Ions and Charged Particles in Nonpolar Media

Ian Morrison
Cabot Corporation

Seiner Memorial Lecture
Carnegie Mellon University
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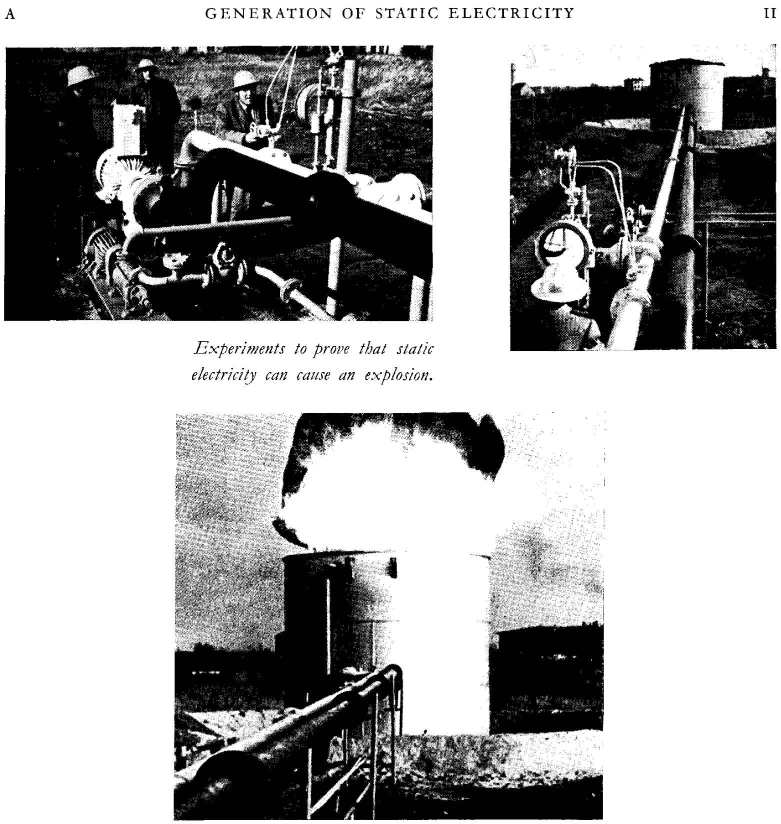
Charges at low conductivity!

image: ArtToday.com

Generation of static electricity



A GENERATION OF STATIC ELECTRICITY II

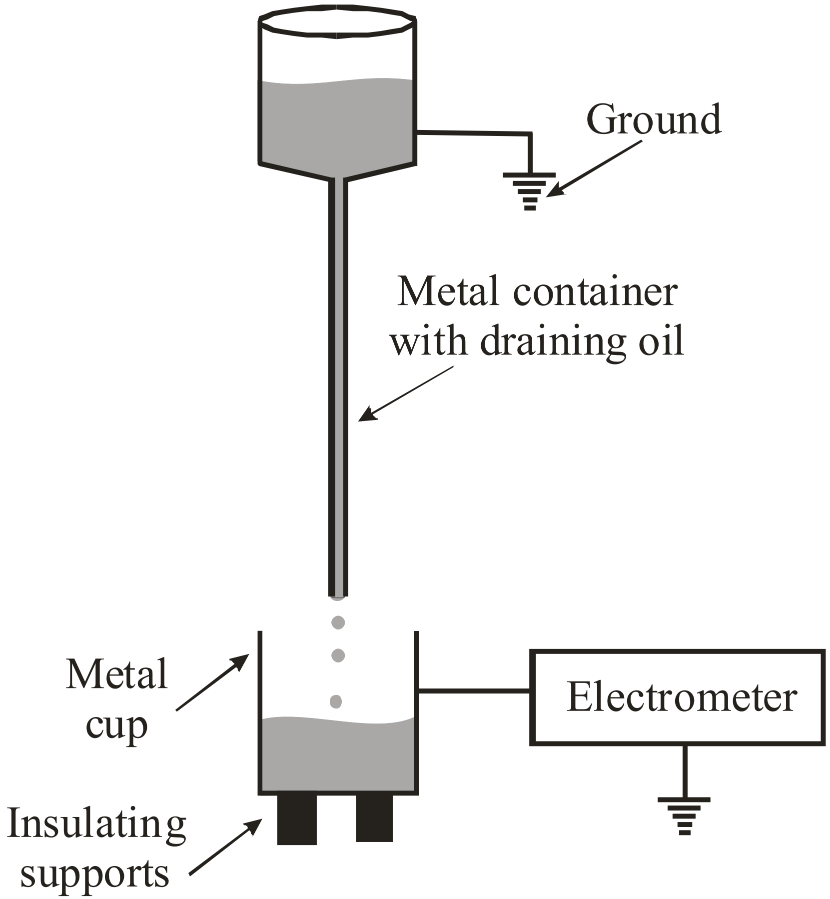
Experiments to prove that static electricity can cause an explosion.

"Early in 1954 a large tank in Shell's refinery at Pernis exploded 40 minutes after the start of a blending operation in which a tops-naphtha mixture was being pumped into straight-run naphtha…

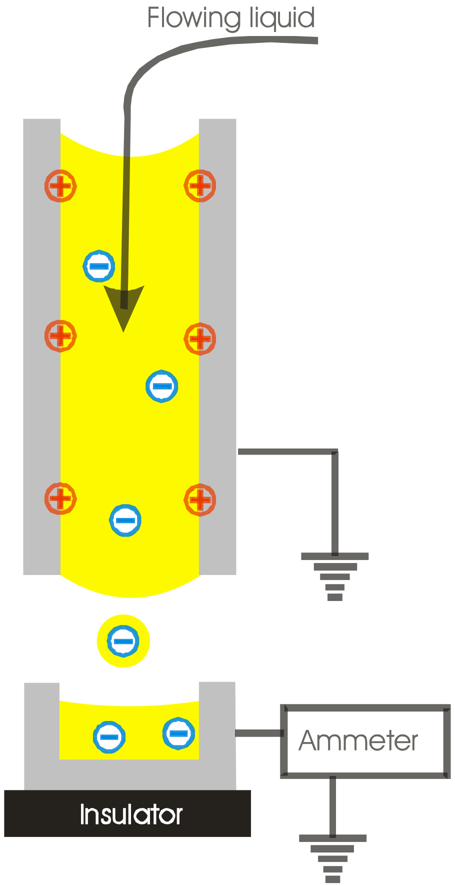
On the following day …again an explosion occurred 40 minutes …"

Electrostatic in the Petroleum Industry
Klinkenberg and van der Minne (1958)

