

The Pennsylvania State University
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**ELECTROPHORETIC DEPOSITION:
FUNDAMENTALS, MECHANISMS AND EXAMPLES
WITH AN IN DEPTH EXAMINATION OF THE
ION DEPLETION EFFECT**

A Thesis in
Materials Science and Engineering
by
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ABSTRACT

The research and analysis for this thesis have been directed toward two major goals: to better understand the process of electrophoretic deposition (EPD) and to demonstrate its utility. This is also the order in which these two topics are addressed in the writing of this thesis.

In order to define the limits of the problem, the first chapter is devoted to a description and definition of what is, and is not, EPD. Here EPD is defined as consisting of three steps. The first is the creation of a charge balanced suspension of electrostatically charged particles in a solvent where some mechanism acts to keep the particles from floccing together during the time necessary to perform EPD. The second step is to create and maintain a DC electric field within the bulk of the solvent causing the electrostatically charged particles to move by electrophoresis toward an electrode. The final step is then to induce a change the nature of the suspension next to the electrode so that particles come into contact with each other and form a rigid deposition.

Chapter 2 then gives an outline of the scientific background necessary for understanding each of the three steps defined in Chapter 1. In order to make the complexity of the EPD system intellectually manageable, it is broken down into three components; solvent, particles, and electric field. Even though the scientific literature specifically on EPD is relatively modest, the literature on the binary interactions between each of these components (solvent-electric field, solvent-particle, etc.) is both extensive and elucidating. Previous reviews on EPD have concentrated almost exclusively on solvent-particle interactions. This thesis shows the vital importance of electrochemical reactions at the deposition electrode in understanding the mechanisms of deposition.

This approach also allows the categorization of mechanisms of EPD already demonstrated in the literature as well as the prediction of new mechanisms not previously demonstrated. To do this a list of mechanisms to prevent particles from floccing in the bulk suspension is compared to a list of effects that can be induced in the suspension at the deposition electrode. The list of specific near-electrode effects that can cause particles from specific types of suspensions to floc or coagulate at the electrode then becomes a list of the possible mechanisms of EPD. One of the most interesting of these mechanisms, ion depleted enhanced - automatic leveling deposition, was chosen for in-depth analysis.

The first step in this analysis is to obtain a complete understanding of the suspension from which the particles are to be deposited. This is done in Chapter 3 for alumina powder in ethanol with added HCl. Here it is shown that in the absence of dissolved ions alumina develops a significant positive surface charge in ethanol by the dissociative adsorption of ethanol molecules to the surface and the preferential desorption of ethoxide ions from the surface. The addition of HCl leads to a large rise in surface charge due initially to the reduction in ethoxide activity. After this initial rise the surface charge is set by a competitive adsorption equilibrium of chloride and ethoxide ions to positive surface sites on the powder.

Chapter 4 is then devoted to analyzing the deposition of alumina from this system. The first part of this chapter is detailed analysis of the conduction layer next to the cathode, the deposition electrode for the positively charged particles. The development of ionic and charge gradients, and the inevitability of a transition to convective transport at the electrode is shown for the electrolyte in the absence of particles. It is then shown that the dramatic change in conduction behavior in the presence of particles can be accounted for by the stabilization of an ion depleted, unbalanced charge conduction layer. Extremely high voltage gradients in this layer then exert a strong consolidating force on the positively charged alumina particles, compacting them into a densely packed deposited layer. This high gradient also leads to a strong equilibrating force to maintain a uniform thickness of the compact deposited layer, the automatic leveling effect.

The second objective here has been to demonstrate the potential utility of EPD in addressing current problems in the manufacture of electroceramic devices. This is undertaken in Chapter 5 with a complete description of the process to form suspensions, deposit particles, process these depositions into final form and to characterize the component created. The direct electrostatic deposition of silver/palladium powder is used to demonstrate the ability of EPD to create both very thin layers and very narrow conductor lines that can be measured on the scale of the particles used to create them. The electrophoretic deposition of PZT is used to demonstrate the formation of an intermediate thickness film with well controlled stoichiometry.

In the final chapter the thesis concludes with a discussion of what still needs to be done to advance the understanding and application of EPD.

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Introduction to the On-Line Version 2009

When I finished this thesis in early 2004 I regarded it as the best scientific introduction to EPD at the time, and to my knowledge it still is.

However, even though I thought it would be very helpful to people first exploring EPD, I have been slow in posting it to the web. This is due in part to having little time to revisit the thesis, but in larger part due to my dissatisfaction with the completeness of explanation it offered. I continued to see effects in my own work and in the work of others which were not covered by the theories presented in the thesis. It gradually became clear to me that to understand the results of the wide variety of experiments that have been reported under the heading of EPD, it is vital to understand the behavior of colloids which are neither fully dispersed nor rigidly deposited.

In my thesis I adopted a fairly strict definition of EPD. This definition requires that the system begin as a stable dispersion of particles which can move independently, and that the end result be a rigid deposit of particles contacting each other at their primary minimum. It was not a conscious decision at the time, but by adopting this definition I was able to avoid making explicit two very significant assumptions.

The first of these assumptions regards dispersion. In the thesis section on dispersion I listed the standard methods for keeping particles far enough apart that they are not pulled together irreversibly by the London-van der Waals force. The implicit assumption was that if the attractive energy between two particles was less than a small multiple of the thermal energy of the solvent, Brownian motion would be sufficient to assure that the particles do not become irreversibly attached to each other, and the particles could therefore be considered to move independently. However, as the volume fraction of particles in suspension rises, the interaction between particles changes from simple two particle interactions to multiparticle interactions where crowding and momentum transfers become significant. At the extreme, particles can pack together to the point that the suspension becomes a pseudoplastic solid. These particles are not deposited, the energy barrier between them is not overcome, and with an adequate volume of solvent they will spontaneously diffuse apart. These particles technically remain dispersed - that is all of the particles are separated by a layer of solvent - even while the dispersion behaves as a solid.

The second implicit assumption is that if the barrier between the particles does not keep them far enough apart, the L-vdW force will inexorably pull the particles into contact at their primary minimum, a contact that is rigid and brittle. However in some cases the interaction between the solvent and the surface is stronger than the attraction between the particles. A layer of solvent then remains between the particles. In this case, even though the particles are bound together by the L-vdW force, the contact between the particles is lubricated. The particles are able to rotate and slide past each other. At high volume fractions they will form a solid capable of large plastic deformation without losing cohesion (i.e. without cracking). At low volume fractions they can form a gel which does not sediment or phase separate but which flows at such a low applied shear force that it can be mistaken for a fully dispersed colloid.

So what is needed to complete the scientific background necessary for understanding EPD? It is the science necessary to describe the behavior of these “Condensed Colloids”, colloids with a particulate volume fraction generally greater than 30% and with non-Newtonian shear behavior.

The first step in explaining these colloids is to extend the discussion of the van der Waals forces to include quantitative approximations. A quantitative understanding is vital because the behavior of these colloids depends not just on the nature of these forces but on the ratios of these forces on the angstrom to nanometer scale.

This then leads into a discussion of the solvent/particle interface. The Keesom and Debye vdW forces at a solid interface can alter the structure of a solvent. In polar solvents, this alteration can be so significant that the nanometer of solvent at the interface will have significantly different properties from the bulk solvent. These solvent/solid interactions have been most extensively considered in the literature of wetting, but the focus needed here is primarily on wetting considered on the nanoscopic scale.

The next step is to consider how this altered solvent layer reacts as two particles come together. This should be divided into three cases: when the solvent is completely squeezed out of the contact point, when a monolayer of solvent remains and when the system is stable with a layer several molecules thick. If the solvent is completely removed, the dry contact points between the particles will have mechanical properties approaching those of the material making up the particles. If a monolayer of solvent remains, the

contact point will be much weaker and particles will be better able to roll and possibly slide past each other. If several molecular layers remain between the particles at the contact point, the contact will be lubricated allowing the particles to easily roll and slide past each other while also providing an elastic connection between the particles.

The micromechanics of the contact point between particles then needs to be translated into the mechanical behavior of the colloid. Since the usual objective of EPD is to maximize the consolidation of the particles, we are most interested in the compressive strength of the particulate component of the colloid. However, this property is rarely measured. Shear strength is more easily and far more often measured for colloids, therefore it would be more useful if a connection between shear and compressive strengths could be drawn.

The compliment to the compressive strength of the particulate component of a colloid is the compressive force acting on those particles. In EPD the particles move independently. Their migration in an electric field toward the deposition electrode is well described by straightforward and well-tested electrokinetic theories. In a condensed colloid, the particles by definition do not move independently. Electrokinetic effects chain up to act on multiple particles which also act mechanically on each other. The high viscosity of the condensed colloid will stabilize the solvent against large scale convection. This allows ionic concentration gradients to develop, modifying electric fields and osmotic pressures.

It is because the consolidation of condensed colloids is so fundamentally different from EPD that it should be separated from EPD and referred to as either electrophoretic consolidation (EPC) or simply electrocasting. However, because many processes are a combination of EPD and EPC and because even processes which are purely electrocasting have been identified in the literature as EPD, it is not possible to fully understand EPD without understanding EPC as well.

Finally, there is the subject of drying. It is rare for EPD or EPC to produce a fully dense deposit prior to drying. If a low density, rigid deposition is formed, $\approx 30\text{vol}\%$, it will almost inevitably crack during drying. If a high density, rigid deposit is formed, 40-50vol%, cracking can frequently be avoided. However, the highest density coatings are formed when the particles are not rigidly deposited. It occurs when the particles are

consolidated on the deposition electrode in a solvated pseudoplastic slurry. This condensed colloidal slurry has enough shear strength to allow it to be removed from the deposition apparatus, but the particles are still able to re-arrange during drying, achieving near theoretical maximum random packing density. However, this is not a panacea. If the shear yield strength of the drying deposit is too high in relation to the crack initiation and propagation energy, the coating will achieve high density as a collection of cracked flakes.

EPD and EPC are surprisingly complex phenomena. Understanding all of the phenomena exhibited by experiments in this field requires an understanding of phenomena in a wide variety of scientific subject areas. As time allows, I will elaborate on the topics above and more, both on this site and through additional journal publications. The long term goal is a complete introduction to the relevant existing science. This will firstly promote novel, clearly designed experiments focused on gaps in understanding, and secondly, provide those tasked with developing new EPD/EPC systems a logical basis for designing and improving processes.

Jonathan Van Tassel, 2009

Symbols used in Chapter 2Abbreviations

DEBL	Diffuse electrostatic boundary layer
EHD	Electrohydrodynamic
EPD	Electrophoretic deposition
RHE	Reversible hydrogen electrode
P-B	Poisson-Boltzmann
P-P	Polymer - Polymer
P-S	Polymer - Solvent

Latin Symbols

A_{131}	Hamaker constant for two surfaces 1 separated by a medium 3.
a	Particle radius (m)
c	Molar concentration of dissolved salt (gram mol equivalent/dm ³)
C_{∞}	Characteristic ratio for polymer chain flexibility
D	Diffusion coefficient ()
e	Elementary charge (1.602E-19 C)
E	Electric field (V/m)
\mathbf{E}	Reduced electrophoretic mobility (non-dimensional)
F	Faraday constant (96,534 C/mol)
F	Force (N)
g	Gravitational acceleration (9.8 m/s ²)
h°	Planck constant (6.63x10 ⁻³⁴ J•s)
h	Surface to surface separation distance (m)
h	Height in a sedimenting suspension (m)
J_o	Flocculation rate (s ⁻¹)
k	Boltzman Constant (1.381x10 ⁻²³ J/K)
k_o	Chemical reaction rate constant
K	Chemical equilibrium rate constant
l	Number of particles in an agglomerate or floc
l_o	Length per polymer repeat unit
m	Number of particles in an agglomerate or floc
m_o	Weight per polymer repeat unit
n	Refractive index
n	Number of repeat units in a polymer chain
n_i	Number density of ion i (m ⁻³)
n_{iref}	n_i at $\psi = 0$
P	Pressure (Pa)
q	Surface charge density (C/m ²)
Q	Total surface charge on a particle (C)
r	Center to center particle separation distance
$\langle r^2 \rangle^{\frac{1}{2}}$	Root mean square (rms) end to end length of a polymer chain
T	Temperature (K)

t_c	Characteristic time for doublet formation (s)
u_E	Particle electrophoretic mobility ($\mu\text{m}\cdot\text{cm}/\text{V}\cdot\text{s}$)
u	Convective velocity (m/s)
u_o	Convective velocity (m/s)
y	Reduced particle potential at shear layer (non-dimensional)
z	Ion valence with sign \pm

Greek Symbols

α	Transfer coefficient for electrochemical reactions at a surface
α	Intermolecular expansion factor for dissolved polymer
ϵ_o	Permittivity of free space ($8.854\text{E}-12 \text{ C}^2/\text{J}\cdot\text{m}$)
ϵ_r	Relative dielectric constant
ζ	Particle Potential at Shear Layer (mV)
μ	Solvent Viscosity (Poise)
η	Overpotential necessary to drive electrochemical reactions at a finite rate (V)
κ	Inverse Debye length (m^{-1})
κ	Solvent Conductivity
ν	Ion electrophoretic mobility
ν_e	Infrared cut-off frequency
ρ_∞	Number density of dissociated molecules of a binary salt in bulk solution (m^{-3})
τ	Polymer bond angle
ϕ	Electrostatic potential (V)
ϕ^o	Standard electrostatic potential relative to RHE (V)
Φ	Particle volume fraction
Φ	Particle interaction energy (kT)
ψ	Rational electrostatic potential (V)

Chapter 2

Mechanisms of Deposition

2.1 Introduction

As was stated in Ch. 1, electrophoretic deposition (EPD) can be broken down into three steps: 1) the formation of a stable, charged suspension; 2) electrophoretic transport of the particles to the deposition electrode; and 3) deposition. The theoretical basis for the first two steps has received considerable attention and these processes are fairly well understood. **(1,2,3)**

The third step, deposition, has been the subject of far fewer theoretical treatments and is still not well understood. This is in part due to the fact that there is no one single mechanism of deposition and in part due to this being a complex combination of colloidal chemistry and electrochemistry studied primarily by materials scientists. To make the complexity of this system more tractable, this chapter breaks down the system into three basic components. These components are then discussed first as binary interactions of each of the components before putting all three together to describe the various mechanisms of deposition that can occur in particular systems.

This analysis breaks an EPD system down into three fundamental components: the particles to be deposited, the suspending solvent, and the applied electric field. The binary interactions are then:

Solvent-Electric Field — An EPD cell is fundamentally a conducting electrochemical cell in which particle deposition occurs. This electrochemical conduction can dramatically change the composition of the solvent and the electric field gradients in the cell.

Particle-Solvent — A brief discussion of how particles develop an electrostatic charge in a solvent.

Particle-Electric Field — An electrostatically charged particle will experience a force in an electric field, however, the oppositely charged fluid around the particle will experience an equal and opposite electrostatic force. The particle and the fluid then move in opposite directions. The thickness of the charged layer of solvent around the particle determines its electrophoretic mobility.

Particle-Particle — Particles in a solvent will inevitably experience a London-Van der Waals (L-VdW) attraction. There must be some mechanism to counteract this attraction to keep the particles from floccing prior to deposition.

These phenomena are then all put together to examine what electrophoretic and electrochemical effects can be combined with which stabilization methods to allow the creation of an adherent deposition of the desired density.

Finally, some of the effects that can occur after deposition will be briefly discussed, both before and after the deposition voltage is turned off, as well as after removal of the deposition from the bath.

2.2 Conduction in a Fluid

The EPD cell is fundamentally an electrochemical cell in which electrophoretic deposition takes place. Understanding how and why particles do or do not form a deposit depends almost entirely on understanding the ionic distribution, and therefore the electric field distribution, in the deposition cell. This not only determines the electrophoretic motion of the particles but the electrohydrodynamic (EHD) convection of the solvent which can move ions and particles at speeds up to four orders of magnitude faster than simple electrophoresis. The following examples will consider a simple parallel plate electrochemical cell.

2.2.1 Non-Conducting System - No Dissolved Ions

The first and simplest case is that of a solvent with no dissolved ions and no electrochemical reactions. Here the solvent will act as a simple dielectric and the potential will change linearly between the electrodes.

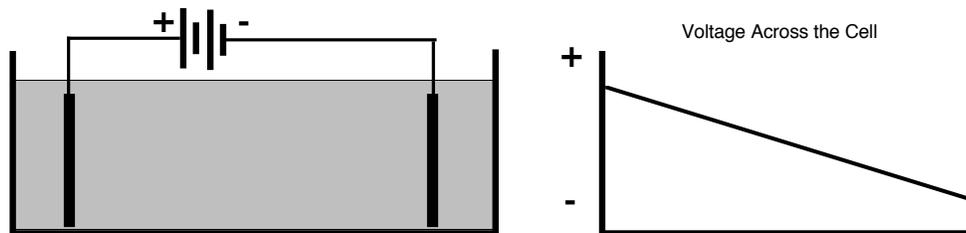


Fig 2.1 Voltage across a cell with no dissolved ions

2.2.2 Non-Conducting System - Dissolved Ions

In the second case the solvent has a concentration of ions but no chemical reactions occur at the electrodes. This case is commonly referred to as that of an ideally polarizable electrode. Ions will migrate toward the oppositely charged electrodes where some may adsorb to the surface of the electrode, reducing the electric field at the surface. Ions that remain dissolved will move toward the electrode until that motion is balanced by concentration diffusion away from the electrode. This charged layer will be referred to here as the Diffuse Electrostatic Boundary Layer (DEBL). In standard terminology (30)

the DEBL term used here corresponds to the diffuse portion of the electrical double layer. The electrical double layer refers to an interface between two oppositely charged layers. When the interface is between a solid and liquid this double layer refers to the charge at the surface of the solid and an oppositely charged layer in the solvent. The layer in the solvent may also be broken into two layers, a Stern or compact layer which does not move relative to the surface and a diffuse layer which remains fluid and can move relative to the surface. With the interjection of a Stern layer this interface is sometimes referred to as the triple layer. It is unfortunately very common that the term 'Double Layer' is used to refer to only the diffuse portion of the electrostatic double or triple layer. The term DEBL is used here to clearly identify the nature of the layer referred to and to distinguish it from electrochemical boundary layers which can exist as well.

