# Polarization of Electrodes by Doped Nonpolar Media

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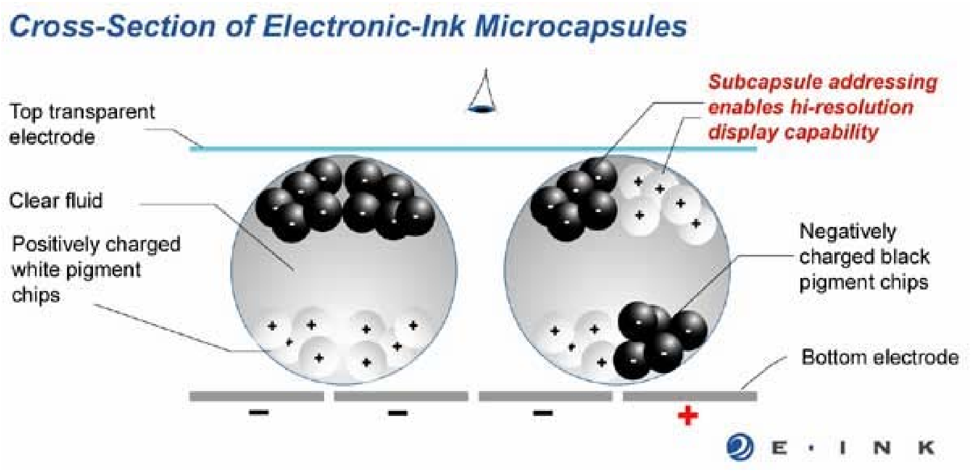
We tend to think of highly nonpolar fluids as being free of charges, but they can contain a significant amount of charge. One dramatic illustration of this charge is provided by explosions which have occurred during the tranporting of petroleum products. Flow of charged hydrocarbons can create a streaming potential large enough to produce a spark that ignites the explosion.

Today I am going to decribe a simple technique for measuring the ionic strength of nonpolar media. It is based on polarization of electrodes. The ionic strength determined by this technique will be confirmed by measuring the double-layer repulsion between a sphere and a plate, then deducing the Debye length.

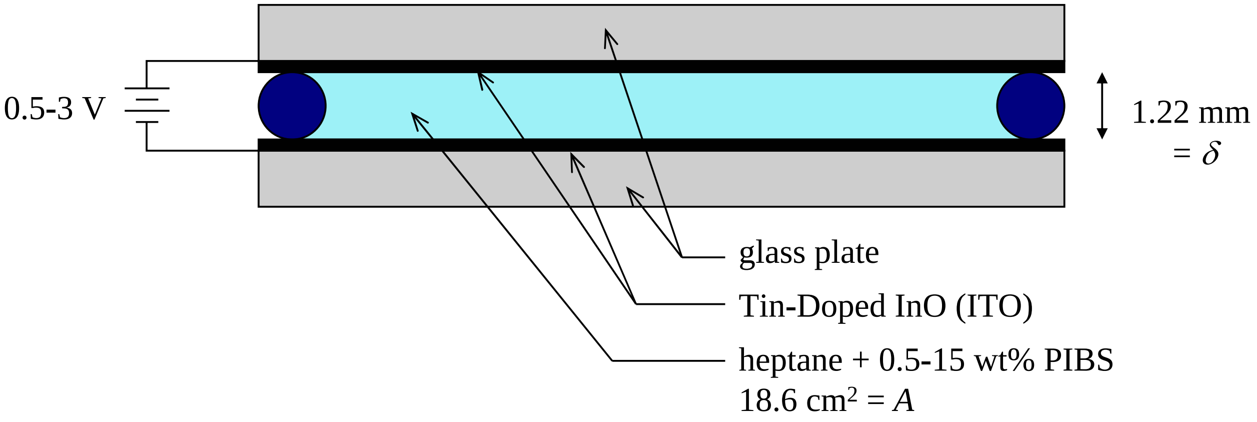
# Motivation



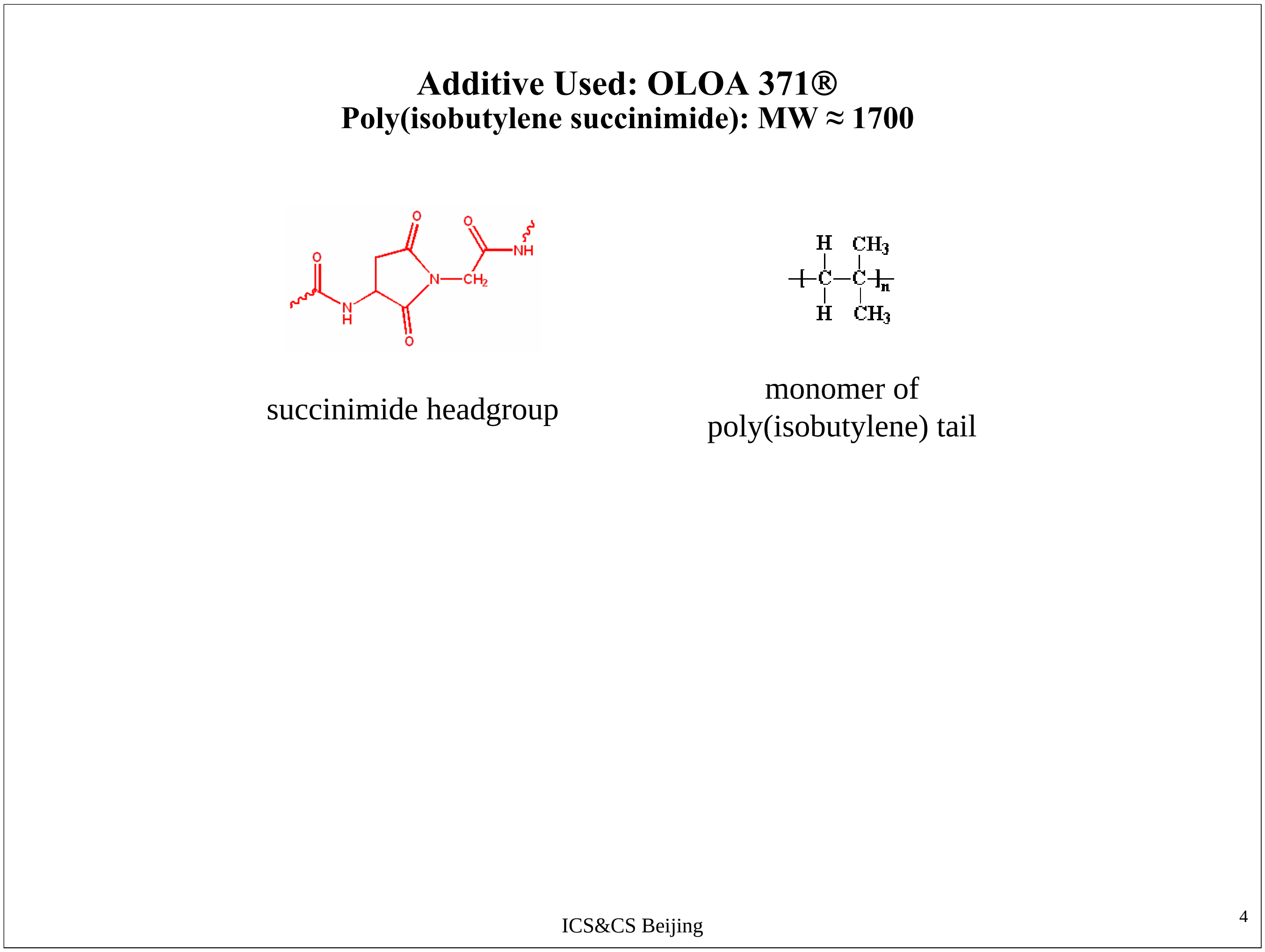
While charging of aqueous solutions has been extensively studied by colloid scientists, charging of nonpolar media is much less studied. Yet there are many applications. One of these is imaging on highly flexible displays which has been pioneered by companies like E-Ink.

This slide was downloaded from E-Ink's website and shows the basic mechanism for imaging. Capsules of 100 micron diameter contain black and white pigment particles which are oppositely charged. The direction of an applied electric field determines the color of an individual pixel. The fluid these particles are dispersed in is a nonpolar media.

# Polarization Apparatus



We used two parallel plate electrodes which sandwich the fluid which is heptane doped with a charging agent. The electrodes are tin-doped indium oxide – or ITO – which is a transparent semiconductor which is deposited on a glass substrate. The transparency is not important for the polarization experiments but is needed for the confirmation studies which employ TIRM.



