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Issues in Assessing the Fate of Manufactured Nanomaterials in Porous Media

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Acknowledgments

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Peter Hatto, Co-chair of the OECD Steering Group 4 Section 1 Working Party
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Disclaimer

Although this work was reviewed by EPA and approved for presentation, it may not necessarily represent official Agency policy.

For purposes of this discussion, a manufactured nanomaterial (MN) is any particle, substance, or material that has been engineered to have one or more dimensions in the nanoscale and that takes advantage of properties at the nanoscale. The nanoscale refers to dimensions typically in the size range of 1 to 100 nanometers.

MNs can be viewed as soluble, insoluble and sparingly soluble:

- Soluble MNs can be treated as any other compound with respect to their aquatic and toxicological properties.
- Insoluble MNs will potentially migrate as aqueous suspensions— many research (including toxicological) issues involved.
- Sparingly soluble MNs also should be assessed as to whether they generate aqueous toxicant concentrations in excess of toxicological guidelines.

Overlap between OECD 100 and EPA 830 series test guidelines:

OECD	EPA
102 Melting Point/Melting Range	830.7200
113 Thermal Stability	830.6317, .6320
109 Density of Liquids and Solids	830.7300
101 UV-VIS Absorption Spectra	830.7050
104 Vapour Pressure	830.7950
105 Water Solubility	830.7840, .7860
107 K_{ow}, Shake Flask Method	830.7550
110 Pcl.Size Dist./Fibre Length/Diam.	830.7520
112 Dissociation Constants in Water	830.7370
117 K_{ow}, HPLC Method	830.7840, .7860
123 K_{ow}, Slow-Stirring method	830.7840, .7860
103 Boiling Point	830.7220
114 Viscosity of Liquids	830.7100

Recommended new test guidelines:

Guideline	Purpose	Procedures
Specific surface area	Toxicity	BET available
Ψ_{zeta} & Hamaker const.	Aggregation	Available
Surface charge	Toxicity	Available
Catalytic properties	Toxicity	Need development
Comp., purity, etc.	Composition	Already addressed???
Aggreg/agglom	Tox - F&T	Can be developed
Crystalline phase	Tox - F&T	Available
Dustiness	Atm. Transport	Available?
Fat solubility	Toxicity	OECD proc. Available?
Grain size, shape, etc.	Toxicity	Can be developed
Surface chemistry	Tox. - F&T	Research issue
Water solub./dispersivity	F&T	Need development
Surface tension	F&T	Available
Abiotic hydrol./photodeg.	F&T	Need development

Insufficient information exists for estimating the likelihood that metal oxide nanomaterials will adsorb (or stick) to immobile surfaces when introduced into aquifers.

Sufficient information does exist however to perform a preliminary assessment of whether these products are likely to self-aggregate in natural waters.

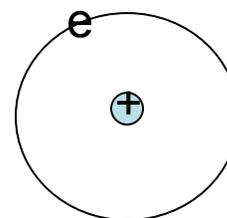
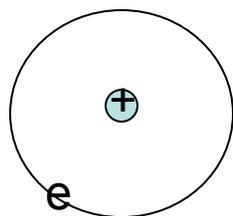
The principle assumption in this work is that nanomaterial aggregates are less likely than individual particles to migrate in aquifers.

Derjaguin-Landau-Verwey-Overbeek (DLVO) Theory of Colloidal Particle Stability

According to DLVO theory, particles in water possess a net electrostatic charge due to among other things, the adsorption of ions from solution. Associated with this net electrostatic charge is an electrostatic potential. Two similarly charged particles in water will experience a net electrostatic repulsive force and tend to remain separated.

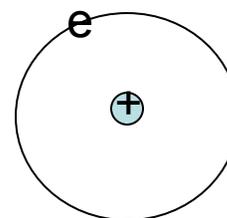
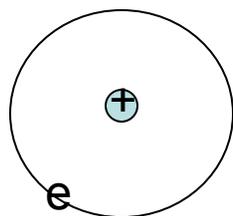
In contrast, if two particles are brought closely enough together, attractive forces from London/Van der Waals/Keesom forces will overwhelm the repulsive forces and the particles will stick together.

Origin of the attractive interactions



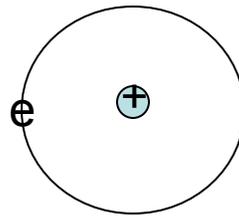
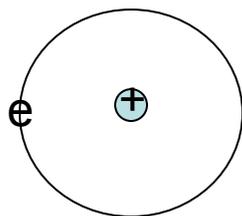
When two atoms are far apart (> 100 nm), the electrons are uncorrelated.

Origin of the attractive interactions



When two atoms are far apart (>100 nm), the electrons are uncorrelated.

When two atoms are close together (i.e., < 10 - 100 nm), the electron motions become correlated and induced dipole attractions are observed.



The same holds for assemblages of atoms...

The DLVO total energy of interaction between two particles in water is:

$$\Delta G_{\text{total}} = \Delta G_{\text{repulsion}} + \Delta G_{\text{attraction}}$$

According to Shaw (1992), expressions for estimating these two energy terms are:

$$\Delta G_{\text{attraction}} = -H \cdot r_{\text{pcl}} / 12X$$

$$\Delta G_{\text{repulsion}} = \frac{32\epsilon r_{\text{pcl}} k^2 T^2 \gamma^2}{z^2 e^2} \text{EXP}(-\kappa \cdot X)$$

H = Hamaker constant, X = distance between pcls.,
 $\gamma = (\text{EXP}(ze\Psi/2kT) - 1) / (\text{EXP}(ze\Psi/2kT) + 1)$

Under conditions where $\Delta G_{\text{total}} = 0$ and $d(\Delta G_{\text{total}})/dX = 0$, at room temperature one may arrive at (Shaw, 1992):

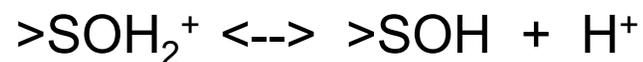
$$\text{CCC} = \frac{3.84\text{E-}39 \cdot \gamma^4}{H^2 z^6} \quad (\text{moles/dm}^3)$$

where CCC represents the Critical Coagulation Concentration (or minimum ionic strength needed to cause the particles to clump together).

In order to estimate the CCC, one needs values for the temperature (T), surface potential (Ψ), the Hamaker constant (H) and the valence of the counterion (z).

