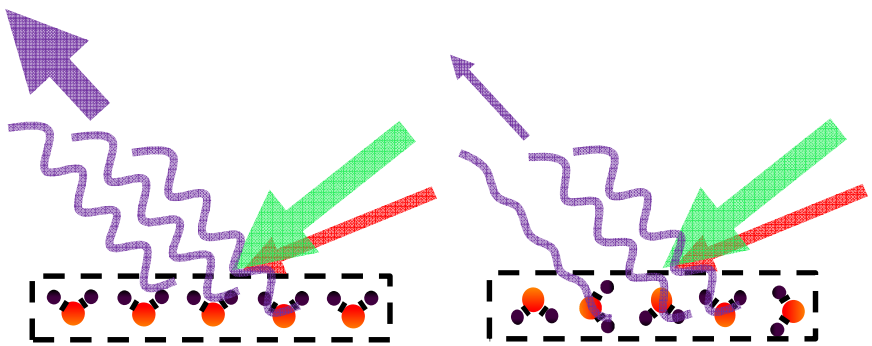
FIG. 2. Density profiles ($\times 10^5$) of KI, KBr, and KCl, from left to right.

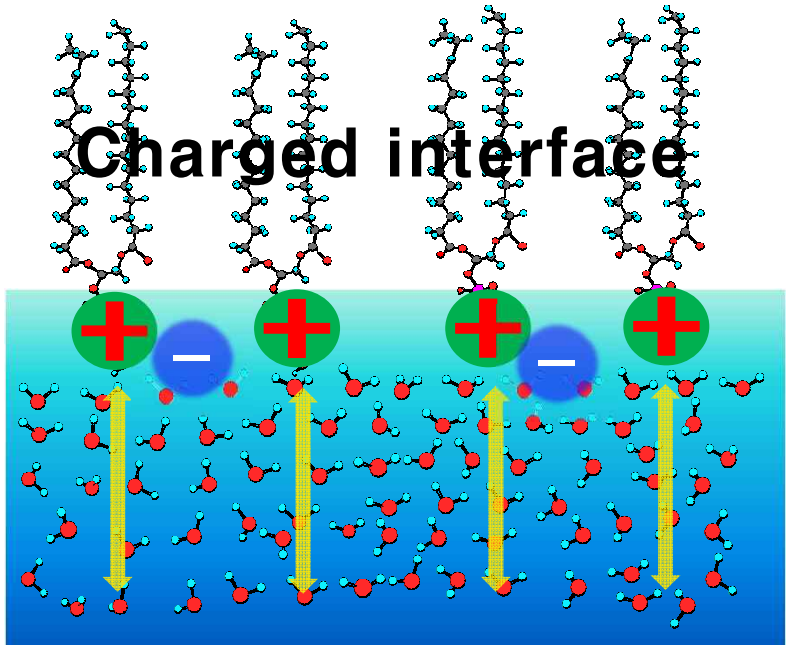
Experimental system – adsorption of halide ion at charged surface



1,2-dipalmitoyl-3-trimethylammonium-propane

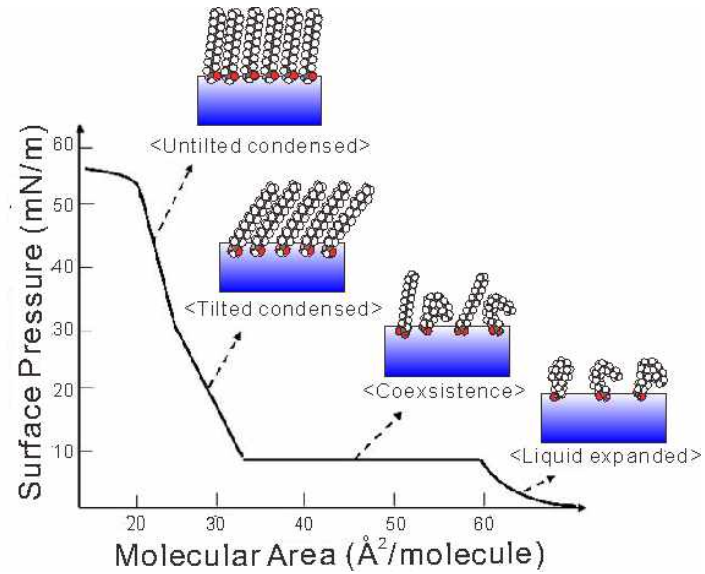
(DPTAP)