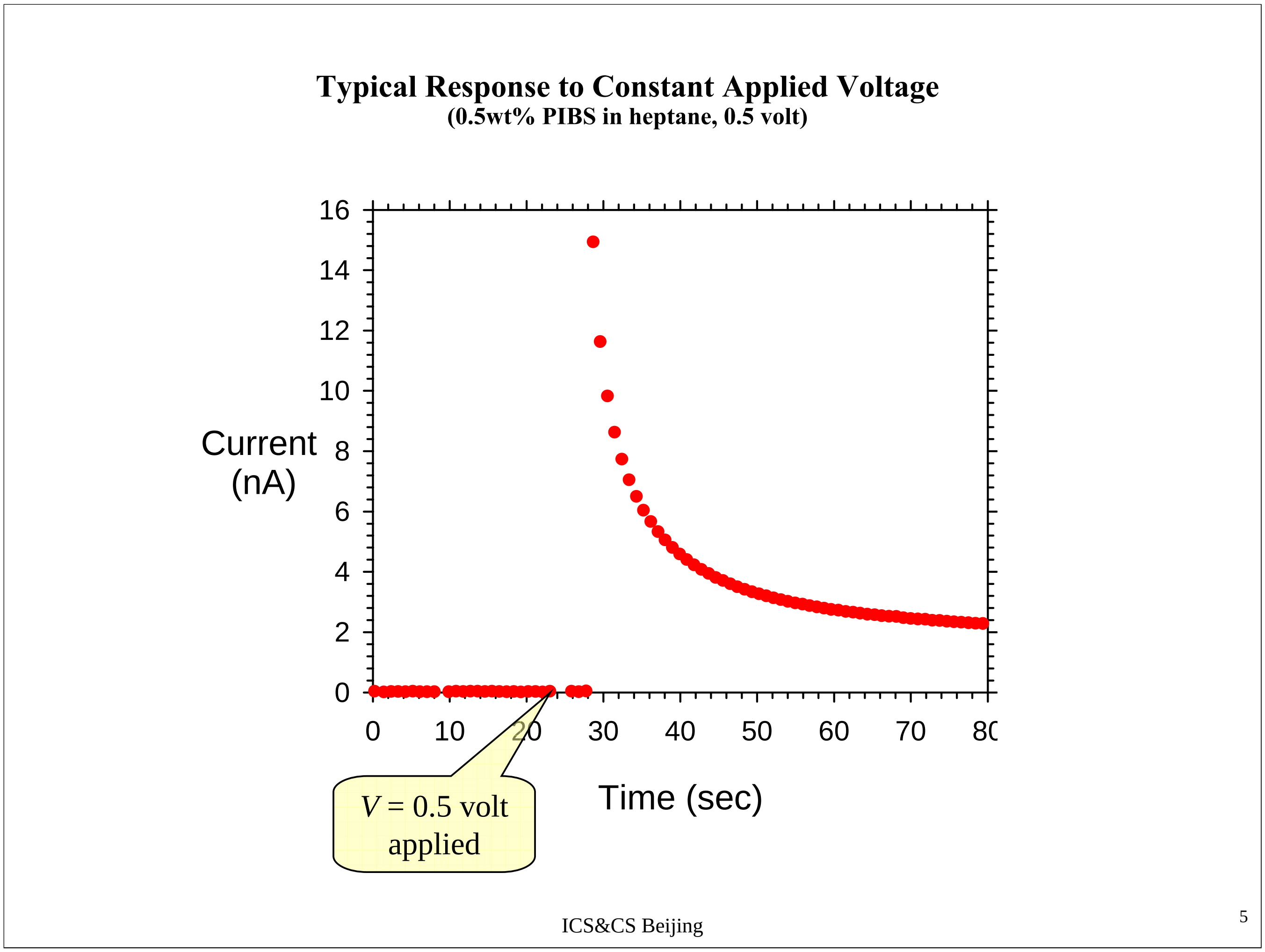
## Additive Used: OLOA 371®

### Poly(isobutylene succinimide): MW ≈ 1700

succinimide headgroup

monomer of
poly(isobutylene) tail

The charging agent is commerical product: polyisobutylene succinimide, an amphipatic molecule having a molecular weight of about 1700, although there is substantial polydispersity.

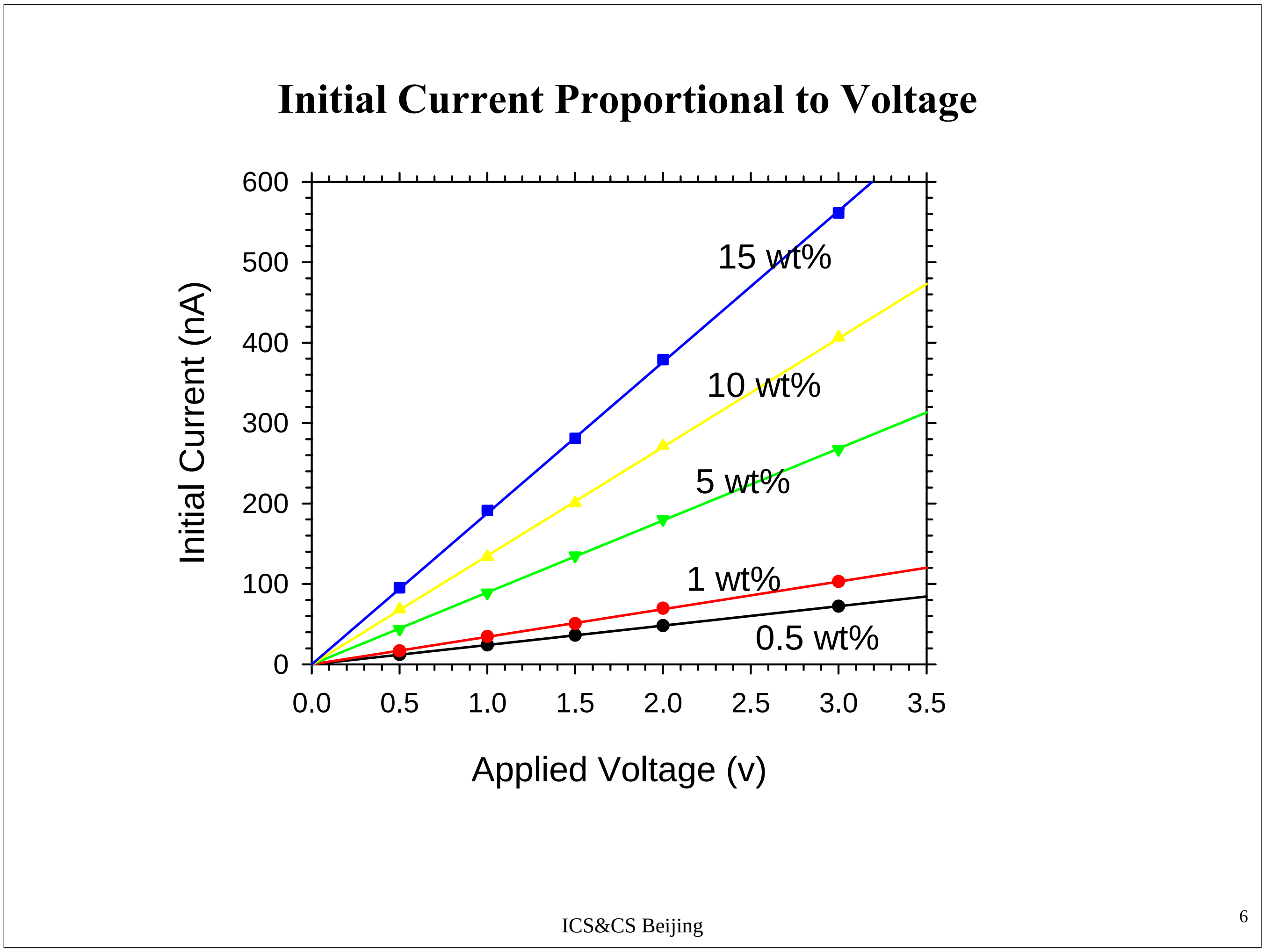


## Typical Response to Constant Applied Voltage

**(0.5wt% PIBS in heptane, 0.5 volt)**

*V* = 0.5 volt applied

This slides shows a typical polarization experiment. At about 28 seconds, we applied a constant half volt between the two electrodes. A significant electrically current is observed which indicates the presence of charge carriers in the heptane. The current is observed to decay monotonically with time owing to the accumulation of opposite charges on the two electrodes.