The source of the surface charge on metal oxide nanomaterials:

Metal oxide surfaces exposed to aqueous solution react with the hydronium ion via reactions of the following type (using the 2 pK model):

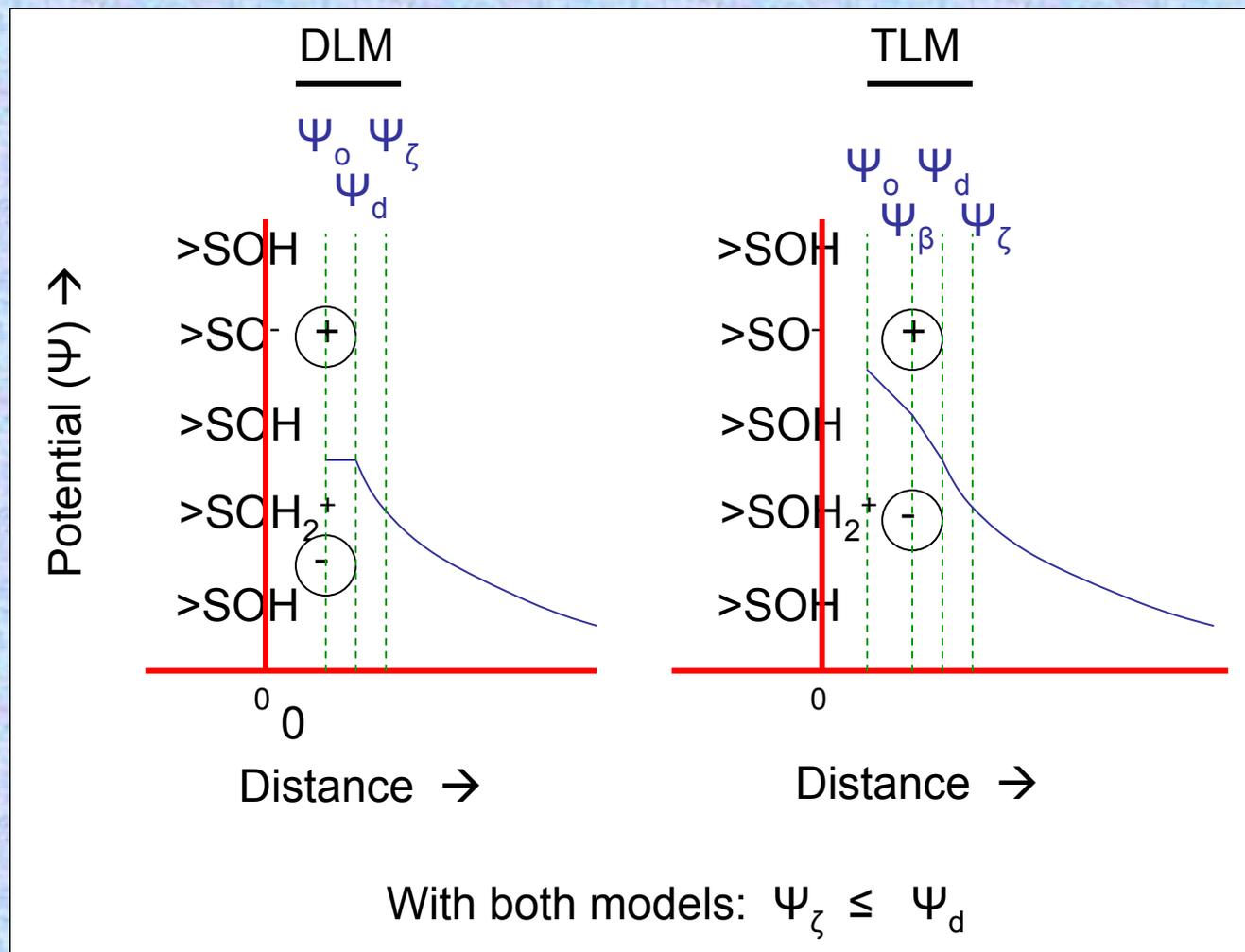


The corresponding mass action expressions describing these reactions are:

$$K_{a1} = \frac{[>SOH]a_{H^+} \text{EXP}(-e\Psi/kT)}{[>SOH_2^+]}$$

$$K_{a2} = \frac{[>SO^-]a_{H^+} \text{EXP}(-e\Psi/kT)}{[>SOH]}$$

Ψ_ζ and geo-chemical speciation modeling



Estimating the surface potential (Ψ) of nanomaterials in aqueous suspension

- * Nernst equation
- * Gouy Chapman relationship between charge density and Ψ
- * Approximate analytical solution published by Ohshima et al. (1986)

Nernst equation:

$$\Psi = (\text{pH}_{\text{zpc}} - \text{pH})2.303kT/e$$

where $2.303kT/e$ equals 59 mV at room T.

Taking derivatives:

$$\partial\Psi/\partial\text{pH} = \sim - 59 \text{ mV/pH unit at room T}$$

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However, derivatives of the negative logarithm of the K_{a1} expression yields:

$$\partial\Psi/\partial\text{pH} = (- 59 \text{ mV})\{1 - \partial[\log([\text{>SOH}]/[\text{>SOH}_2^+])]/\partial\text{pH}\}$$

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Gouy-Chapman planar solution to the Poisson Boltzmann equation:

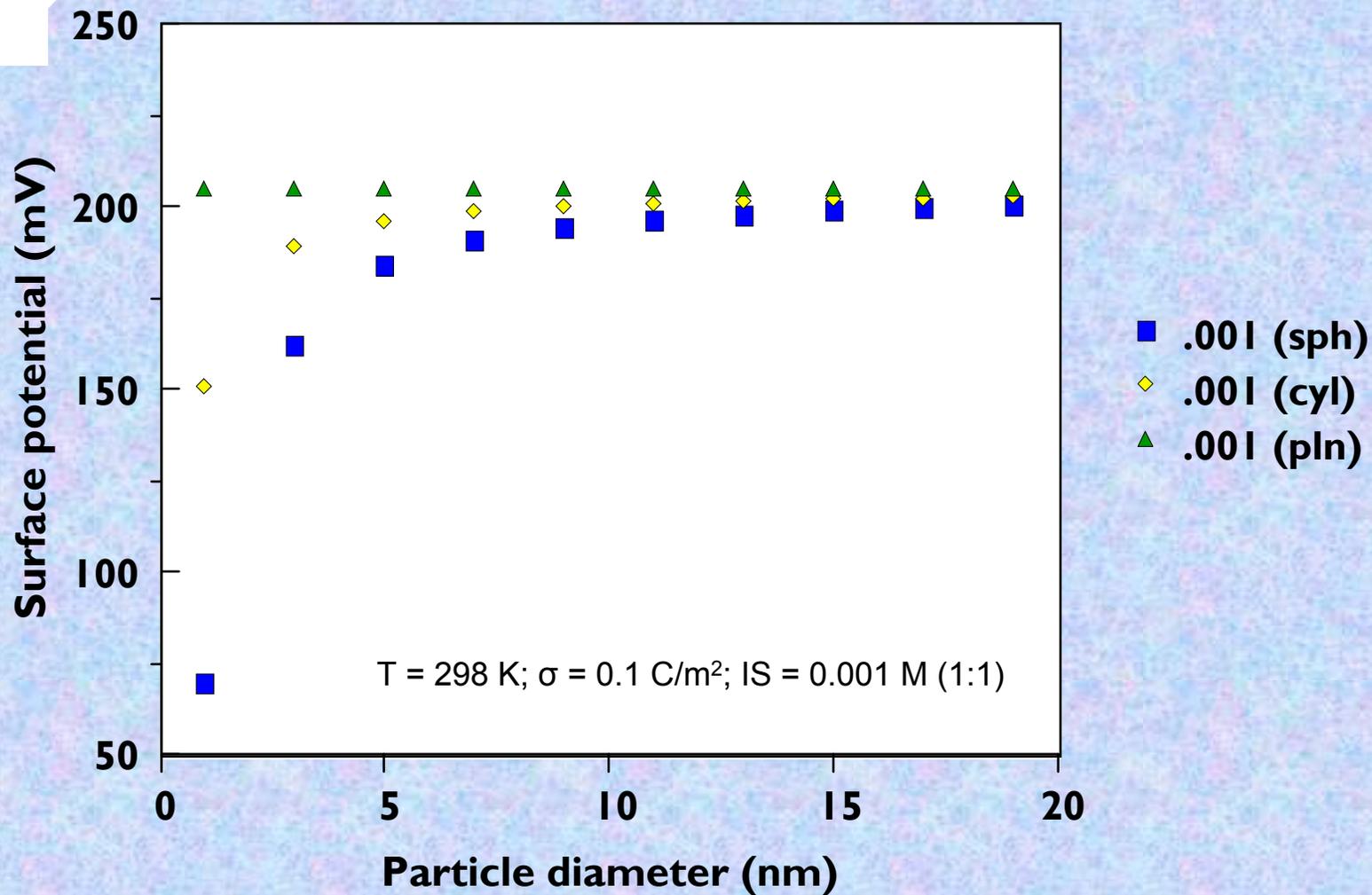
First estimate the charge density (C/m²):