While the concentration of adsorbed ions on the electrode surface will depend on specific ion-surface interactions, the profile of ions in solution near the surface can be described by combining an equation for the gradient of an electric field as a function of ionic concentration with an equation for the ionic concentration as a function of the electric field. The Poisson equation describes the Laplacian of the electrostatic potential, the gradient of the electric field, as a function of net ionic concentration:

$$\nabla^2\psi = \nabla E = -\frac{e}{\epsilon_r\epsilon_o} \sum_1^N z_j n_j. \quad \text{Poisson Eq.} \quad [2.1]$$

Where ψ is the rational electrostatic potential, that is the potential relative to a bulk solution potential of zero, E - the electric field, e - the charge of an electron, z_j - the charge on ion j , n_j - the number density of ionic species j , N - the total number of ionic species present, and $\epsilon_r\epsilon_o$ -the permittivity of the solvent. The Boltzmann equation then describes the gradient of the ionic concentration as a function of the electric field:

$$\nabla \ln n_j = -\frac{ez_j}{kT} E = -\frac{ez_j}{kT} \nabla\psi \quad \text{Boltzmann Eq.} \quad [2.2]$$

with the solution

$$n_j = n_{jref} \exp(-ez_j\psi/kT), \quad [2.3]$$

here n_{jref} is the concentration of the ionic species n_j at the reference condition where the electrostatic potential is zero; $\psi = 0$. Putting these equations together forms the Poisson-Boltzmann (P-B) equation which describes the shape of the electric field and distribution of dissolved ions around a charge in a solvent with dissolved ions:

$$\nabla^2\psi = \nabla E = -\frac{e}{\epsilon_r\epsilon_o} \sum_1^N z_j n_{jref} \exp(-ez_j\psi/kT) \quad [2.4]$$

Poisson-Boltzmann Equation

If the electrolyte is symmetric, that is where there is an equal number of positive and negative ions in the reference state and the charges on the ions are equal and opposite, +1/-1 or +2/-2, the identity $\sinh p = (e^p - e^{-p})/2$ can be used to write the P-B equation as:

$$\nabla^2 \psi = \nabla E = \frac{2ezn_{jref}}{\epsilon_r \epsilon_o} \sinh(ez\psi/kT) \quad [2.5]$$

If a planar electrode is assumed with a perpendicular vector x , this has the solution (2, §4.7):

$$\Psi(x) = 2 \ln \left(\frac{1 + \exp(-\kappa x) \tanh\left(\frac{1}{4} \Psi_s\right)}{1 - \exp(-\kappa x) \tanh\left(\frac{1}{4} \Psi_s\right)} \right) \quad [2.6]$$

If a planar electrode is assumed with a perpendicular vector x and the sinh function is linearized* assuming a low surface potential ($\psi < 30$ mV) for the electrode relative to the bulk solution, the result is the Debye-Hückel approximation of the P-B equation:

$$\frac{d^2 \psi}{dx^2} = \frac{2e^2 z^2 n_{jref}}{\epsilon_r \epsilon_o kT} \psi \quad [2.7]$$

The decay of the potential from a flat charged surface to a neutrally charged solvent can then be described by

$$\psi = \psi_s \exp(-\kappa x) \quad [2.8]$$

where x is the distance from the surface, ψ_s is the rational electrostatic potential at the surface and κ is the Debye parameter which has the units of m^{-1} . (Eq.s [9] & [10]) The inverse Debye parameter is referred to as the Debye length and is the distance from a flat plate where the voltage will drop by $1/e$ or 63%. A very frequently used unitless parameter in colloidal electrostatics and electrostatics is κa , the radius of a particle, a , divided by the Debye length. The resulting parameter gives an index of the thickness of the electrostatic layer around a particle relative to the surface curvature. The thinner the layer relative to particle curvature the more the surface can be approximated by flat plate assumptions (large κa). The thicker the layer relative to particle curvature the better it can be approximated as a point charge (small κa).

$$\kappa = \left[\frac{2e^2 z^2 n_{jref}}{\epsilon_r \epsilon_o kT} \right]^{\frac{1}{2}} \quad \text{Debye Parameter for Symmetric Electrolytes} [2.9]$$

$$\kappa = \left[\frac{\sum_1^N e^2 (z_j)^2 n_{jref}}{\epsilon_r \epsilon_o kT} \right]^{\frac{1}{2}} \quad \text{Generalized Debye Parameter} \quad [2.10]$$

(* The linearization of the sinh function leads to an overestimation of the potential of $\approx 13\%$ at 25 mV, 40% at 50 mV and 65% at 75 mV, all at 25°C.)

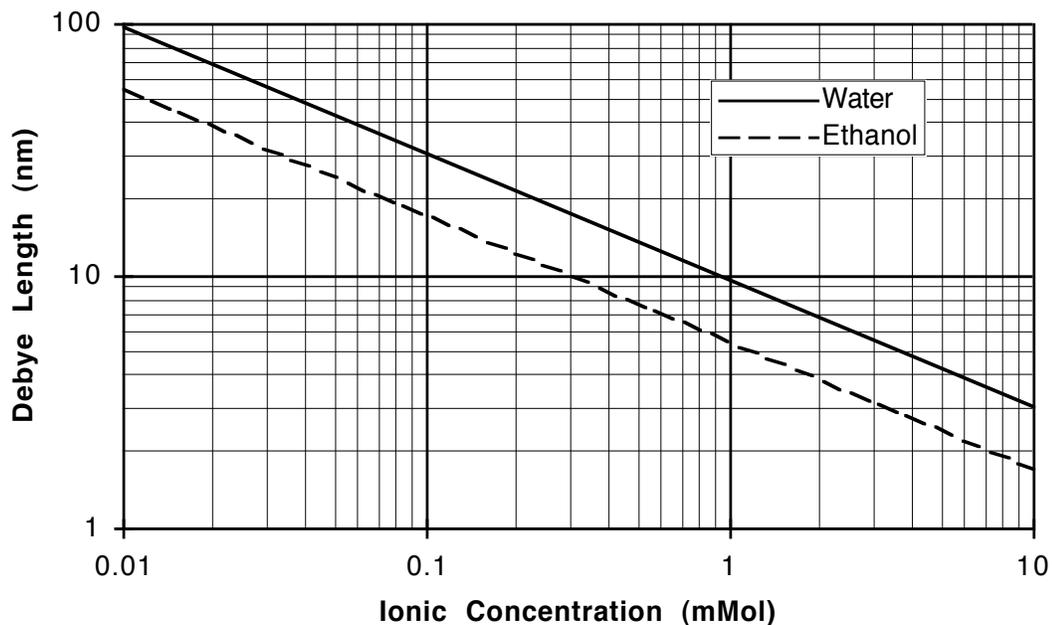


Fig. 2.2 Debye Length for a symmetric 1-1 electrolyte in water and ethanol.

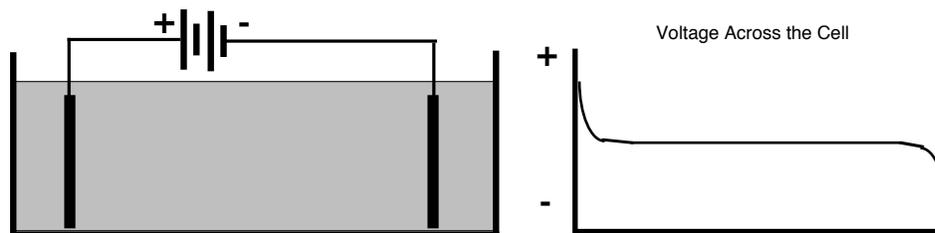


Fig. 2.3 Schematic of voltage distribution across an electrochemical cell with a concentration of ions but with no electrochemical reactions occurring at the electrodes. Almost the entire voltage drop across the cell will be confined to two very thin layers next to the electrodes.

As can be seen from the plot of the Debye length as a function of ionic concentration in Fig. 2.2, this characteristic length is measured on a nanometer scale. Given that the voltage decay is exponential on this scale it can be seen that even at very low ionic strengths almost the entire voltage across the cell will be confined to very thin layers immediately adjacent to the electrode surfaces. This is shown schematically in Fig. 2.3.

So when an electrode is placed into a solvent with dissolved ions, the surface may adsorb some ions with a preference for one polarity or another and thereby develop a surface charge (§ 2.3 below). When a voltage is applied to the electrode, it will attract

positive ions and repel negative ions dissolved in the solvent. The result is that the concentration of positive ions in solution at the surface goes up and that of negative ions goes down. This situation is illustrated in Fig. 2.4. This concentration effect in addition to an electrostatic effect increases the ratio of adsorbed positive ions to negative ions.

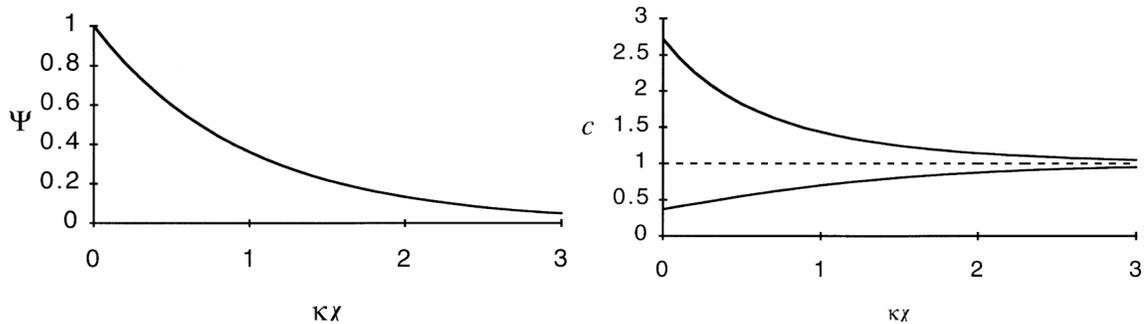


Fig. 2.4 Potential Distribution and Ionic Concentration at an Electrode for a non-dimensional surface potential of 1.0. This corresponds to a potential of 25.7 mV at 298°C. (eq. [6])

If no chemical reactions take place, then when the applied voltage is removed current will flow back out of the electrode as positive ions move away from the surface and the mirror charge within the electrode is reduced. This is the basic principle of electrolytic capacitors or "super capacitors". Very large surface area electrodes are separated by a salt solution. The maximum voltage is kept low to minimize chemical reactions and enormous dielectric polarizations are made possible by the forward and backward motion of positive and negative ions in the salt solution.

2.2.3 Conduction in a Solvent

In the previous section it was assumed that no electrochemical reactions take place at the electrodes, however, in any cell containing a solvent with dissolved ions some conduction will occur.

Solvents, with the exception of liquid metals, are ionic conductors. For conduction to occur ionized atoms or molecules must be oxidized (lose electrons) at the anode and be reduced (gain electrons) at the cathode. Current then is carried by migration of these ions through the solvent. In an electrolytic capacitor the objective is to minimize these reactions since they represent a dielectric loss, and at low voltages some systems can have extremely low currents. Conversely, in electrochemical production processes the objective will be the maximum current at the minimum voltage.

For EPD there must be a significant voltage gradient in the bulk solution for electrophoretic migration of the particles to occur. This means that there must be a

conduction current in amperes usually at least one order of magnitude higher than the conductivity of the cell in seimens. If the conduction current is lower than that, most of the voltage across the system will be concentrated in the thin double layers. There will be little or no voltage gradient in the bulk to drive the particles to the deposition electrode.

Electrolytic conduction can occur by either production or consumption of ions at the electrodes. Ions then move from one electrode to another by a combination of three mechanisms: *Migration* - this is the motion of an ion due to the force caused by its charge in the local electric field; *Diffusion* - net motion of ions due to random motion of individual ions with a concentration gradient of those ions in the solvent; and *Convection* - motion of the solvent and ions together due to either density differences in a gravitational field or net electrostatic charge on a unit of solvent in an electric field. The sum of these components are shown in order as the three terms of the Nernst-Planck equation:

$$i = -F^2 \nabla \phi \sum z_j^2 |v_j| c_j - F \sum z_j D_j \nabla c_j + Fu \sum z_j c_j \quad [11]$$

Nernst-Planck Equation for Current Flux

Where i is the current in Amperes, F - the Faraday constant, ϕ - the electrostatic potential, v_j - the mobility of ion j , c_j - the molar concentration of ion j , and D_j - the diffusion coefficient of ion j , and u - the convective velocity of the solution. Although these three components of conduction appear as a simple summation, each of the terms is related to the others by the Poisson equation [2.12], which relates charge concentrations to electric field gradients, and the equation for electrostatic body force, Eq. [2.13], which relates electric field and charge concentration to one of the forces driving convection (the other forces being gravity or mechanical stirring).

$$\nabla^2 \phi = -\frac{F}{\epsilon_r \epsilon_o} \sum_1^N z_j c_j \quad \text{Poisson Eq.} \quad [2.12]$$

$$F = -E \sum_1^N z_j n_j \quad \text{Electrostatic Body Force} \quad [2.13]$$

To drive the current flow in an electrolytic cell a voltage must be applied between the electrodes. The total voltage across the cell can be broken down into six components: ϕ - electrode potential, η_{sa} , η_{sc} - electrode overpotential at the anode and cathode, η_{Ω} - ohmic potential, and η_{ca} , η_{cc} - concentration overpotential at the anode and cathode respectively.

$$V = \phi + \eta_{sa} + \eta_{sc} + \eta_{\Omega} + \eta_{ca} + \eta_{cc} \quad [2.14]$$

These will be treated in order in the following sections., §2.2.4 to §2.2.7.

2.2.4 Electrode Potential

The electrode potential is the electrostatic potential of a metal electrode in a solution at zero current. This potential is measured relative to a reversible hydrogen electrode. Understanding the nature of this potential provides a basis for understanding the electrode overpotential and boundary layer behavior to be discussed later.

When a metal electrode is immersed into an electrolyte solution electrochemical reactions will begin immediately. A commonly used example is that of a copper electrode in a copper sulfate/water solution. When the copper is immersed in the solution it will immediately begin to dissolve.



This dissolution will generate a current

$$i = zFk_o^f a_m \quad [2.16]$$

where k_o^f is the dissolution rate constant and a_m is the activity of the metal. Likewise, cupric ions from the solution will precipitate onto the solid metal



Which will generate a current in the opposite direction

$$i = -zFk_o^b a_{\text{Cu}^{2+}} \quad [2.18]$$

If the currents from the dissolution and precipitation reactions are not balanced an electrostatic charge will quickly build up on the electrode, either attracting or repelling cupric ions from the solution. A double layer will form, and the charge on the electrode will increase until the activity of the cupric ions at the surface has reached a value where the net current is balanced:

$$zFk_o^f a_m - zFk_o^b a_{\text{Cu}_s^{2+}} = 0 \quad [2.19]$$

where the activity of the cupric ion at the surface, $a_{\text{Cu}_s^{2+}}$, is given by the Boltzmann equation;

$$a_{\text{Cu}_s^{2+}} = a_{\text{Cu}_z^{2+}} \exp\left(-\frac{2e}{kT}\psi_o\right) \quad [2.20]$$

where $a_{\text{Cu}_z^{2+}}$ is the activity of the cupric ion in the bulk of the solution and ψ_o is the surface potential relative to the bulk of the solution.

It is obvious that equation [15] simplifies to a chemical equilibrium equation

$$K = \frac{a_{\text{Cu}_s^{2+}}}{a_m} \quad [2.21]$$

where K is the ratio of the forward and backward reaction rates. Then using the Boltzmann equation we can solve for the potential necessary to maintain a constant surface activity of the cupric ion for any activity of the ion in the bulk of the solution.

$$\psi_o = \frac{kT}{ze} \left[\ln \left(\frac{a_{Cu_z^{2+}}}{a_m} \right) - \ln(K) \right] \quad [2.22]$$

Because of the difficulty and uncertainty of the measurement of surface potential relative to the bulk solution, electrochemical measurements are almost always measured relative to another electrode. The standard electrode in this scheme is the reversible hydrogen electrode (RHE). This is a platinum surface exposed to both the solution and 1 atmosphere pressure of H_2 gas, usually bubbled across the platinum surface in the solution. This electrode is assigned a potential of zero for a 1 molar activity of the hydronium ion (H_3O^+) in aqueous solution. The standard potential for a copper electrode is then defined as the potential relative to the RHE for copper metal in a solution containing 1 molar activity of Cu^{2+} ions. If the electrode metal is pure copper and is free of adsorbates, then it is assigned an activity of 1. The constant $\ln(K)$ term in equation [22] is combined with the constant term for the offset of the RHE to give the standard electrode potential, ϕ^o , for copper in aqueous solution.

$$\phi = \phi^o + \frac{kT}{z_+e} \ln \left(\frac{a_{Cu_z^{2+}}}{a_m} \right) \quad [2.23]$$

This is now the well known Nernst equation for equilibrium at a metal electrode. The reason for the above derivation is to illustrate the central nature of the diffuse electrostatic boundary layer in the in the determination of the potential at an electrode.