# Initial Current Proportional to Voltage

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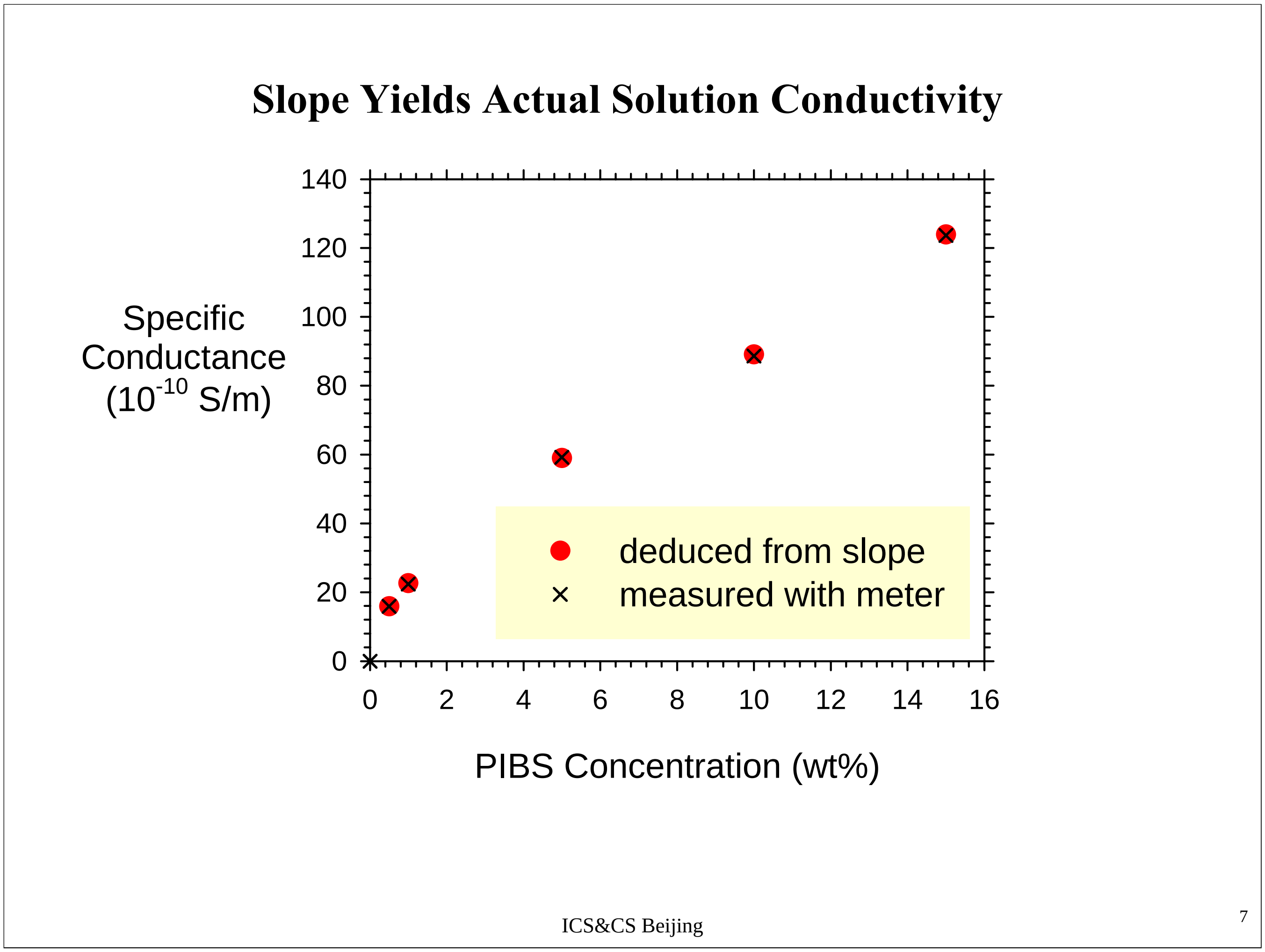
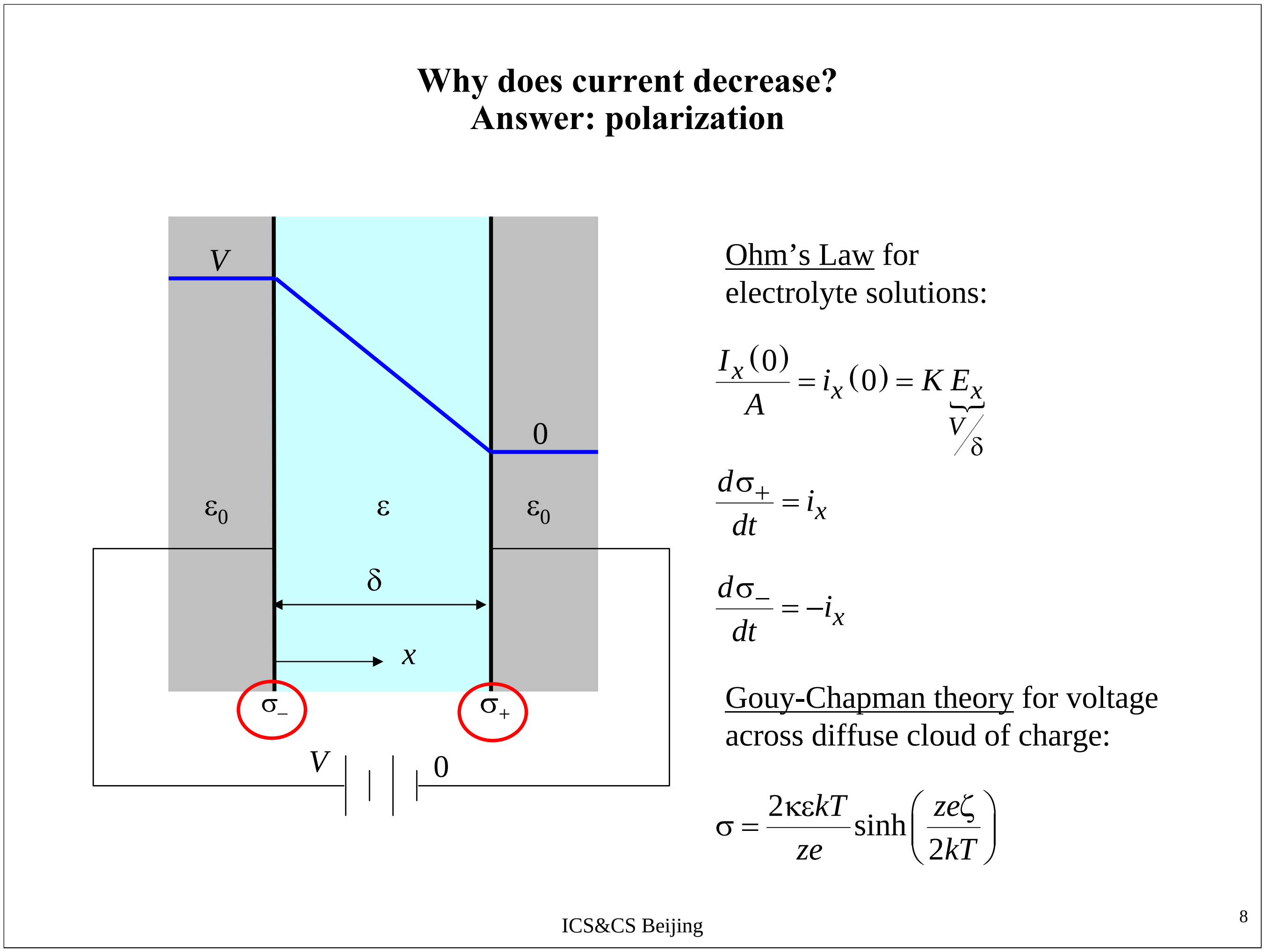
The initial current depends on the voltage and the concentration of charging agent. Here we see that current is directly proportional to applied voltage for each of the 5 different concentrations of the PIBS surfactant, as you would expect from Ohm’s law.

For each concentration, we regressed the slope.



## Slope Yields Actual Solution Conductivity

Multiplying by the geometrical cell constant, the slope can be converted into the specific conductance of the solution, indicated by the red dots on this slide. The conductance deduced from the slope is within experimental error of the specific conductance measured independently with a conductivity meter and indicated by the black x's on this slide.