$$\sigma = ([>\text{SOH}_2^+] - [>\text{SO}^-])F/(SC*SSA)$$

Then use the following analytical relationship:

$$\sigma = (8n_0\epsilon kT)^{1/2}\text{SINH}(ze\Psi/2kT)$$

As will be demonstrated, this relationship ignores radial effects and will overestimate the surface potential for spherical nanoparticles.



Legacy SCMs use the Gouy-Chapman planar solution to the P-B eqn; may overestimate potentials for smaller spheres and cylinders...

Estimating the surface potential (Ψ) of nanomaterials in aqueous suspension

- * ~~Nernst equation~~
- * ~~Gouy Chapman relationship between charge density and Ψ~~
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Ohshima et al (1986) spherical approximate analytical solution to the Poisson Boltzmann equation:

$$I = 2 * \text{SINH}(y_s/2) [1 + 2 / (A * \text{COSH}^2(y_s/4) + 8 * \ln(\text{COSH}(y_s/4)) / (A^2 * \text{SINH}^2(y_s/2)))]^{1/2}$$

$$I = - dy/d\varepsilon|_{\varepsilon=0} \quad y_s = e\Psi_s/kT$$

$$A = \kappa * r_{pcl} \quad \kappa = \text{recip. Debye length}$$

This relationship is rated as being accurate to within a few percent for a value of $\kappa * r_{pcl}$ as small as ≈ 0.1

Ionic Strength of Natural Waters

From the literature, the following values of the ionic strength of natural water were used in this work (Loux and Savage, 2008):

Rain water $1\text{E-}5$ to $5\text{E-}4$ M (Rothert, 1999; Sequeira, 1995)

Freshwater $5\text{E-}4$ to 0.1 M

Saline water 0.1 to 0.6 M

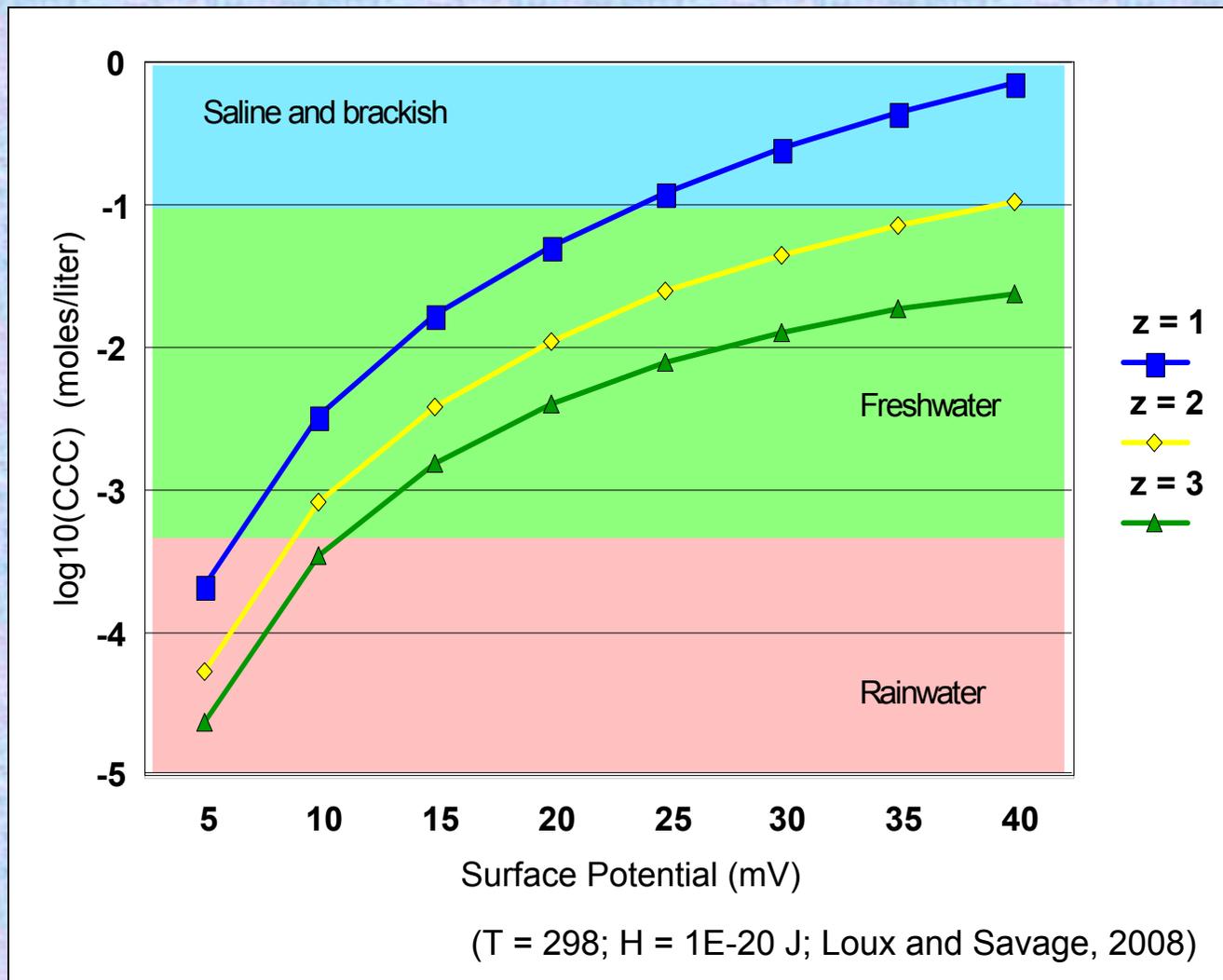
Marine water 0.6 to 1.0 M

Selected, literature-reported, non-retarded Hamaker constants (A_{121}) for metal oxides and biocolloids in water. (Loux and Savage, 2008)

Material	non-retarded Hamaker constants in H ₂ O	Reference
Al(OH) ₃	12.6E-20 J	Visser (1972)
SiO ₂	0.16E-20 J	Ackler et al. (1996)
Fe(OH) ₃	17.7, 20E-20 J	Visser (1972)
TiO ₂ (rutile)	6 ± 2E-20 J	Larson et al. (1993)
TiO ₂ (anatase)	2.5E-20	Visser (1972)
TiO ₂ (ave.)	5.35, 5.65E-20 J	Bergstrom (1997)
TiO ₂	~5.3E-20 J	Shibata et al. (2002)
ZnO	1.89, 2.24E-20 J	Bergstrom (1997)
biocolloids	3E-21 to 4E-20 J	Keller and Auset (2007)
OM coated hematite	4.6E-21 J	Mylon et al. (2004)

Some literature reported surface properties of metal oxides in water. Loux and Savage, 2008.

