Session 2: Ions and Charged Particles in Nonpolar Media

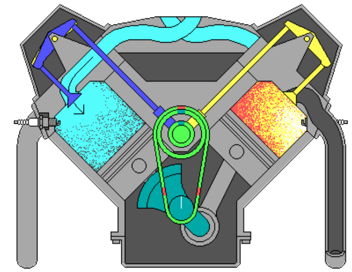
Ian Morrison
Cabot Corporation

The American Chemical Society

image: ArtToday.com

Nonpolar, electrocratic applications:

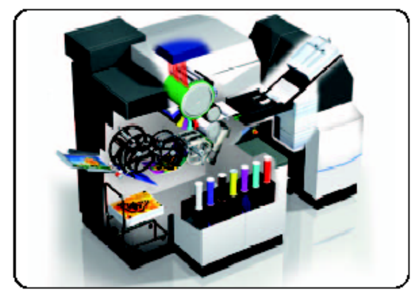
- Carbon in engine oils:



http://www.autoshop-online.com/auto101/eng1.html

- Liquid immersion printing:

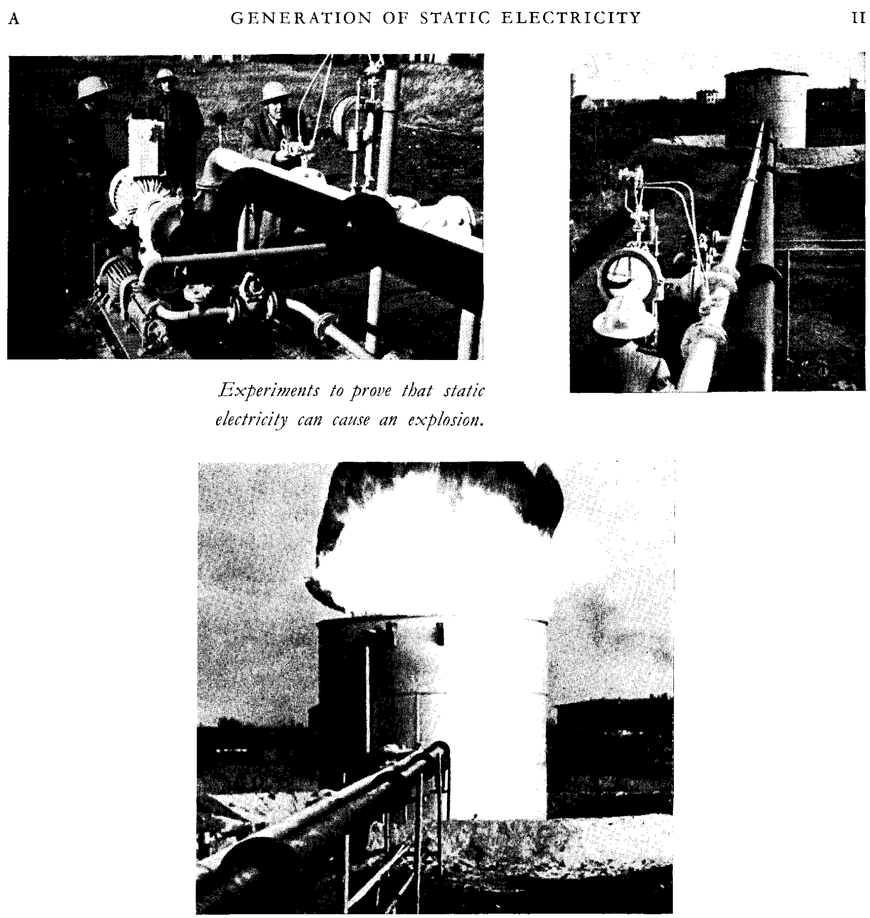
HP Indigo

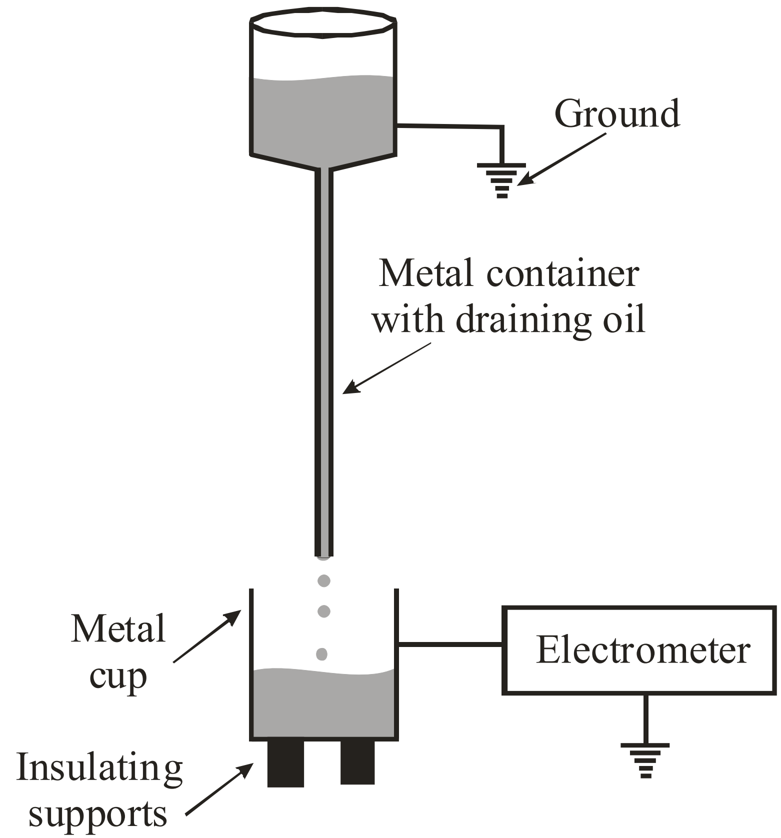


- Electrophoretic displays:

E Ink / Philips

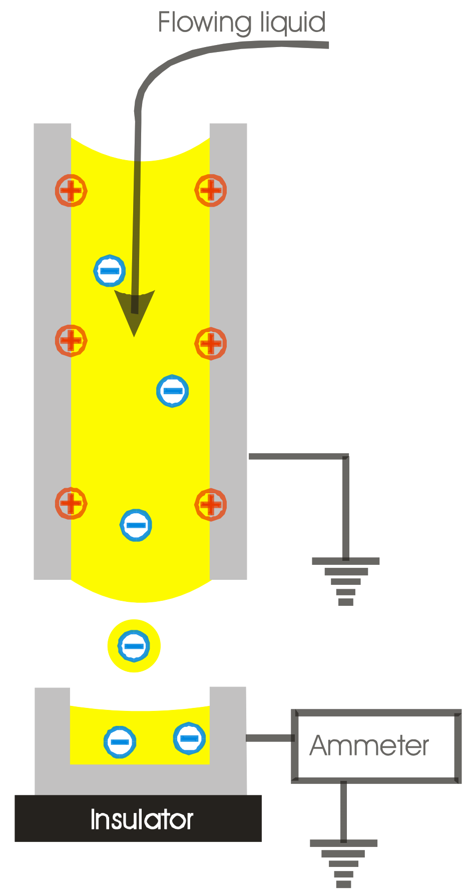
The charging capacity of oil



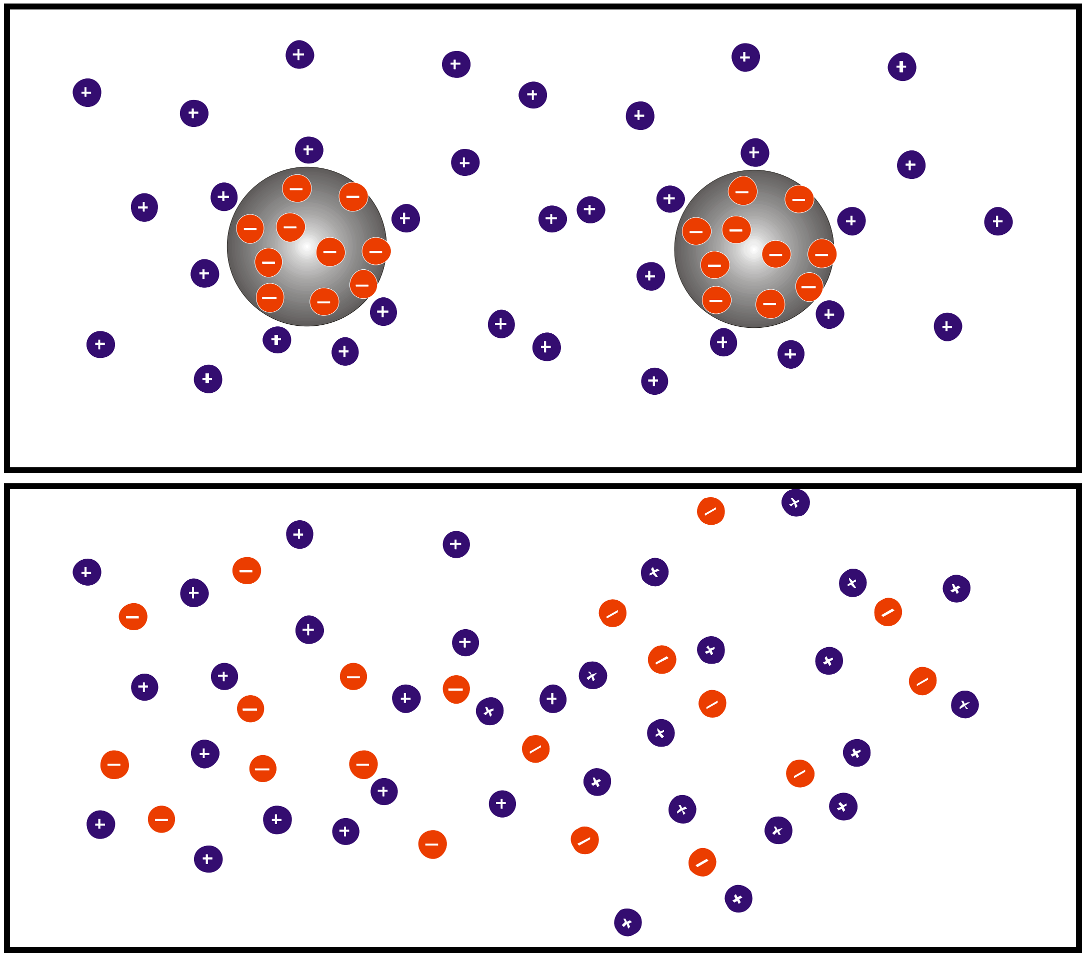


Klinkenberg and van der Minne (1958)

Separation of charges with liquid flow



Charges in water



Ion pair association

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

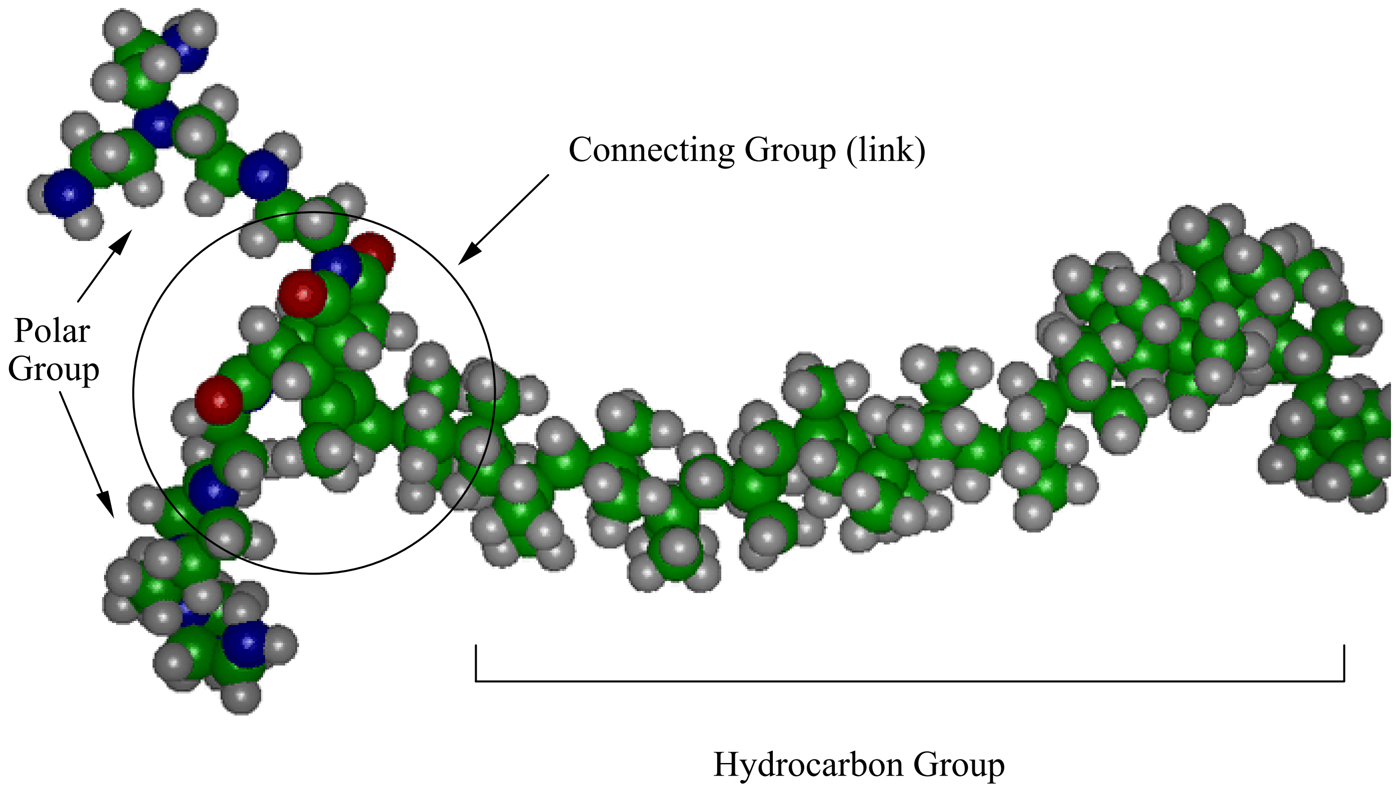
$$E_{coul} = \frac{-e^2}{4\pi\varepsilon_r\varepsilon_0 d}$$

In water: $\varepsilon_{H_2O} \simeq 80 \text{ hence } d > 0.7nm$

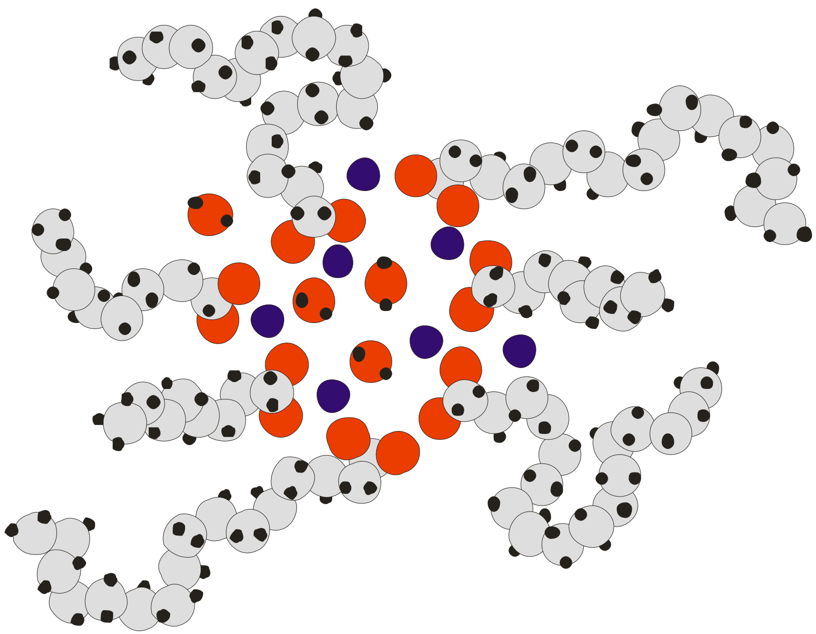
In oil: $\varepsilon_{oil} \simeq 2 \text{ hence } d > 27nm$