# Why does current decrease?
# Answer: polarization

Ohm’s Law for electrolyte solutions:

$$\frac{I_x(0)}{A} = i_x(0) = K\underbrace{E_x}_{V/\delta}$$

$$\frac{d\sigma_+}{dt} = i_x$$

$$\frac{d\sigma_-}{dt} = -i_x$$

Gouy-Chapman theory for voltage across diffuse cloud of charge:

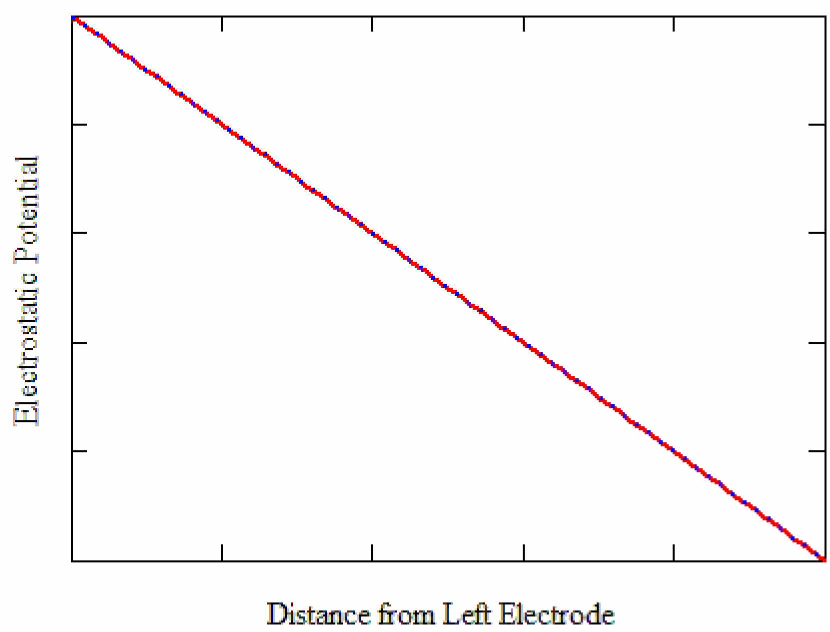
$$\sigma = \frac{2\kappa\varepsilon kT}{ze}\sinh\left(\frac{ze\zeta}{2kT}\right)$$

We have just seen that the initial current obeys Ohm’s law, which suggests that the electrostatic potential varies linearly between the two voltages applied to the electrodes as shown by the blue curve in this figure. Mathematically, the current divided by the area of the electrodes equals the specific conductance mutiplied by the electric field, which is just the applied voltage drop divided by the electrode spacing.

So why does the current decrease with time? In the absence of any redox reactions on the electrode surface, the ionic charge carriers in the heptane do not give up their charge upon reaching the electrode surface. Rather they accumulate there as a charge cloud next to the electrode which grows with time. Opposite charges accumulate at the two electrodes.

According to Gouy-Chapman theory, there will be a voltage drop across each charge cloud, which represents the zeta potential associated with that diffuse cloud.

# Polarization Causes Weakening of Electric Field in Bulk of Solution



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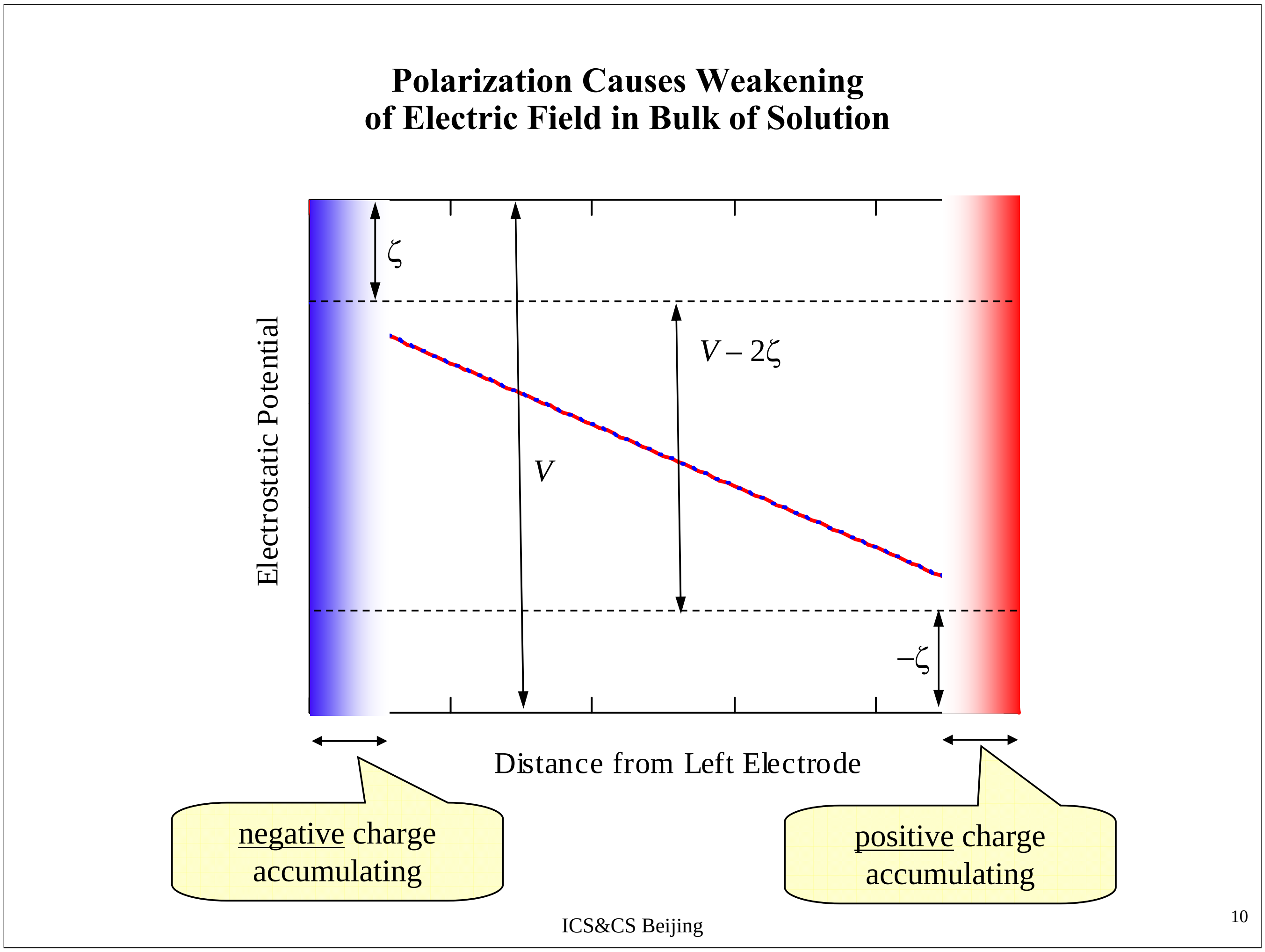
This animation suggests how the initially linear voltage profile evolves with time as the charges build up next to each electrode. Notice that the electric field in the electrically neutral bulk solution decreases with time. This is what causes the decrease in current with time.