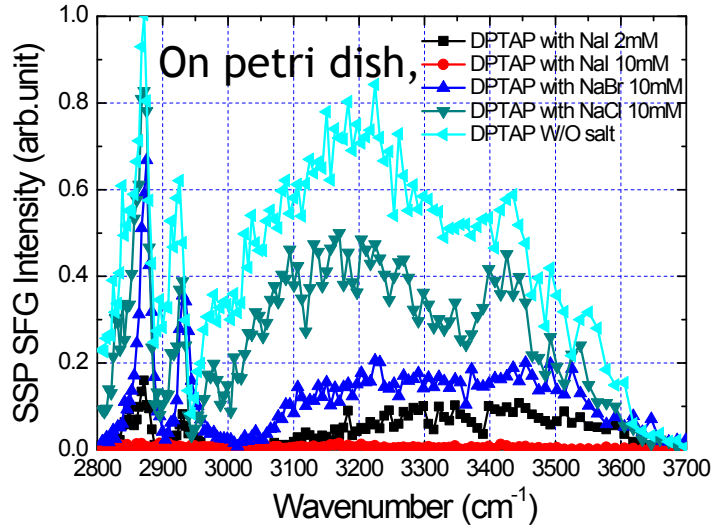


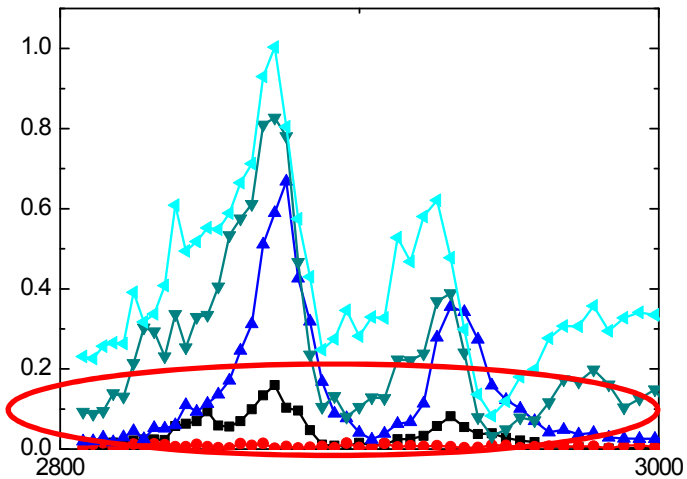


$$\vec{P}^{(2)} \propto \sum_{i,j,k} N_s \sum_{\xi,\eta,\zeta} \alpha^{(2)}_{\xi\eta\zeta} < (\hat{\xi}\cdot\hat{i})(\hat{\eta}\cdot\hat{j})(\hat{\zeta}\cdot\hat{k}) >$$