Typical oil "electrolyte"

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



Oil “electrolytes” form inverse micelles



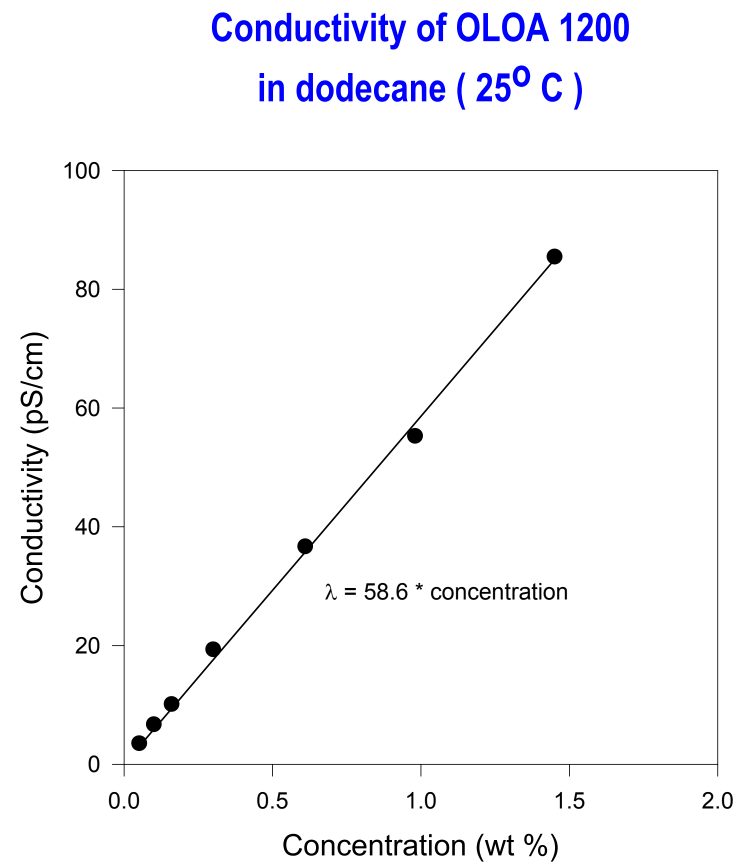
The micelle core is highly polar.

The diameters are 10’s of nanometers.

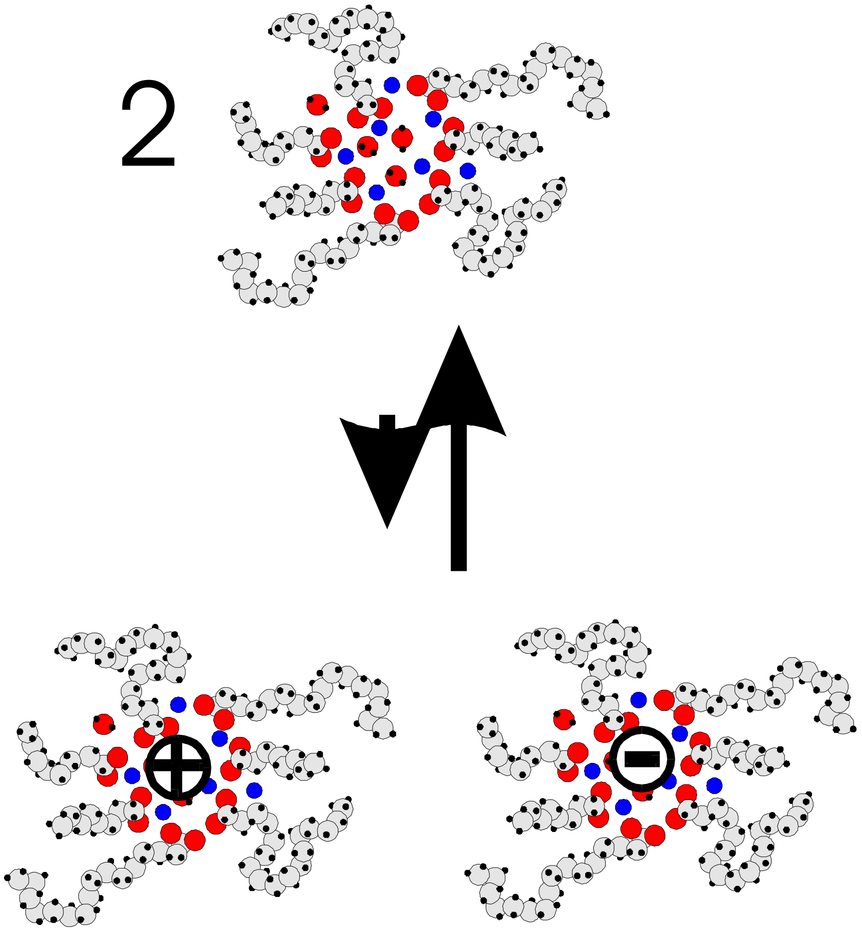
Single polymer molecules may be sufficient.

Linear conductivity of nonpolar electrolytes?

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



Creation of charged micelles:

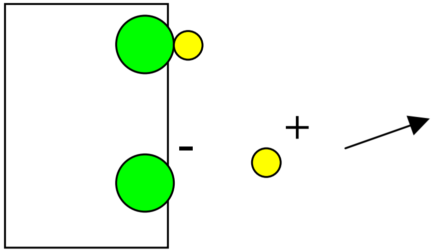


Micelles exchange ions with each other and with surfaces.

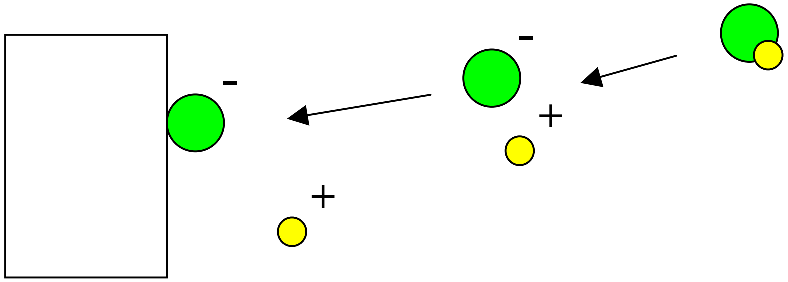
The equilibrium is a dynamic balance.