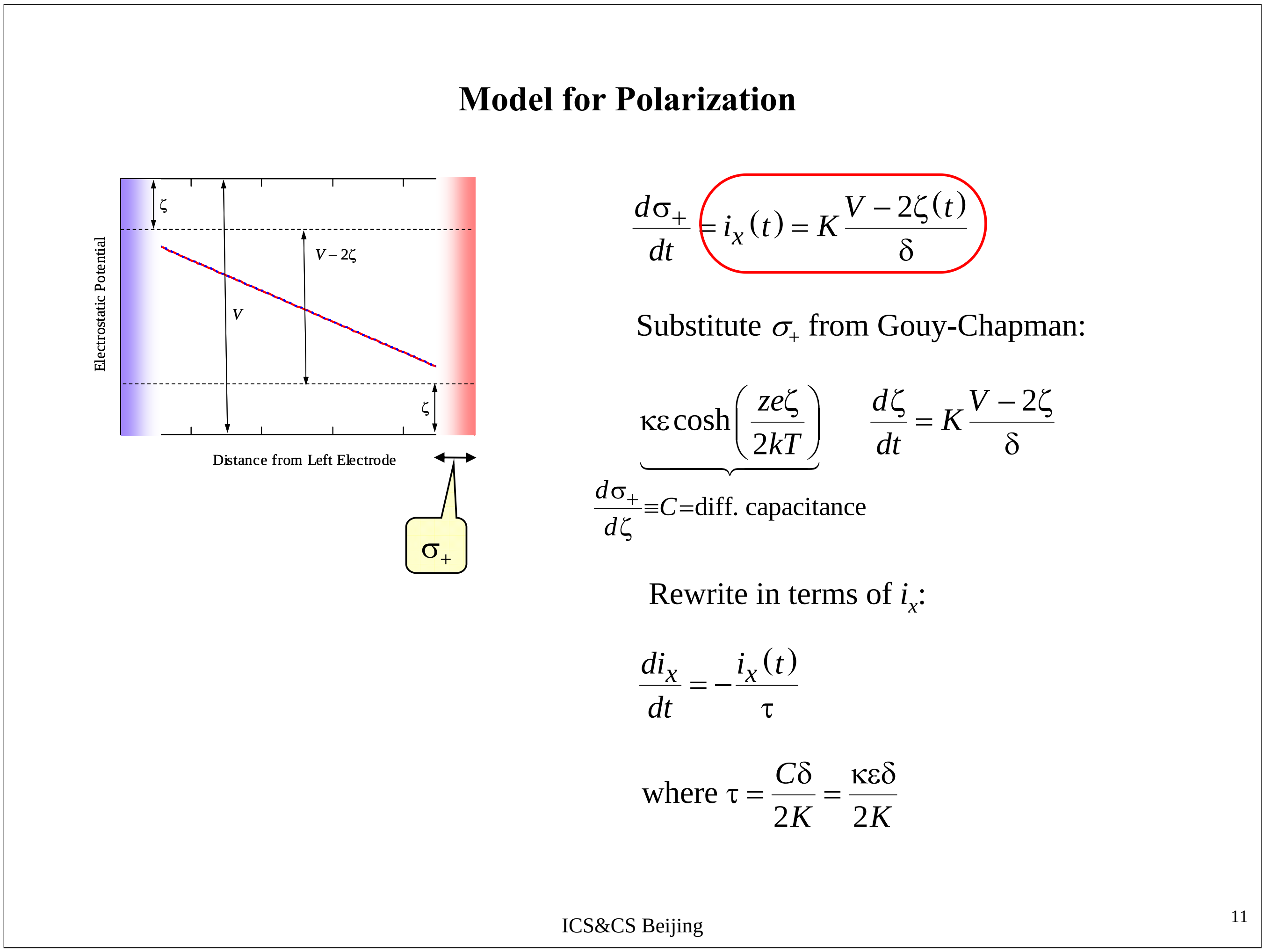


## Polarization Causes Weakening of Electric Field in Bulk of Solution

negative charge accumulating

positive charge accumulating

The diffuse cloud of charge turns out to be very thin compared to the one millimeter electrode spacing. Then the equal but opposite zeta potentials of the two clouds subtract from the total applied voltage, erode the electric field in the bulk solution and decreasing the current.



## Model for Polarization

$$\frac{d\sigma_+}{dt} = \boxed{i_x(t) = K\frac{V-2\zeta(t)}{\delta}}$$

Substitute $\sigma_+$ from Gouy-Chapman:

$$\underbrace{\kappa\varepsilon\cosh\left(\frac{ze\zeta}{2kT}\right)}_{\frac{d\sigma_+}{d\zeta}\equiv C=\text{diff. capacitance}}\quad\frac{d\zeta}{dt} = K\frac{V-2\zeta}{\delta}$$

Rewrite in terms of $i_x$:

$$\frac{di_x}{dt} = -\frac{i_x(t)}{\tau}$$

where $\tau = \frac{C\delta}{2K} = \frac{\kappa\varepsilon\delta}{2K}$

So here is our model for interpreting these polarization experiments. Ohm’s law is applied with the electric field being the applied voltage minus the zeta potential drop across the two charge clouds divided by the electrode spacing. The instantaneous current density gives the rate of charge accumulation next to the electrode.

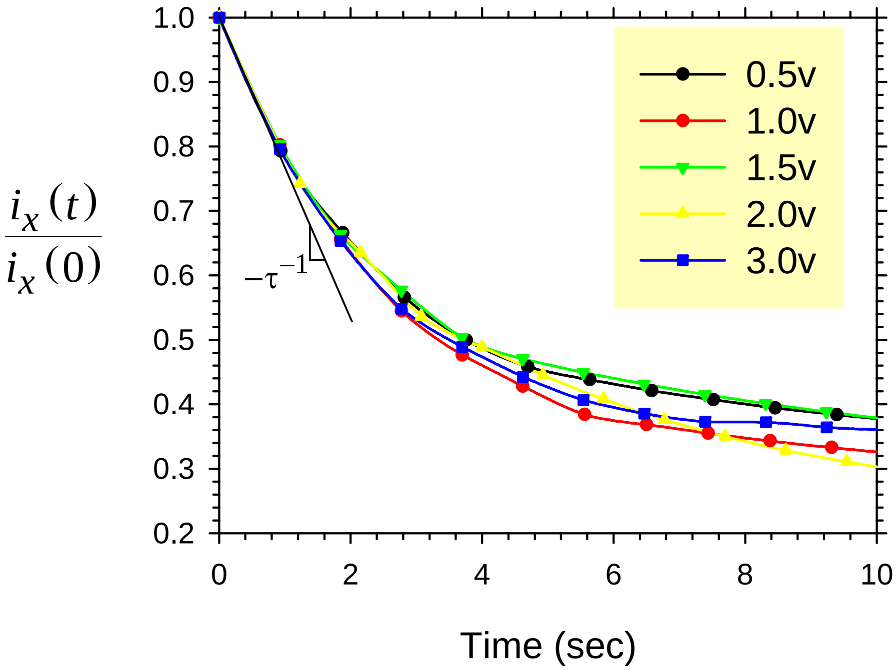
Using Gouy-Chapman theory to relate charge density to zeta potential, we can obtain an expression for the rate of change in the zeta potential. The coefficient of the time derivative of zeta potential represents the change in charge per unit change in zeta potential – in other words, the differential capacitance of the charge cloud.

Using the red-circled relationship, we can express zeta potential in terms of current density. Rewriting the last equation in terms of current density yields a simple differential equation describing how current decreases with time.

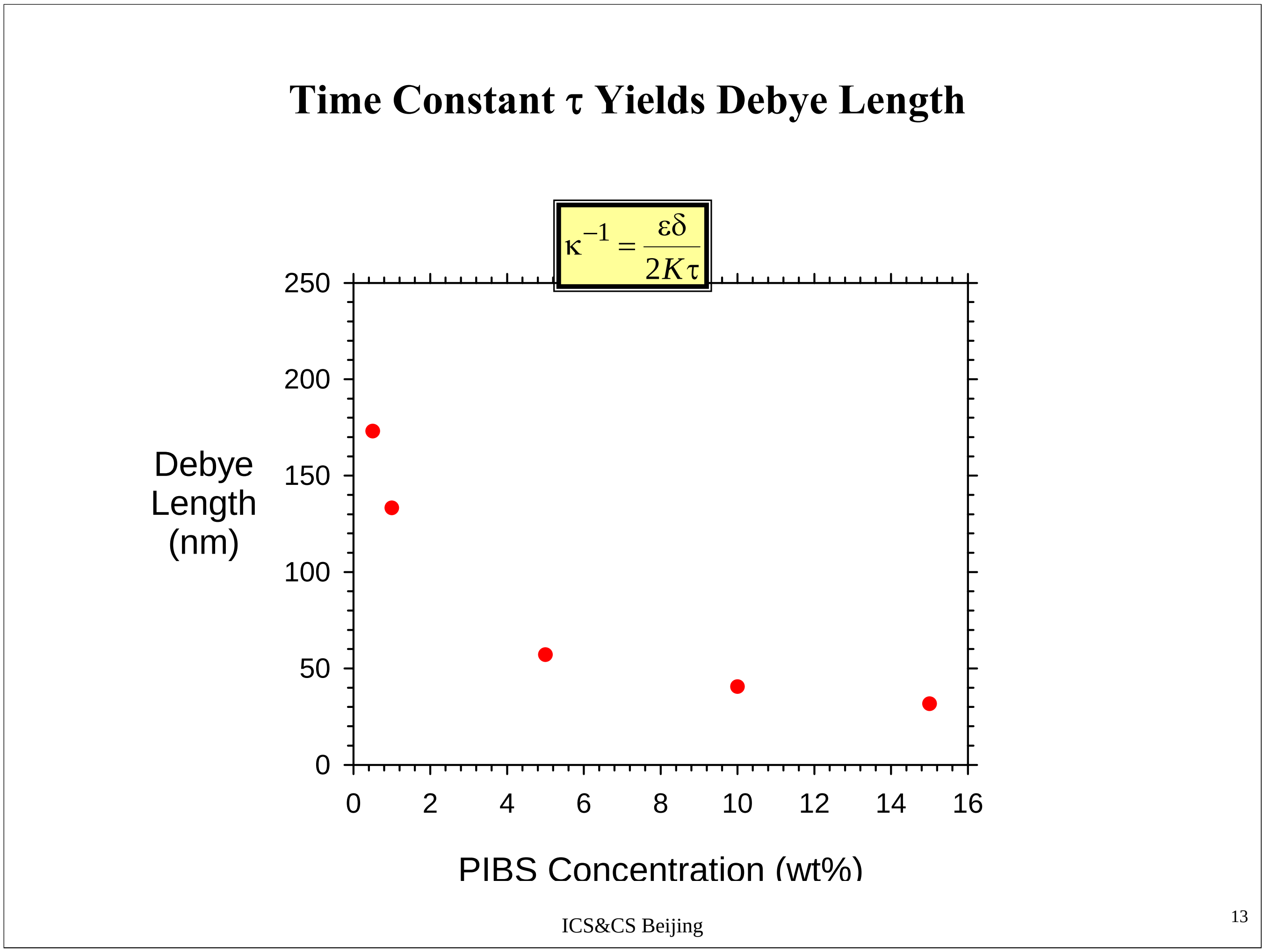
Notice the characteristic decay time $\tau$ depends on the differential capacitance divided by the specific conductance of the solution. If the initial zeta potential is zero, then the differential capacitance is just the Debye parameter times the permittivity of the solution. Thus the initial rate of decay can yield the Debye length and ionic strength of the solution.