Metal Oxide	Ns (sites/nm ²)	pKa1	pKa2	Reference
TiO ₂ (rutile)	5-15.5	3.7	8.2	Koretsky (2000)
	10	3.7	8.2	Sverjensky & Sahai (1996)
TiO ₂ (anatase)		4.98	7.8	Schindler (1981)
am. silica	10	-1.1	8.1	Sverjensky & Sahai (1996)
silica	.06-.58			Huang (1981)
γ-Al ₂ O ₃	10	6.3	9.8	Sverjensky & Sahai (1996)
FeOOH (goethite)	8.7-20	7.5	10.2	Koretsky (2000)
"	10	7.5	10.2	Sverjensky & Sahai (1996)
ferrihydrite	10	7.5	10.2	Sverjensky & Sahai (1996)
"	2.31	7.29	8.93	Dzombak and Morel (1990)
ZnO	10	7.7	10.5	Sverjensky & Sahai (1996)

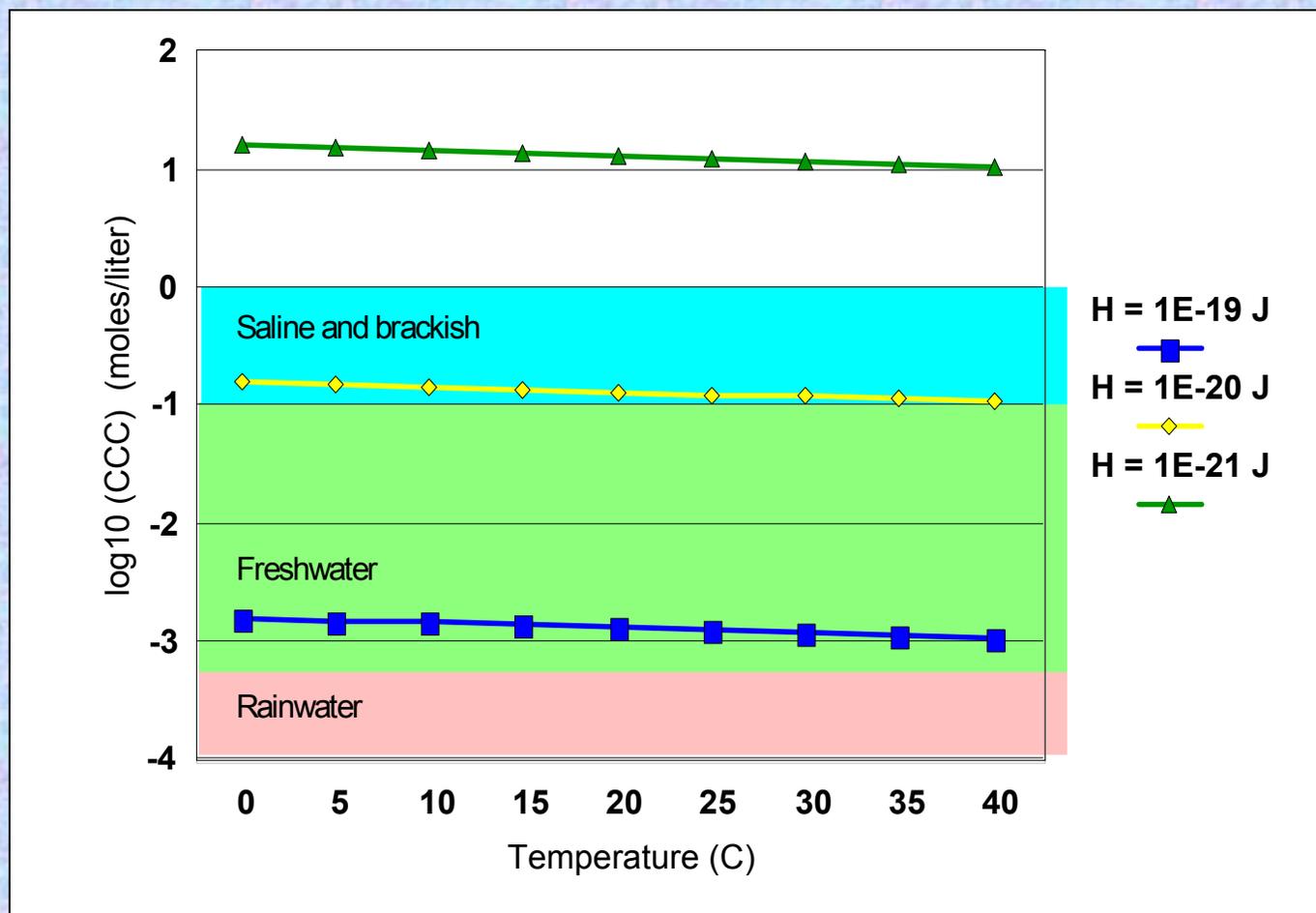


Loux and Anderson (2001) postulated that the absolute value of the surface potential of natural surfaces was likely to have a value less than kT/e (25 mV).