Particle charging in polar media

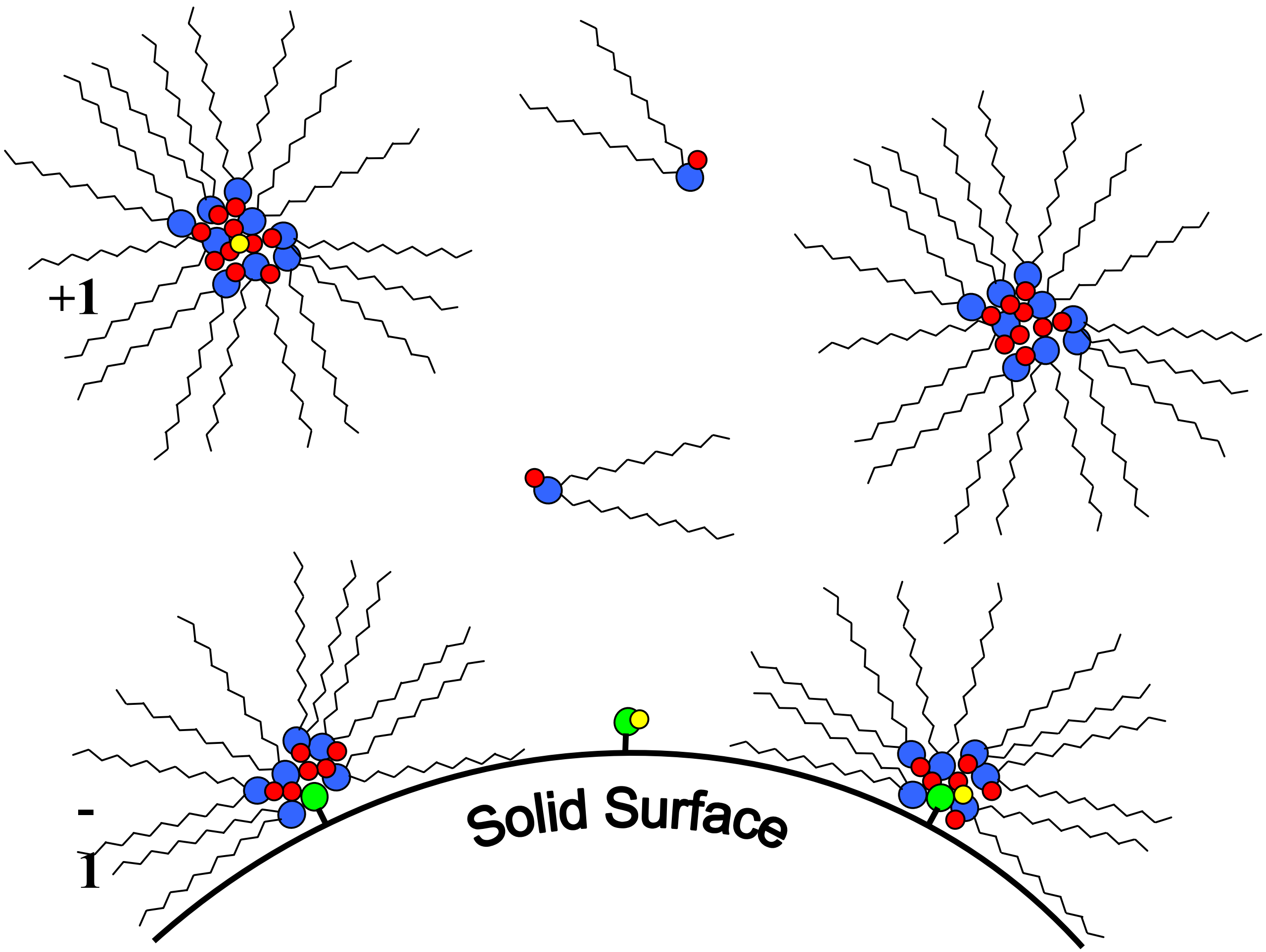
– Charges by surface dissociation



– Charges by surface adsorption

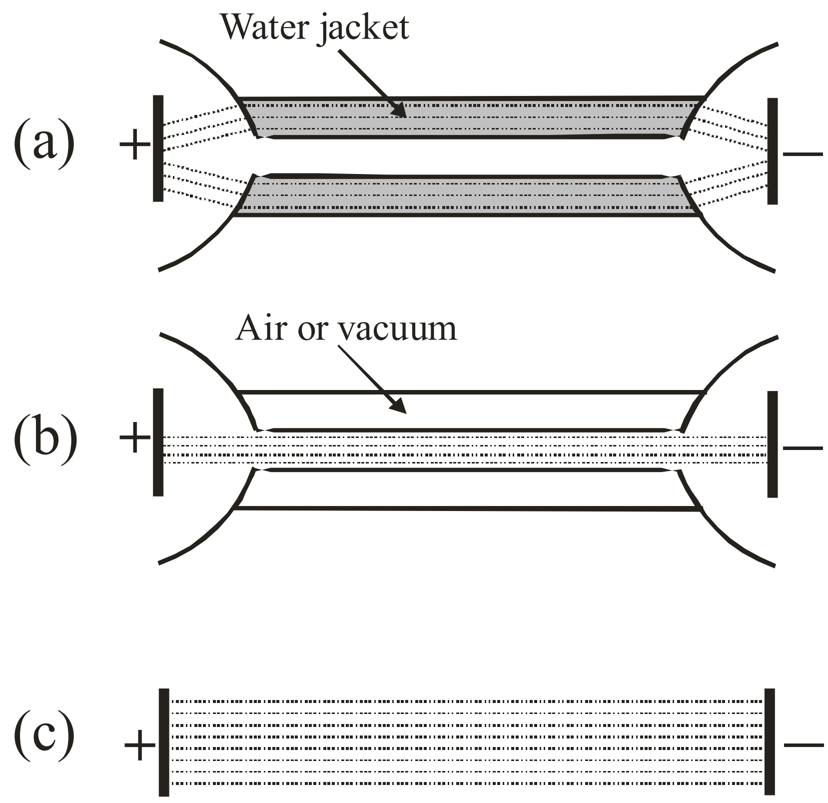


Particle charging in nonpolar media

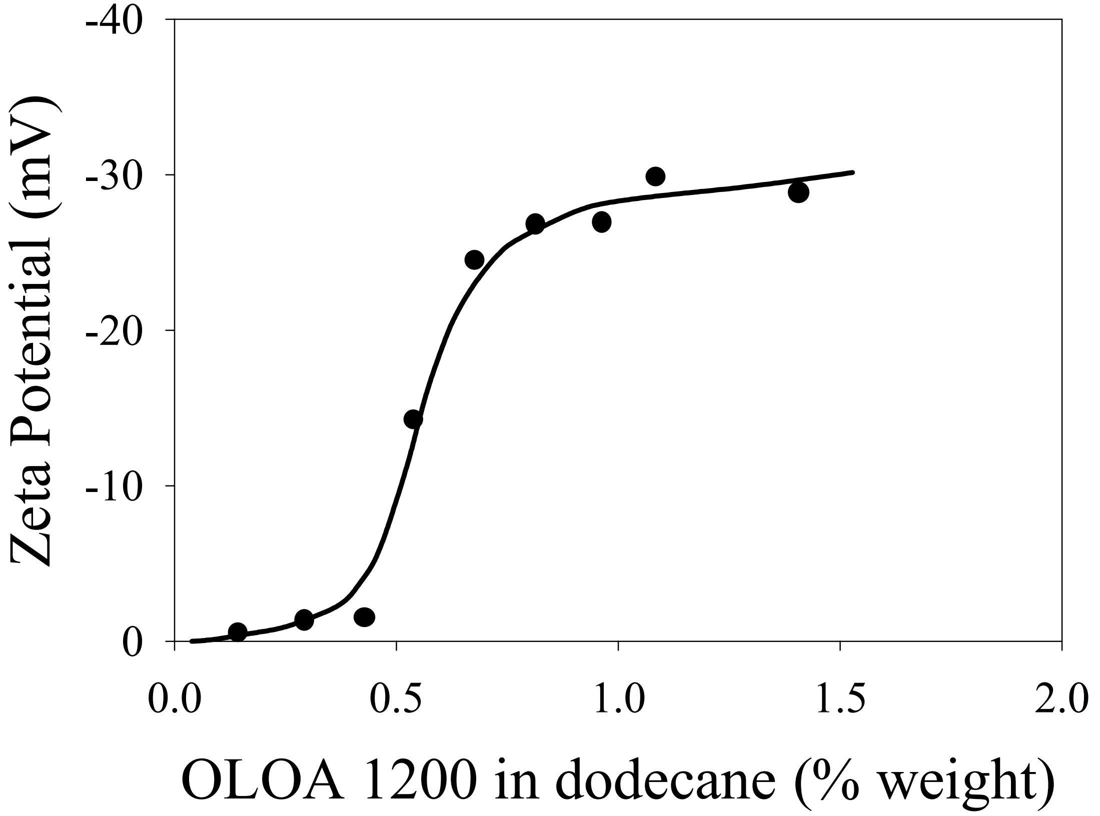


Electrophoresis in nonpolar liquids

Electrophoresis is fundamentally no different in oil than in water, except, you must avoid constant temperature baths!

