In Pursuit of the Elusive Bound Site Activity Coefficient

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Introduction

Diffuse Layer Models (DLMs) are widely employed to describe the acidity behavior of bound reactive sites on metal oxides, NOM, polyelectrolytes and latex beads:

$$>SOH \Longleftrightarrow >SO^{-} + H^{+}$$

$$K_{a1} = \frac{[>SO^{-}]a_{H^{+}}EXP(-e\psi/kT)}{[>SOH]}$$

Historically, these mixed concentration/activity expressions assume bound site activity coefficients: 1) cancel out in the quotient, 2) equal 1 (i.e., ideal behavior), or 3) are represented in the exponential term.

Following Chan et al. (1975), the electrochemical potentials of these species are given by:

$$u_{H+} = u_{H+}^{o} + kT\ln([H^{+}]) + kT\ln(\gamma_{H+}) - e\Psi$$

$$u_{>SOH} = u_{<SOH}^{o} + kT\ln([>SOH]) + kT\ln(\gamma_{>SOH})$$

$$u_{>SO-} = u_{>SO-}^{o} + kT\ln([>SO-]) + kT\ln(\gamma_{>SO-}) - e\Psi$$

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Due to moving a mobile ion from bulk solution where Ψ=0 to the interface where Ψ ≠ 0.

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$$u_{>SO-} = u_{>SO-}^{o} + kTln([>SO-]) + kTln(\gamma_{>SO-}) - e\Psi$$

Due to the creation of a charged site in a region of constant potential Ψ.

Problem: If one creates a mass action expression from these electrochemical potentials (assuming that charging energies are the only significant non-ideal excess free energy term), one arrives at:

$$K_{a1} = \frac{[>SO^-]a_{H+}EXP(-2e\psi/kT)}{[>SOH]}$$

where 1 eΨ is due to the hydronium ion and 1 eΨ is due to the creation of a charged site in a region of constant potential Ψ.

Incorporation of counterion condensation into the electrochemical potentials:

$$u_{H+} = u_{H+}^{o} + kT\ln([H^{+}]) + kT\ln(\gamma_{H+}) - e\Psi$$

$$u_{>SOH} = u_{<SOH}^{o} + kT\ln([>SOH]) + kT\ln(\gamma_{>SOH})$$

$$u_{>SO-} = u_{>SO-}^{o} + kT\ln([>SO-]) + kT\ln(\gamma_{>SO-}) - (1-\tau)\, e\Psi$$

Loux (1999, 2000, 2006) modified the bound site charging energy term to include counterion condensation (τ; where $0 \le \tau \le 1$)

Assuming that charging energies are the only significant non-ideal excess free energy term, at high charge densities and constant τ the new mass action expression is:

$$K_{a1} = \frac{[>SO^{-}]a_{H+}EXP(-(2-\tau)e\psi/kT)}{[>SOH]}$$

where (1-τ)eΨ is the new charging energy term. Note that as τ approaches 1, this expression collapses into the historical approach.

Activity coefficients for ions in bulk solution are obtained from charging energies in the Debye-Huckel Limiting Law (DHLL) for spherical ions. The DHLL is derived under the following assumptions:

1) $e\Psi \ll kT$

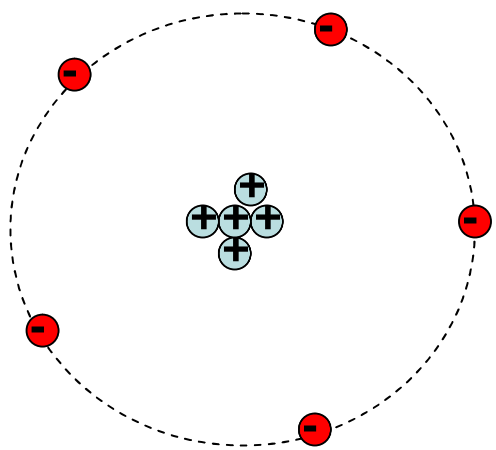
2) $1/\kappa \gg r_{ion}$

3) ***the charge in the diffuse layer can be represented as a hollow charged sphere $1/\kappa$ distant from the surface of the ion.***