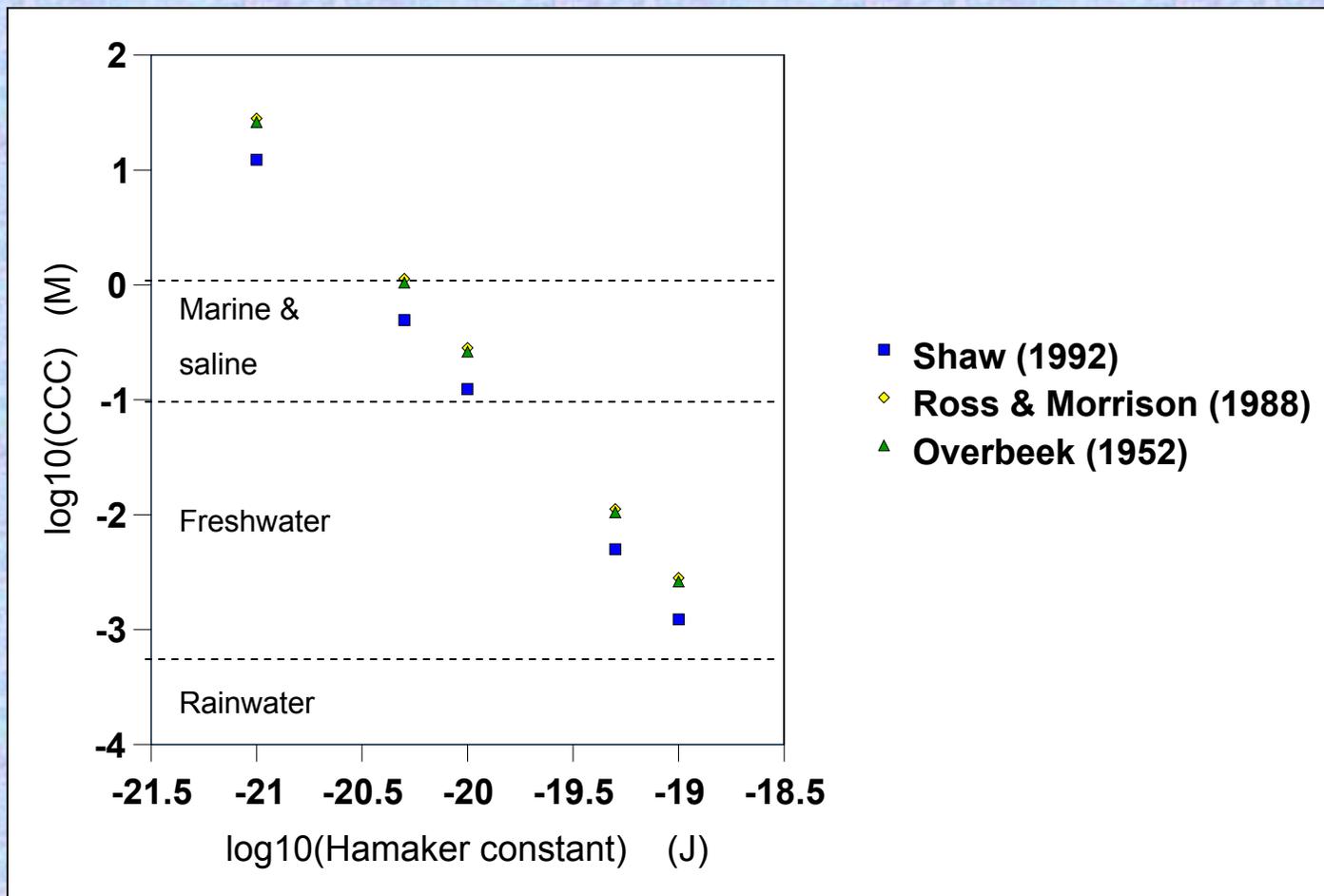
Literature-reported zeta potentials for environmental surfaces.

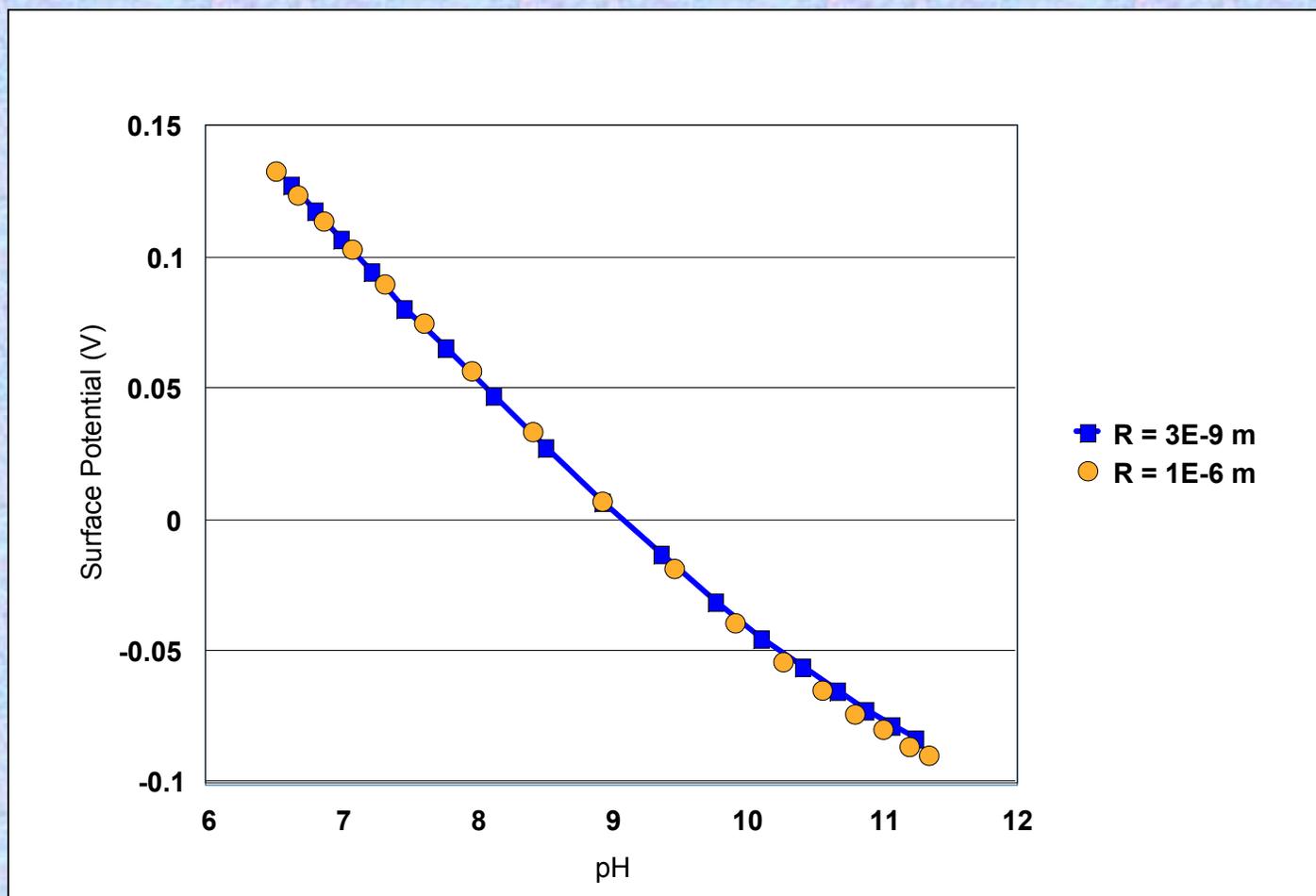
Zeta pot. (Ψ_{ζ} , mV)	Comments
-21.6 to -31.2	Uncontaminated aquifer sediments (Bunn et al., 2002)
-21.3 to -35.4	Uncontaminated aquifer colloids (Bunn et al., 2002)
-23.7 to -34.9	Contaminated aquifer sediments (Bunn et al., 2002)
-20.3 to -25.5	Contaminated aquifer colloids (Bunn et al., 2002)
-16.5 to -22.5	Soil colloids (Sequaris and Lewandowski, 2003)
$\sim +0.62$ to -24.2	Soil colloids, $20^{\circ} \pm 0.5$ C, pH = 6.5, 0.35 mM CaCl ₂ (Kjaergard et al. 2004)
-25 to -42	Kaolinite, pH range 3-11 (Yukselen and Kaya, 2004)
-10 to -15	Colloidal particles in rain (Malyshev et al., 1994)

(Loux and Savage, 2008)