## When Normalized, Initial Slope Is Independent of Voltage

(0.5wt% PIBS in heptane)



So here are some experimental results showing the instantaneous current normalized by the initial current for several different applied voltages. Notice that by normalizing in this way, the initial slope is independent of applied voltage, yielding a single value for the differential capacitance, Debye length and ionic strength. The curves deviate at later times because the differential capacitance is increasing at a rate which depends on the voltage.

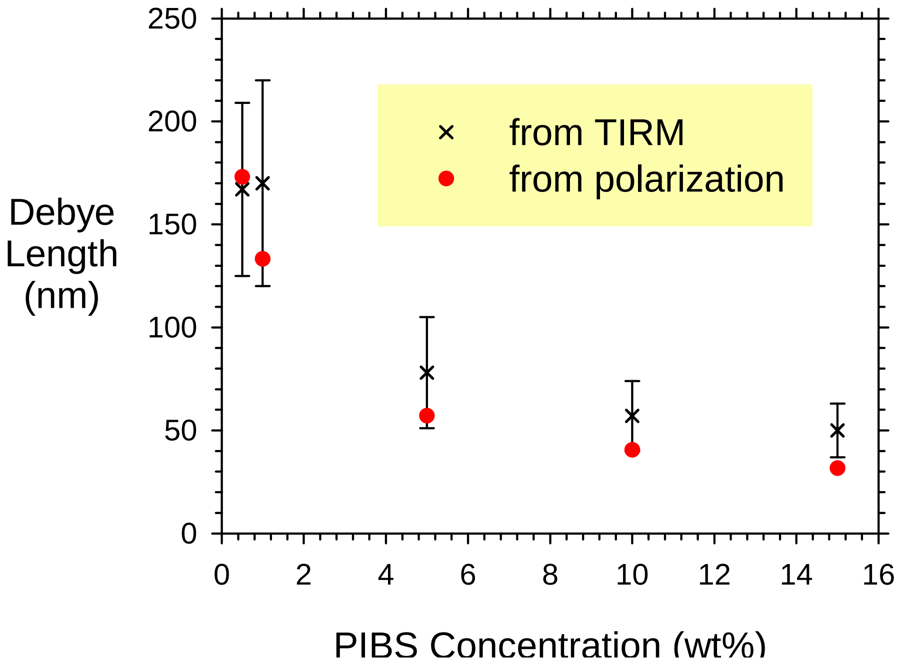


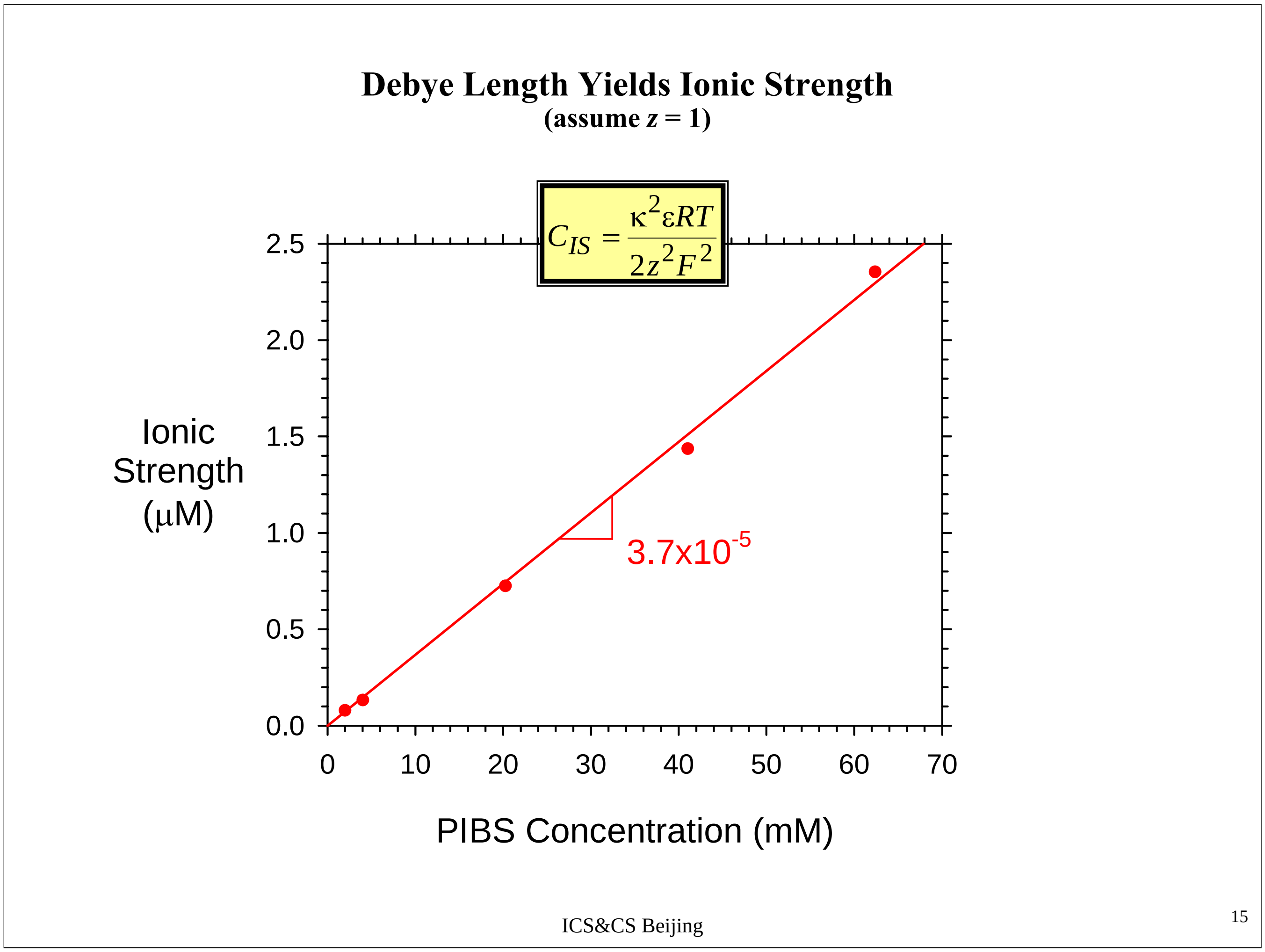
# Time Constant τ Yields Debye Length

$$\kappa^{-1} = \frac{\varepsilon\delta}{2K\tau}$$

So here are those Debye lengths inferred from the initial slope at different surfactant concentrations. Are they correct? We used TIRM to measure the potential energy profile between a