DHLL

(Hunter, 1987)

—1/κ—



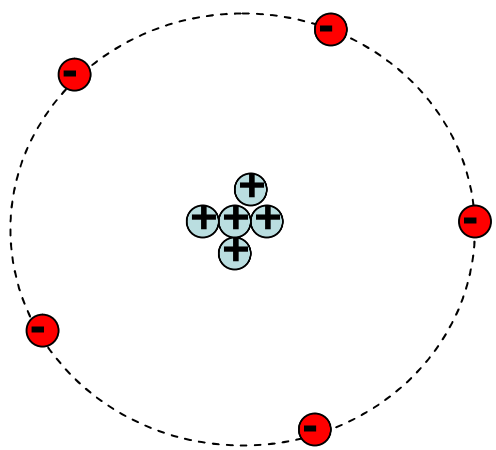
$$e\Psi_d << kT$$

$$\Psi_d = \frac{Q_p}{4\pi\varepsilon r_{pcl}} - \frac{Q_p}{4\pi\varepsilon(r_{pcl} + 1/\kappa)}$$

DHLL

(Hunter, 1987)

$|$— $1/\kappa$ —$|$



$e\Psi_d \ll kT$

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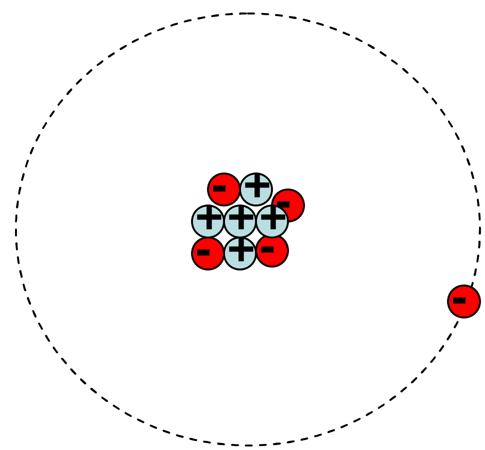
Present work

$|$— $1/\kappa$ —$|$



$e\Psi_d \gg kT$

$$\Psi_d = \frac{Q_p}{4\pi\varepsilon r_{pcl}} - \frac{\tau Q_p}{4\pi\varepsilon r_{pcl}}$$

Estimation of the charging energy terms:

DHLL

$$\Delta G = {}_0\!\int^{ze} [\kappa Q_d/4\pi\varepsilon]dQ$$

$$= (ze)^2\kappa/8\pi\varepsilon$$

Present work

$$\Delta G = {}_Q\!\int^{Q\pm e}[(1-\tau)Q/4\pi\varepsilon r_{pcl}]dQ$$

$$= (1-\tau)(\pm 2eQ + e^2)/8\pi\varepsilon r_{pcl}$$

$$= \pm(1-\tau)e\Psi$$

Assumptions:

$e\Psi << kT$

$1/\kappa >> r_{ion}$

Q >> e and constant τ, most charge neutralization from CC

Estimation of the activity coefficients:

DHLL	*Present work*
$\ln(\gamma) = -\Delta G/kT$	$\ln(\gamma) = -\Delta G/kT$
$= -(ze)^2\kappa/8\pi\varepsilon kT$	$= -/+(1-\tau)e\Psi/kT$

Comparison between the DHLL and the present approach.

In applications of the the DHLL, $\tau \neq 0$; e.g., for a 1:1 ion pair, $\tau = 1$, $\Delta G = 0$ and $\gamma = 1$. Therefore, a more accurate DHLL potential expression (with no change in computational accuracy) is given by:

$$\Psi_d = \frac{(1-\tau)Q_p}{4\pi\varepsilon r_{pcl}} - \frac{(1-\tau)Q_p}{4\pi\varepsilon(r_{pcl} + 1/\kappa)}$$

Or the present approach is a truncation where:

$$|-\tau Q_p/4\pi\varepsilon r_{pcl}| >> |-(1-\tau)\kappa Q_p/4\pi\varepsilon|$$

(i.e., CC dominates charge neutralization).