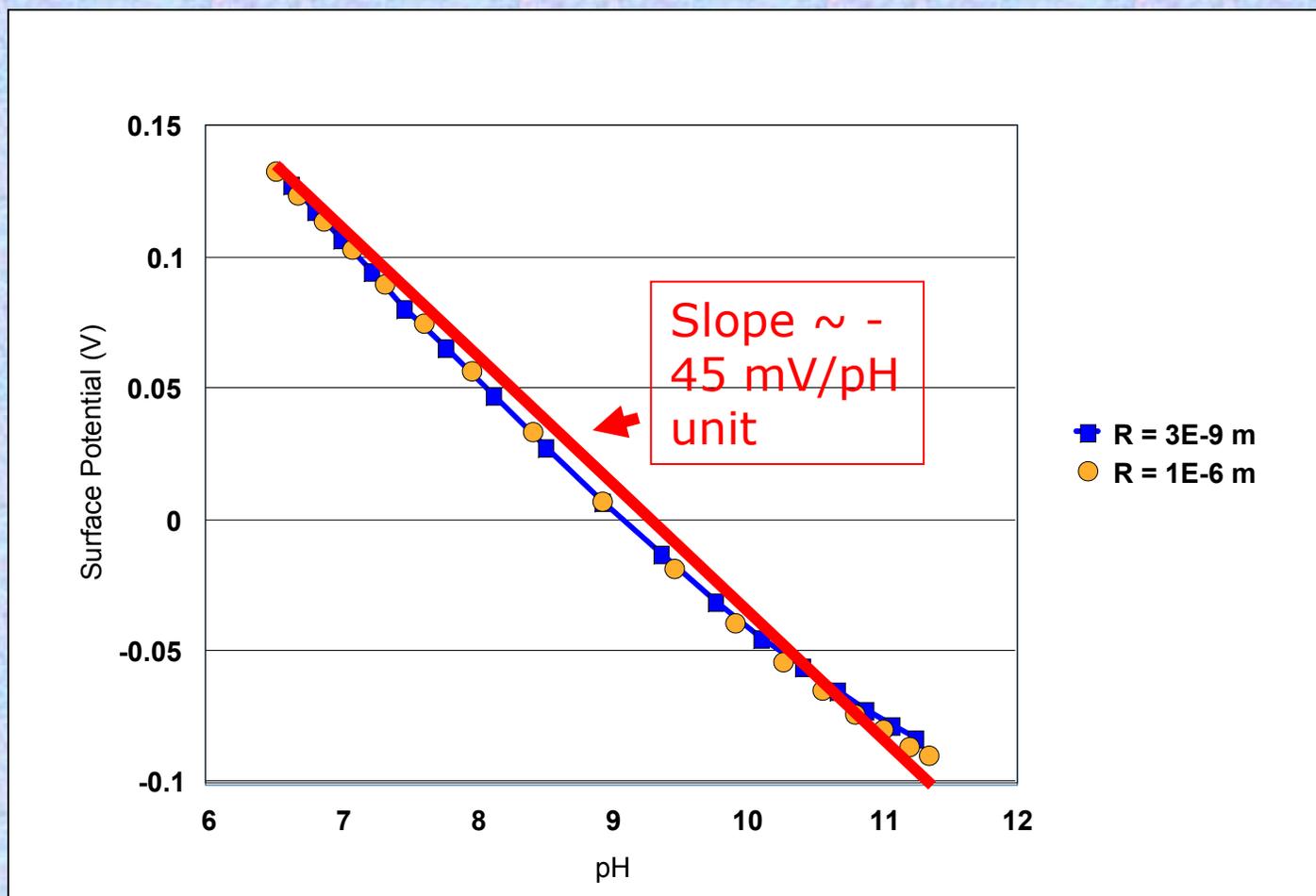


Estimated Critical Coagulation Concentration (moles/l) as a function of system T and Hamaker constant. $|\Psi_0| = 25 \text{ mV}$; $z = 1$. (Shaw, 1992). Loux and Savage, 2008.