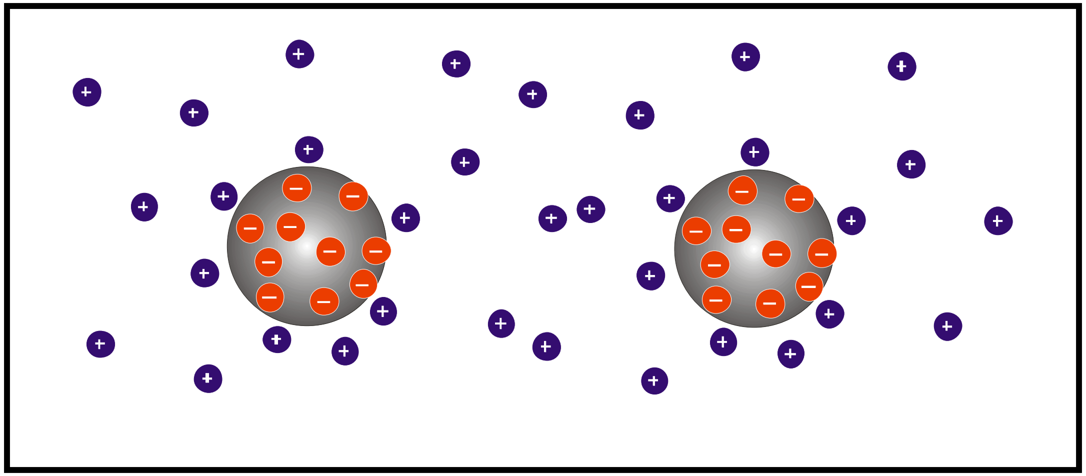
The charging capacity of oil



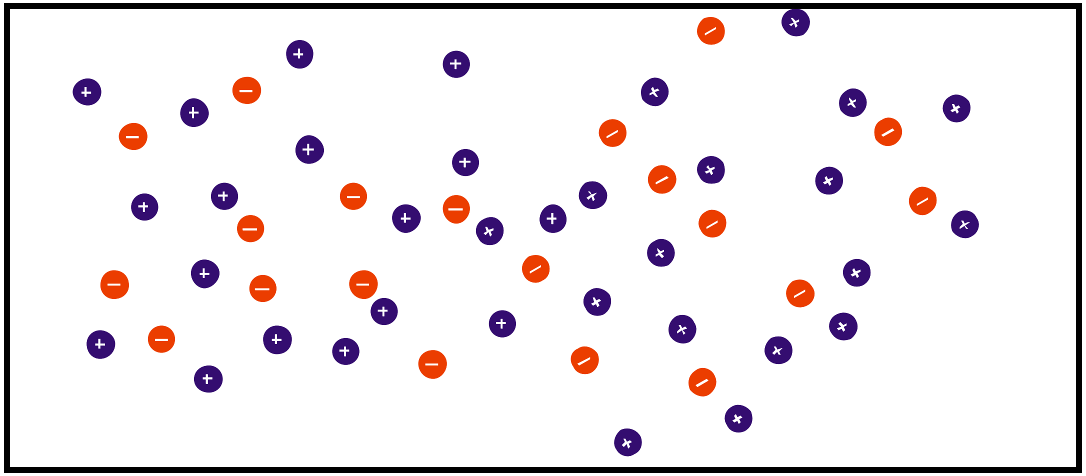
Separation of charges with liquid flow



Charges in water



Dispersion stability is described by DLVO theory.



Suppose all the ions were free. What explains the stability?

Ion pair association

$$E_{coul} = \frac{-e^2}{4\pi\varepsilon_r\varepsilon_0 d}$$

Ions will associate if they get closer than an energy that corresponds to -*kT.*

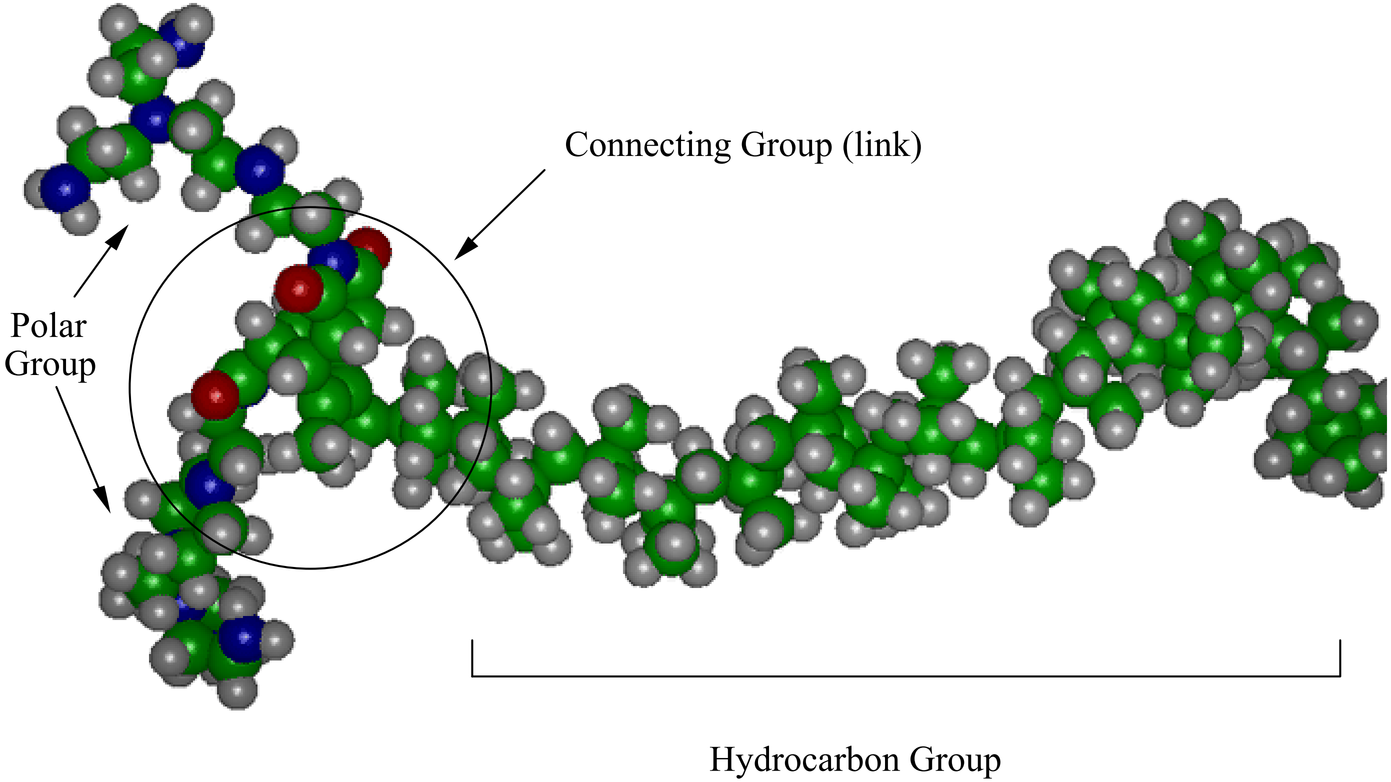
In water: $\varepsilon_{H_2O} \simeq 80 \;\text{ and } d \gg 0.7nm$

In oil: $\varepsilon_{oil} \simeq 2 \;\text{ and } d \gg 27nm$

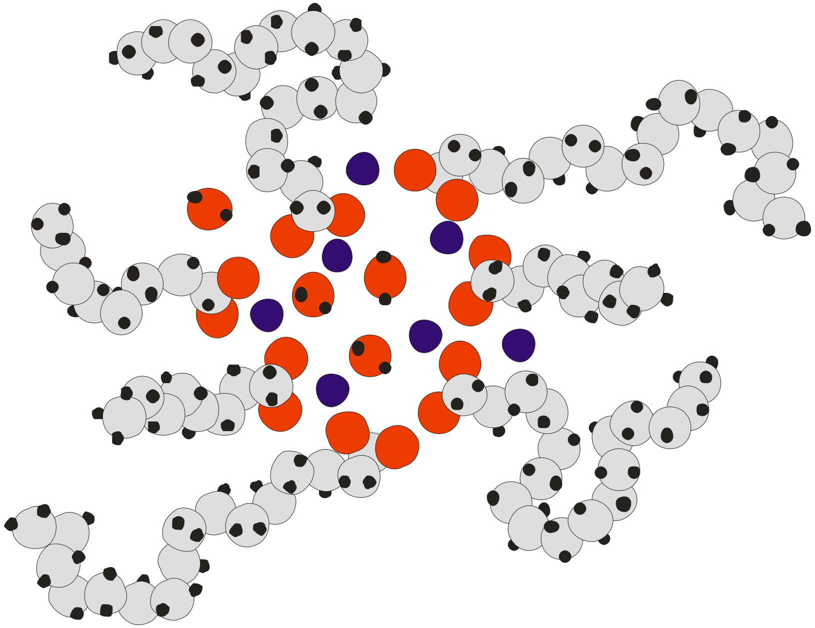
Electrostatic attraction is longer range in oil than in water.

Typical oil "electrolyte"

Polar Group: amine, amide, imide, acid, salt



Oil “electrolytes” can form inverse micelles



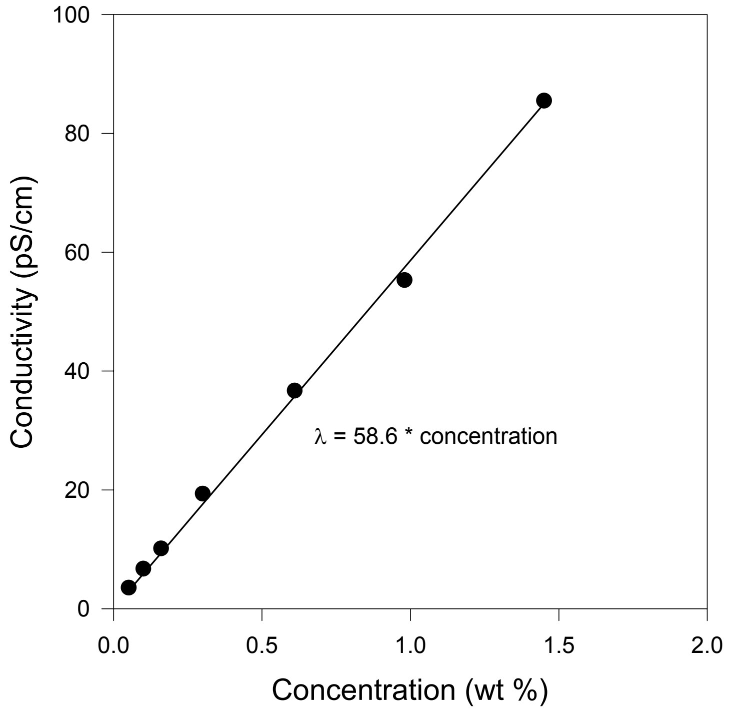
The micelle core is highly polar. Possibly like a molten salt?