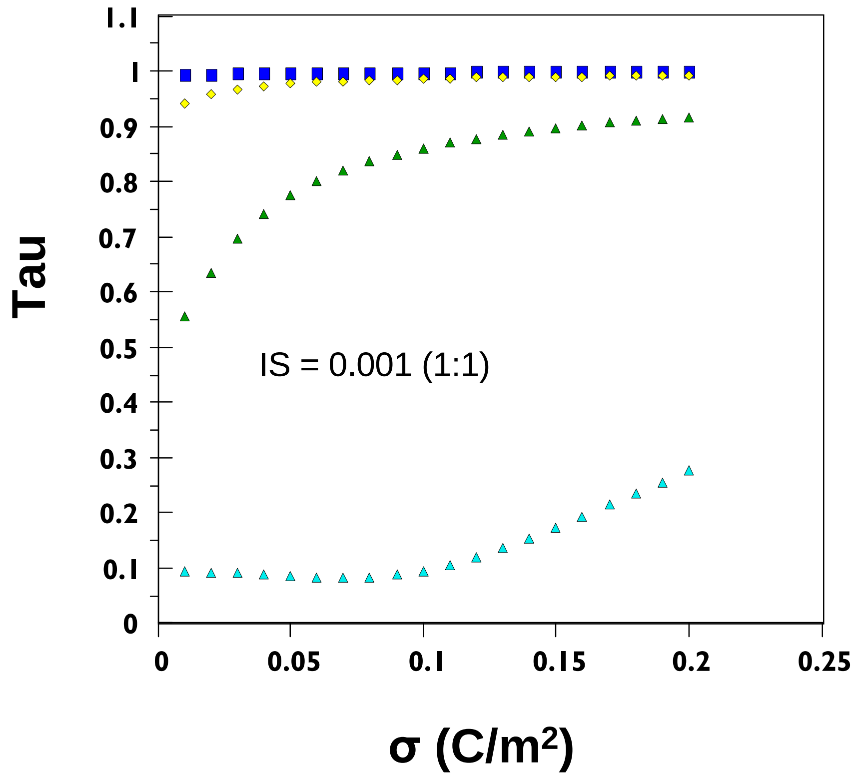
Methods

Surface potential estimates for spherical particles were obtained using the approximate analytical solution to the P-B equation published by Oshima et al. (1982). $T = 298$ K.

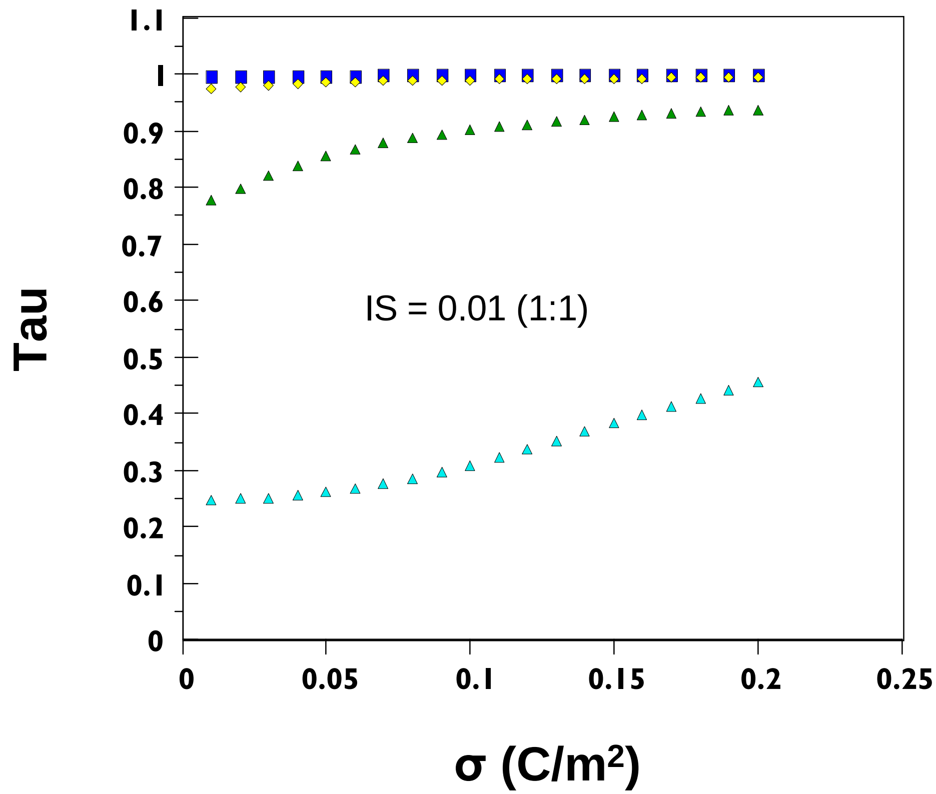
Following Loux (2006): $\tau_{PB} = (\Psi_{Coul.} - \Psi_{PB})/\Psi_{Coul.}$