# Debye Lengths from Polarization Agrees with TIRM





## Debye Length Yields Ionic Strength

**(assume z = 1)**

$$C_{IS} = \frac{\kappa^2 \varepsilon RT}{2z^2F^2}$$

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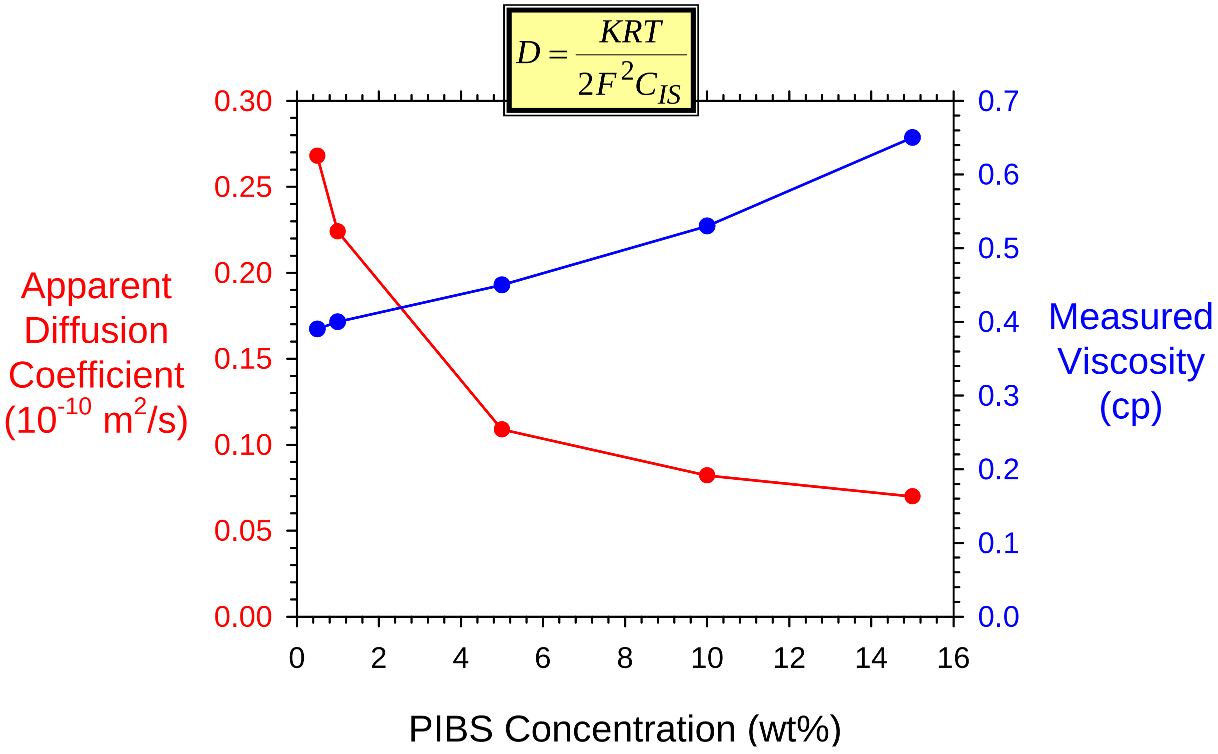
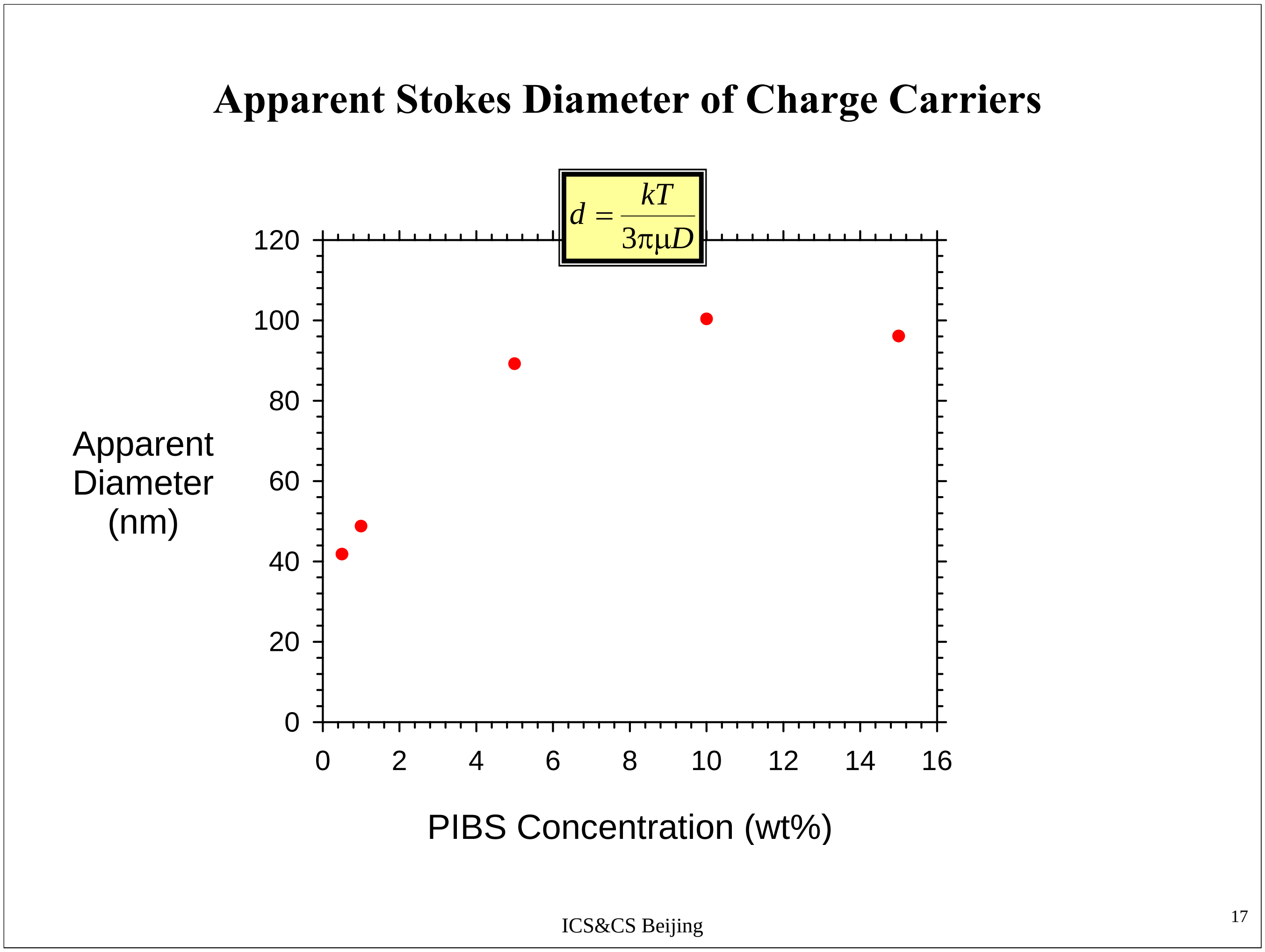
# Mobility of Charge Carriers Decreases More than Viscosity Increases

$$D = \frac{KRT}{2F^2 C_{IS}}$$





# Apparent Stokes Diameter of Charge Carriers

$$d = \frac{kT}{3\pi\mu D}$$

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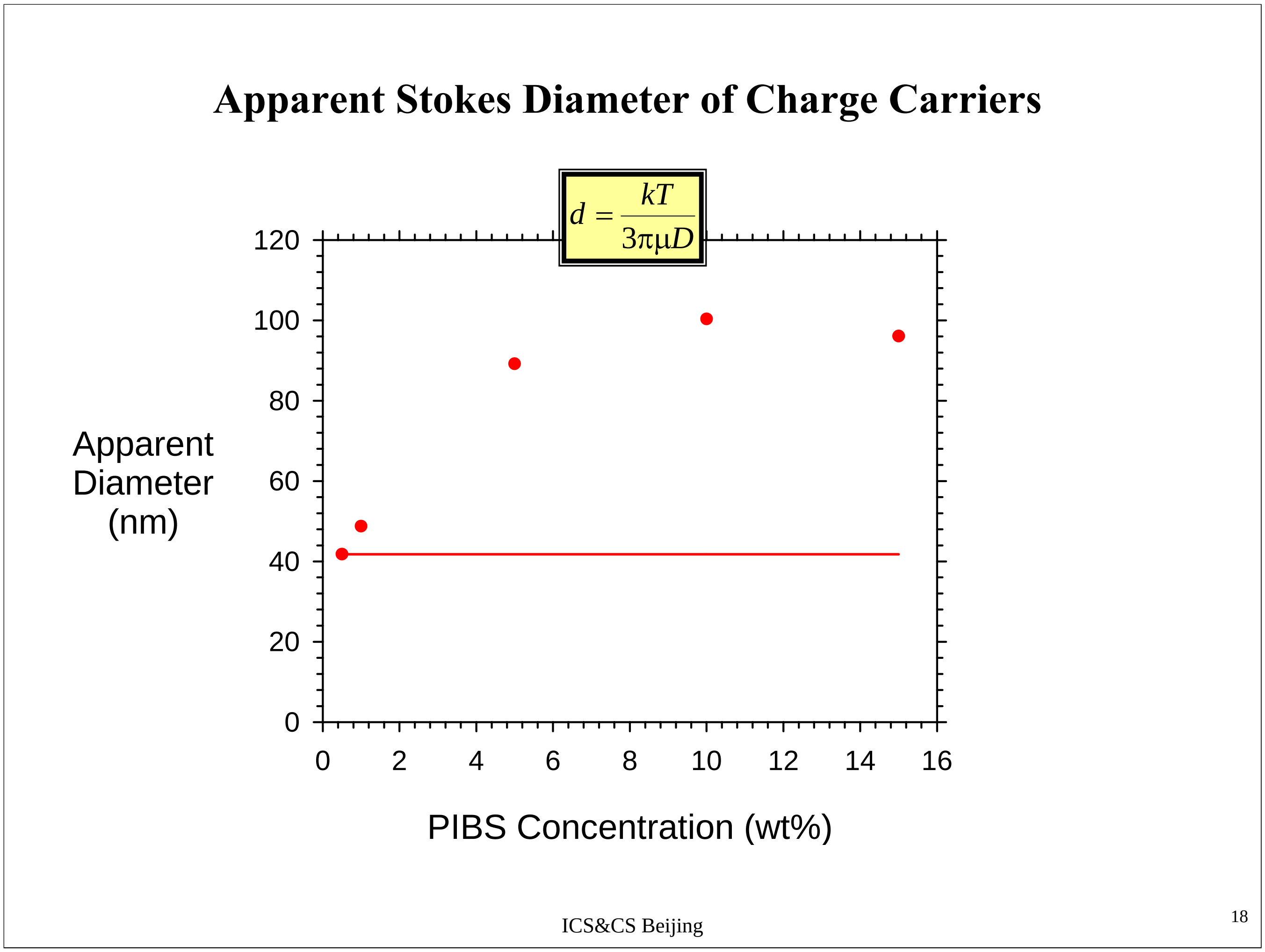
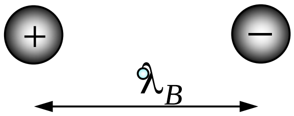