The one thing that has been skipped in this treatment is the true nature of what is meant by "surface" and "at the surface". Sometimes the surface is simply an exposed layer of atoms of the underlying solid with solvent molecules and ions colliding randomly with that surface. Frequently that surface will attract an ordered layer of solvent molecules and it is only on the other side of this layer that the solvent behaves like a fluid in random motion. The difficulty is that this ordered layer will act as a dielectric — frequently a spontaneously polarized dielectric. This means that the potential measured within the metal of a metal electrode can be very different from the potential one molecular layer away in the solvent. An extreme example of this is the behavior of water at a platinum surface. Molecular dynamic simulations done by Heinsinger (4) showed that water molecules will spontaneously orient with the oxygen end toward a crystalline platinum surface. In an uncharged system this spontaneous polarization is sufficient to cause a

potential jump of 1.1 Volts over the 3 Å thick single molecule thick layer of surface water. Thus a metal surface can attract a hydration or solvation sheath just like a metal ion in solution.

This ordered molecular layer at the metal surface, referred to as the Helmholtz layer, will also have a capacitance. In the case of platinum in water the orientation of the molecules at the surface leave this with a relatively low dielectric constant, ≈ 5 , but given the thinness of this layer the capacitance will be at least $15 \mu\text{F}/\text{cm}^2$. Polarization of a second layer of water can then boost the differential capacitance of this layer to more than $40 \mu\text{F}/\text{cm}^2$. Over a range of voltages this capacitance is close enough to a constant that its effect can simply be incorporated into the constant term of the Nernst equation (5). However, for accurate calculation of surface activities, it is the potential on solvent side of this layer that should be used. Therefore here ψ_o will be defined as the potential on the solvent side of this layer with ψ_m being the potential inside the metal, both terms being relative to the solvent potential in the bulk of the solution. So the total potential between the inside of the metal and the solvent will be broken down into two components $\psi_m - \psi_o$ the potential drop from the inside of the metal to the outside of the Helmholtz layer and ψ_o the potential across the diffuse electrostatic boundary layer (DEBL). The terms "at the surface" will mean immediately adjacent to the Helmholtz layer on the solvent side while "on the surface" will mean either in physical contact with the surface or incorporated into the structure of the Helmholtz layer.

2.2.5 Electrode Overpotential

In order to move the system beyond equilibrium and initiate a current flow, a voltage in addition to the equilibrium potential has to be applied. The usual procedure to measure this voltage is to place two electrodes of the same material as close together as possible in the electrochemical bath. A current is then driven between one electrode and a third separate electrode. The voltage difference between the two identical electrodes at various current levels is then recorded as electrode overpotential. The objective in placing the electrodes as close together as possible is to minimize ohmic and concentration voltages between the electrodes. Ideally the overpotential is measured with the exact same conditions prevailing immediately outside the double layers of each of the electrodes.

When this overpotential is applied to an electrode, the change in voltage will cause a change in the activity of ions at the surface. This change can be approximated by the Boltzmann relation. Although this approximation is frequently used without qualification, it should be noted that this equation is an equilibrium equation being applied to a dynamic

system. The diffusion of reactant and product ions in and out of the double layer will change the concentration and potential profile of this layer. Because at medium and high ionic strengths this layer is very thin compared to the speed of diffusion, it has been shown that this has only a minor effect on the double layer profile, (6). How well this holds true in very low ionic strength solvents will need to be demonstrated.

So to a first approximation the activity of an ion near the electrode surface will be given by

$$a_s = a_\infty \exp\left(-\frac{ze}{kT}\psi_o\right) \quad [2.24]$$

However, the reaction rate of an ion at the surface is not linearly related to its activity. The rate of reactions involving electron exchange at an electrode will be a function of the potential across the Helmholtz layer (5). The greater the potential drop across the Helmholtz layer the lower the reaction rate. This reaction rate can be written as:

$$k_o^f = B \exp\left(\frac{ze}{kT}\alpha(\psi_m - \psi_o)\right) \quad [2.25]$$

where B is a theoretical reaction rate at zero potential at the surface, and α is called the transfer coefficient and is a value between 0 and 1, most often it is measured to be 0.5. (z is the charge on the reacting ion assuming that the reaction is between an ion of charge z and a neutrally charged species, i.e. involves a charge transfer of $|z|$ electrons.)

If we now make the simplifying assumptions that both the potential across the Helmholtz layer and across the diffuse double layer are linear functions of the electrode potential, the potential can be written as $\phi + \eta$, the standard potential at a particular molar concentration plus the overpotential. All of the constant terms can now be collected into a catchall term, i_o , called the exchange current. The variable term is then an exponential function of the overpotential times a proportional term, α , the transfer coefficient.

$$i = i_o \exp\left(-\alpha \frac{ze}{kT}\eta\right) \quad \text{Tafel Equation} \quad [2.26]$$

Eq. [2.26] is often referred to as the Tafel equation which was determined empirically and is valid in many cases for overpotentials greater than 50-100 mV.

If the reaction is symmetric there will be both a cathodic and an anodic reaction occurring at the same time. The net current in either direction can then be approximated by the so called Butler-Volmer equation:

$$i = i_o \left[\exp\left(\alpha_a \frac{ze}{kT}\eta\right) - \exp\left(-\alpha_c \frac{ze}{kT}\eta\right) \right] \quad \text{Butler-Volmer Equation} \quad [2.27]$$

where i is the total current, i_0 is the exchange current, α_a , α_c are the anodic and cathodic transfer coefficients, and η is the electrode overpotential.

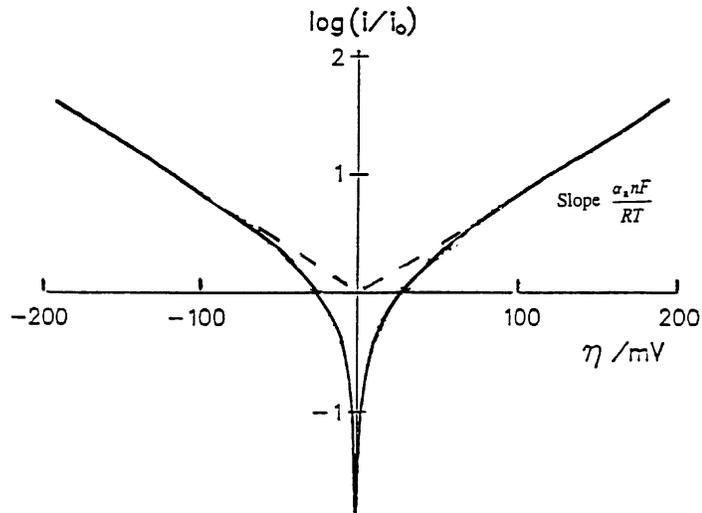


Fig. 2.5 Tafel plot of current-overpotential for a symmetric reaction. (from 7)

From the perspective of EPD the most important conclusion from this analysis is that, except in very rare coincidences, there will be a double layer at the surface of the deposition electrode. Furthermore, since EPD usually involves the application of tens of volts, not a few hundred millivolts, to a suspension with ionic strengths measured on a fractional millimolar scale, the double layer at the deposition electrode will both be relatively thick, tens of nanometers, and very highly charged. This can lead to a condition where even though the electrode is negatively charged and particles in suspension are positively charged, their interaction will be repulsive and the particles cannot be made to deposit on the electrode. This is a result of the dramatic charge density difference that can exist between the particle and the surface of a conducting electrode (8).

On the other hand, a clear understanding of the nature of the electrode DEBL allows its manipulation. By matching the electrode metal, solution composition and applied voltage/current, the electrode diffuse layer can be manipulated or even eliminated, the electrode brought to the potential of zero charge. Thus at one voltage/current particles can be brought to the vicinity of the electrode, allowed to rearrange in a 'floating' layer above the electrode, then the voltage/current changed to allow the particles to contact the electrode and deposit. This understanding will be important for the production of ordered monolayers, deposition on sub micron patterned electrodes, and even controlled single particle depositions.

2.2.6 Ohmic Potential — η_{Ω}

The Ohmic potential across a cell is due to the intrinsic resistance of the solvent to electrical conduction. This conduction in the solvent will occur by electrophoretic migration of ions under the influence of the external applied electric field. This ionic migration is resisted by random collisions between the ions and other molecules in the solvent. Because the mechanism of resistance is the same as in an electronic conductor there is likewise a linear relationship between electric field and current, which can be written as Ohm's law:

$$i = \kappa \nabla \phi \quad [2.28]$$

where κ is the conductivity of the solvent. This will apply in areas of the solution where charge is balanced and there are no concentration gradients.

A simple analysis of the conductivity will illustrate most of the significant effects in ohmic conduction. The total current will be the sum of the flux of positive and negative ions:

$$i = z_+ c_+ F u_+ + z_- c_- F u_- \quad [2.29]$$

where c_{\pm} is the molar concentration and u_{\pm} is the velocity of the ions. Since this has been defined to be in a region of charge balance then:

$$z_+ c_+ + z_- c_- = 0 \quad [2.30]$$

giving:

$$i = z_+ c_+ F (u_+ + u_-) \quad [2.31]$$

The velocity of the ions can then given by:

$$u_i = -z_i v_i \nabla \phi \quad [2.32]$$

where v_i is the electrophoretic mobility of the ion. This mobility in turn can be approximated by:

$$v_i = \frac{D_i z_i e}{kT} \quad [2.33]$$

where D_i is the diffusion coefficient for ion i . These equations then can be combined to give the final form of this approximate formulation of conductivity in term of the diffusion coefficients of the ions:

$$\kappa = \frac{eF}{kT} \sum D_i z_i^2 c_i \quad [2.34]$$

The purpose of this analysis is to show the close relationship between migration and diffusion. Electrophoretic migration of ions being simply a type of diffusion in an electric field. In particular migration and diffusion are effects that operate on the same order of magnitude and it is only in special cases where one can be considered without the other.

Of course eq. [2.34] is only a rough approximation of the ionic conductivity of a solution. The actual conductivity will be reduced by interactions between the ions which reduce the mobility of individual ions. Very accurate values for the conductivity of ionic solutions can be calculated using the Fuoss-Onsager equation [2.35]. The values of the various terms in this equation are described more fully in Appendix A.

$$\Lambda = \Lambda_o - S(c\gamma)^{1/2} + E'c\gamma \ln(6E'c\gamma) + Lc\gamma - K_A c\gamma^2 \Lambda \quad [2.35]$$

2.2.7 Concentration Overpotential — η_c

Also known as concentration polarization — This is the final component of the total cell voltage as given in eq. [2.14]. This potential arises due to ionic concentration gradients in the solution outside of the DEBL's. These gradients are in turn caused by the electrochemical reactions occurring at the electrodes where ions are either produced, consumed or blocked. This can cause either a change in ionic composition or an increase or decrease in ionic strength.

An example of a change in chemical composition is the case of a neutral salt such as KCl in an electrolyzable solvent such as water. When a voltage is applied to the cell K^+ ions will migrate toward the cathode and Cl^- ions toward the anode. K^+ ions approaching the cathode will not react, but will be blocked from further migration by the cathode surface. This will lead to an accumulation of K^+ in the solution near the cathode. Cl^- ions migrating away from the cathode will be replaced by OH^- ions produced by electrolysis of the solvent. Thus the accumulation of K^+ will be electrically balanced by the production of OH^- . K^+ will continue to accumulate until migration toward the cathode in the electric field is balanced by the concentration diffusion away from the cathode. The result is that at the cathode KOH will accumulate at a higher concentration than that of KCl in the starting solution. Likewise at the anode an accumulation of Cl^- ions will be electrically balanced by H_3O^+ ions produced by electrolysis at that electrode.

If this process is continued without convection, eventually the cell will be divided into two regions, one on the cathode side containing KOH and on the anode side HCl. Conduction will occur by migration of OH^- ions away from the cathode and H_3O^+ ions away from the anode. They then meet and neutralize forming water in the middle of the cell. The relative migration of K^+ and Cl^- ions toward the cathode and anode will be balanced by concentration diffusion away from the electrodes. The total number of ions in the cell will have doubled. This division of the cell into purely basic and acidic sides will rarely be seen in practice. These concentration gradients will lead to slight ionic charge imbalances. The electric field will result in an electrostatic body force on these unbalanced

charge regions in the cell. These forces can then initiate convection and convective mixing in the cell.

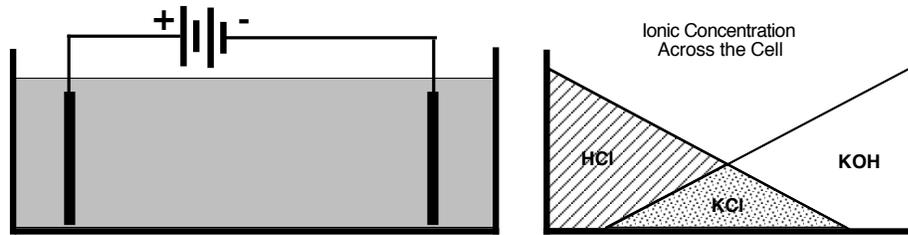


Fig. 2.6 Ionic concentration and composition across the cell.

What is significant here for electrophoretic deposition is that electrochemical reactions can have several effects. It can increase or decrease the ionic concentration at the electrode, in this case increasing the ionic concentration at both electrodes. It can change the ionic composition near the electrode, in this case the hydrogen ion activity (pH), and it can induce EHD convection, changing transport mechanisms in the cell.

2.2.8 Limit Current Behavior

Much larger concentration overpotentials can occur in a different case where an ion is produced at one electrode and consumed by reaction at the opposite electrode. An example of this would be conduction in a Brønsted acid solution where the anion does not participate in the electrochemical reactions. This is the case that will be examined more closely in Ch. 4 where the electrolyte is hydrochloric acid in an ethanol/water solvent. Here the acid dissociates into chloride ions and predominantly hydronium ions. During conduction hydronium ions will be consumed at the cathode, producing H₂ gas and water. On the other side of the cell H₃O⁺ ions will be produced by electrolysis of the water in the solvent. Cl⁻ ions will remain mostly passive in the solvent, primarily just providing charge balance to the H₃O⁺ ions.

The first case to consider here is that of equilibrium conduction of a HCl electrolyte in the absence of convection. The following analysis was first published by Levich in 1962 (9). In an equilibrium conducting state with no convection, the chloride ions will migrate in the electric field toward the anode. However, since no chloride ions are produced or consumed in the cell, for the concentrations to be in equilibrium the migration in one direction must be balanced by diffusion in the other. So at equilibrium the net motion of the chloride ions will be zero and they will not contribute to conduction in the solution.

$$i_{Cl} = 0 = F^2 z_{Cl}^2 v_{Cl} c_{Cl} \frac{d\phi}{dx} - F D_{Cl} z_{Cl} \frac{dc_{Cl}}{dx} \quad [2.36]$$

This means that the total current in the cell will be due to migration and diffusion of the H_3O^+ ions.

$$i_{H^+} = -F^2 z_{H^+}^2 v_{H^+} c_{H^+} \frac{d\phi}{dx} - FD_{H^+} z_{H^+} \frac{dc_{H^+}}{dx} \quad [2.37]$$

Returning to the simple description of ionic mobility:

$$v_i = \frac{D_i z_i e}{kT} \quad [2.38]$$

allows Eq. [2.36] to be rewritten as

$$\frac{d\phi}{dx} = \frac{kT}{z_{Cl}^2 F e c_{Cl}} \frac{dc_{Cl}}{dx} \quad [2.39]$$

Eq.s [38] & [39] can now be substituted into Eq. [2.37] to give:

$$i_{H^+} = -F^2 z_{H^+}^2 \frac{D_{H^+} z_{H^+} e}{kT} c_{H^+} \frac{kT}{z_{Cl}^2 F e c_{Cl}} \frac{dc_{Cl}}{dx} - FD_{H^+} z_{H^+} \frac{dc_{H^+}}{dx} \quad [2.40]$$

Which simplifies to :

$$i_{H^+} = -FD_{H^+} z_{H^+} \left(\frac{z_{H^+}^2}{z_{Cl}^2} \frac{c_{H^+}}{c_{Cl}} \frac{dc_{Cl}}{dx} + \frac{dc_{H^+}}{dx} \right) \quad [2.41]$$

At this point it is possible to introduce the assumption of quasi-neutrality.

Although positive and negative charge are never perfectly balanced in conduction in the presence of a concentration gradient, this assumption is that the quantity of unbalanced charge is negligible in comparison to the total ionic concentration. The validity of this assumption was shown by both Levich and Newmann (9,7), and it remains valid down to very low total ionic concentrations. This assumption is expressed mathematically as:

$$c_{H^+} \approx \frac{z_{Cl}}{z_{H^+}} c_{Cl} \quad [2.42]$$

When this is substituted into Eq. [41] all of the terms involving the concentration or valence of the anion cancel out, and the result is:

$$i_{H^+} = -2FD_{H^+} z_{H^+} \frac{dc_{H^+}}{dx} \quad [2.40]$$

From this equation it can be seen that the maximum continuous current due to both electrophoretic migration and concentration diffusion is only two times what it would be for diffusion alone in the same gradient.