The diameters are 10’s of nanometers.

Single polymer molecules may be sufficient.

Conductivity of oil electrolytes

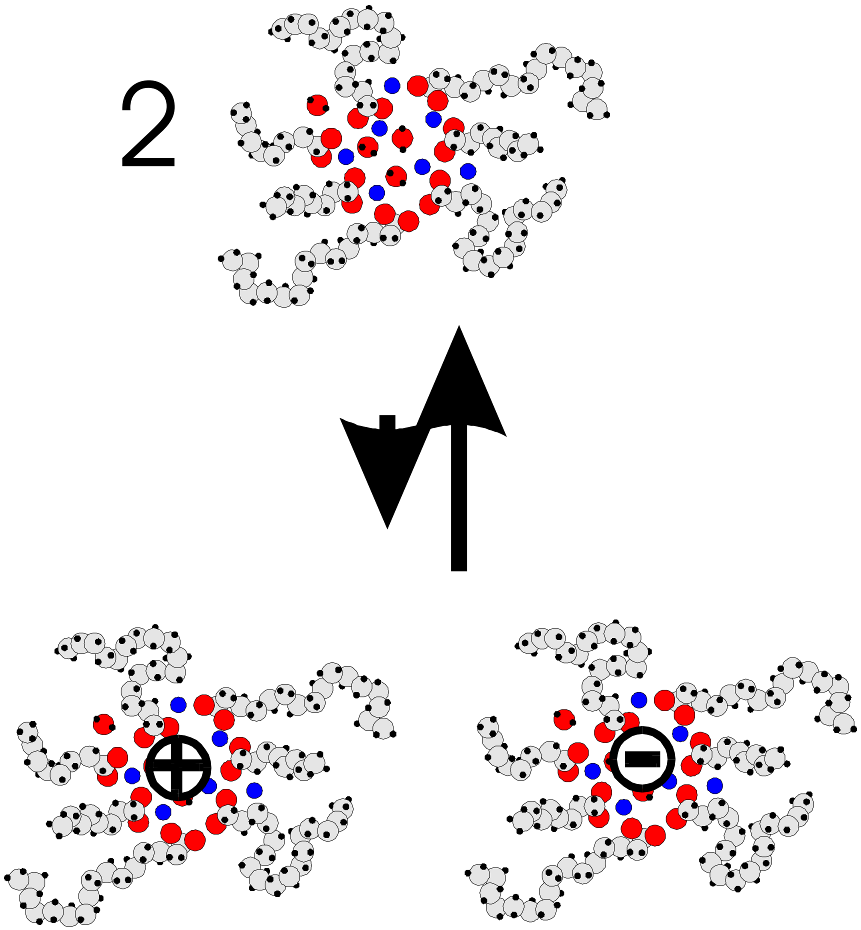
Conductivity of OLOA 1200
in dodecane (25^{o} C)



A problem:

The conductivity of weak electrolytes should vary with the square root of concentration.

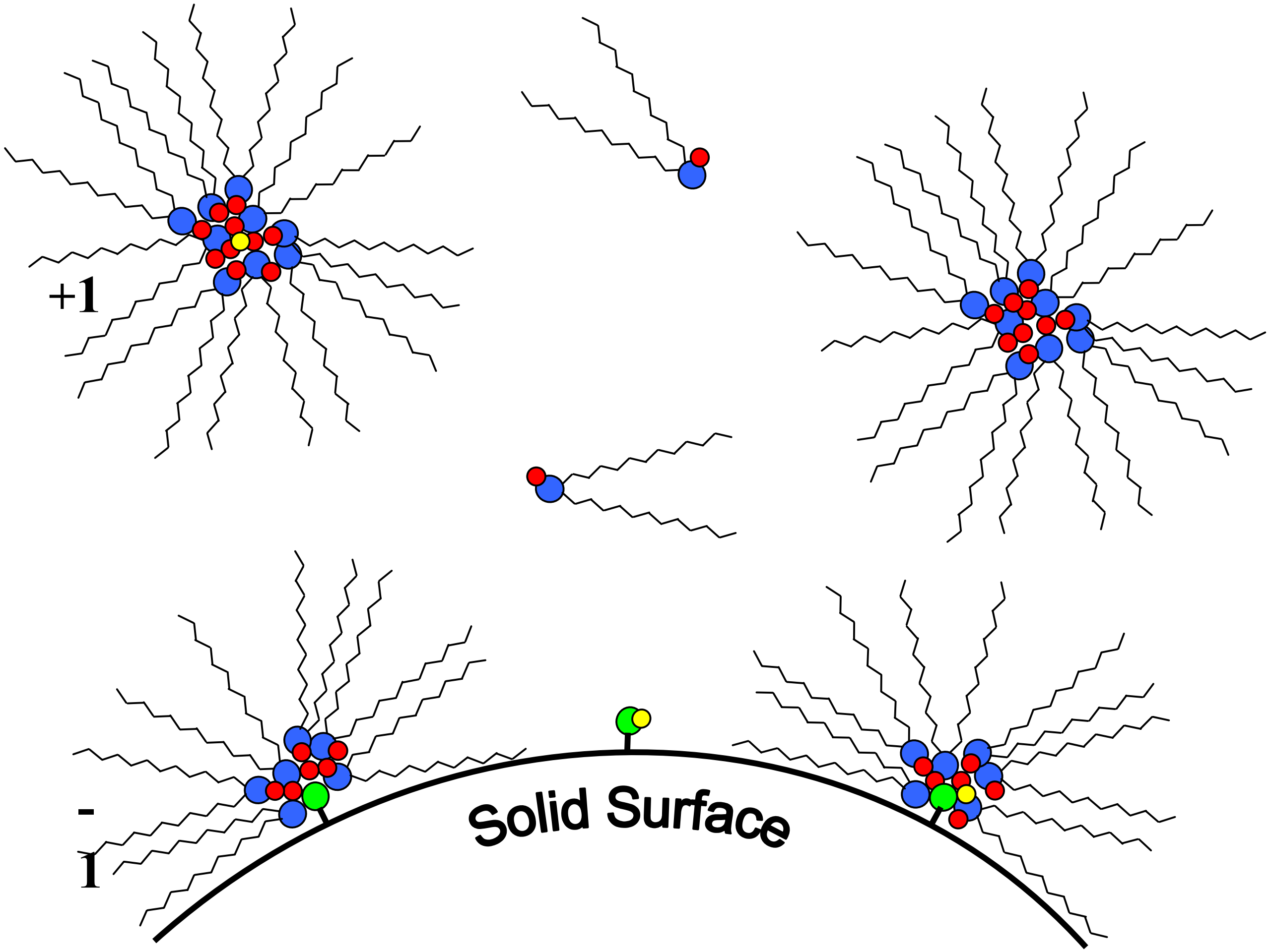
Creation of charged micelles:



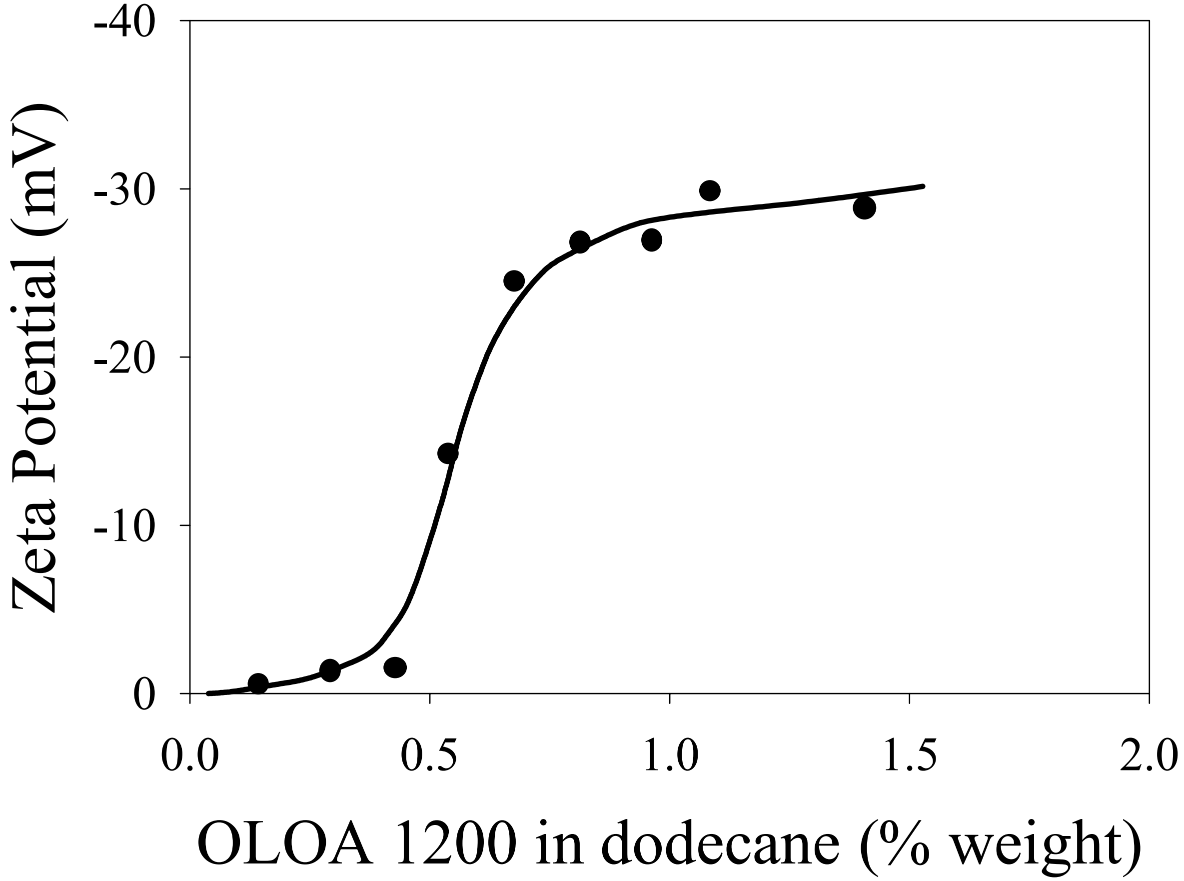
Micelles exchange ions with each other and with surfaces.

The equilibrium is a dynamic balance.

A mechanism for the charging of particles in oil:

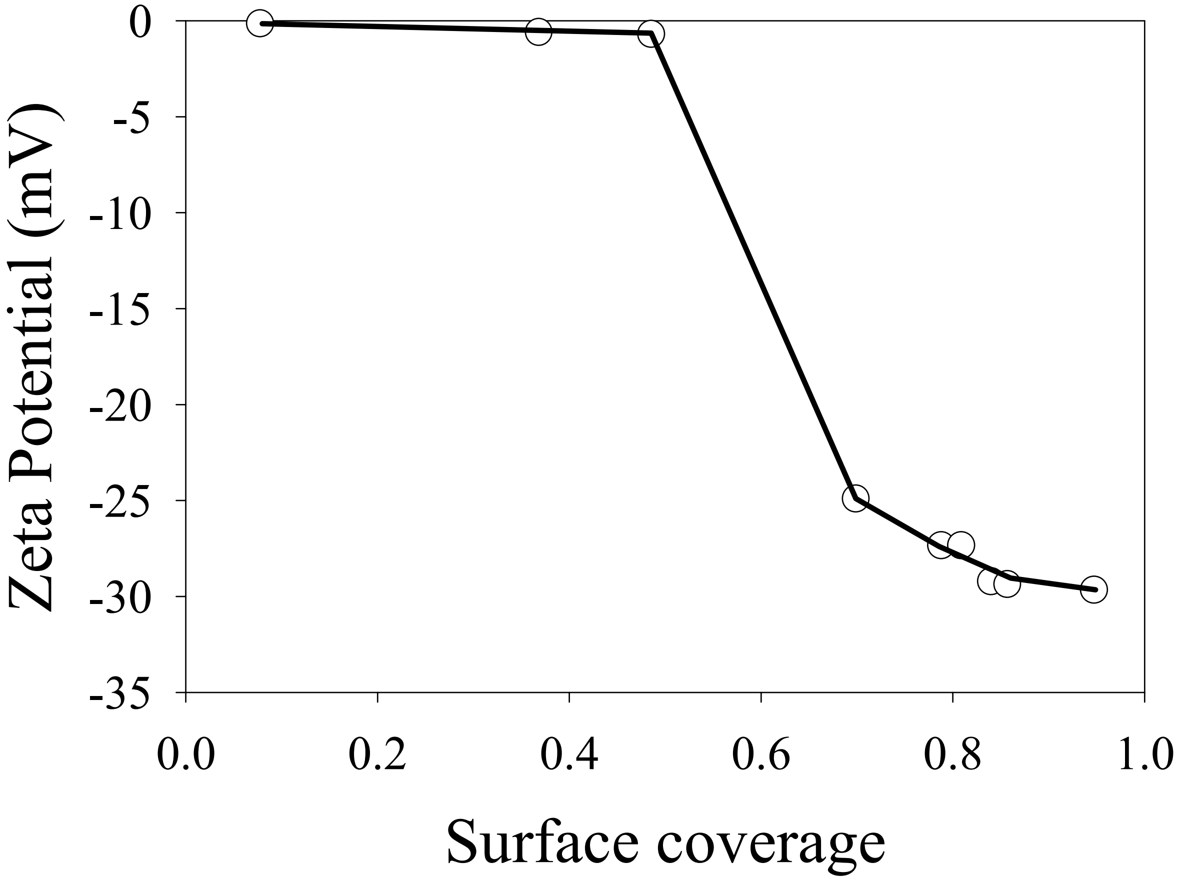


Electric charge on carbon black particles in oil

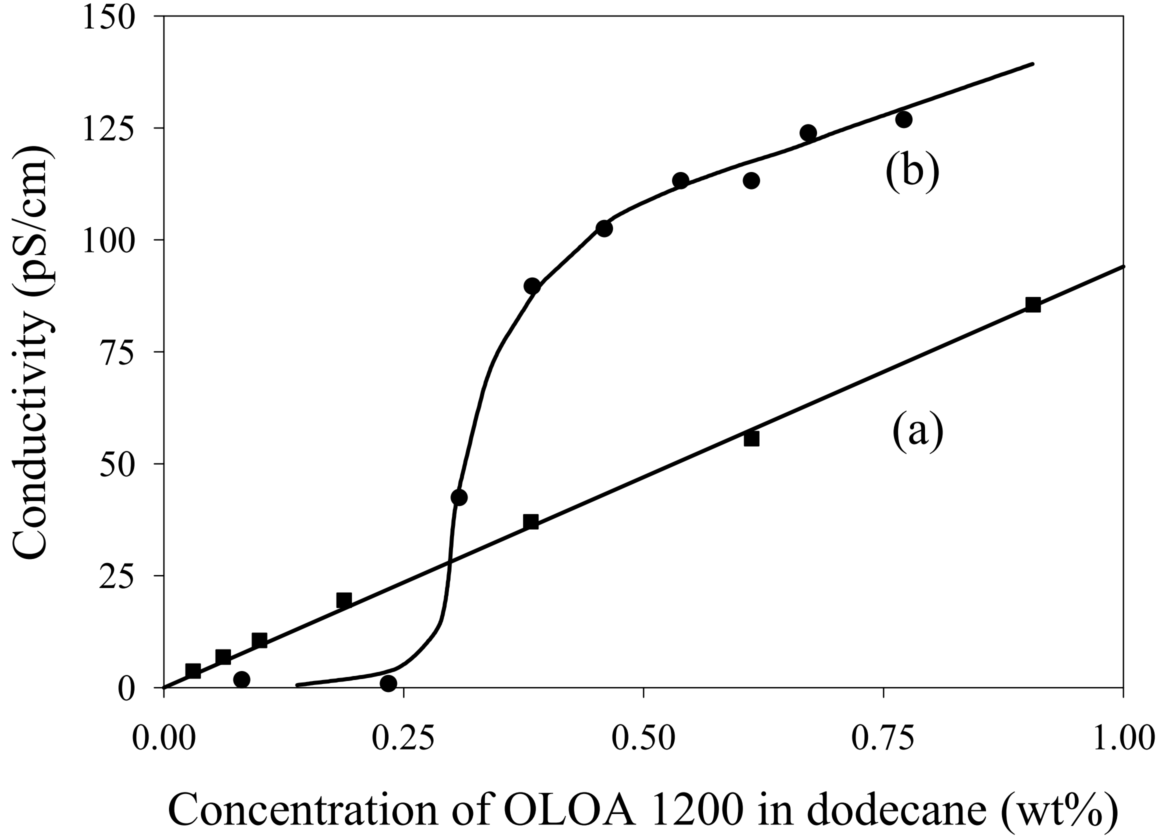


Zeta Potential and Adsorption

OLOA 1200 on Carbon black (2% vol) in Isopar

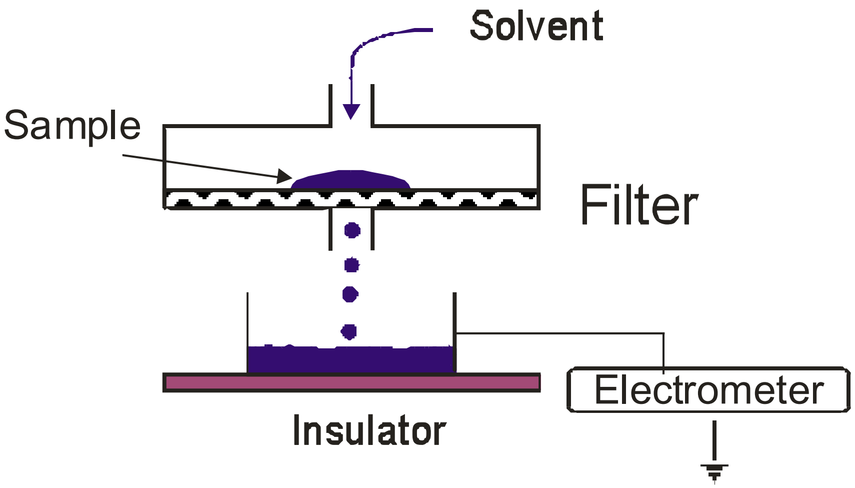


Conductivity of CCA in dodecane: (a) alone, and (b) in the presence of carbon black particles

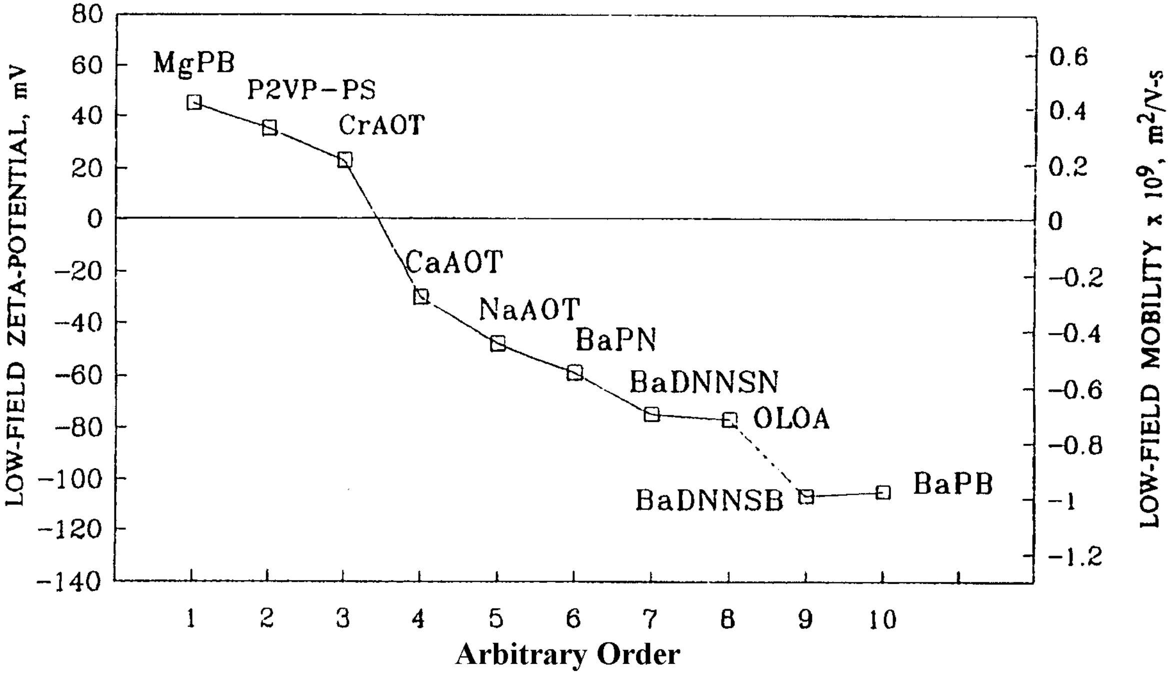


Morrison, I.D.; Ross, S. *Colloidal Dispersions: Suspensions, Emulsions, and Foams*; John Wiley & Sons: New York; 2002; p.320

Number of charges on particles.

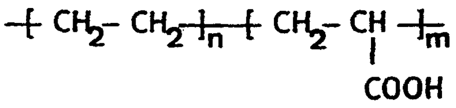


Effect of Micelle Core Chemistry on Charging



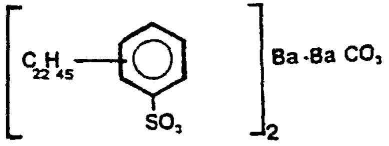
Chen, Wen-Jang, *Stabilization and Electrostatic Deposition of Aqueous and Non-Aqueous Polymeric Colloids;* UMI: Ann Arbor, 1988

PE/PAA

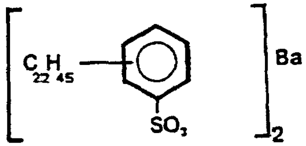


$$-[CH_2-CH_2]_n-[CH_2-\underset{COOH}{CH}]_m-$$

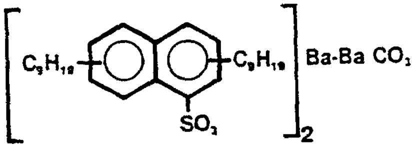
BaPB



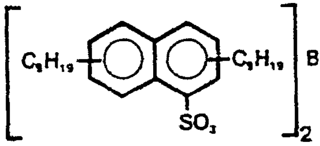
BaPN



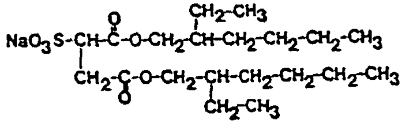
BaDNNSB



BaDNNSN



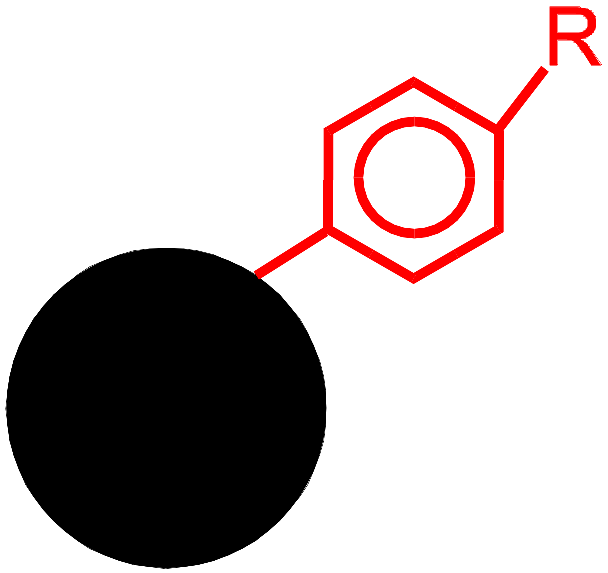
NaAOT



What are we suggesting?

Nonpolar systems behave like polar systems when inverse micelles create a dynamic “nano-polar environment” for the surface sites and their counterions.

Cabot's Belmont blacks



Covalently attached chargeable sites.