# Apparent Stokes Diameter of Charge Carriers

$$d = \frac{kT}{3\pi\mu D}$$

## Bjerrum Length

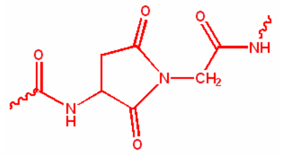
**(separation at which electrostatic attraction = *kT*)**



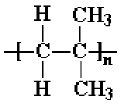
$$\lambda_B = \frac{e^2}{4\pi\varepsilon kT}$$

| In water: | In heptane: |
|---|---|
| $\varepsilon = 78\ \varepsilon_0$ | $\varepsilon = 2\ \varepsilon_0$ |
| $\lambda_B = 0.7$ nm | $\lambda_B = 28$ nm |

# Additive Used: OLOA 371®
## Poly(isobutylene succinimide): MW ≈ 1700

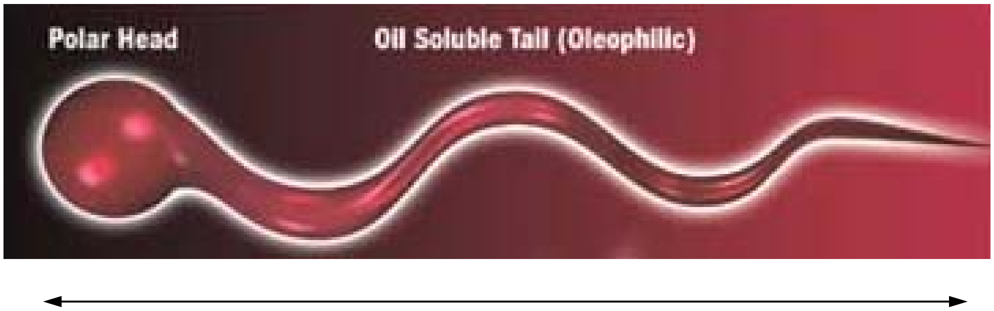


succinimide headgroup



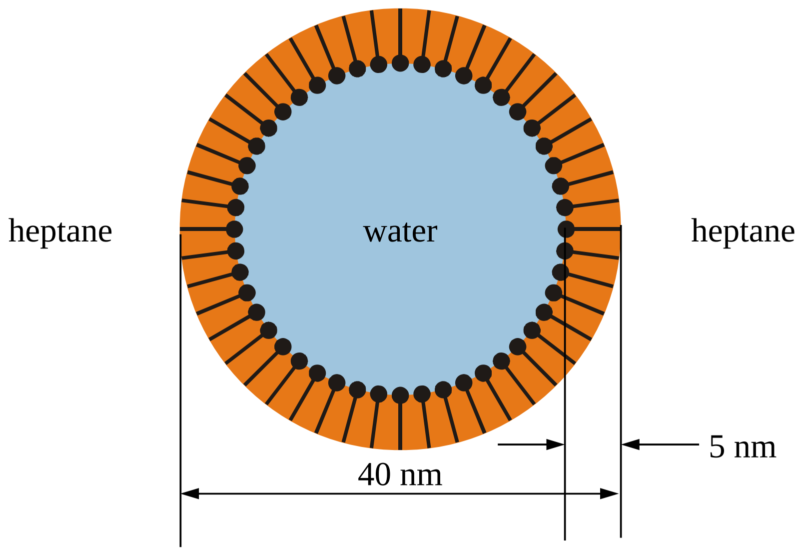
$$\left[ \overset{\text{H}}{\underset{\text{H}}{\text{C}}} - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}} \right]_n$$

monomer of
poly(isobutylene) tail



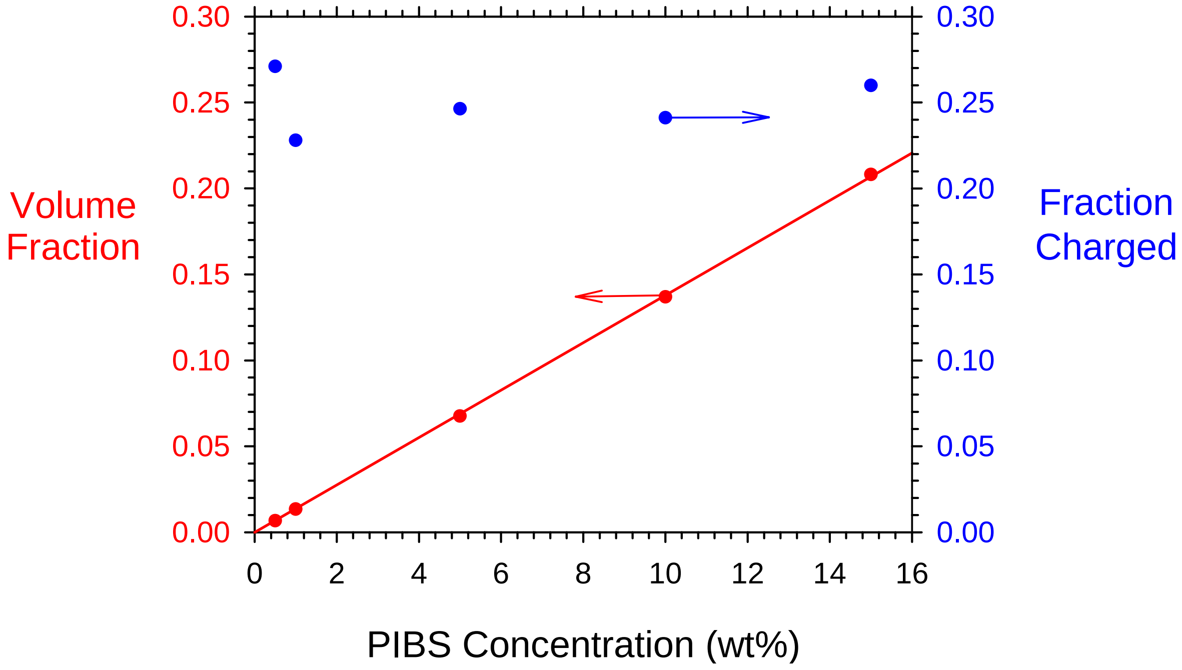
5 nm

## Charge Carriers are Large Micelles which Solubilize Water

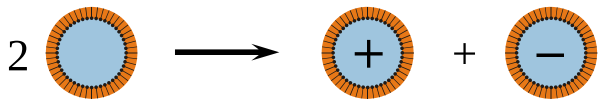


$$\boxed{N_{agg} = \frac{V_{\text{shell}}}{\bar{v}_{\text{PIBS}}} \approx 6900}$$

# Volume Fraction of PIBS Micelles



# Possible Charging Mechanism: Proton Transfer



$$K_{eq} = \frac{C_{+}C_{-}}{C_{0}^{2}}$$

$$C_{total} = C_{0} + C_{+} + C_{-}$$

$$C_{+} = C_{-}$$

$$\alpha \equiv \frac{C_{+}}{C_{total}} = \mathrm{const}$$

fraction of micelles charged is independent of PIBS concentration

# Conclusions

- Electrode polarization is a simple and effective method to deduce ionic strength for nonpolar fluids (confirmed by TIRM)
- Charge carriers are 40 nm micelles of PIBS
- Increase in viscosity with [PIBS] consistent with volume fraction of micelles
- Fraction of micelles charged is independent of [PIBS]: suggests proton transfer between 2 neutral micelles