Because τ monotonically approaches a maximum value with increased charge density, maximum values of τ (or τ_{max}) were estimated using a Michaelis-Menten type plot of σ/τ vs. σ where the slope equals $1/\tau_{max.}$

Results



"τ" as a f(r_{pcl} and σ): r_{pcl} = 1.0 µm (blue boxes), 0.1 µm (yellow diamonds), 0.01 µm (green triangles), and 0.001 µm (aquamarine triangles).



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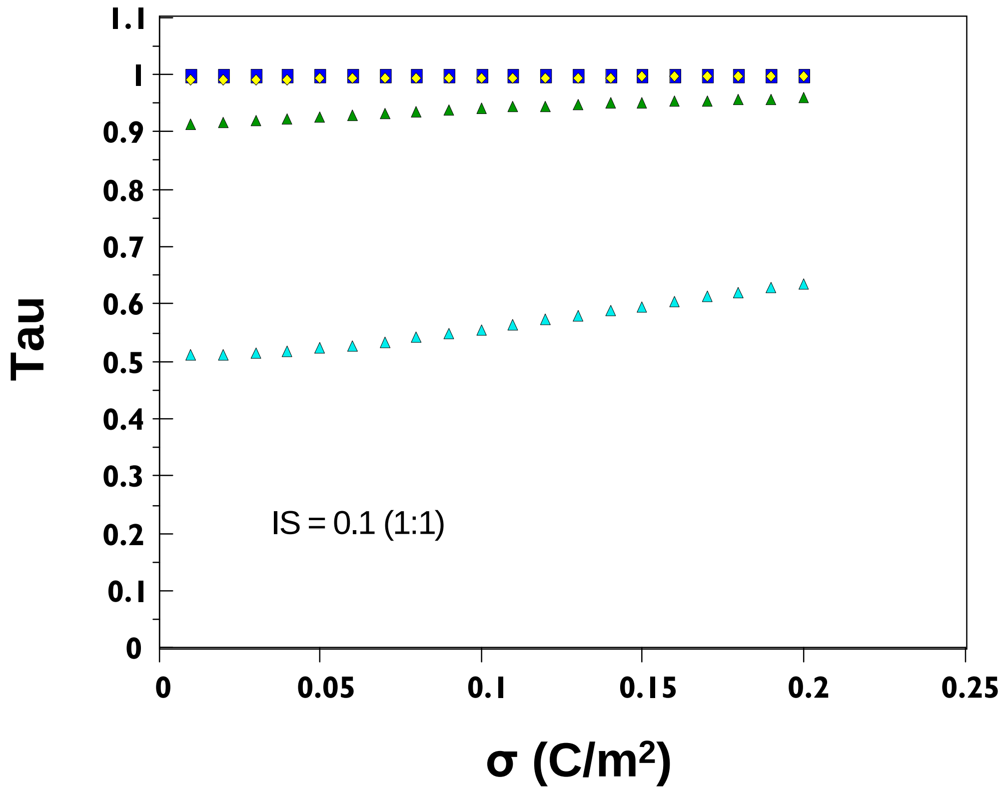