When this is applied to a simple parallel plate electrochemical cell with a plate separation of d , this equation can be integrated from $x=d$, the anode, to a point x distance from the cathode. This then gives the following formula for the concentration across the cell as a function of the cation concentration at the anode, $c_{H_0^+}$,

$$c_{H^+} = \frac{i}{2FD_{H^+} z_{H^+}} (x - d) + c_{H_0^+} \quad [2.41]$$

This then shows a simple linear concentration gradient across the cell.

The problem with this equilibrium conduction in a charge balanced solvent is that the limiting current possible in the absence of convection is very low, as is the voltage that will induce this current. If the concentration gradient between the two electrodes is linear then as the voltage is raised there will be a point where at the ionic concentration at the anode will rise to twice the initial average in the cell. This concentration then declines linearly to zero at the cathode. Since negative concentrations are not possible this will be the point at which the cell is conducting the maximum current possible under the above assumptions. This maximum current is given by:

$$i_{\text{lim}} = 2 \frac{FD_{H^+} z_{H^+}}{d} c_{H_0^+} \quad [2.42]$$

In this treatment the formal charges of the ions have been carried through, even though the stated case of HCl the charges are simply +1/-1. However, by carrying through the charges, the mathematics become valid for a simple salt having any valence combination where an ion of one polarity is produced at one electrode and consumed at the other and opposite ion does not react. The appropriate values for the ion which carries the current can be substituted for the values indicated for the hydronium ion in the above analysis, and the values for the non-reactive ion can be substituted for the chloride ion. This will lead to the same result regardless of the valence of the ions. The current will only be two times the diffusion current for the charge carrying ion in the same concentration gradient.

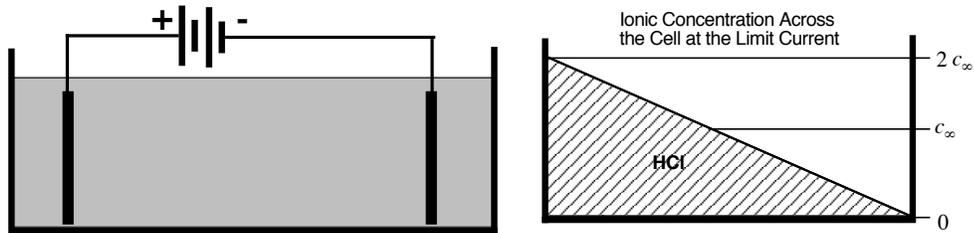


Fig. 2.7 At the limit current the ionic concentration across the cell will decrease linearly across the cell to almost zero at the electrode where the ions are consumed.

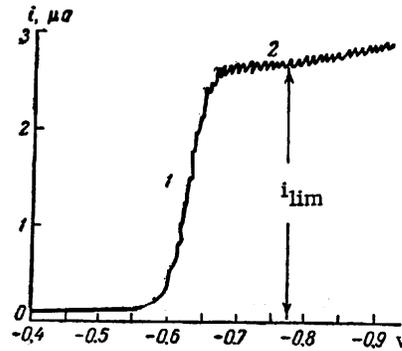


Fig. 2.8 Example limit current behavior (1) Ohmic region below the limit current, (2) limit current region, additional voltage does not induce significant additional current. (from Levich (9)).

Obviously the concentration at the cathode will not go to zero as a current will continue to flow. However, as the concentration approaches zero several other effects become significant, violating the assumptions above.

2.2.9 Beyond the Limit Current

It is useful here to take a qualitative look at an equilibrium approach to this limit current, and analyse what happens when the voltage is raised beyond the point necessary to induce the limiting current.

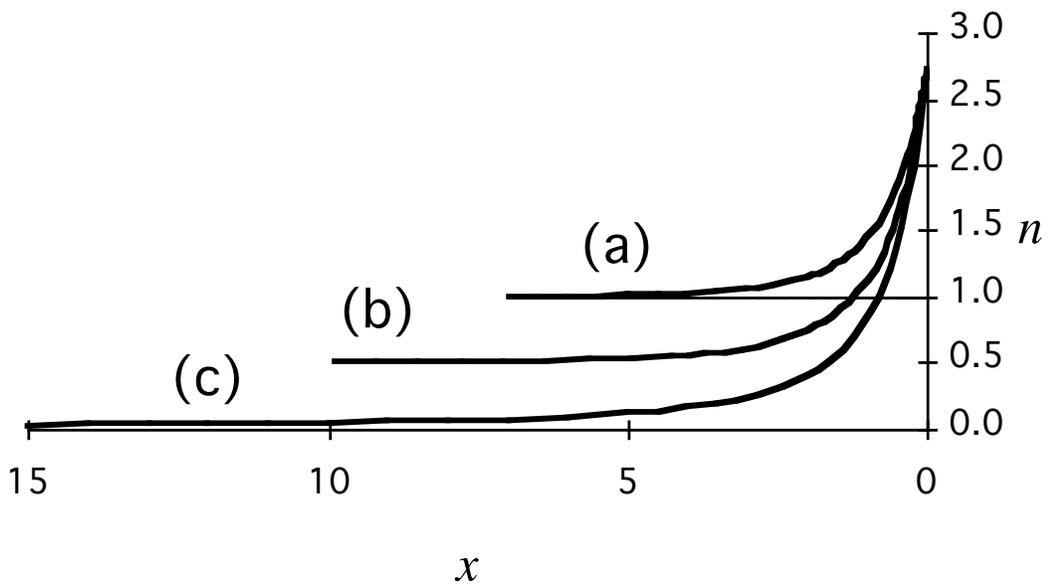


Fig. 2.9 Ionic concentration profiles in the DEBL at an electrode with constant surface activity. (a) initial concentration in the bulk solution, (b) concentration outside the DEBL one half initial concentration, (c) concentration outside the DEBL 0.01 of initial. Potentials calculated using eq.s [6],[3]

Assuming that the equilibrium rational electrode potential of the cathode is negative, the diffuse boundary layer at zero current will as shown by line (a) in Fig. 2.9. When a voltage is applied to induce an equilibrium current of one half the limit current, the concentration across the cell will be as shown by line (b). The concentration outside the cathode DEBL will have dropped by one half. This means that the DEBL thickness will increase by a factor of $\sqrt{2}$. The voltage across the DEBL will have to increase by $kT/e \ln 2$ just to maintain the same concentration of positive ions at the electrode ($kT/e = 25.7\text{mV}$ at 25°C). The additional overvoltage necessary to drive the conduction reactions forward will depend on the exchange current for the reduction reaction at this electrode.

Fig. 2.9 (c) shows the situation approaching the limit current. If the concentration outside the boundary layer is now 1% of the initial concentration then the boundary layer thickness will have increased by a factor of 10 and the voltage across the diffuse layer will have to increase by 120 mV just to maintain the equilibrium concentration at the electrode surface. Again there will have to be a significant overvoltage in addition to this to drive the electrochemical reactions at the electrode.

As the cell approaches the theoretical limit current, additional voltage will all be concentrated across the DEBL. With each increase in voltage the concentration outside the DEBL will decrease. This decrease will have very little effect on the concentration gradient in the bulk of the cell and, therefore, very little effect on the total current through the cell. With little change in current there will be little change in the ohmic or concentration potential drop across the cell. This decrease in concentration will, on the other hand, have a large effect on the DEBL. In a non-conducting DEBL concentration diffusion away from the electrode will be balanced by electrophoretic migration toward the electrode. In a conducting DEBL migration must predominate over diffusion for there to be a net current flowing to the electrode. At the innermost edge of the DEBL concentrations are high enough that this is a minor effect. At the outer edge this can become the dominant effect. As the concentration goes down the outer edge of the DEBL will flatten and expand until the concentration gradient reverses. In this outer region both concentration diffusion and migration act to move the positive ions toward the cathode.

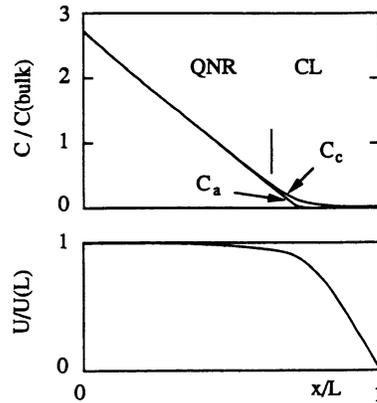


Fig. 2.10 Equilibrium ionic concentration (C) and potential distribution (U) across the cell at a voltage above that necessary to elicit the limit current in the absence of convection. Electrode boundary layers are not depicted. Cell is divided into the quasi neutral region (QNR) and charged layer (CL). Thickness of the charged layer is exaggerated. (From Chazalviel (10))

So, in equilibrium conduction absent convection, at a voltage just beyond the onset of the limit current, the cell can be broken down into four regions: 1) the Anode Boundary Layer - because of the increase in ionic concentration outside this layer, this DEBL will simply get thinner and has little effect on overall cell behavior; 2) the Quasi-Neutral Region - here the ionic concentration can be well described by the analysis of Levich assuming charge balance as discussed above; 3) the Charged Layer - this layer has a very high voltage gradient, 1 to 10 MV/m, a cation concentration gradient declining toward the cathode, a thickness that can be measured on a micron scale, and an almost complete absence of anions; and 4) the Cathode Diffuse Layer - here the voltage gradient is even higher than in the charged layer but the thickness will only be a few tens of nanometers. This difference between this layer and the charged layer is that the cation concentration gradient rises toward the cathode surface in this layer.

2.2.10 Imposition Voltage/Current Above the Limit Current

The prior discussion has focused on equilibrium conduction at each point up to the onset of convection. A more realistic case for EPD is where a current or voltage well beyond the limit current is suddenly imposed on the system. The situation where a voltage greater than that necessary to elicit the limit current will be discussed below. This problem has been analyzed numerically by Chazalviel (10). The concentration of the two types of ions was calculated based only on the Nernst-Planck and Poisson equations with no convection. The electrode boundary layers were included in the analysis with the

assumption of an infinite exchange current, therefore the boundary layer voltage was enough to maintain the same surface concentration as at zero current.

When the voltage is first applied to the cell, the instantaneous current will be determined only by the ohmic resistance of the solution, $i = V\kappa$. This current will immediately begin to drop as some of the voltage is taken up by the cathode and anode DEBL capacitances. The current across the cell will still be determined only by the ohmic resistance of the solution but the voltage driving the current will be reduced by the double layer voltages. Once significant electrochemical reactions begin at the electrodes there will begin a depletion of hydronium ions at the cathode and an accumulation of chloride ions at the anode. This situation is shown as the black line in Fig. 2.11.

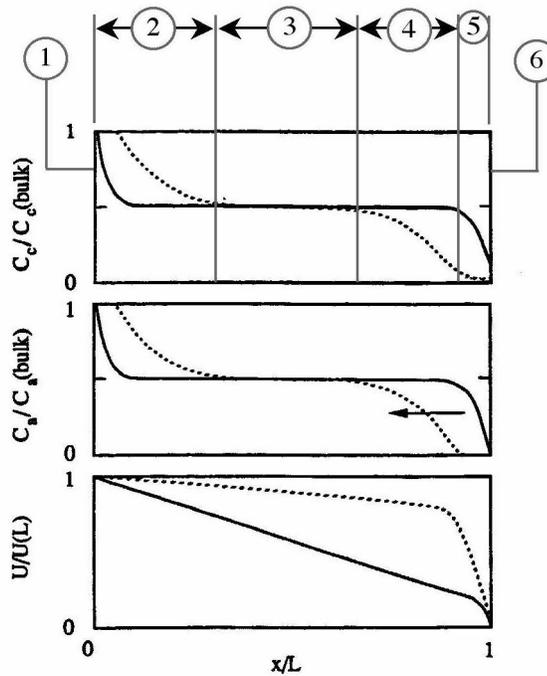


Fig. 2.11 Ionic concentration (C) and potential distribution (U) across the cell at two times after the imposition of a voltage above that necessary to elicit the limit current. Electrode boundary layers are not depicted. Cell is divided into six layers numbered as identified in text. (Adapted from Chazalviel (10))

The accumulation of chloride ions at the anode will increase the solution conductivity in this region but will have little impact on the total voltage across the cell. On the other hand, the depletion region near the cathode will have a dramatic effect on the cell voltage distribution. The concentration gradient region outside of the cathode DEBL will have a lower conductivity than the bulk and therefore will account for a larger and

larger portion of the cell voltage. Likewise, as mentioned previously, as the ionic concentration drops outside the DEBL, the voltage across the DEBL increases as well.

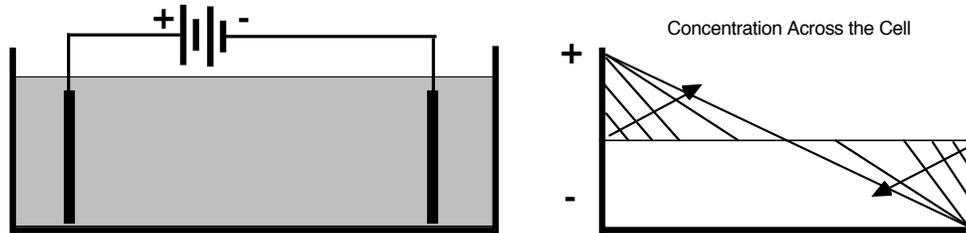


Fig. 2.12 Dropping concentration gradient near the cathode at the initiation of conduction.

This cathode concentration gradient zone will grow as shown in Fig. 2.12. The current will not change dramatically during the growth of this zone therefore the slope of the concentration gradient will remain the same with the width of the zone growing. The solution will remain predominantly charge balanced in this gradient zone until the concentration approaches zero near the boundary layer. The thickness of the gradient region when this will occur can be estimated using Eq. [42] where d will be the thickness of the gradient zone and i_{lim} the current across the cell prior to the formation of the charged layer. Once the gradient layer has reached this thickness the concentration outside the cathode DEBL will drop to the point where this layer will split into two regions. One next to the electrode surface where the concentration of positive ions declines away from the surface, and another much thicker region where the anion concentration rises again moving away from the surface. This second zone is what Chazalviel refers to as the 'charged layer' and the concentration profile of this region is given schematically in Fig. 2.10. In both of these regions there is an almost complete absence of anions.

The resulting concentration and voltage profiles are shown as the dotted line in Fig. 2.11. In this case of non-equilibrium conduction the cell can be separated into six regions of charge/concentration/potential. Going from left to right in Fig. 2.11 these are: 1) the anode boundary layer, 2) the anode gradient layer, 3) the bulk solution, 4) the cathode gradient layer, 5) the charge layer, and 6) the cathode boundary layer. Together the anode and cathode gradient layers and the bulk solution form what Chazalviel has termed the 'Quasi Neutral Region'. At long times these regions will merge into one gradient and the current will reach a minimum which is the limit current for the cell. Any voltage in excess of what is necessary to elicit this very low limit current will be taken up by the very high voltage gradient of the charged layer.

This is a theoretical profile based on the complete absence of convection in the cell. This is actually a very difficult condition to achieve. Chazalviel describes his calculated concentration profile as "unphysical", and Levich in describing the limit current region as shown in region 2 of Fig. 2.8 comments:

"... a motionless solution can be achieved in practice only in exceptional cases, for example, where the solution is immobilized by the addition of gelatin or agar-agar." (9)

To this list could also be added filter material or a porous packing of particulate material. Each of these will act strongly to damp convective motion of the fluid. The necessity for very strong viscous damping of convection in order to see these effects indicates that there must be equally strong forces driving the fluid into convection.

2.2.11 Transition to Convective Transport

In any region where the concentration diffusion and electrophoretic migration are in the same direction there will be a net driving force for convection. A concentration gradient driving diffusion in the same direction as migration will be referred to here as a favorable gradient. So any layer with a favorable gradient will be able to lower its net free energy by bulk motion of the fluid within the layer.

Beyond there just being a driving force for convection, for convection to actually occur the energy released by convection must be greater than the energy consumed by the fluid's viscous resistance to convection. Because the cell is a closed system and will behave as an incompressible fluid, convective transport must occur by circular vortices. That is, motion of fluid in one direction must be balanced by an equal volume moving in the opposite direction. While vortices can and do grow larger than the region they start in, the initial vortex will not be larger than the layer that generates it.

The smaller the vortex, the greater its energy dissipation per unit volume. The energy available to drive the vortex will also be volumetric, going up as the cube of the diameter of the potential vortex. Because of the geometric relationship between energy available and energy dissipation there will likely be a critical thickness of the unstable conduction layers where they will quickly trip into convective motion due to infinitesimal inhomogeneities in conduction or concentration.

Accurate estimates of the critical thicknesses of these layers will rely on future analysis and numerical modeling, however, the stability of each of the six conducting

layers enumerated above and the scale at which they will become unstable to convection can be estimated.

In both the electrode diffuse electrostatic boundary layers the concentration gradients will be unfavorable, so these layers will be highly resistant to convective motion.

The charge layer near the cathode is marked by both a favorable concentration gradient and an electric field on the order of one to ten million volts per meter. Because of the very high energy available in this layer it is likely to break into convective motion when it reaches a thickness of only a few tens of nanometers. The rapidity of the transition of this layer to convective flow explains the difficulty of observing the limit current behavior without some mechanical means of suppressing convection such as gelatin or packed filter material.