Typical charge control agents

CCA1:

Soluble tail: Polyhydroxystearic acid

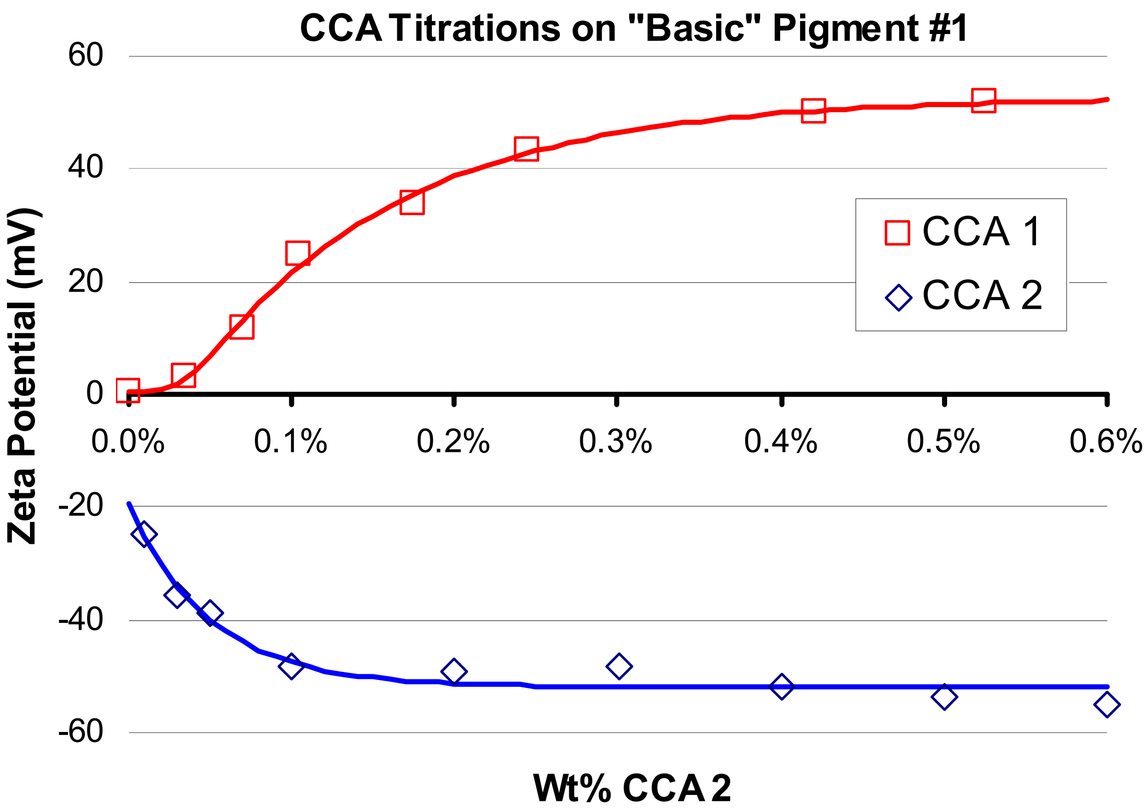
Head group: Quaternary ammonium - methyl sulfate

CCA2:

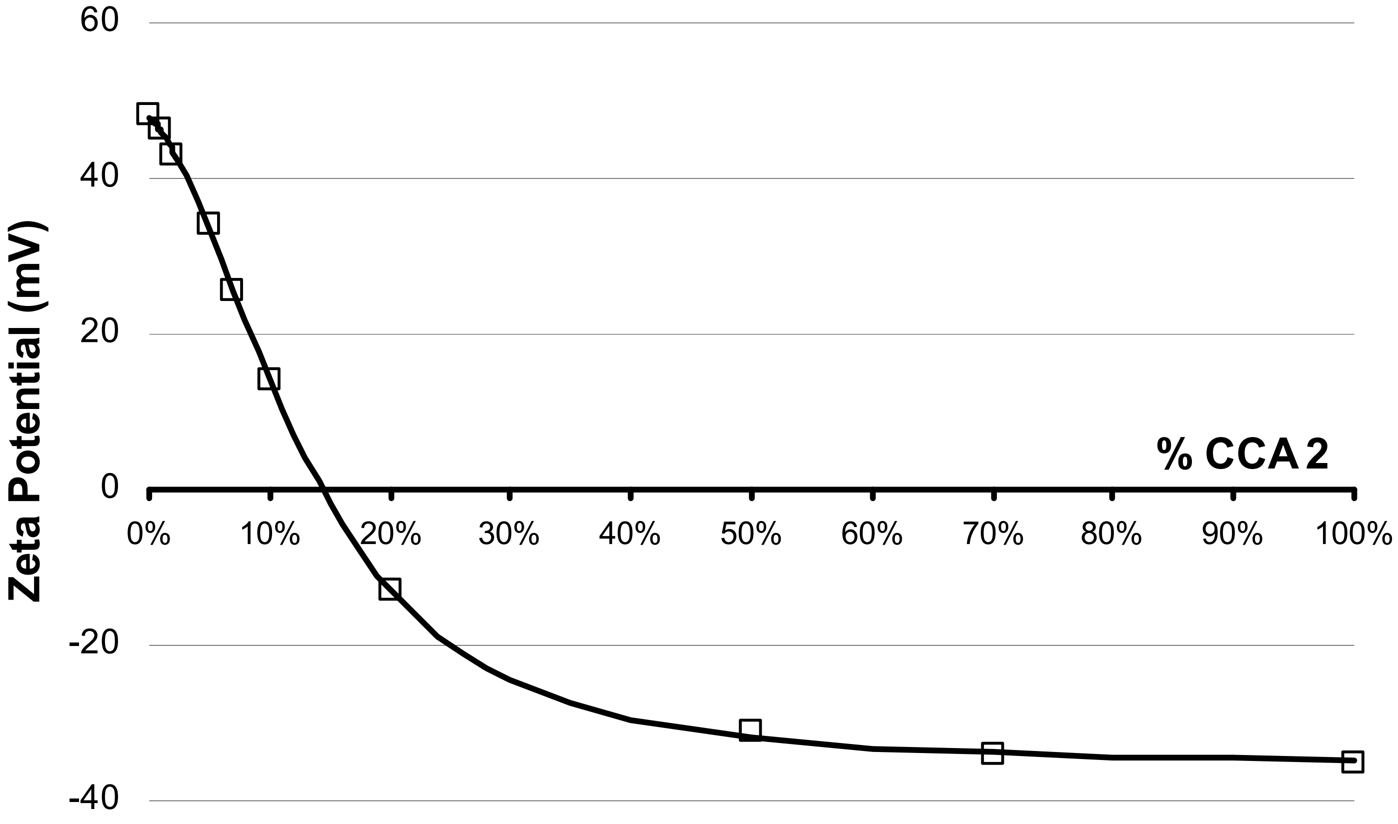
Soluble tail: C13 Hydrocarbon chains

Head group: Sodium sulfosuccinate

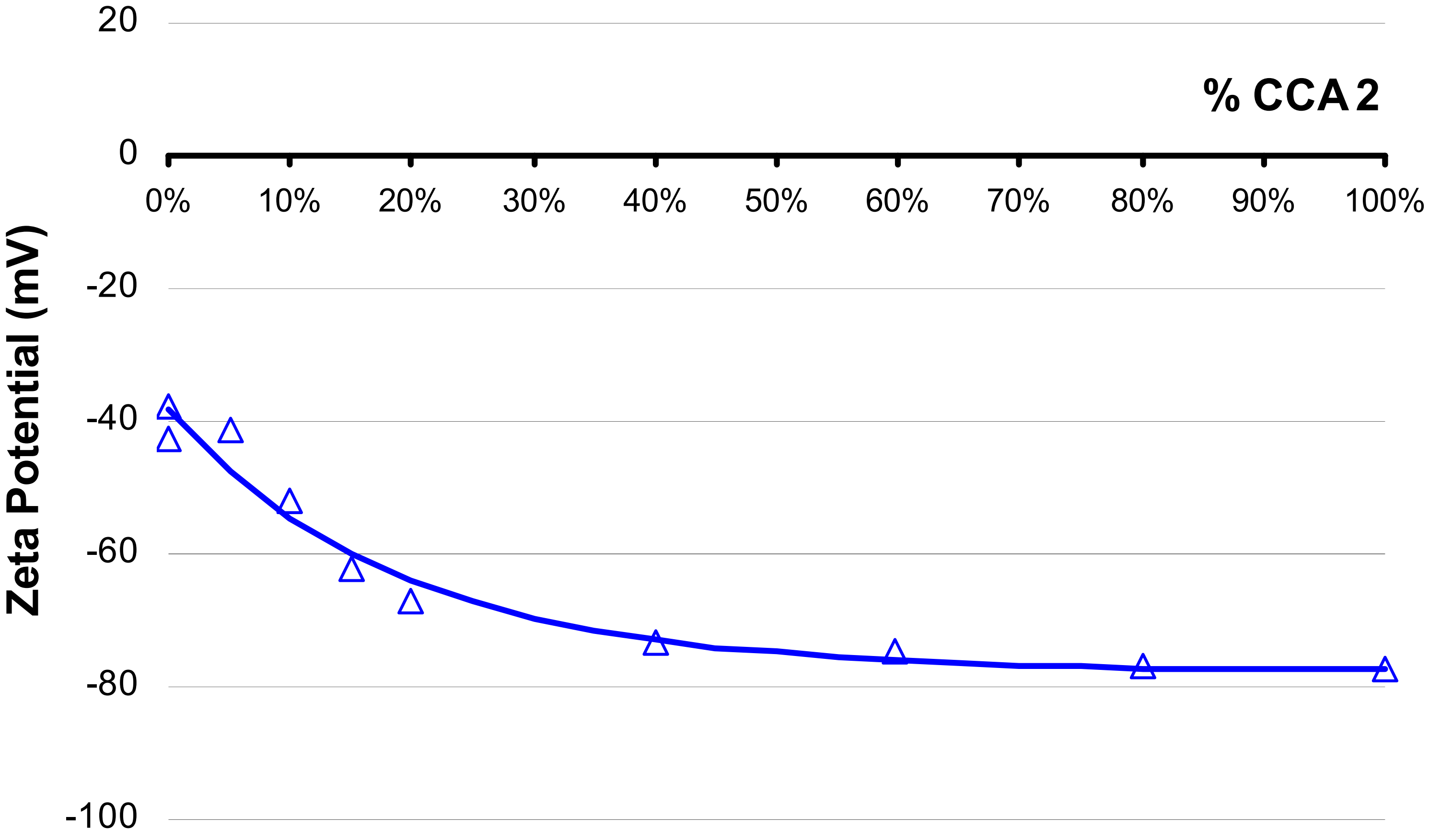
Charging of a
"Basic" Belmont carbon black