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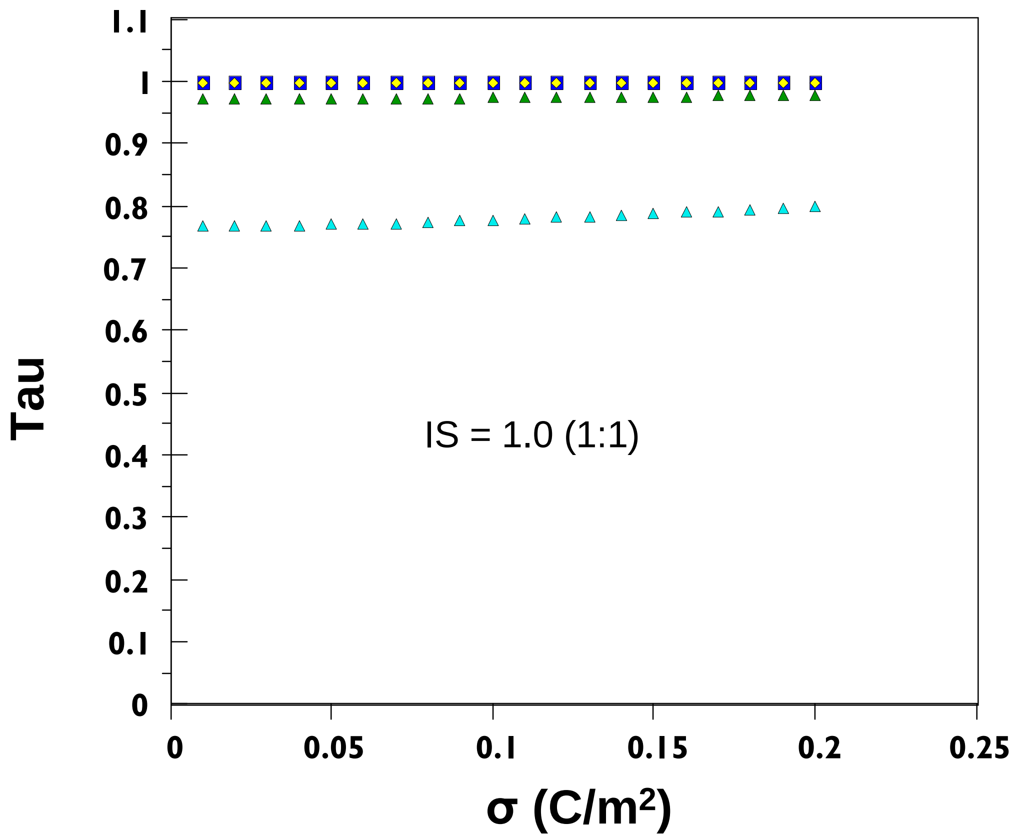