The situation is somewhat more complicated for the gradient layers in the quasi-neutral region. Here the concentration of the cation and anion is almost identical with the concentration gradient favorable for one and unfavorable for the other. The key for understanding convective instability in this region is that the imbalances in the ionic concentration here, while insignificant from a chemical point of view, can have a large electrostatic effect on the conducting fluid. Wherever there is a change in the conductivity of the solution there must be a change in the voltage gradient in order for a uniform current to flow through the cell. However, a change in the voltage gradient implies an accumulation of unbalanced charge. The interaction of this electrostatic charge with the electric field will produce a body force on the solution.

In the cathode gradient layer where the ionic concentration drops, the conductivity drops and there is an increased voltage gradient. This increase in voltage gradient is due to a slight excess positive charge accumulating in the solution at the edge of this layer. There is then a force on this layer toward the cathode due to the local electric field. However, the local electric field will also be a function of the distance between this charged layer and the cathode. If at one point the layer moves closer to the cathode, the potential gradient between this layer and the cathode will increase. The motion of one portion of the fluid toward the cathode will displace fluid, forcing another portion of the charged layer away from the cathode, and decreasing the potential gradient between it and the cathode. Thus the fluid moving toward the cathode experiences an increased force toward the cathode while the fluid moving away experiences a decreased force. This then creates a vortex which will grow progressively mixing the fluid from the gradient layer with the bulk solution and blending out the concentration difference between the gradient layer and the

bulk solution. The scale at which this layer becomes unstable to convection is likely to be measured in tens of microns.

The anode gradient layer will rely on the same effect, however, because of the much lower changes in voltage gradient the forces will be at least an order of magnitude lower than at the cathode. Thus this layer will be unstable at a scale of hundreds of microns to several millimeters.

2.2.12 Convective Transport

As the voltage is raised across a cell there are a series of convective flow patterns that can be expected. These are shown diagrammatically in Fig. 2.13. This is assuming a simple rectangular cell with the gravitational vector pointing downward to the bottom of the page.

At the lowest voltage, well below that necessary to induce the limit current, there will be no convection and a uniform concentration gradient will form across the cell. At a slightly higher voltage a single large vortex will form essentially filling the cell. This vortex will usually be initiated by a density gradient in the fluid. The ionic concentration gradient across the cell will make the solvent more dense at the anode and less dense at the cathode. The solvent will then rise at the cathode and fall at the anode, kicking off a circular vortex driven by both gravitational and EHD forces. (Fig. 2.13 a) This bulk vortex will contribute dramatically to ionic transport across the cell and will allow currents much higher than the limit current to be carried across the cell without the need for any other convective motion.

At higher voltages a gradient layer will form at the cathode initiating smaller vortices at the surface. (Fig. 2.13 b) These vortices will be on a scale of a few hundred microns to a few millimeters in size. They may roll across the surface, swept along by the flow of the bulk vortex or can be pinned in place by surface irregularities. These vortices will combine to even further increase ionic transport across the cell. This set of vortices works very effectively to mix the solution across the cell, preventing the formation of large concentration gradients. This allows a current several orders of magnitude higher than the limit current to be carried across the cell.

At even higher voltages this pattern will also become unstable. The gradient layer vortices will not provide sufficient transport to prevent the formation of an unbalanced charge layer at the cathode surface. Once this charge layer reaches the critical thickness it will break into vortices. (Fig. 2.13 c) These vortices will combine and grow outward into the gradient layer. Once these vortices reach a certain size an unbalanced charge layer will

form again, generating new vortices which themselves will grow away from the cathode surface. The surface flow will then be characterized by continuous, chaotic formation and growth of vortices that are ultimately swept away by the bulk vortex.

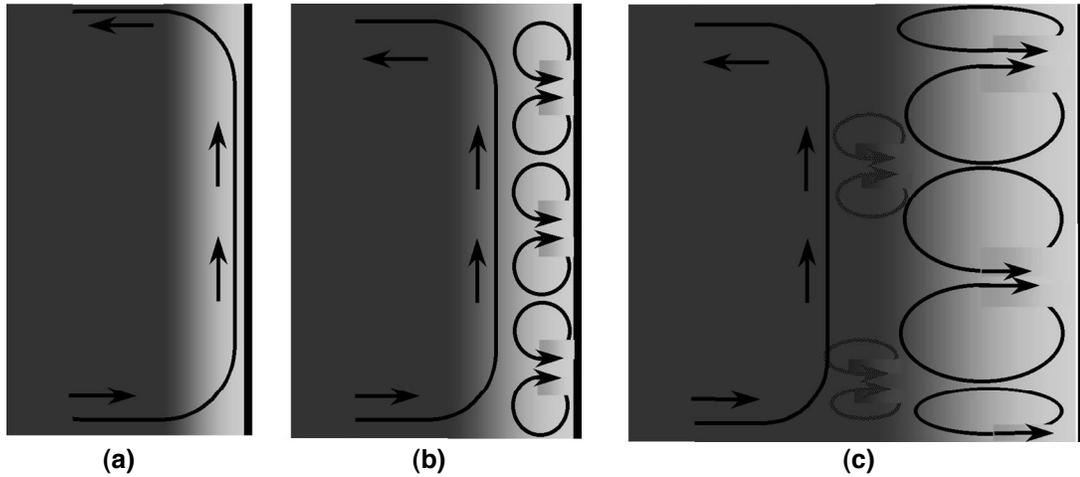


Fig. 2.13 Modes of convection in a simple rectangular cell.

At even higher voltages it is possible for the bulk vortex to split into smaller vortices, but the main effect will be the growth of the chaotic layer near the cathode until it fills the entire cell.

2.2.13 Conduction Summary

There are three main points from the preceding discussion that are particularly relevant for the understanding of EPD

1. There is an equilibrium diffuse electrostatic boundary layer at the surface of the deposition electrode. This boundary layer will change during conduction but only under very special circumstances will it disappear. During conduction this layer will usually have a potential drop an order of magnitude higher than the potential of the particles to be deposited. The potential of the electrode relative to the solvent at equilibrium and during conduction is system dependent and cannot be predicted a priori.

2. At any but the very lowest voltages there will be some level of EHD convection in the cell. This can provide significant mixing in the cell.

3. Where convection is suppressed large voltage and concentration gradients can develop.

2.3 Developing Surface Charge

The development of a particle surface charge is essential for the process of EPD. Without an electrostatic charge on the particle different from that of the solvent the particles will not move in an applied electric field. Also, obviously, electrostatic stabilization (§ 2.6.2) will not work without an electrostatic charge on the particle. Beyond this, understanding the mechanisms of charge formation will also help in understanding the adsorption of polymers and surfactants to the surface for steric stabilization (§ 2.6.3).

There are several ways in which particles in solution can develop a surface charge. These are not exclusive and frequently act to oppose one another. What these mechanisms have in common is that they all will involve interactions with ions in solution.

2.3.1 Dissolution/Precipitation

In this case a pure solid is in equilibrium with dissolved ions of the same material in solution. This is most typically a metal in equilibrium with ions of the same metal in solution. Using the example of copper given above (§ 2.2.4), in pure water copper will dissolve as Cu^{2+} ions leaving behind two electrons. This will continue until the negative charge on the copper particle is sufficient that the concentration of Cu^{2+} ions attracted back to the surface creates an equilibrium between dissolution and precipitation. Likewise, in a strong copper sulfate solution, cupric ions will precipitate onto the copper particles until the particles develop a sufficient positive surface charge to repel the Cu^{2+} ions, reducing the surface concentration to equilibrium again.

This case of simple dissolution/precipitation requires that the material be a conductor, with electrons moving in and out of the conduction band of the solid, generating a non-localized surface charge.

2.3.2 Selective Dissolution/Precipitation

This is the typical case for ionic solids where there is a different solubility for each of the ions. The classic example of this is silver iodide where the surface charge can be precisely controlled by the ratio of dissolved silver and iodide ions in solution. One ion will preferentially precipitate and the other dissolve until the accumulated surface charge drives the concentrations at the surface to the equilibrium Ag^+/I^- ratio. In this case the material does not need to be conductive, and usually is not. The surface charge is due to ions at specific sites of unbalanced charge.

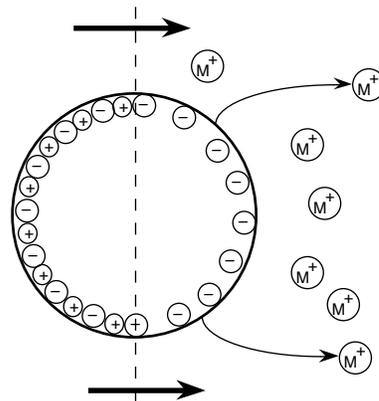


Fig. 2.14 Surface charge created by preferential dissolution.

2.3.3 Selective Adsorption

In this case there is a pre-existing concentration of ions dissolved in the solvent. If one ion has a greater adsorption energy than the oppositely charged ion it will preferentially adsorb to the surface giving the particle the charge of that ion. At very low ionic concentrations in the solvent the surface charge will adjust to bring the ionic concentration ratio at the surface to the ratio of the ionic adsorption energies. However this is a process that also depends on the concentration of adsorption sites available on the surface. As the concentration of ions in solution is raised the number of free adsorption sites for the preferentially adsorbed ion will go down – the surface will become saturated. This changes the surface ionic equilibrium ratio and causes the surface potential to go down. This suppression of surface charge can occur even at very low ionic concentrations in the solvent.

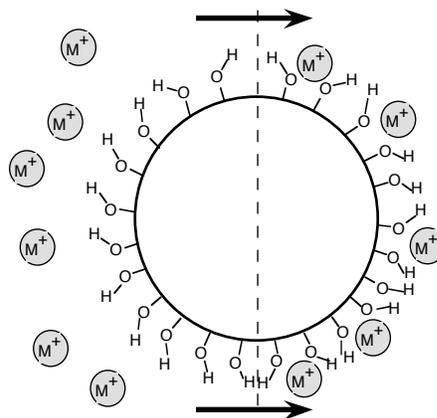


Fig. 2.15 Surface charge created by selective adsorption.

2.3.4 Surface Catalysis

Here there will be a molecular species in solution which is ionizable but is not ionized. This can include molecules of the solvent itself. The ionizable molecule is adsorbed to the particle, dissociated into two ions one of which remains adsorbed and one which returns to solution.

There are two mechanisms by which this dissociation can take place. The first is an interfacial process which is driven by the difference between the solid surface and the solvent. An uncharged molecule or polymer which is soluble in solution adsorbs to the particle surface. The soluble portion of this molecule then redissolves into the solvent either taking a charged entity from the surface or leaving a charged moiety behind. While the most frequent charged entity that is exchanged is a proton in a Brønsted acid/base reaction, the entity can be virtually any charged ion such as Na^+ or SO_4^- .

The second type of charging catalysis is where the particle surface itself acts as the ionizing catalyst. An example of a non-polar catalyst is the platinum metal surface where H_2 is dissociatively adsorbed as two hydrogen atoms. These atoms are then removed from the surface by water molecules becoming dissolved hydronium ions, leaving behind a negative charge on the platinum. An example of a polar catalytic surface is alumina (Ch. 3) where ethanol molecules are dissociatively adsorbed to negative and positive surface sites as a proton and an ethoxide ion. The ethoxide ion is then more easily desorbed from the surface leaving a slight preponderance of protons and therefore a positive surface charge on the particle. There is little practical difference between interfacial and surface catalysis other than that the surface catalytic effect may more easily be poisoned by strongly adsorbing atoms or molecules occupying the surface catalytic sites.

2.3.5 Special Case - Hydroxide Surface

A very commonly offered example of selective dissolution/precipitation surface charging is that of proton exchange with a hydroxide surface. Because of the humid, oxidizing conditions present in most laboratory environments, metals that are not already metal oxides will frequently form an oxide surface. Of these oxides, many will be stable as hydroxides - particularly in aqueous solution. The charging mechanism is then based on the Brønsted acid/base concept. These surface hydroxide groups can act as either proton donors or acceptors. This leads to the familiar 'S-curve' behavior in aqueous suspensions, with the particles positively charged in acidic conditions and negatively charged in basic. This hydroxide surface model is a specific example of the ionizable surface group model of surface charge regulation elaborated by Healy and White in 1978. (31)

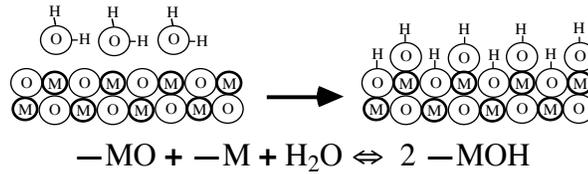


Fig. 2.17 Hydration of a metal oxide surface.

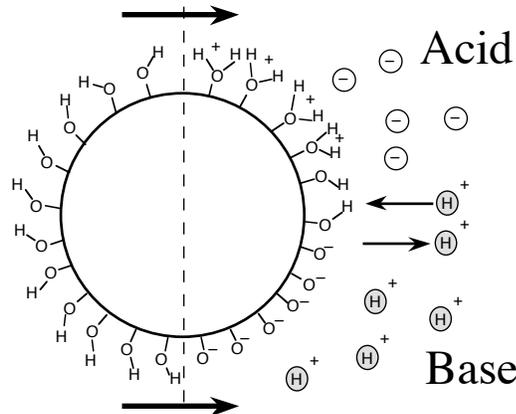


Fig. 2.18 Surface charge regulated by proton acceptance/donation.

However, this case is not as simple as it appears. As pointed out by Hunter (2, p 20, p 280) the Nernst equation does not apply in these cases. The surface charge density measured by acid/base titration is orders of magnitude higher than that measured by electrokinetic methods. There must be an additional adsorption/desorption mechanism to reconcile the two measurements.

This same case is analysed for alumina in ethanol/water in Ch. 3. Here it will be shown that surface charging is far more dynamic and complex than the simple adsorption/desorption of protons to and from the surface hydroxide layer. (11)

2.3.6 Compensating Effects

As mentioned at the beginning of this section, these effects will often act to counter one another. This is primarily due to action of the DEBL. If the particle begins to develop a positive charge, positive ions will be repelled from the surface while negative ions are attracted to it. The increased concentration of negative ions at the surface increases the likelihood of their adsorption, decreasing the positive charge. The decreased concentration of positive ions will increase their rate of dissolution from the surface, again reducing positive charge.

A dramatic example of this effect is the etching of polarized ceramics. **(12)** On a single crystal surface in an acidic solution, positively poled surfaces will dissolve at a dramatically higher rate than negatively poled surfaces, with the dissolution of surfaces parallel to the polarization dissolving at an intermediate rate. This can be explained by different surface charges appearing on oppositely polarized surfaces. If the positively polarized surfaces have a more positive surface charge than negatively polarized surfaces, the solution concentration of positively charged metal ions will be much lower at positively polarized surfaces and higher at negatively polarized surfaces. This would result in the rapid dissolution of metal ions from the positively poled surfaces, exposing oxygen ions which are converted to soluble hydroxides. The higher concentration of metal ions at the negatively poled surface would then act to slow the equilibrium dissolution rate of metal ions from this surface. This differential etching strongly suggests that it may be possible to use electrophoretic effects to orient and align electrically polarized particles.

2.4 Electrophoretic Motion of Particles

An isolated particle with a total charge of Q in a solvent will experience a force F due to an externally applied electric field E_∞ : $F = QE_\infty$. This force will cause the particle to accelerate until the viscous drag force is equal to the electrostatic force: $F = QE_\infty = 6\pi\mu a u_E$. Where μ is the solvent viscosity; a is the particle radius; and u_E is the velocity of the particle. By substituting in the electrostatic relationship between charge and surface potential, $Q = 4\pi\epsilon_r\epsilon_0 a\zeta$, we obtain the Hückel formula for the particle velocity in terms of the surface potential at the shear layer, ζ , and which is independent of the particle radius:

$$u_E = \frac{2}{3} \frac{\epsilon_r \epsilon_0}{\mu} \zeta E_\infty \quad \text{Hückel formula for Electrophoresis} \quad [2.43]$$

where ϵ_r is the relative dielectric constant of the solvent and ϵ_0 is the current permittivity of our locally observable universe.

However, an electrostatically charged particle in a solvent is rarely isolated. Most often the suspension is charge balanced; there is no net electrostatic charge. This means that for every unit of charge on the particle there will be an opposite unit of charge on an ion in solution. If the only ions in the solvent are the charged ions necessary to balance the charge on the particle surfaces, then the ion clouds around the particles will be so diffuse that they have little effect on the behavior of the particles, and the Hückel formula will still be valid.

This formula begins to lose its validity as the concentration of independent ions in the solution goes up. Instead of a large diffuse cloud of counterions spread throughout the solvent, the charged surface of the particle will form a polarized layer around itself with one polarity of ion reduced in concentration compared to another. Thus there will be a layer of fluid surrounding the particle that will have a charge equal and opposite that of the particle surface. In this case where an electric field is applied, the particle will experience a force in one direction while the fluid in the layer immediately adjacent to the particle will experience an equal and opposite force. As a result the particle will begin to move in one direction while the fluid boundary layer around it is pumped in the opposite direction.