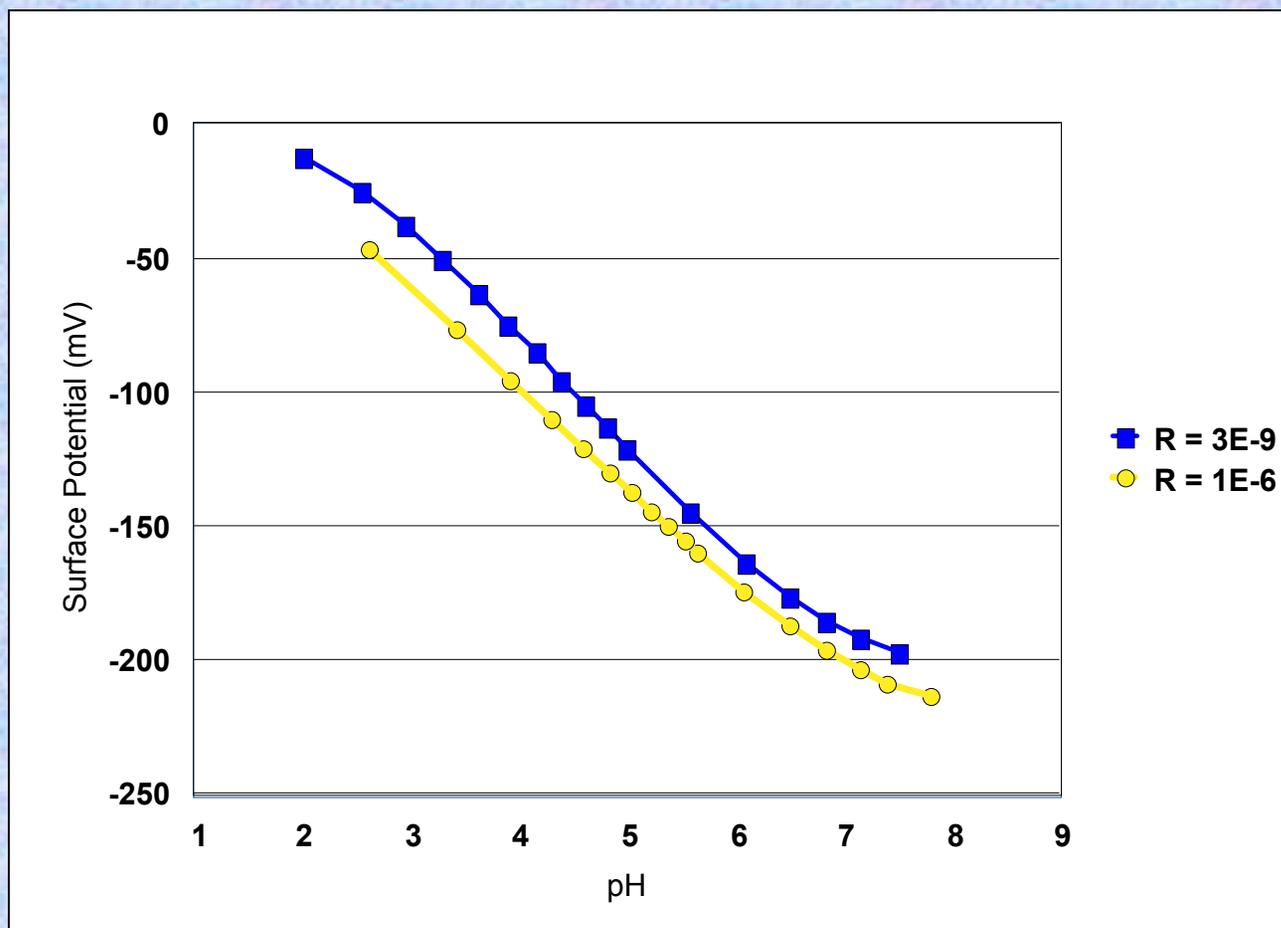




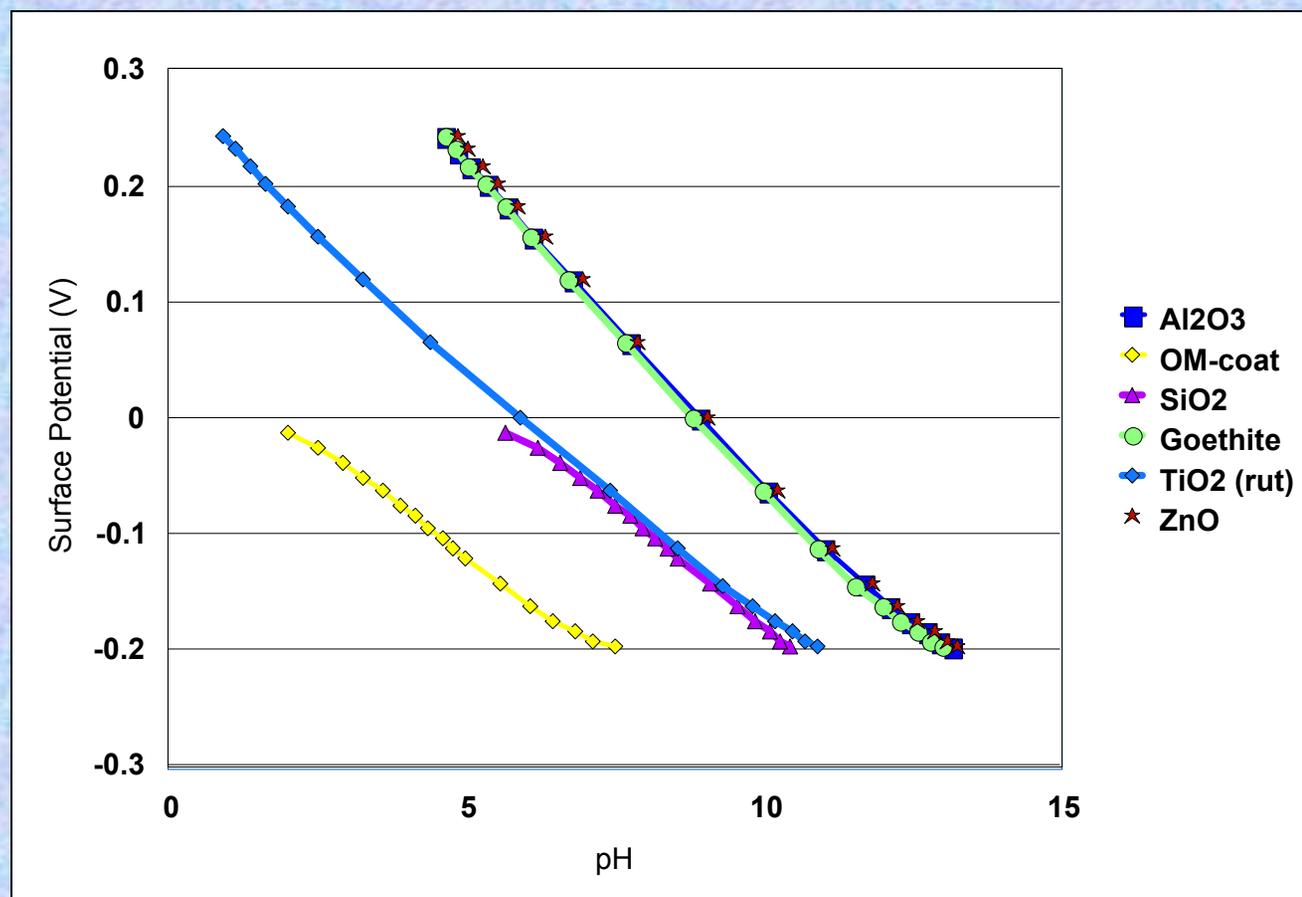
Surface potential as a function of pH for an Al_2O_3 substrate (gibbsite). $T = 298^\circ \text{K}$, $IS = 0.1 \text{ M (1:1)}$, $r_{pcl} = 3\text{E-}9$ and $1\text{E-}6 \text{ m}$, $pK_{a1} = 7.5$, $pK_{a2} = 10.4$, $\text{Sigmax} = 1.6 \text{ C/m}^2$. Loux and Savage, 2008.