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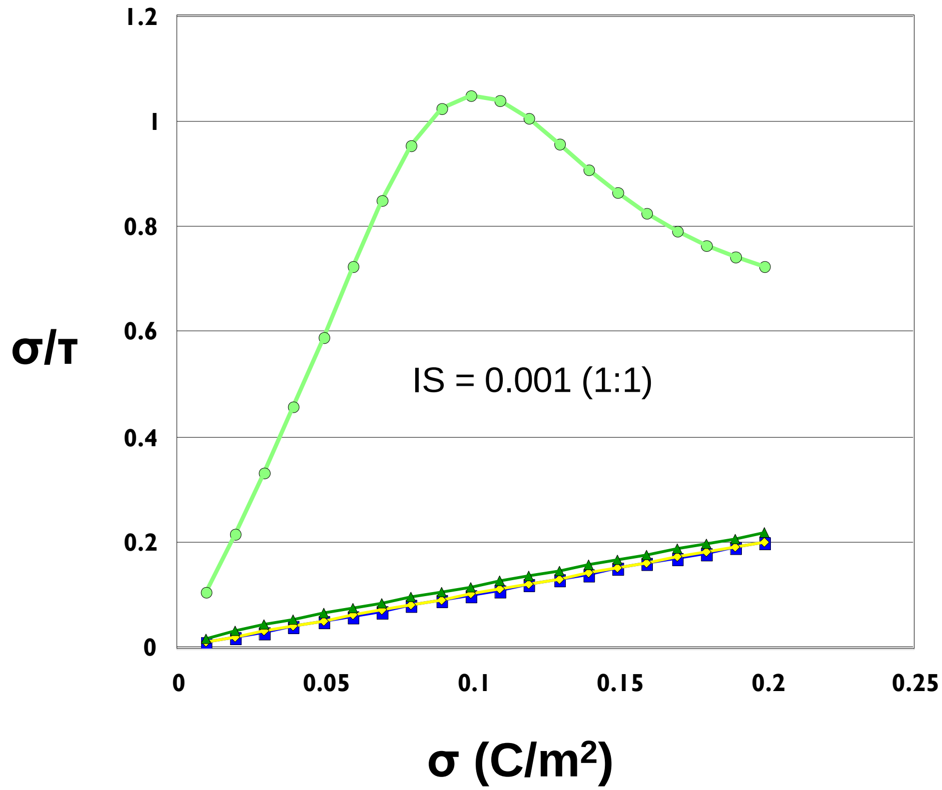
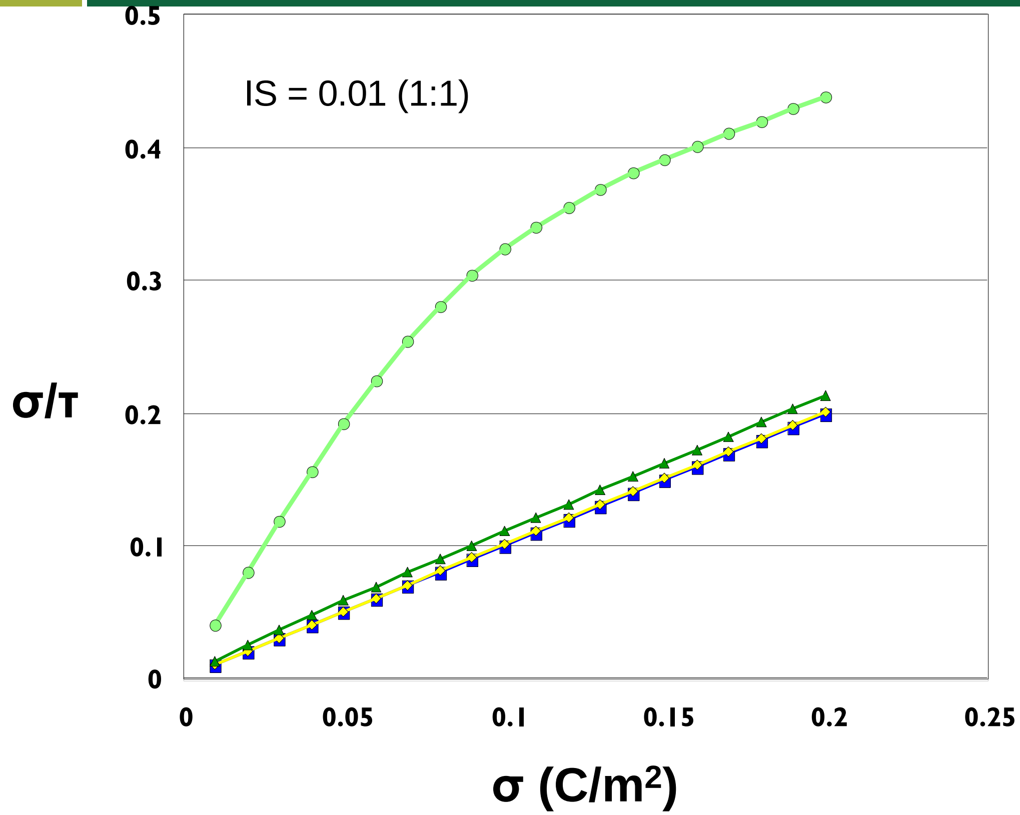