Smoluchowski analyzed this problem for very thin boundary layers in 1903 (13). The resulting formula is very similar to the Hückel formula and is again shown to be independent of the particle radius:

$$u_E = \frac{\epsilon_r \epsilon_0}{\mu} \zeta E_\infty \quad \text{Smoluchowski Formula for Electrophoresis} \quad [2.44]$$

The formulae are identical with the exception that for the same surface potential the particle in the thick (Hückel) boundary layer case will move 50% faster than the thin (Smoluchowski) case. In the thin boundary layer case the electrohydrodynamic pumping of the charged boundary layer in the direction opposite the motion of the particle adds significantly to the hydrodynamic drag. However, to maintain the same surface potential the net charge, and therefore the electrostatic force, is much higher on the particle in the thin boundary layer case. For example a 300nm diameter Ag/Pd particle with a surface potential of 40mV in acetic acid where the ionic strength is very low (Ch. 4.5), will have a total charge of 47 nC/m². For an alumina particle in ethanol (Ch. 3.5) with a surface charge of 42 mV and a 8.6 nm boundary layer thickness, the surface charge density is 1.1 mC/m². In the thin boundary layer case the surface charge is more than 20 times higher at the same surface potential. This means that the electrostatic force on the particle in the thin boundary layer case will also be 20 times higher even though the electrophoretic velocities are similar.

The Smoluchowski and Hückel formulae addressed the electrophoretic motion of particles with very thin and very thick boundary layers. In 1931 Henry (14) developed a formula for the motion of particles over the entire range of boundary layer thicknesses:

$$u_E = f(\kappa a) \frac{2}{3} \frac{\epsilon_r \epsilon_o}{\mu} \zeta E_\infty \quad \text{Henry Formula for Electrophoresis} \quad [2.45]$$

The values for the function $f(\kappa a)$ are shown graphically in Fig 2.19 below where κ is the inverse Debye length, a measure of the thickness of the boundary layer. (Eq.s [9] & [10]) This is an analytic solution of the problem, and, as such, Henry had to ignore some effects in order for the problem to remain mathematically tractable. This does not affect the validity of his solution, but restricts it to particles with low surface potentials.

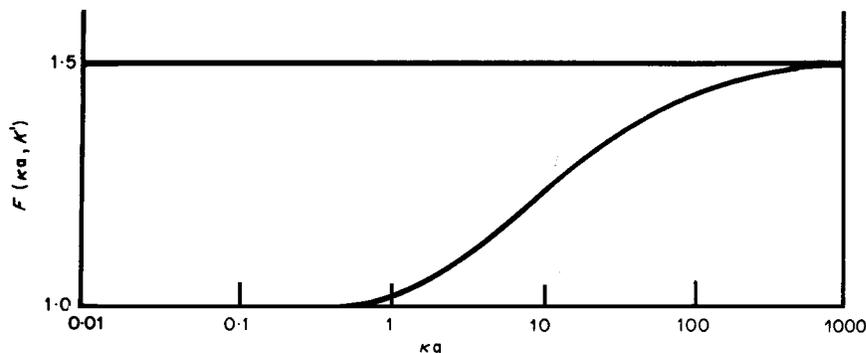


Fig. 2.19 $f(\kappa a)$ of Henry (14) from Hunter (2).

Two effects that were left out of Henry's treatment were polarization of the boundary layer and ion diffusion into and out of the polarised fluid around the particle. Higher surface potentials mean a higher charge in the boundary layer and therefore a greater ion imbalance. When an external electric field is applied, the particle/boundary layer will polarize with the boundary layer shifting relative to the particle. This eliminates the symmetry of the system on one axis and distorts the external electric field. Furthermore, as it is pumped around the particle, solvent will be entering and leaving the boundary region. The solvent entering the boundary layer around the particle will contain a balance of positive and negative ions and will become part of the charged boundary layer by ionic diffusion in or out of the solvent. Likewise, on the other side of the particle charged solvent will be pumped away from the particle. This solvent will remain charged for the time it takes for oppositely charged ions to interdiffuse and eliminate the imbalance. This electrohydrodynamic pumping of fluid around the particle combined with finite diffusion times will add to the polarization of the particle/boundary layer system.

The complete problem was solved using a computational algorithm by O'Brien and White in 1978 (15). Their results for particles in a 1-1 electrolyte, in this case KCl in water, are shown in Fig 19 a) & b). These charts are indexed on the non-dimensional mobility:

$$E = \frac{3\mu e}{2\varepsilon_r \varepsilon_o kT} \cdot u_E \quad [2.46]$$

and non-dimensional surface potential:

$$y = \frac{ez\xi}{kT} \quad [2.47]$$

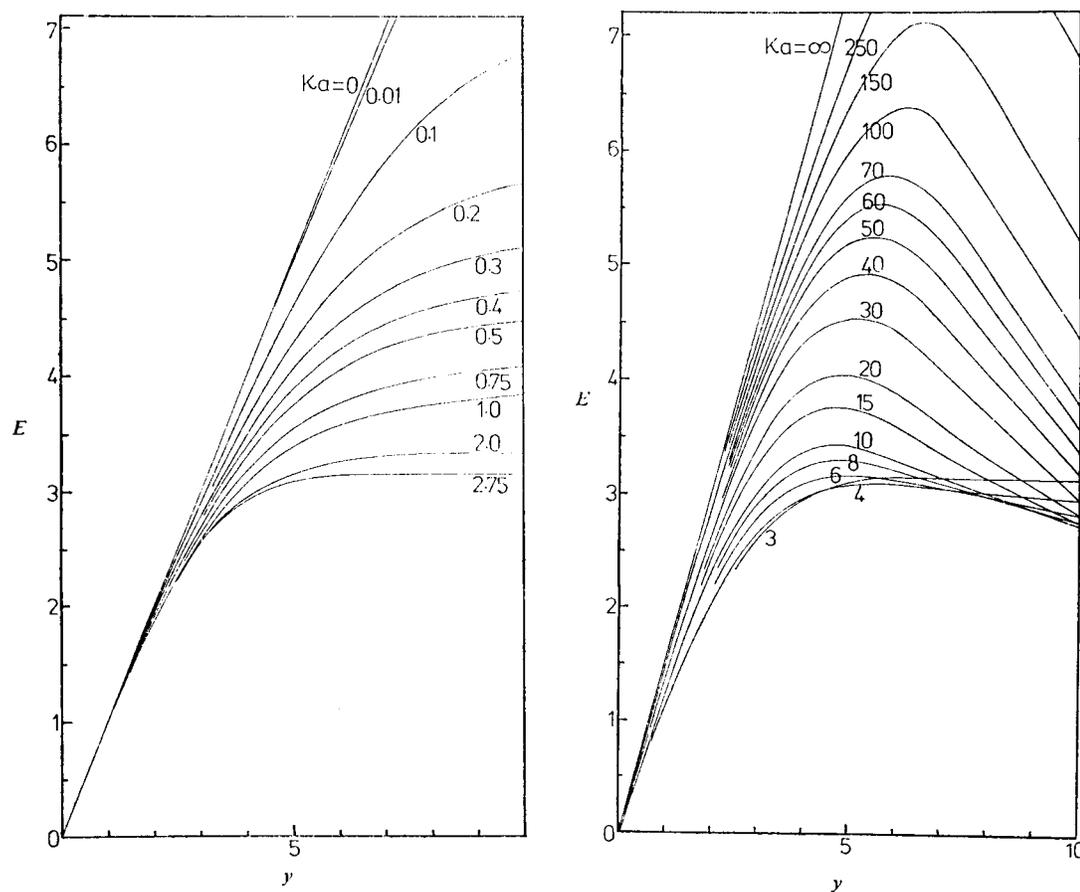


Fig. 2.20 The relationship between non-dimensional surface potential, y , and non-dimensional electrophoretic mobility, E , based on the ionic mobility of KCl in water. From O'Brien and White (15)

2.5 Creation of a Stable Suspension of Particles

The first step in EPD is the creation of a stable, charged suspension of the powder to be deposited, and the first step to be taken here will be to define 'suspension' and 'stability'.

A suspension most broadly defined is any discrete phase - solid particles, liquid droplets or gas bubbles dispersed in a continuous liquid or gas phase. A suspension is a 0 – 3 composite where the phase suspended is not interconnected in any direction and the suspending phase is continuous in three dimensions and interposed between the each of the units of the suspended phase. A suspension can be anything from soap bubbles floating in air to uranium dioxide precipitates floating in liquid lead oxide. However, to keep the scope of this paper reasonable the suspensions considered here will all consist of solid particles in a liquid at room temperature and pressure.

Stability in the case of colloidal suspensions is very different from thermodynamic stability. The thermodynamically stable state for most of these suspensions is for the particles to be stuck together and sitting at the bottom of their container underneath the liquid. Stability in the case of suspensions is a relative measure of the resistance of the suspension to achieving this thermodynamic equilibrium. This is a relative measure since a suspension may be stable for only a few minutes or it may be stable for many years, yet either suspension may be stable enough or too stable for a particular purpose.

The two forces that act against the stability of a suspension are gravity and the van der Waals force (vdW). For particles denser than the suspending solvent gravity will continuously pull the particles toward the bottom of their container. The vdW force will draw particles together and cause them to stick to one another. There are two types of force that can be used to preserve the suspension. One is macroscopic agitation; stirring, shaking, sound waves, etc. The other is the thermal energy of the solvent acting on the microscopic scale where the physical energy of agitation of the solvent molecules can impart kinetic energies on the scale of kT , the Boltzmann constant times the absolute temperature.

Table 2.1 Properties of some materials considered here.

Material	Density	Refractive Index	Dielectric Constant
Quartz (α)	2.65	1.45	3.75
Silica Glass	2.2	1.6	3.8
Mica (Muscovite)		1.6	7.0
Alumina	3.97	1.75	10
Zirconia	5.68	2.15	12.5
Barium Titanate	6.02	2.4	3,000
PZT	8.0	2.5	800
Titania	4.23	2.6	114
Silver 70/Palladium 30	11.0		~
Gold	19.3	3.1	~
Ethanol (20°C)	0.789	1.361	25.3

2.5.1 Gravitational Sedimentation

A spherical particle suspended in a fluid will experience a downward force due to gravity:

$$F_g = \frac{4}{3} \pi a^3 \Delta \rho g \quad [2.48]$$

where a is the particle radius and $\Delta \rho$ is the particle density minus the density of the fluid. This force will cause the particle to accelerate downward until the gravitational force is balanced by the viscous drag of the fluid. All of the flows that we encounter here will be laminar, so the drag on the particle can be calculated using the Stokes equation: $F_d = 6\pi\mu a u_0$. The particles will reach an equilibrium velocity, u_0 , when the forces are equal, Eq (2.1). The equilibrium sedimentation velocities for several materials in ethanol as a function of particle size is shown in Fig. 2.1.

$$u_0 = \frac{2a^2 \Delta \rho g}{9\mu} \quad [2.49]$$

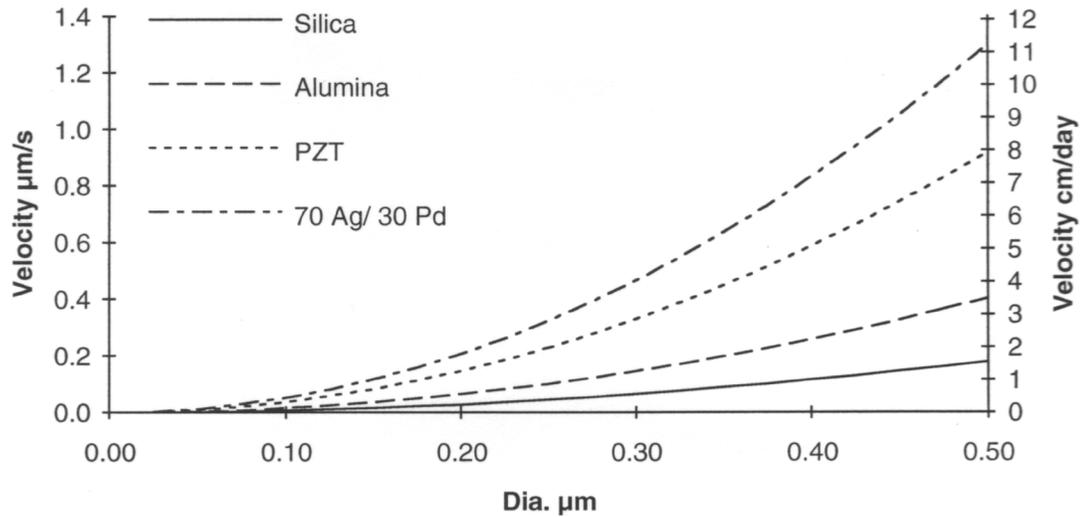


Fig. 2.21 Sedimentation velocity for particles in ethanol.

While the particle falls due to gravity like a macroscopic particle, it will also behave like a very large molecule. That is, it will have an average thermal kinetic energy of $\frac{3}{2}kT$, – the Boltzmann constant times the absolute temperature. A water molecule for example weighing $\approx 3.0 \times 10^{-23}$ g with a kinetic energy of $e_k = \frac{1}{2}mV^2 = \frac{3}{2}kT$ will on average be moving at 520 m/s at room temperature (approximately 1,160 miles per hour). In contrast, a 150 nm diameter alumina particle that weighs 5.65×10^{-14} g, will move at an average velocity of 1.5 cm/s (or 0.033 miles per hour).

However, neither a solvent molecule nor the particle can go very far at this speed before hitting other solvent molecules and transferring their momentum to the solvent. This momentum transfer is the definition of viscous drag and, in equilibrium, will conform to the Stokes equation above. So a particle in suspension will pick up a kinetic energy of some small multiple of kT from a collision with a solvent molecule. This momentum will be dissipated by viscous forces on a nanosecond time scale (1, §3.2). Thus the particle will have an average velocity of 1.5 cm/s with the direction changing randomly every few nanoseconds. While each impulse and decay is invisible, the result of many submicroscopic motions leads to the visible translation known as Brownian motion. Integrating these random kinetic impulses and viscous damping leads to the Stokes-Einstein equation for particle diffusion:

$$D_o = \frac{kT}{6\pi\mu a} \tag{2.50}$$

To form a suspension that is stabilized by this random motion due to thermal energy the flux of particles downward due to gravity must be balanced by the flux of particles upward due to diffusion. If the concentration of particles at height h in a suspension is c_h , then in equilibrium

$$c_h u_0 + D_0 \frac{dc_h}{dh} = 0. \tag{2.51}$$

This can be integrated easily to give the equilibrium concentration at a height h in terms of the concentration at the bottom of the container:

$$c_h = c_0 \exp\left(\frac{u_0}{D_0} h\right) = c_0 \exp\left(\frac{-m_p g h}{kT}\right). \tag{2.52}$$

The height over which the concentration of an equilibrium suspension will drop by 95% is shown for a few materials in ethanol in Fig. 2.2. For example, for 0.27 μm diameter alumina particles (at the extreme end of the alumina line) given a sediment density of 55% at the bottom of a suspension, the particle concentration will drop by 95% at a little over 100 μm above the sediment and will drop to a few parts per thousand within 0.2 mm of the sedimented layer. It is only for particles well below 100 nm that significant quantities can be held in suspension by Brownian motion.

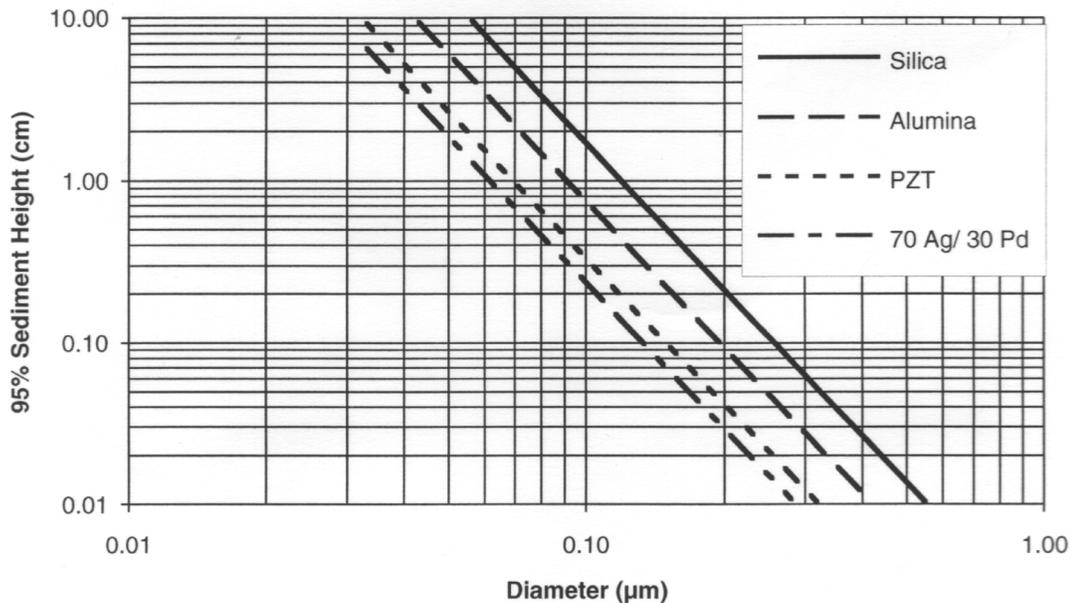


Fig. 2.22 Height over which the density of particles in suspension will drop by 95%, based on the equilibrium between Brownian diffusion and gravitational sedimentation.