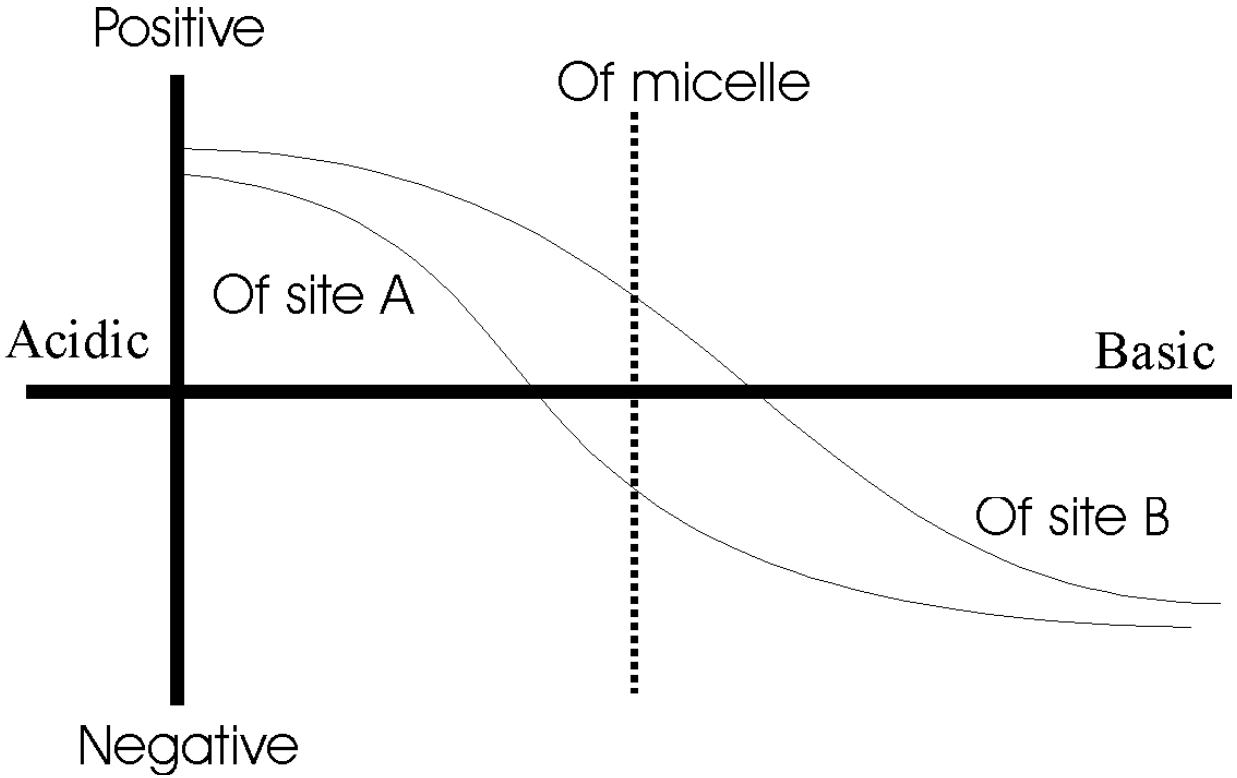
Charge titration with “mixed” micelles



“Acidic” Pigment with mixed micelles

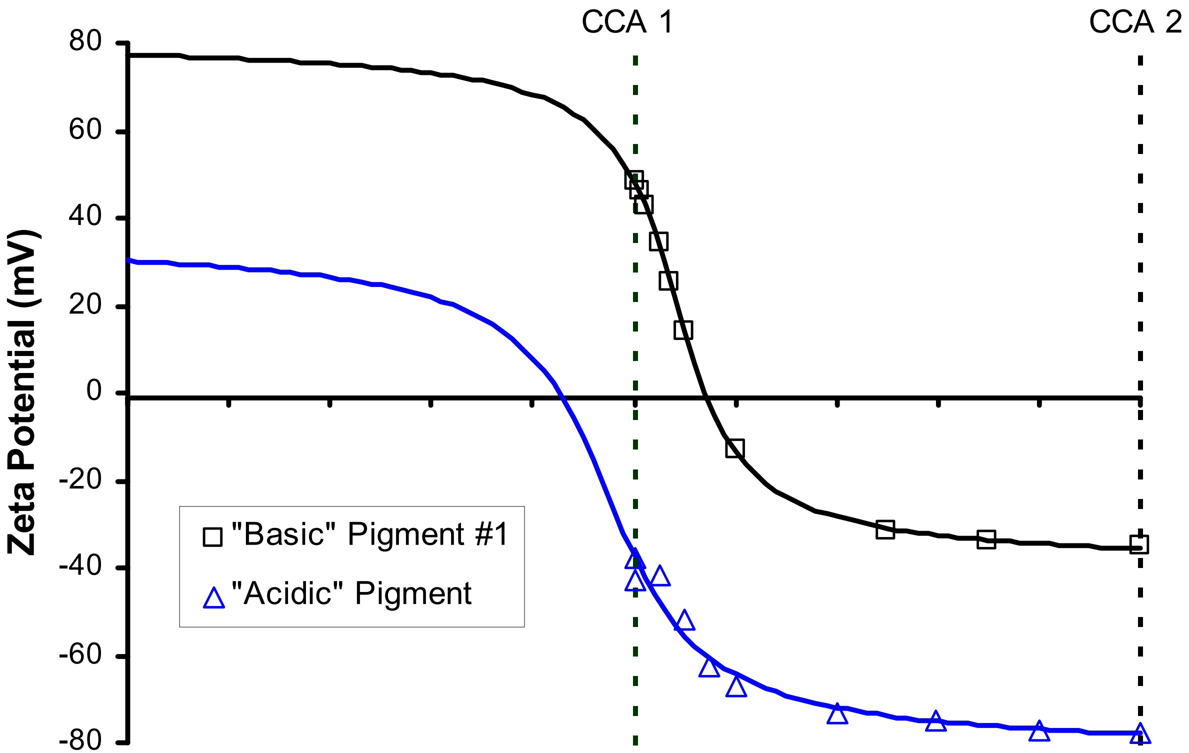


Chemistry of charge creation



The sign and magnitude of the charge depends on the chemistry of the micelle.