Michelis-Menten plots: r_{pcl} = 1 μm (blue boxes), 0.1 μm (yellow diamonds), 0.01 μm (green triangles); and 0.001 μm (aquamarine circles). Slope = 1/ τ_{max}.



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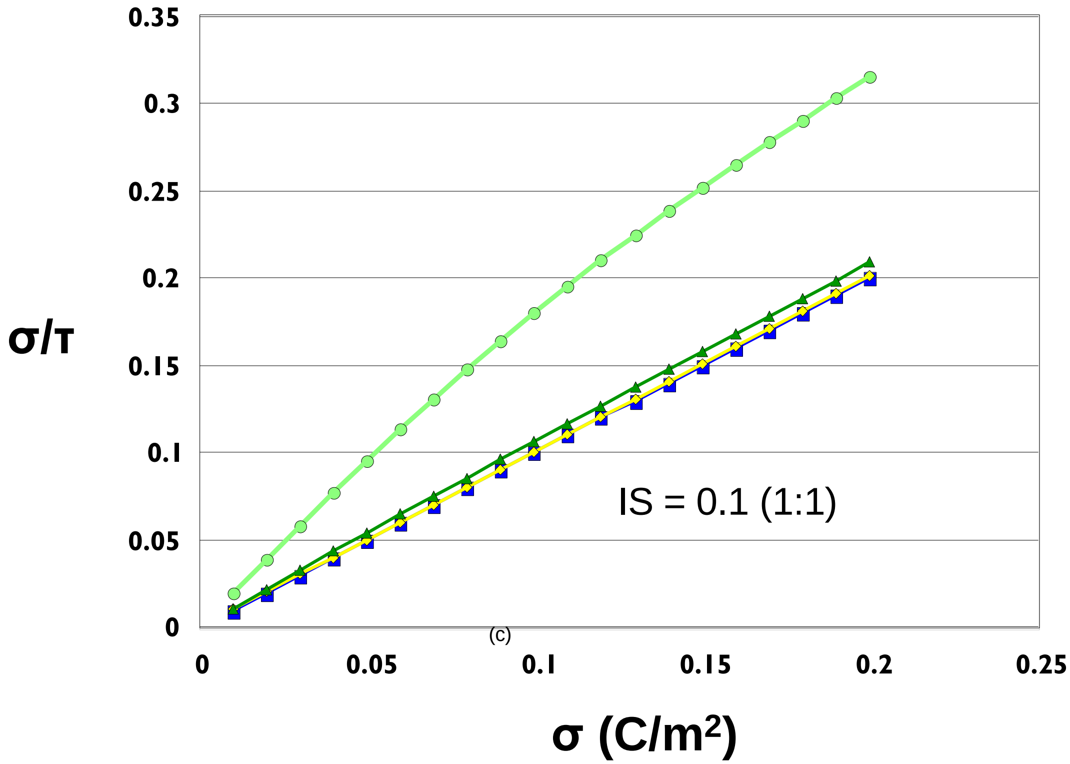