There are two non-dimensional numbers that can be used to characterize the sedimentation of a suspension. The number that characterizes how the suspension will sediment is the Péclet number for sedimentation

$$Pe = \frac{u_0}{D_0} H = \frac{4/3 \pi r^3 \Delta \rho g}{kT} H, \quad [2.53]$$

where H is the total depth of the suspension. Large Péclet numbers ($Pe > 1000$) will indicate a suspension dominated by free sedimentation. Auzerais et al. (16) calculated the density profiles for the sedimentation of a suspension with $Pe = 8500$ and this is shown in Fig. 2.23. This Péclet number would be equivalent to an alumina powder with a diameter of $0.28 \mu\text{m}$ in ethanol and a total depth of 10 cm. The second non-dimensional number is the characteristic time for sedimentation, t^* . This is the total height of the suspension divided by the Stokes sedimentation velocity for the particle,

$$t^* = \frac{H}{u_0} = \frac{9\mu}{2a^2\Delta\rho g} H \quad [2.54]$$

For the $0.28 \mu\text{m}$ particle in 10 cm of ethanol mentioned above, this time is ≈ 51 hours.

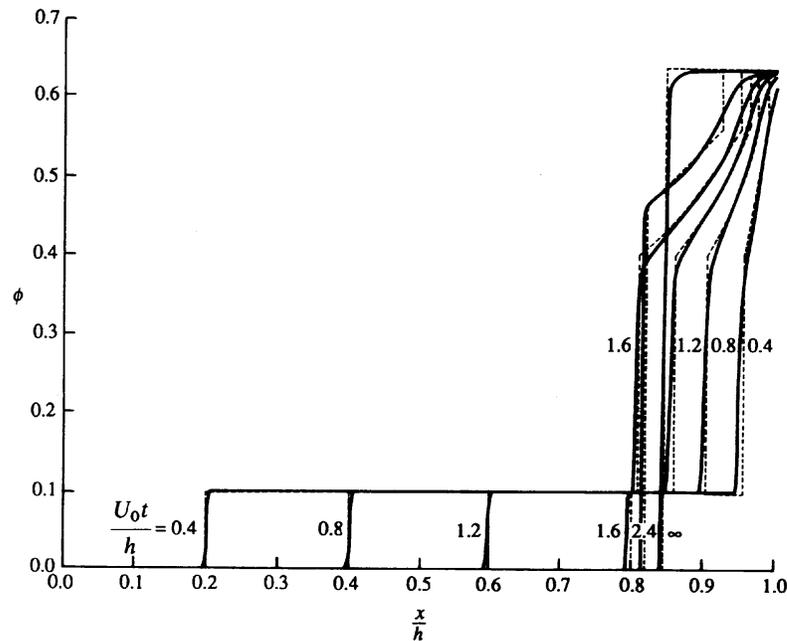


Fig 2.23 Concentration profiles for various times, $Pe = 8500$, initial volume density 10%, x/h relative distance from top of suspension, ϕ particle volume fraction. (from 16)

In the case illustrated it will take t^* or about two days for the boundary of the clear layer to drop halfway down the container. This is only half the velocity that particles would drop in very dilute suspensions. This is because at finite concentrations there will be a backwash of rising fluid due to displacement by the sedimenting particles and fluid pulled downward by the particles' drag plus near field interactions between the flow fields around the particles. Auzerais et al. developed an empirical estimate for this velocity for

finite density suspensions, U , as a function of the Stokes settling velocity and the particle volume fraction, ϕ ,

$$U = U_0(1 - \phi)^{6.55} \quad [2.55]$$

The conclusion to be drawn from this discussion is that most of the suspensions of sub-micron particles used in EPD are not in fact stable relative to gravitational sedimentation. However for EPD all that is necessary is a quasi-stability for a few minutes to a few hours to perform the depositions. Moreover, if the suspension is stirred periodically then it effectively becomes stable for as long as stirring continues.

2.5.2 Floccing

The next form of stability is preserving the individual particles as entities that can move independently within the suspension. The problem here is the Van der Waals (VdW) forces which will pull particles together if they pass too close to each other. Since the particles approach each other from random directions they will stick together in randomly arranged three dimensional structures or flocs.

Here it is useful to make a distinction between coagulation and flocculation as outlined very clearly by Napper (17, p.3). A 'coagulum' in Latin is a curd, as in cheesemaking. This implies a fairly uniform, dense lump. In Latin 'floccus' is a tuft of wool and describes a very loose, low density structure.

Coagulation is a process in which the primary particles will come together in a densely packed clump. This implies that the particles are able to rearrange themselves within the agglomerate. Particles must be able to slide and rotate past on another as they enter the agglomerate to find a well packed position.

In flocculation particles or flocs collide randomly and are frozen into place where they contact. This leads to a low density, fractal structure as shown on several scales in Fig. 2.4 below.

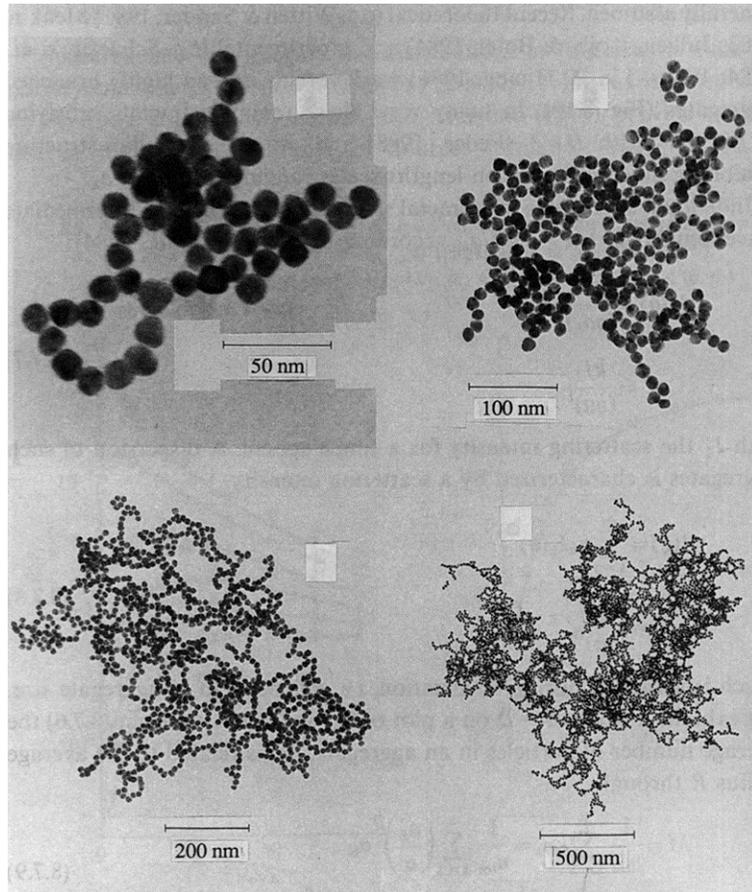


Fig. 2.24 Typical Floc Structures From (18) as reproduced in (2, p.282)

There are three types of agglomeration of a dispersed phase that lead to three different densities of the agglomerate. The first type is coalescence where the dispersed phase is liquid or gas. When particles touch they flow into each other and the density of the agglomerate is the same as that of the initial particles. The growth rule for this type of agglomerate is simply:

$$l = \left(\frac{a_l}{a_o} \right)^3 \quad \text{Coalescence growth rule} \quad [2.56]$$

where a_o is the radius of the initial particles and a_l is the radius of an agglomerate of l particles.

The second type is, as mentioned, coagulation. Here solid particles will be able to move to achieve a uniform packing density that is less than that of the initial primary particles but which does not vary with size. The growth rule for this type of agglomerate is:

$$l = \phi \left(\frac{a_l}{a_o} \right)^3 \quad \text{Coagulation growth rule} \quad [2.57]$$

where ϕ is the packing density of the primary particles in the coagulate, usually between 0.6 and 0.7.

Finally there is flocculation, a fractal process. Particles come together randomly and stick at their first point of contact. This is repeated as flocs come together and stick randomly. This repeated collision of larger and larger units in the same manner gives the floc the type of scale independent structure characteristic of a fractal geometry. As small flocs have a lower density than the primary particles, larger flocs will have a lower density than the smaller flocs they are made up of. This leads to a geometric decline in density as the floc grows. This is described by the same formula but where the exponent d is less than 3.

$$l = \left(\frac{a_l}{a_o} \right)^d \quad \text{Flocculation growth rule} \quad [2.58]$$

There are two problems with these particulate flocs for EPD. The first is that all of the particles in a floc will behave as one large particle. The density of this composite particle will be much less than that of the individual particles, however, the increased size will lead to a sedimentation rate several orders of magnitude larger than for the separated particles. The second problem occurs during EPD. If the particles are electrostatically charged, these flocs can be attracted to the deposition electrode and can be made to deposit. However, in most cases the deposition forces are not strong enough to break the floc structure, and their low density structure will be preserved in the deposition. In the usual case where maximum random packing of the particles is the desired outcome, this is an undesirable outcome.

2.5.3 van der Waals Force

The van der Waals force is made up of three components. The first component is the permanent dipole-permanent dipole or Keesom force. The second is the permanent dipole-induced dipole or Debye interaction. These first two forces are generally ignored in the colloidal literature as particles are almost always assumed to be isotropic. There are, however, many cases where these forces will have a significant effect. Crystalline particles can have different surface charge on different facets, thereby adding a dipolar component to their interaction. (Although this is generally masked for larger particles by the electrostatic double layer.) The dipoles of magnetic particles will certainly interact.

Further, both of these dipoles can be induced in suspended particles with the application of sufficient external fields.

The third force is the dispersion or London force. It is a quantum mechanical force resulting from the exchange of virtual photons between virtual resonant dipoles created in a material on the atomic, molecular and crystal structure level. To obtain the total interaction force, the electromagnetic resonant response of the material is integrated over the electromagnetic spectrum from the infrared through the visible into the ultraviolet. In the vast majority of colloidal suspensions this is the only one of the van der Waals forces that is significant. Since the following analysis will all be based on the assumption of the particles being isotropic spheres, this is the only force that will be considered here.

There are various different formulas for calculating the London-Van der Waals (L-VdW) interaction force between two bodies, depending on their geometry. Each of these formulas is the product of two terms, one is a geometric term which depends only on the shape and separation distance of the interacting bodies, and the second is the Hamaker Constant, which is a function of the electromagnetic properties of the materials that are interacting and of the medium separating them. The formula below from Israelachvili (3) can be used to give an accurate estimate of the Hamaker constant for two bodies of material 1 separated by a solvent 3 (A_{131}). The largest part of this force comes from the second term (>98%), which depends on the relative refractive indices, n , of the materials. The greater the difference between the refractive index of the solvent and the suspended particles, the greater the attraction between the particles.

$$A_{131} = \frac{3}{4} kT \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right)^2 + \frac{3h^0 v_e}{16\sqrt{2}} \frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}} \quad \text{Hamaker Constant Est.} \quad [2.59]$$

The refractive index of the material is used in this formula is a measure of the polarizability of the material. The more polarizable the material the stronger the L-VdW attraction. The difference in refractive index between the particles and the solvent surrounding them is significant because there is also a L-VdW attraction between the solvent and the particles. If the dielectric spectrum of the solvent is the same as that of the particles then the particle-solvent attraction will be the same as the particle-particle attraction. This means that there will be no net particle-particle attraction in that solvent.

Fig. 2.5 below shows the dramatic increase in the attraction energy going from low refractive index materials that have been the subject of a many EPD studies (Al_2O_3 , SiO_2), to some typical electroceramic materials, to metals.

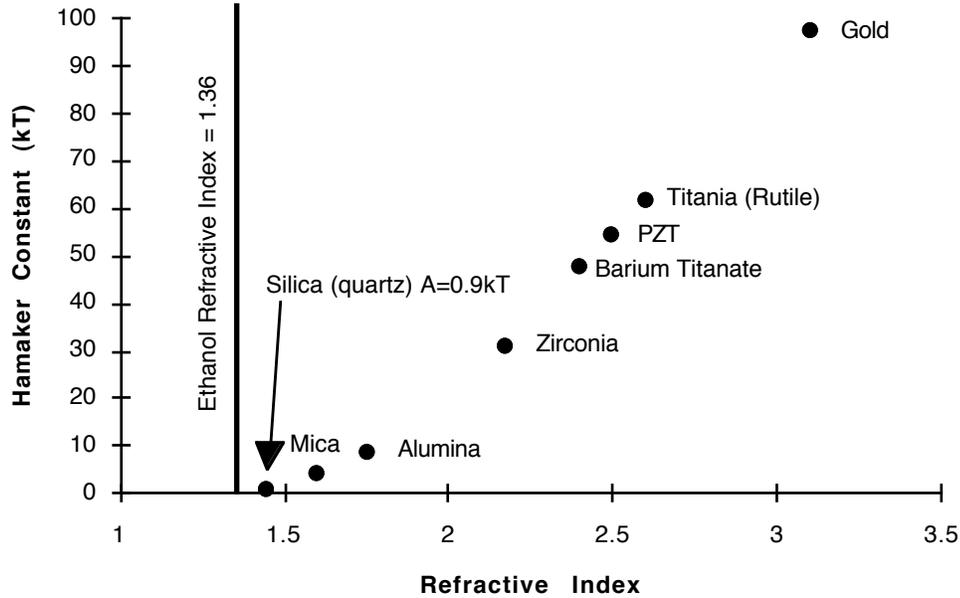


Fig.2.25 Hamaker Constant (A_{131}) vs. Refractive Index for various materials in ethanol.

To get the interaction energy the Hamaker constant is multiplied by a geometric term which accounts for relative proximity of the material in the two bodies being considered. It is essentially a volume integral of material divided by the square of the separation distance. The formula below is for two equal diameter spheres. It has the standard terms for the decrease in the force with separation distance. This does not include a retardation term which accounts for the decrease in the force as the higher frequency interactions fall out of phase with increasing separation. The values calculated in figures 2.26 and 2.27 include an estimation of this retardation effect as presented in (1).

$$\Phi = -A_{131} \frac{1}{6} \left(\frac{2a^2}{r^2 - 4a^2} + \frac{2a^2}{r^2} + \ln \frac{r^2 - 4a^2}{r^2} \right) \quad [2.60]$$

Van der Waals Attraction Energy Between Two Particles of Radius a

The L-VdW force is usually thought of as a short range force and this is valid for most colloidal systems that have been studied quantitatively. These are water-hydrocarbon mixtures, spherical polystyrene and silica particles in water, and the crossed cylindrical mica sheets used by Israelachvili.(3) The interaction energy for two 270 nm diameter silica particles in ethanol will only be less than -5 kT energy units within 5 nm of the surface. For alumina particles of the same size this -5 kT distance increases to 8 nm in ethanol.

Moving to materials with a higher refractive index, the distance jumps by more than a factor of two, such as the value of 20 nm for PZT. The extreme would be gold or other similar metals where this -5 kT distance would be 23 nm or 17% of the particle radius. This illustrates why far more work and care are required to generate stable suspensions of these highly polarizable materials.

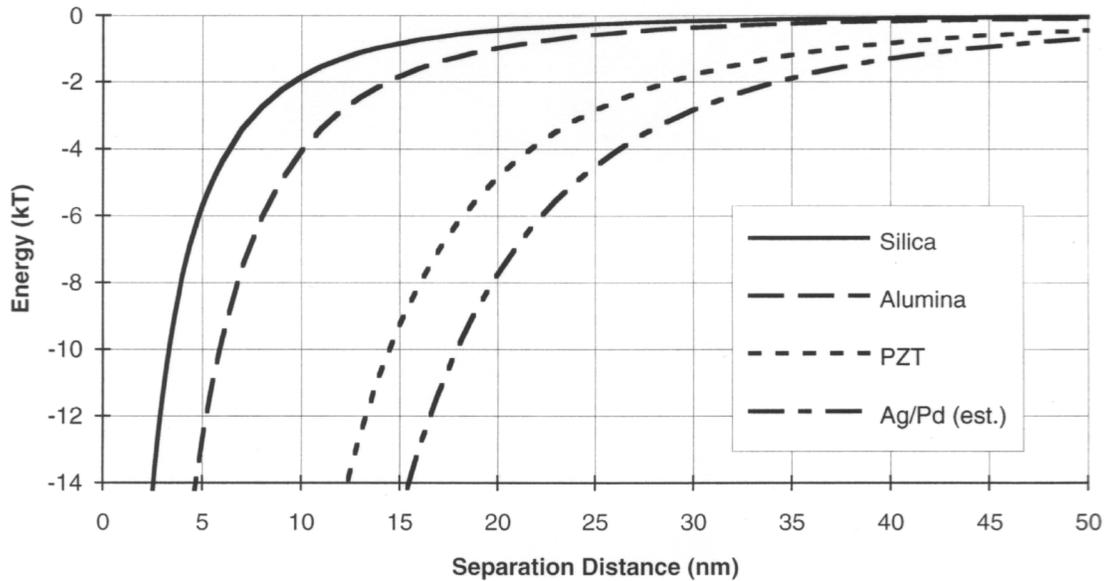


Fig 2.26 Retarded L-VdW energy-distance profiles for two 270 nm dia. spheres in ethanol.