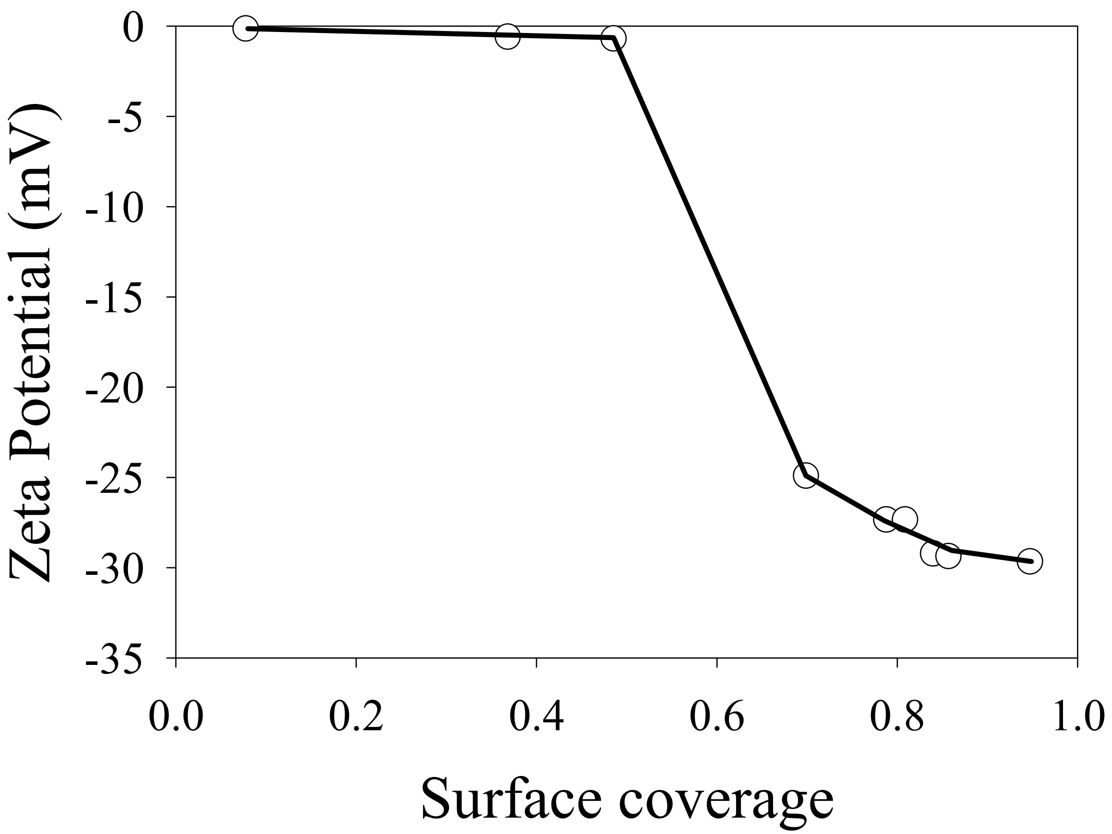


Electric charge on carbon black particles in oil

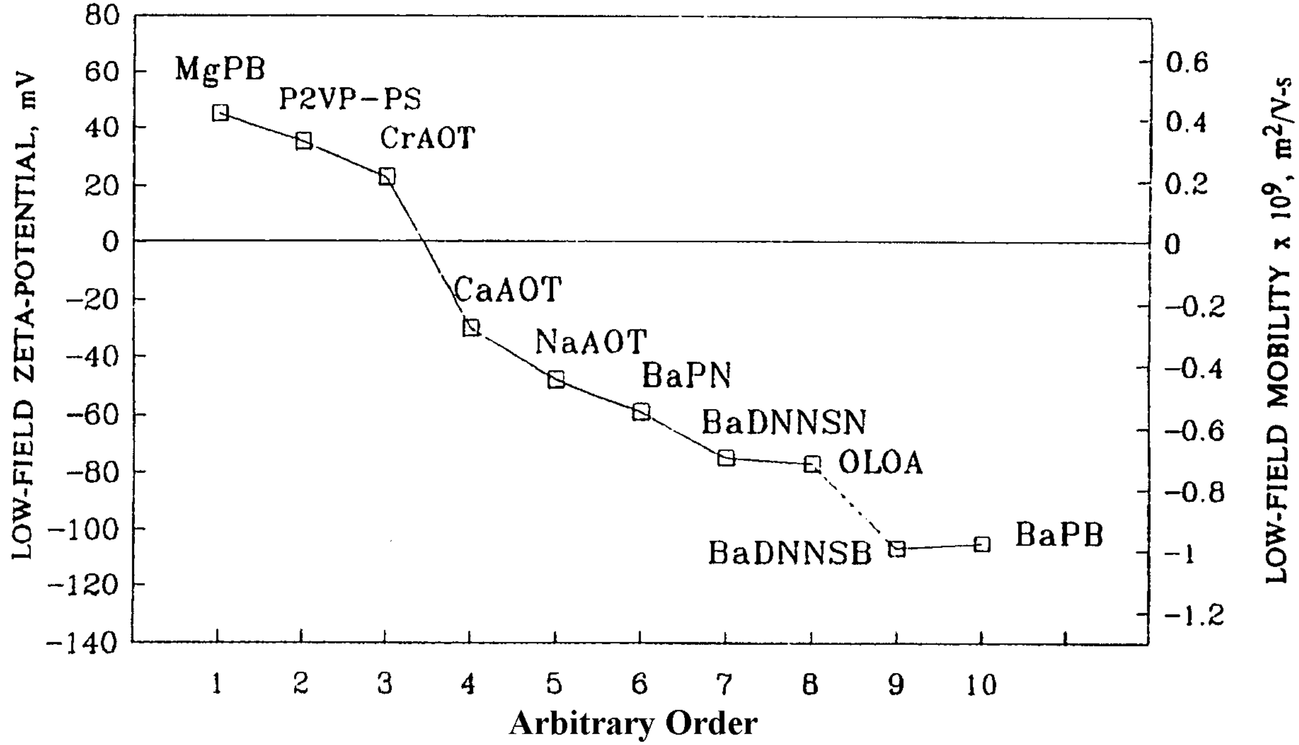


Zeta potential and adsorption

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



Effect of micelle chemistry



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

Nonaqueous pH ranges

Chipperfield, J.R. Non-Aqueous solvents; Oxford Univeristy Press: New York; 1999, p. 34