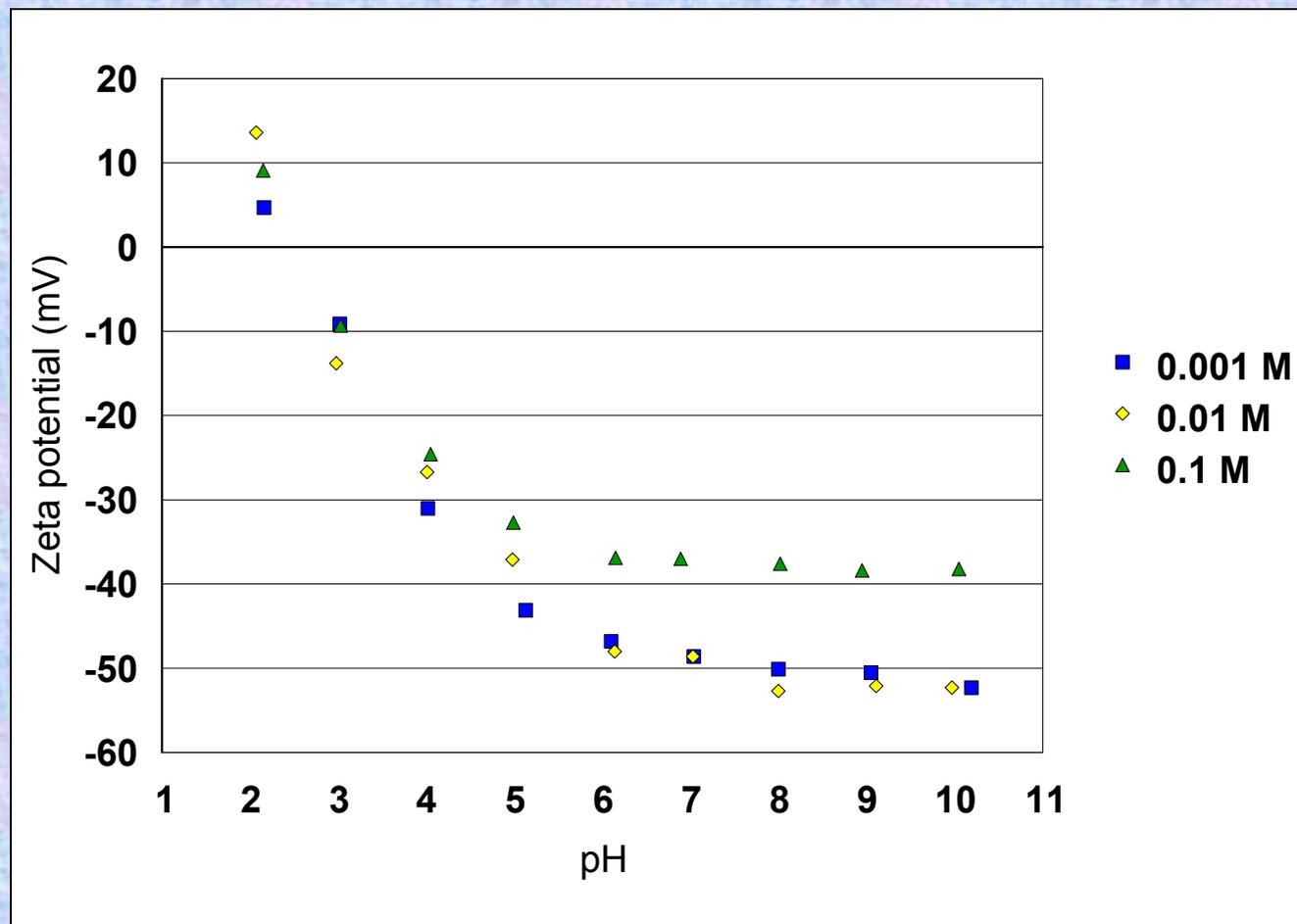


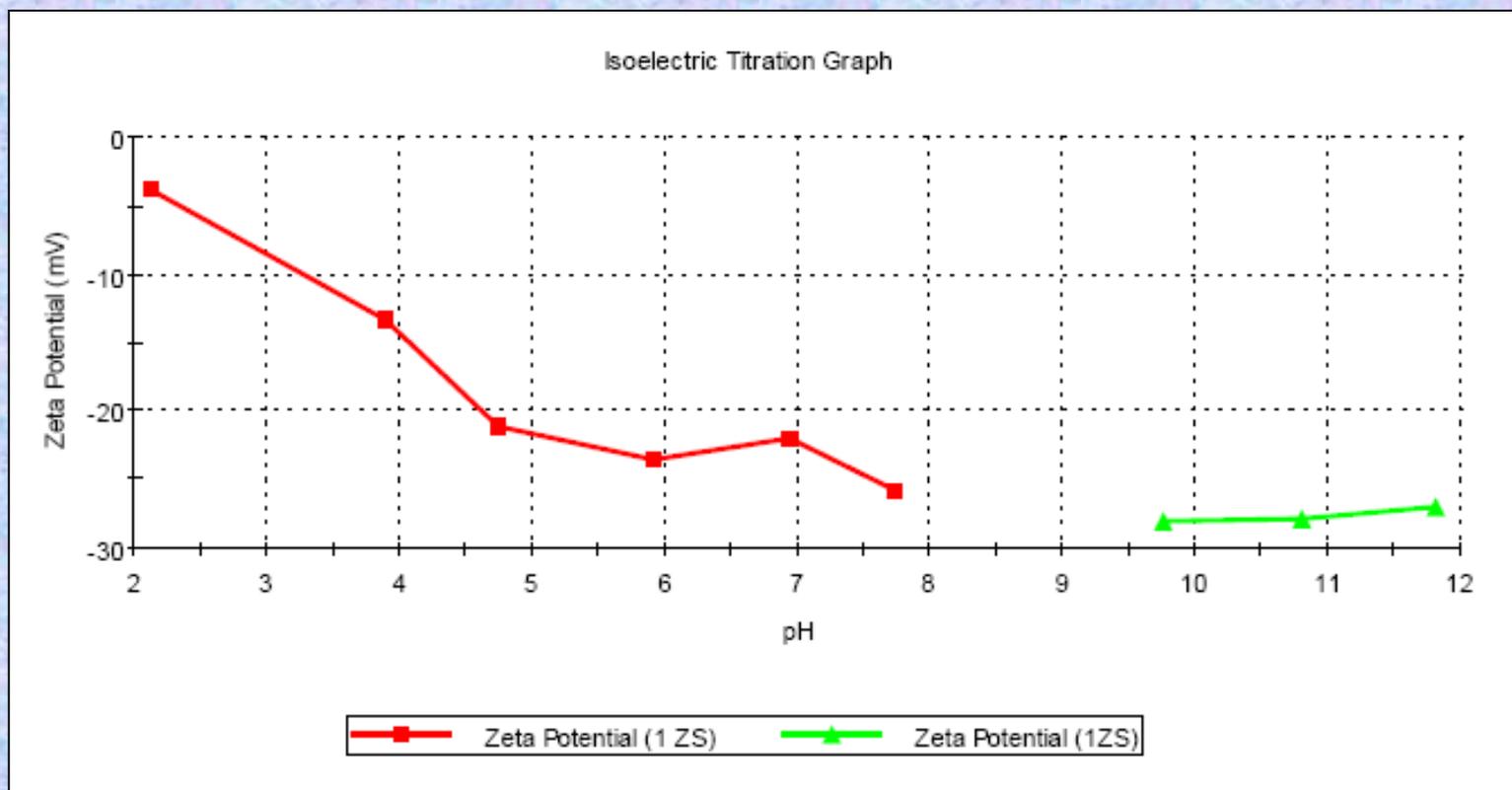
Surface potential as a function of pH for an Al_2O_3 substrate (gibbsite). $T = 298^\circ \text{K}$, $I_S = 0.1 \text{ M (1:1)}$, $r_{\text{pcl}} = 3\text{E-}9$ and $1\text{E-}6 \text{ m}$, $\text{pK}_{a1} = 7.5$, $\text{pK}_{a2} = 10.4$, $\text{Sigma}_{\text{max}} = 1.6 \text{ C/m}^2$. Loux and Savage, 2008.



Ψ_0 as a function of pH for an organic matter coated substrate. $T = 298^\circ \text{K}$, $IS = 0.001 \text{ M}$ (1:1), $r_{pcl} = 3E-9$ and $1E-6 \text{ m}$, $pK_a = 3.5$, assumed monoprotic behavior, $\sigma_{max} = 0.192 \text{ C/m}^2$, organic matter properties from Gustafsson (2001). (Loux and Savage, 2008).







Spectrum of acidity constants reported on single walled carbon nanotubes with and without oxidation (Hemraj-Benny *et al.* (2008).

	pK (mmol/g)	pK (mmol/g)	pK (mmol/g)
Pristine	5.9 (0.087)	8.5 (0.067)	
Ozone-treated	5.7 (0.097)	8.8 (0.043)	10.4 (0.138)
Ozone/H ₂ O ₂	5.1 (0.125)	6.9 (0.038)	9.5 (0.164)

Presumably carbon nanotubes also possess carboxyl and hydroxyl groups that can engender pH-dependent surface charge densities and potentials.

Do colloids aggregate in environmental systems?



Fe^{++} is released from the oxidation of iron sulfide minerals. In turn, this Fe^{++} is oxidized to Fe^{+++} and subsequently precipitates as $\text{Fe}(\text{OH})_3$. When $\text{Fe}(\text{OH})_3$ is precipitated, it passes through a nanoparticle size range.

Coatings of iron oxide, manganese oxide and aluminum oxide have been observed in the sediments of streams in the US.

Mechanistic estimates of the surface (and zeta) potentials of commercial nanomaterials in aquatic media can be obtained using geochemical speciation modeling...

While empirical laboratory zeta potential measurements will be very useful, these measurements should:

- 1) Be conducted in simulated environmental aquatic media.
- 2) Not be extrapolated to diverse environmental aquatic media unless one has a sound mechanistic understanding of what is going on.