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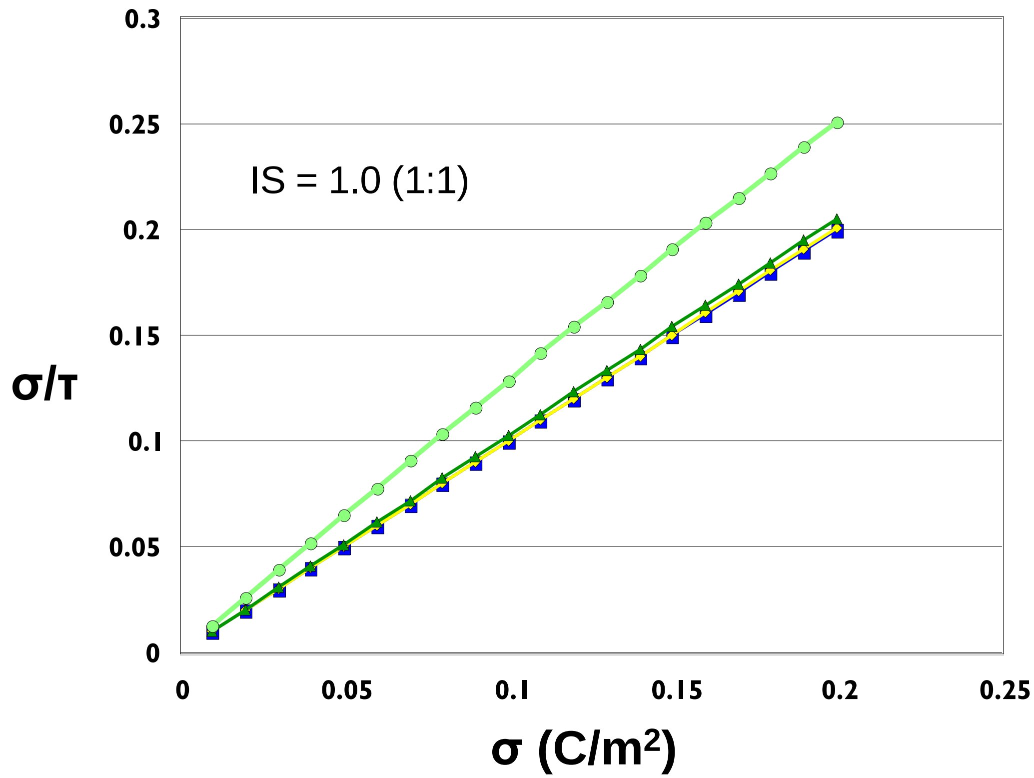

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$\log_{10}(IS)$	Estimates of τ_{max}			
	r_{pcl} = 1 µm	r_{pcl} = 0.1 µm	r_{pcl} = 0.01 µm	r_{pcl} = 0.001 µm
-3	0.9996	0.9955	0.9640	~0.4
-2	0.9996	0.9956	0.9569	~0.5
-1	0.9996	0.9963	0.9629	~0.6
0	0.9998	0.9977	0.9774	0.7990

$\Delta G_{charging} < 0.1e\Psi$
$\Delta G_{charging} > 0.1\ e\Psi$

Conclusions

- *In both the present approach and the DHLL, the principal excess free energy term is an ionic-strength-dependent charging energy term.*
- *The historical mass action expression is supported in systems where $r_{pcl} \geq 0.1$ um and IS ≥ 0.001 M (1:1).*
- *At high σ, the historical expression is supported when $r_{pcl} \geq 0.01$ um and IS ≥ 0.001 M (1:1).*
- *Charging energies are predicted to be significant in all situations where $r_{pcl} \approx 0.001$ um (i.e., charged bound sites are predicted to display non-ideal behavior).*

How significant will be the red term with smaller particles in intermediate charge density situations?

$$\Psi_d = \frac{(1-\tau)Q_p}{4\pi\varepsilon r_{pcl}} - \frac{(1-\tau)Q_p}{4\pi\varepsilon(r_{pcl} + 1/\kappa)}$$

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Specifically:

$$\ln(\gamma) = +(1-\tau)(\pm 2eQ_p+e^2)/(r_{pcl}+1/\kappa)8\pi\varepsilon kT - (1-\tau)(\pm 2eQ_p+e^2)/r_{pcl}8\pi\varepsilon kT$$

??????