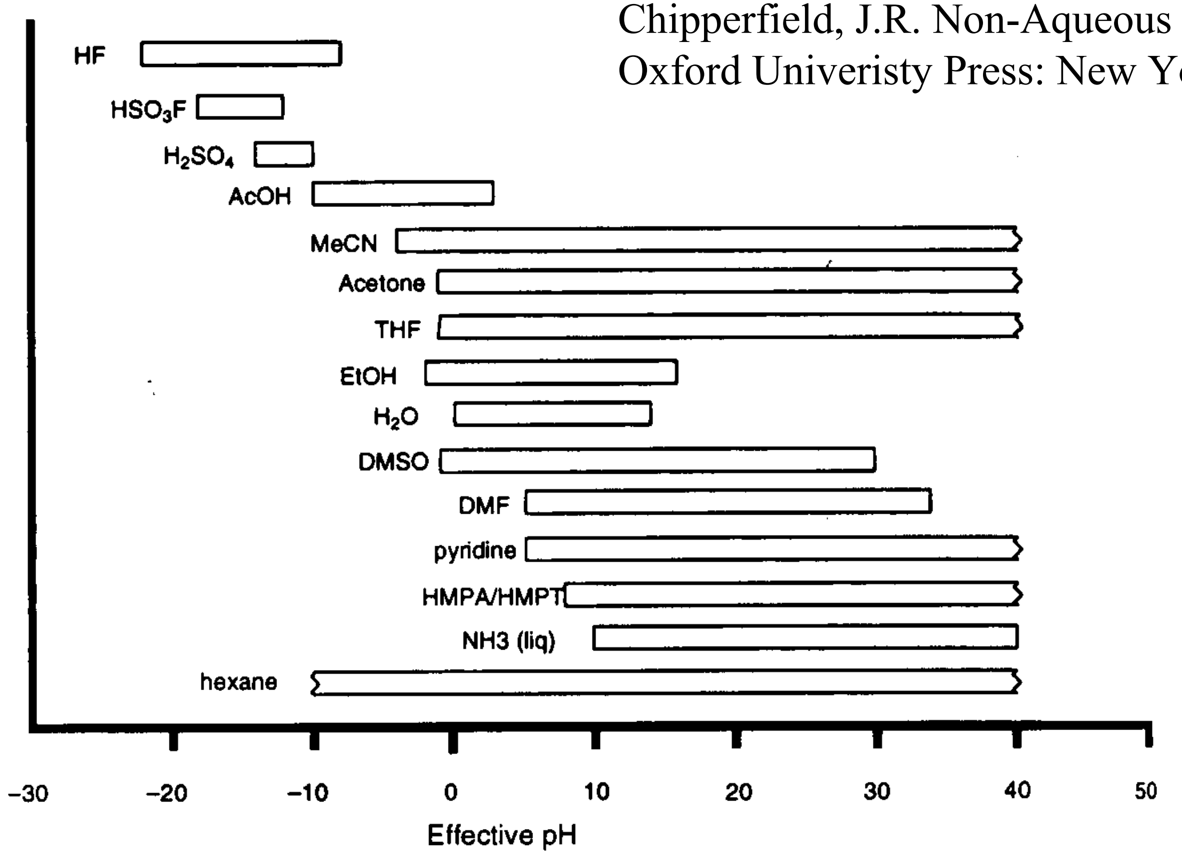
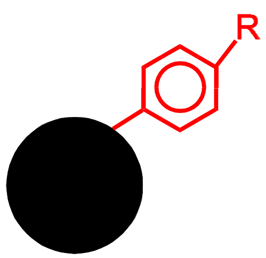
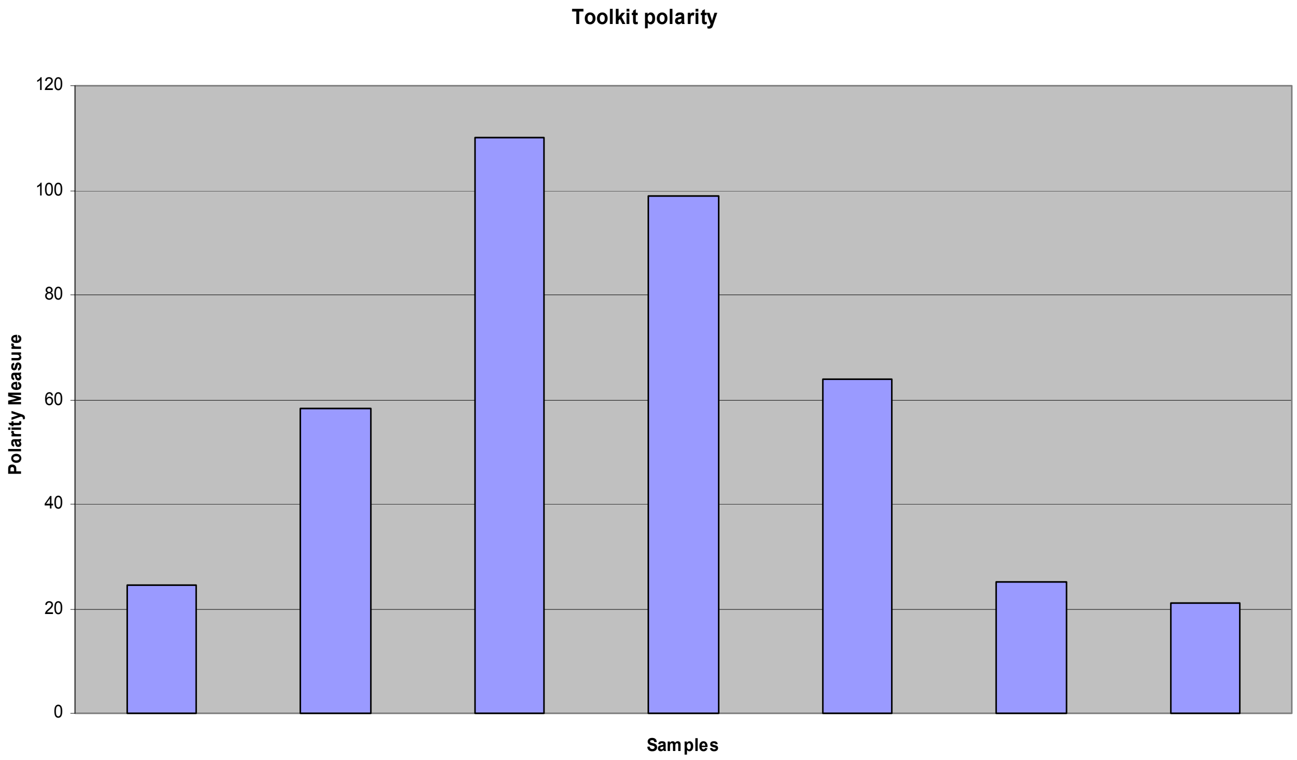


Fig. 2.3 Effective pH ranges for some common amphiprotic and protophilic solvents.

Cabot's modified carbon blacks





Example charge control agents

CCA1:

Soluble tail: Polyhydroxystearic acid

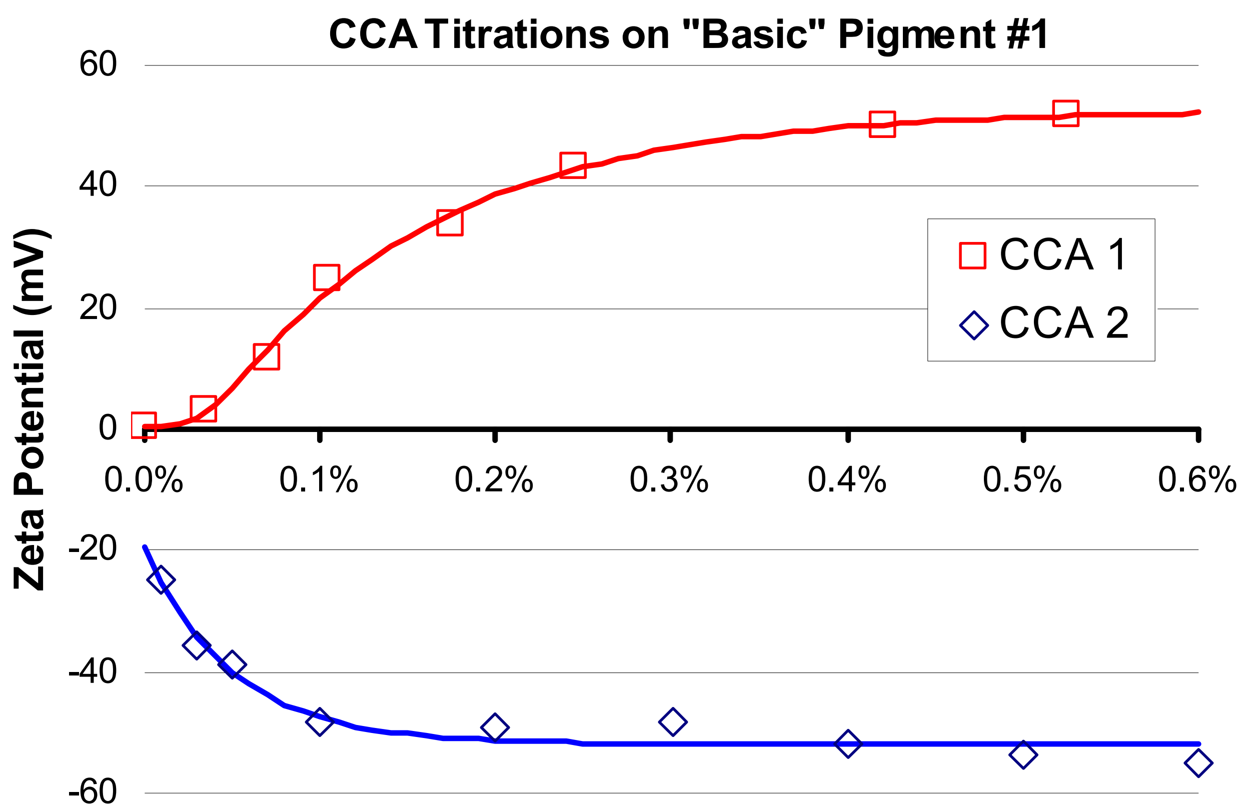
Head group: Quaternary ammonium - methyl sulfate

CCA2:

Soluble tail: C13 Hydrocarbon chains

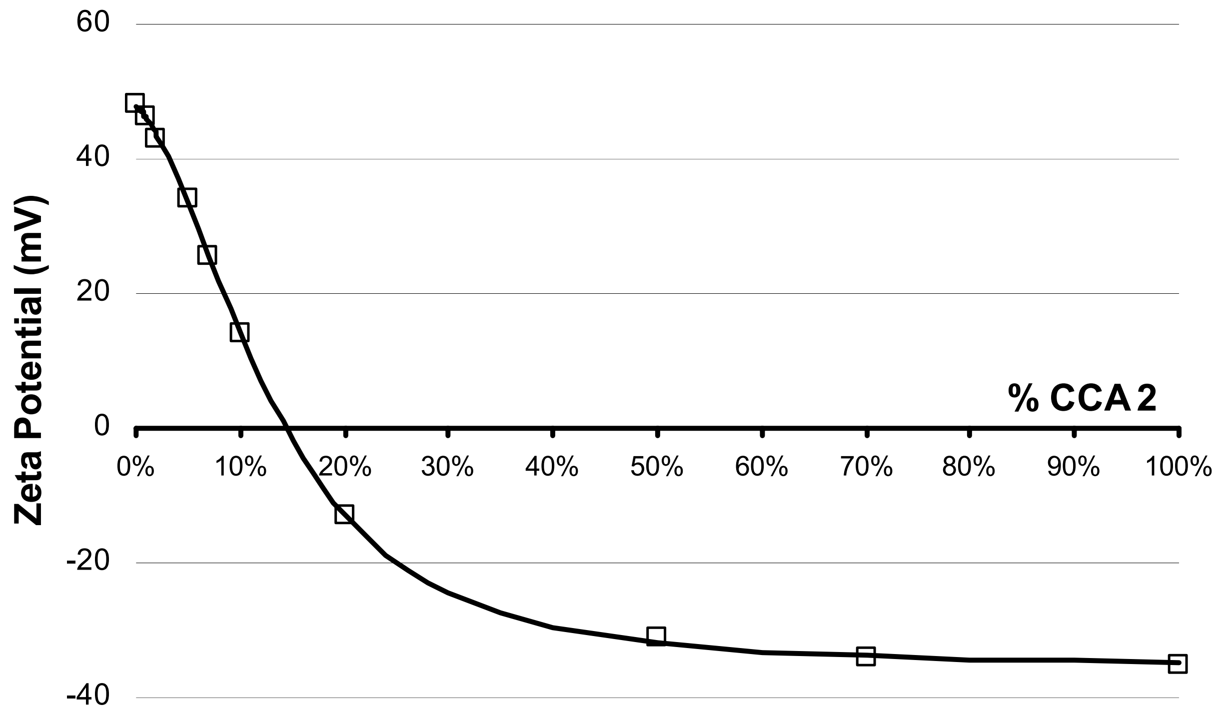
Head group: Sodium sulfosuccinate

Charging of a "basic" carbon black



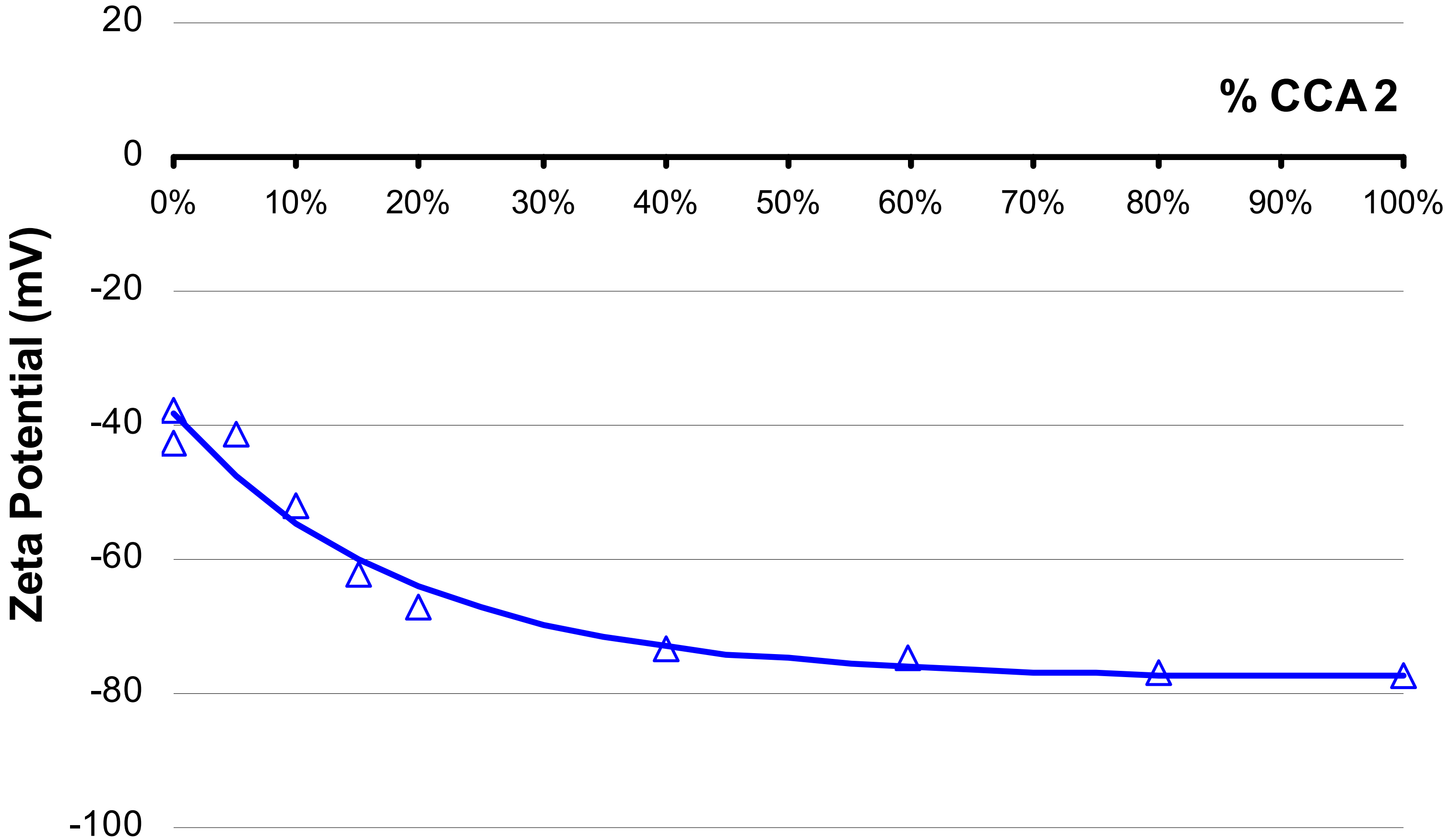
Basic pigment with “mixed” micelles

Start with “acidic” micelles that charge the particles positive.