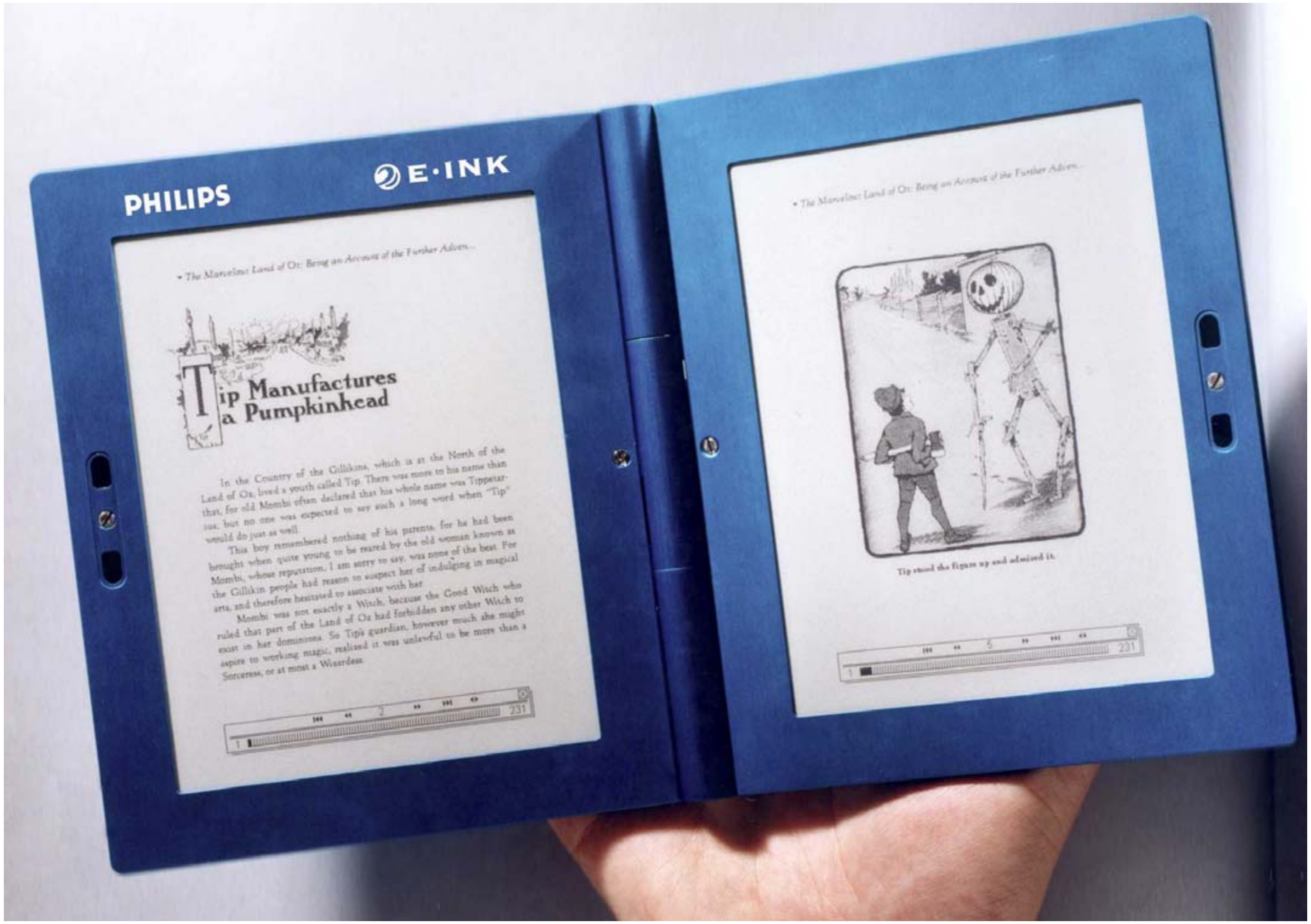
Chemistry of charge creation: Speculation with real data



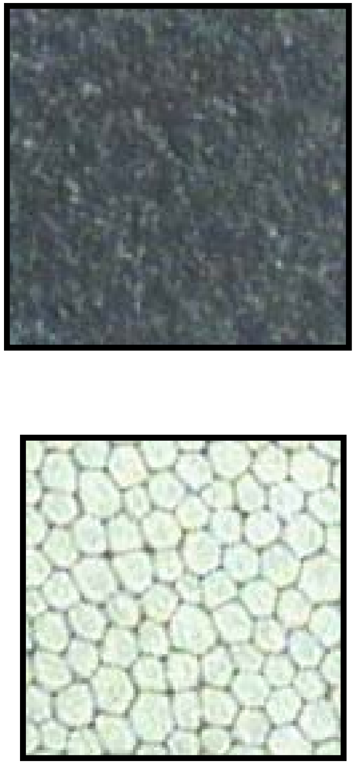
Note the "points of zero charge".

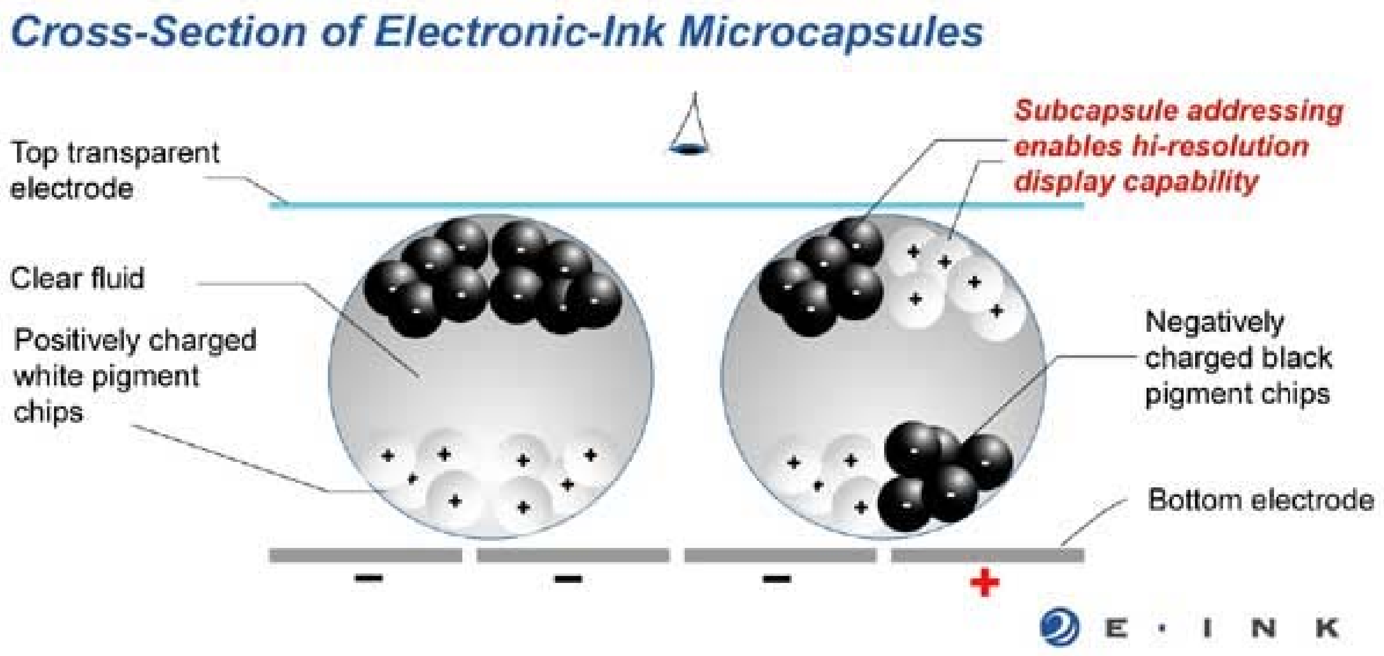
Also, note the conditions for oppositely charged particles.

E Ink electrophoretic display



Liquid ink-based display technology





Length Scales

- To “create” a charge - molecular dimensions, *e.g*. Angstoms
- To “separate” charge-pairs - colloid dimensions, *e.g*. 10’s namometers and larger

Time Scales

- For charge creation - inside a free micelle or adsorbed micelle, very fast?

- For charge separation
  - molecular diffusion between micelles, slow?
  - separation of charged micelles, even slower?

Summary

The physics of charging in nonpolar media is about steric stabilization of the ions.

The chemistry of charging in nonpolar media is about the highly polar core of the inverse micelles.

The chemistry of those cores can be tuned to control the charge on the particles.

This lecture commemorates Jerome Seiner and his contributions to the creation and growth of the Colloids, Polymers and Surfaces Program at CMU.

A most grateful thank you to the Jerry Seiner Memorial Fund.

Collaborators

- Dr. Craig Herb, E Ink Corporation
- Dr. Ralph Kornbrekke, Lubrizol Corporation
- Jeremy O’Brien, Washington U., St. Louis
- Rick Paolini, E Ink Corporation
- Dr. Tonis Oja: Malvern
- Dr. David Cannon: Colloidal Dynamics