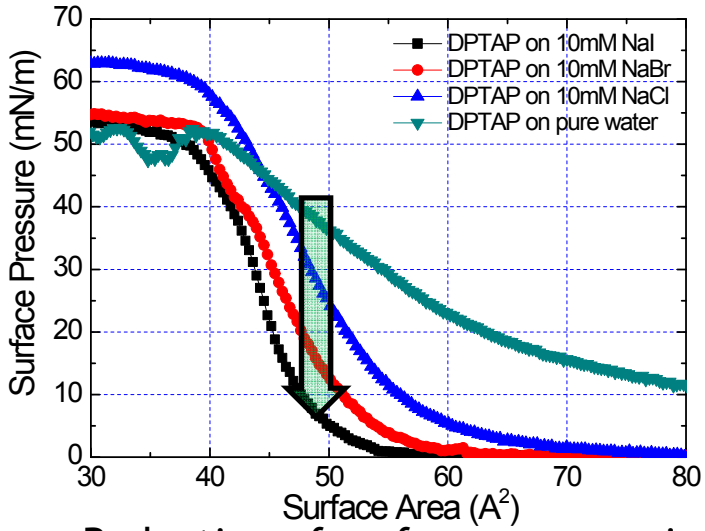
Pressure-Area isotherm





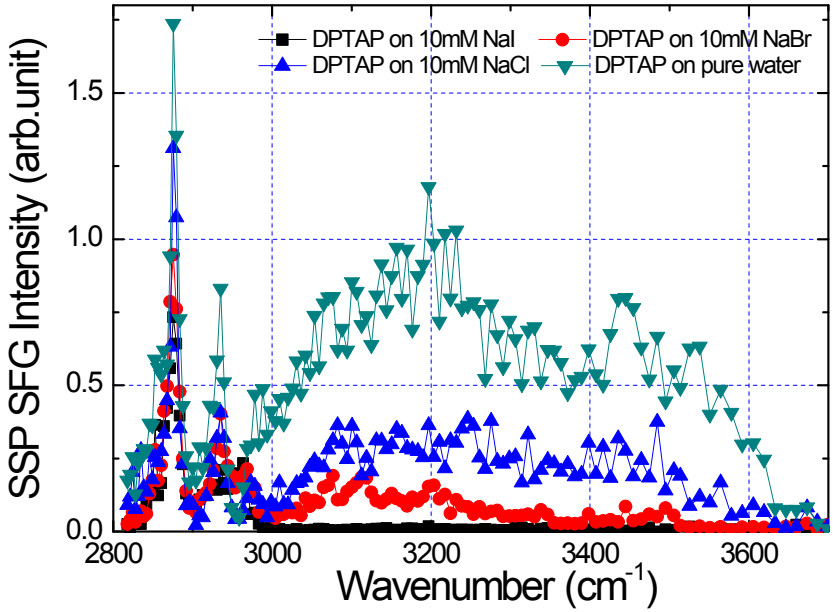


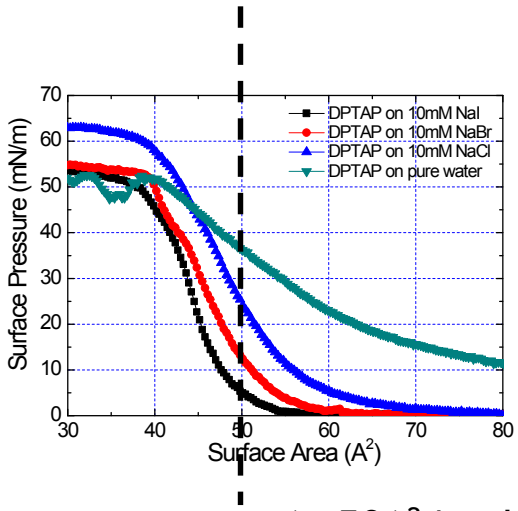
dissolved??



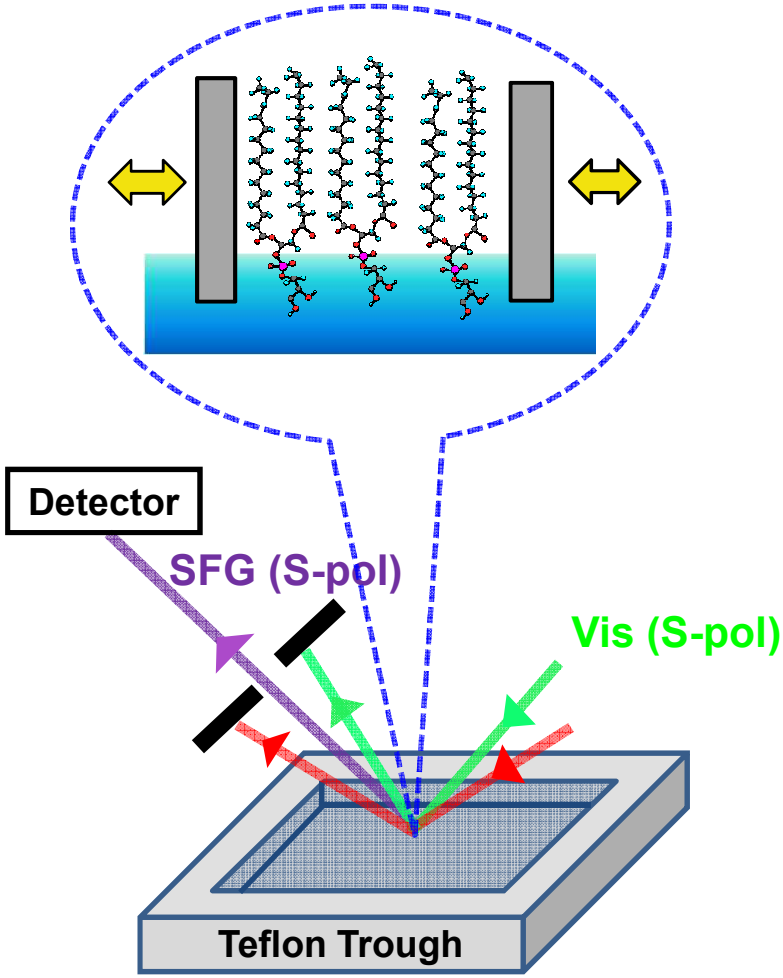
Reduction of surface pressure is due to screening of electrostatic repulsion