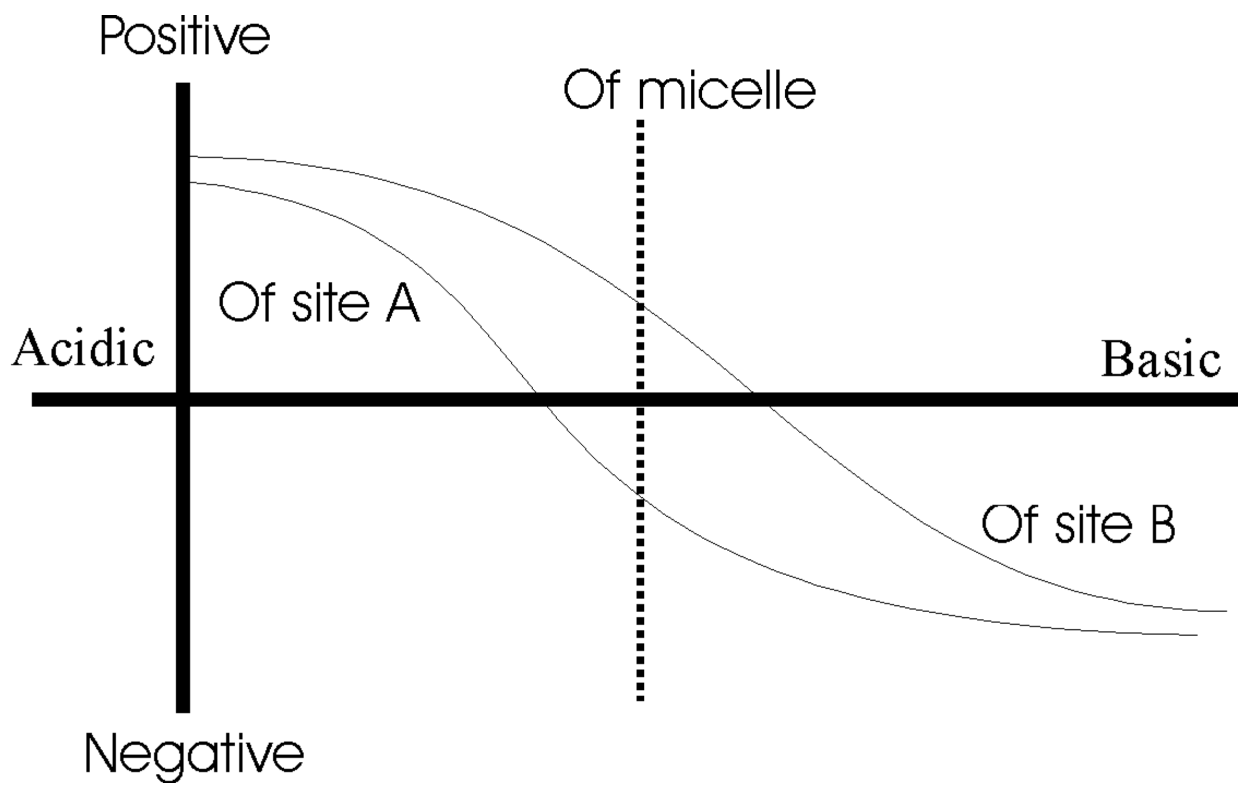


Continue to “basic” micelles that charge the particles negative.

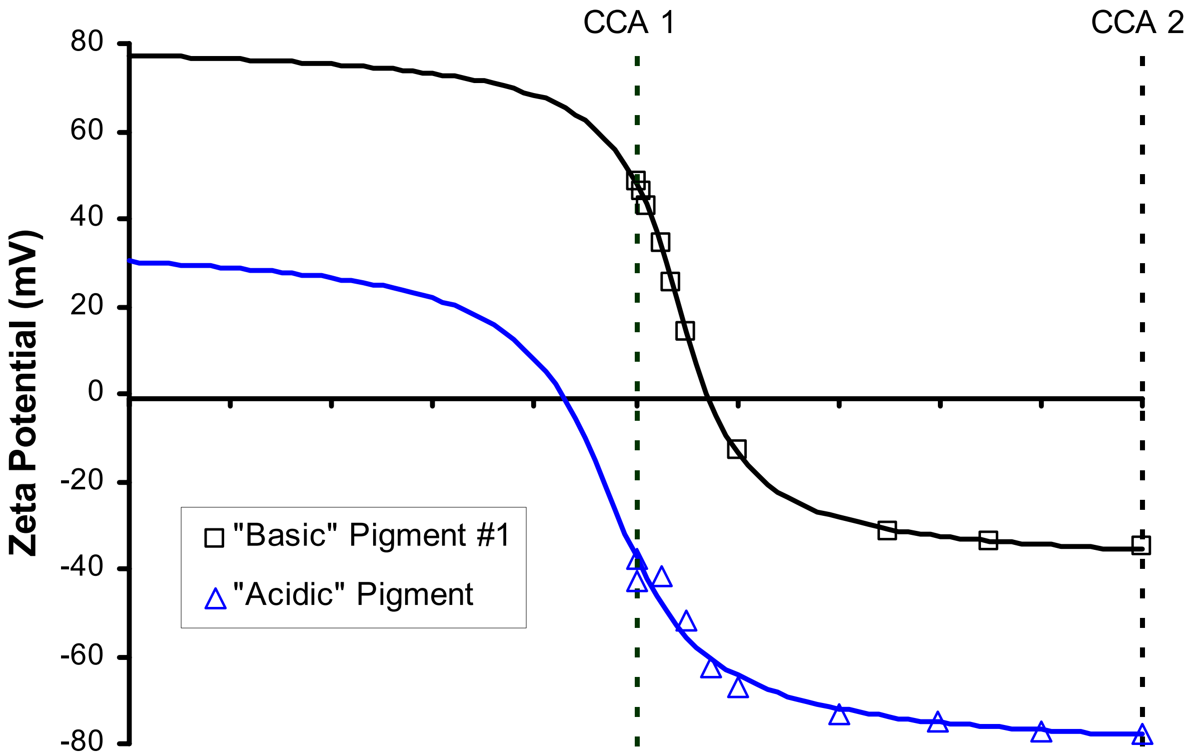
Acidic pigment with mixed micelles



Chemistry of charge creation



Titration of "acidic" pigment and "basic" pigment



Note the conditions for oppositely charged particles.

Note "points of zero charge".

What’s not new?

- Zeta potentials are about the same
- Potential determining ions are potential determining!
- Micellization and adsorption are competitive processes

What's just a change in degree?

- Ion concentrations (DeBye lengths)
- The sizes of ions
- Space charge effects
- Time constants
- Surface charge density (and uniformity)
- When electrodes are blocking

What's really new?

Maybe just dispelling some misconceptions and learning a few new tricks.

But nothing shocking in the electrostatics.

Summary

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

The chemistry of the micelle cores and the particle surface control the charge on the particles.