Surface excess of halide anion at charged surface

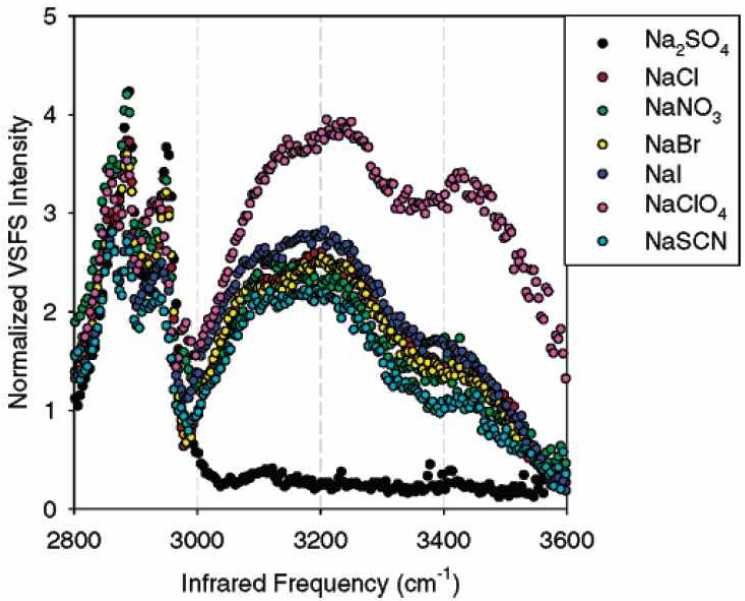




At 50A^2/molecule,



In ODA monolayer……..



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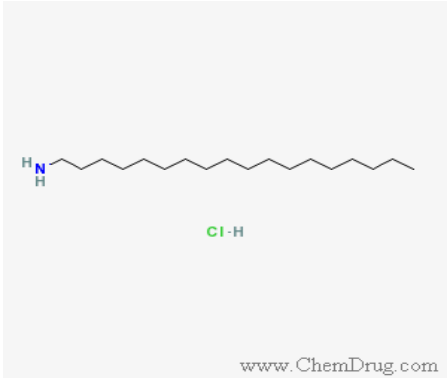

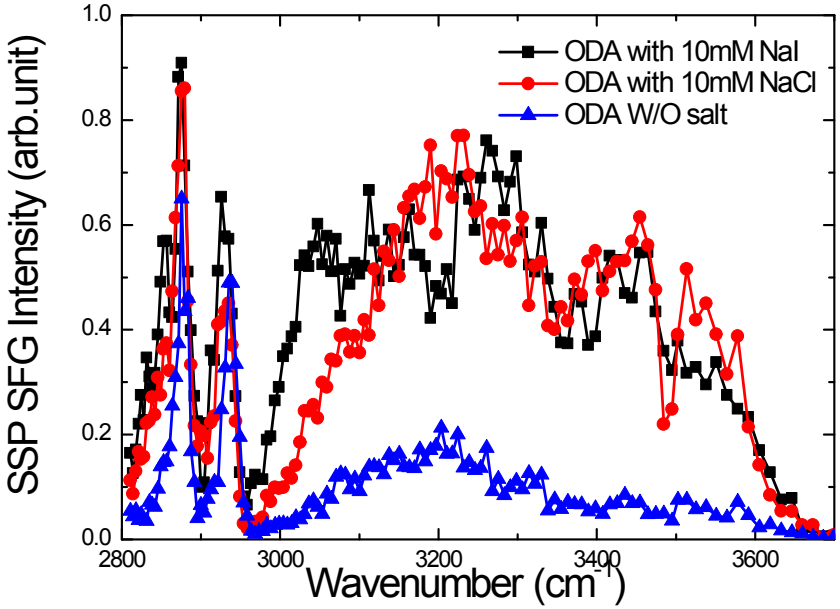

Insertion of salt induce ionization of head group??