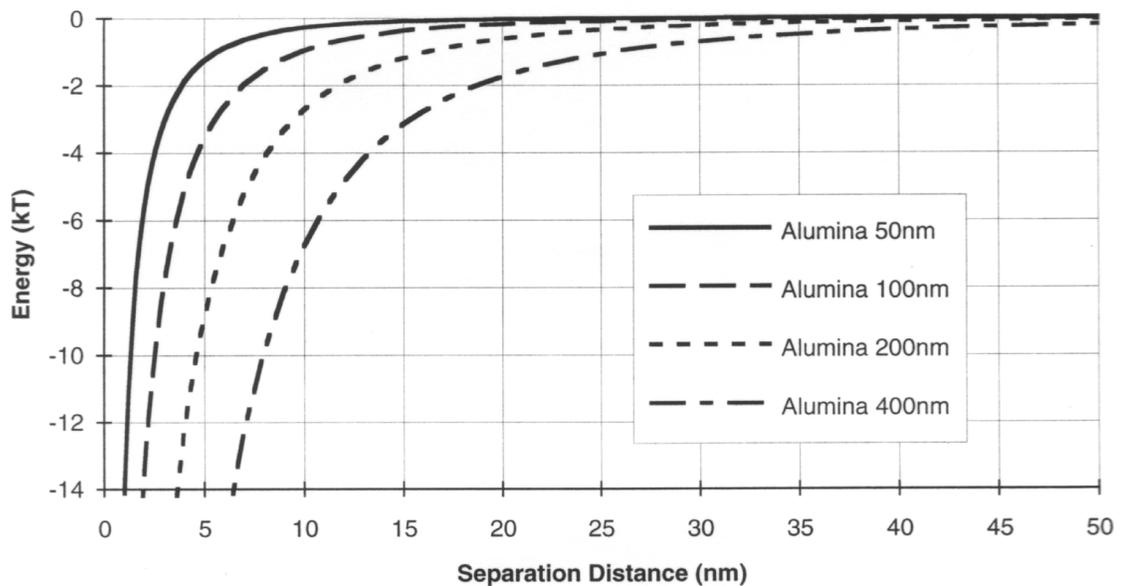


Fig. 2.27 L-VdW energy distance profiles for spherical alumina particles of different diameters in ethanol.

2.6 Stabilization

There are three main categories of stabilization for a particulate suspension: kinetic, electrostatic, and polymeric. These are all simply ways of keeping particles apart on the time scale of interest. Kinetic stabilization is simply to make the suspension sufficiently dilute that Brownian diffusion does not bring the particles into contact at a significant rate. Electrostatic stabilization uses the attraction between fixed charges on the surface of the particles and counter ions in solution to create a pressure layer around the particles which serves as an additional energy barrier keeping the particles apart. Finally in polymeric stabilization the particles are coated with a polymer layer which is thick enough to keep the particles from approaching within range of the L-VdW force, and itself has an insignificant L-VdW interaction in the solvent.

2.6.1 Kinetic Stabilization

Kinetic stabilization relies on the spacing between particles being large relative to the diffusion rate of the particles and the time period of interest. This can either be the time necessary to perform EPD or the sedimentation time for individual particles.

The theory for the rapid coagulation of particles was first developed by Smoluchowski in 1916 (19). The assumptions for this most basic theory are: the particles move only by Brownian diffusion, there is no particle interaction until two particles touch, and when two particles do touch they are irreversibly attached. This was conceptually modeled by assuming a stationary particle in a suspension where each mobile particle in the suspension disappears when it comes into contact with the stationary particle. This allows the instantaneous doublet formation rate to be calculated without the consideration of the effects of triplets, quadruplets, et ceterae.

Mathematically this was modelled as a suspension with a concentration of particles per unit volume, n . Within this suspension there is a sphere of radius, R , two times the particle radius, within which the particle concentration is zero. The rate of diffusion of particles through this surface is then the rate at which interparticle contacts would occur. This is then generalized for the entire suspension by using a diffusion coefficient for mutual diffusion of particles. For symmetric particles this is simply two times the single particle diffusion rate. Finally this is integrated for the time probability of an inter-particle contact over the number of particles per unit volume.

$$J_o = \frac{dn_o}{dt} = \frac{8kTn^2}{3\mu} = n \frac{2\phi kT}{\pi\mu a^3} \quad [2.61]$$

where n is the number density of particles and ϕ is the particle volume fraction.

This expression for the flux of single particles disappearing from the suspension can then be integrated to give the particle concentration at a given time based on the initial particle density, n_0 :

$$n_t = \frac{n_0}{1 + t/t_c} \quad [2.62]$$

where t_c is the characteristic time for doublet formation:

$$t_c = \frac{3}{4} \frac{\mu}{n_0 kT} = \frac{\pi \mu a^3}{\phi_0 kT} \quad [2.63]$$

This is the time in which one half of all single particles will turn to doublets, assuming that only doublets are formed. Of course, doublets, triplets and large flocs cannot be ignored in real systems, but this approach does give an accurate estimate of coagulation rates in the initial stages of coagulation and in very dilute suspensions.

One of the key points highlighted by these formulas is the linear dependence of the coagulation rate on the number of particles per unit volume. This means that the volume fraction must go down as the cube of the particle diameter. Fig. 2.8 below shows the characteristic time for doublet formation in ethanol, $\mu=1.07$ cP, at 25°C. A 1 vol.% suspension of 4 μ m particles will have a characteristic time of ten minutes. For a suspension of 0.4 μ m particles to have the same characteristic time the volume fraction must drop by 10^3 to 10 parts per thousand. For 40 nm particles this drops again to the usually impractical volume fraction of 10 parts per billion.

From this analysis it is clear that there is a window of particle size and volume fraction where a suspension will be stable for long enough to perform EPD, even though there is no force slowing or preventing the particles from coming into contact. The lower limit of particle size will be set by the flocculation rate, the upper limit by sedimentation rate, and the volume fraction by the time it takes to go from turning off the high energy agitation necessary to disperse the particles to the end of deposition.

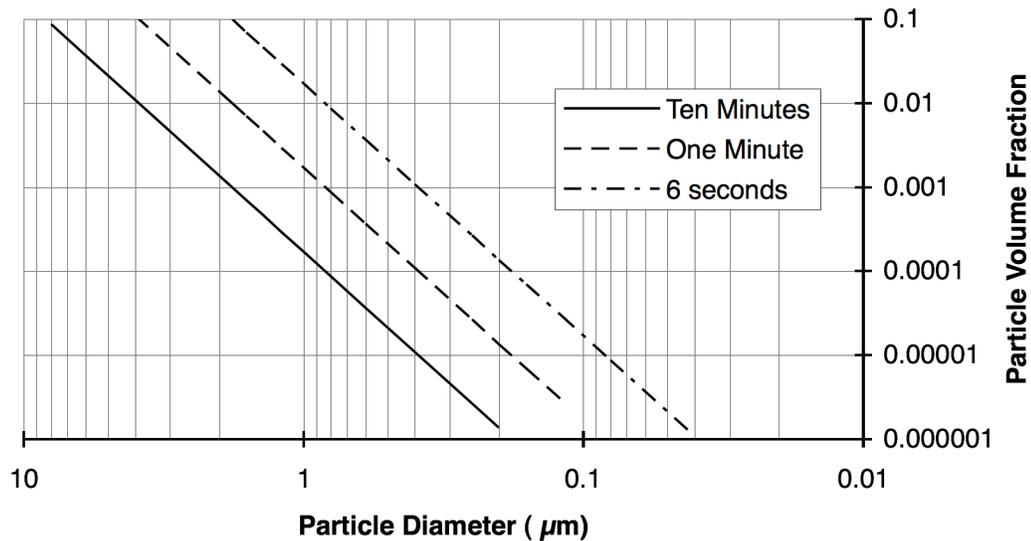


Fig. 2.28 Particle volume fraction as a function of particle diameter for three characteristic times of doublet formation.

Another phenomenon that can be mentioned here is that of a kinetically stable flocced suspension. That is a suspension which consists of flocs but where the flocs are neither growing nor sedimenting significantly on the time scale necessary for EPD. From the treatment above, for a 0.5 vol.% suspension of 0.25 µm diameter particles, the characteristic doublet formation time is only 0.32 seconds. This is approximately the time it will take for one half of the single particles to form doublets. At longer times these doublets will then more slowly combine to form quadruplets, then again more slowly forming octuplets, etc.

Smoluchowski was able to extend his theory for the coagulation of individual particles to multiple particles on the basis of two assumptions. The first was that the hydrodynamic radius of a floc would be the same as the effective capture radius for the floc. Since the diffusion coefficient for a particle is inversely proportional to the hydrodynamic radius, this allowed the statement that $D_l a_l = D_1 a_1$; that is the product of the diffusion coefficient and the capture radius of a floc made up of l particles is the same as the product of the diffusion coefficient and capture radius of a single particle. The great advantage of this assumption is that it is both reasonable and eliminates the need to have any knowledge of the density or geometry of the flocs. A lower density floc will have a larger area for collision and capture of other particles/flocs, but this will be proportionally compensated by the reduction in the floc's diffusion velocity.

While this first assumption cancels the floc density from the equations for the collision of flocs of the same size, it is not eliminated from the calculation for the relative diffusional motion of different sized flocs. This necessitates the second critical assumption, that most of the collisions occur between flocs of similar size such that:

$$a_l + a_m \left(\frac{1}{a_l} + \frac{1}{a_m} \right) = 4, \quad [2.64]$$

where a_l , a_m are the hydrodynamic and capture radii of two colliding agglomerates, l & m . This allows the generalization that $D_{lm} a_{lm} = 2D_l a_l$; where D_{lm} is the relative diffusion rate of a floc containing l particles to a floc of m particles. This equation would, of course, be exact for flocs of the same size: $D_{ll} = 2D_l$.

These assumptions then allowed the analytic solution of the conservation equations for number density of independently moving particles/flocs containing l particles, n_l . The sum of all of the independent particles/flocs as a function of time is found to be

$$\sum_{l=1}^{\infty} n_l = \frac{n_o}{1 + t/t_c}. \quad [2.65]$$

This is the same as equation [62] above with the same t_c . It is only the meaning that is changed.

From this equation it is possible to make an estimate of the time it takes to form $5 \mu\text{m}$ and $10 \mu\text{m}$ flocs. Using an intermediate value for the fractal dimension of 2.25,

$$l = \left(\frac{a_l}{a} \right)^{2.25} \quad [2.66]$$

a suspension with a starting particle size of $0.25 \mu\text{m}$ will generate 5 and $10 \mu\text{m}$ flocs containing 800 and $4,000$ primary particles respectively. To reach this state from an initial primary particle dispersion would take about 5 minutes for $5 \mu\text{m}$ flocs and 20 minutes for $10 \mu\text{m}$ flocs. To go from an average floc size of $5 \mu\text{m}$ to $10 \mu\text{m}$ takes 15 minutes. For the number density of flocs to drop in half again will take a further 30 minutes.

These flocs, of course, will be sedimenting out of the suspension. However, because of their very low density the sedimentation velocity is still low on the time scales here. For the $5 \mu\text{m}$ flocs in this example the particle density within the floc will be only 10 vol. %. If these particles are alumina in ethanol, this will yield a barely noticeable sedimentation rate of 0.25 mm/minute. Ten micron flocs will be only 6% dense, but because of their larger size will have the more noticeable sedimentation rate of 0.6 mm/minute. However, even this sedimentation would be invisible with even the slightest agitation.

Thus we have the situation where even though the particles are 'rapidly' flocculating, because of the very low solids loading frequently used in EPD a kinetically quasi-stable suspension of flocs can be formed. A mechanically dispersed suspension of individual particles will become substantially flocced within seconds of the ending of high energy agitation of the suspension. With a solids loading of a few volume percent or more these flocs will rapidly consume the entire volume of the suspension forming a gel or pseudoplastic paste which would be useless for EPD. Below one volume percent these flocs can reach a state of relatively slow growth and sedimentation. These flocs can easily be deposited electrophoretically. The increased density at the deposition electrode will bring the flocs together in a low density sediment structure.

2.6.2 Electrostatic Stabilization

In the absence of an externally applied voltage, if a surface is charged in a solution then for each unit of charge on the surface there is an opposite charge dissolved in solution. The opposite charges will attract, and the ions in solution will migrate toward the surface until electrophoretic migration is matched by diffusion away from the elevated concentration near the surface. This results in a concentration gradient of ions near the surface governed by the Poisson-Boltzmann equation [4] as described before for electrode surfaces.

This diffuse portion of the electrostatic layer at the surface will have a higher hydrostatic pressure than the surrounding fluid. This can be thought of in two ways. One way is to regard this higher pressure layer as a Maxwell force due to the electrostatic attraction between the charged particle surface and the charged solution in the DEBL. Alternatively this can be regarded as the increased osmotic pressure due to the higher ionic concentration in this layer. Both approaches are merely looking at different sides of the P-B equation.

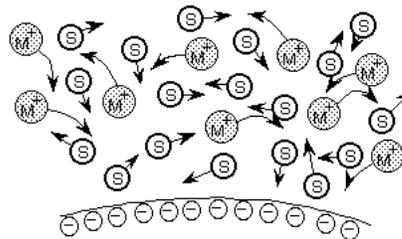


Fig. 2.29 The electrostatic attraction between the counter ions and surface leads to a higher hydrostatic pressure at the charged surface.

So a particle with an electrostatic surface charge will surround itself with a layer with a higher hydrostatic pressure than the bulk of the solvent. As one particle approaches another these higher pressure layers will act as bumpers holding the particles apart. This is the primary mechanism of electrostatic stabilization. Actual electrostatic repulsion between like charges only occurs when the separation between particles is much less than the thickness of the DEBL between the particles. This is usually only significant in suspensions with very low ionic strengths and therefore very thick boundary layers (small κa).

Estimating Electrostatic Repulsion

There are two commonly used approximation methods for calculating the force between electrostatically charged particles: the Derjaguin and the Linear Superposition approximations. Both make different simplifying approximations for the ionic distribution between two spheres, making them valid for different particle separations and diffuse layer thicknesses. Both, however, rely on the same linearization of the P-B equation [2.7] which is the basis of the Debye-Hückel approximation. This means that even in the proper range of diffuse layer thicknesses and particle separations these formulas will only provide good quantitative estimates for relatively low surface potential (< 25 mV).

There are two radial components in the problem of approaching spheres which have prevented the creation of a closed form solution of the interparticle force even with the linearization of the P-B equation. The first is the curvature of the particles themselves. Moving away from a curved surface the volume gradient dV/dr increases. It is only for very thin diffuse layers (high κa) that the surface can be treated as a flat plate. This is the particle radial component. The second significant component is the central plane radial component. To calculate the forces between two particles the hydrostatic pressure is integrated over the central plane separating the particles. When particles approach solvent with the dissolved counter ions is squeezed out from between the particles. This causes charge imbalance in the region of closest approach of the particles. This can lead to both a classical electrostatic like-charge repulsion between the surfaces as well as a strong radial electrostatic field in the central plane between the particles, changing the counter ion distribution and therefore the osmotic pressure distribution.

The Derjaguin approximation is based on an accurate solution of the linearized P-B equation between two flat plates. In exchange for this accurate solution of the P-B equation this approximation ignores both of the radial components. Because of this, it is only valid for thin boundary layers and small particle separations. Furthermore, because it ignores the central plane radial component this estimation method does not work well for

most separation distances at constant surface charge conditions. The exception is for very thin diffuse layers ($\kappa a > 30$) with a particle separation distance greater than κ^{-1} .

The Linear Superposition Approximation replaces the accurate solution for the linearized P-B equation in the Derjaguin formulation with an accurate solution for the diffuse layer around a sphere and estimates the interaction force by summing the ionic concentrations where the diffuse layers overlap. Because this formulation includes the contribution from the particle radial component it will generate accurate estimates for thick diffuse layers and large particle separations. Unfortunately, at particle separation distances of less than $2\kappa^{-1}$ superposition becomes a very inaccurate method of estimating the counter ion distribution and significantly overestimates the interparticle force.

Electrostatic Interaction Energy Approximation Formulae

- Derjaguin Approximation Interaction Potential Energy - Constant Potential

$$\Phi = 2\pi\epsilon_r\epsilon_o\psi_o^2 a \ln(1 + e^{-\kappa h}) \quad [2.67]$$

- Derjaguin Approximation Interaction Potential Energy - Constant Charge

$$\Phi = 2\pi \frac{q^2}{\epsilon_r\epsilon_o} a \ln(1 - e^{-\kappa h}) \quad [2.68]$$

- Linear Superposition

$$\Phi = 4\pi\epsilon_r\epsilon_o \frac{a^2}{h + 2a} \psi_o^2 e^{-\kappa h} \quad [2.69]$$

- Thin Double Layer Linear Superposition

$$\Phi = 32\pi\epsilon_r\epsilon_o \left(\frac{kT}{ze}\right)^2 a \gamma^2 e^{-\kappa h} \quad ; \quad \gamma = \tanh\left(\frac{ze\psi_o}{4kT}\right) \quad [2.70]$$

(From (1))

In 1982 Glendinning and Russel (20) used a combined analytic/numeric scheme to generate accurate solutions for two spheres as a function of diffuse layer thickness and separation distance. They used a solution of the linearized P-B equation in the form of the product of a Bessel equation and a Legendre polynomial expansion. They were then able to use a coordinate translation to put a second sphere into the coordinate system of the first. The result, when truncated, was a system of linear equations which could be solved numerically.

They then compared the results of this calculation to the values of the Derjaguin and linear superposition approximations to generate charts of the percentage deviations between the estimation methods and the accurate solution. From these deviation charts

they created the validity maps in Fig 2.30 below. The regions marked Derjaguin and LSA are where each of the interparticle force approximations are within 10% of the accurate solution. The regions marked 'exact' are where only the accurate solution will generate quantitatively meaningful results. Because the Glendinning and Russel solution is again based on the linearized P-B equation the location of these 10% lines is independent of surface potential with the limitation that they are only valid themselves for low surface potentials (< 25 mV).

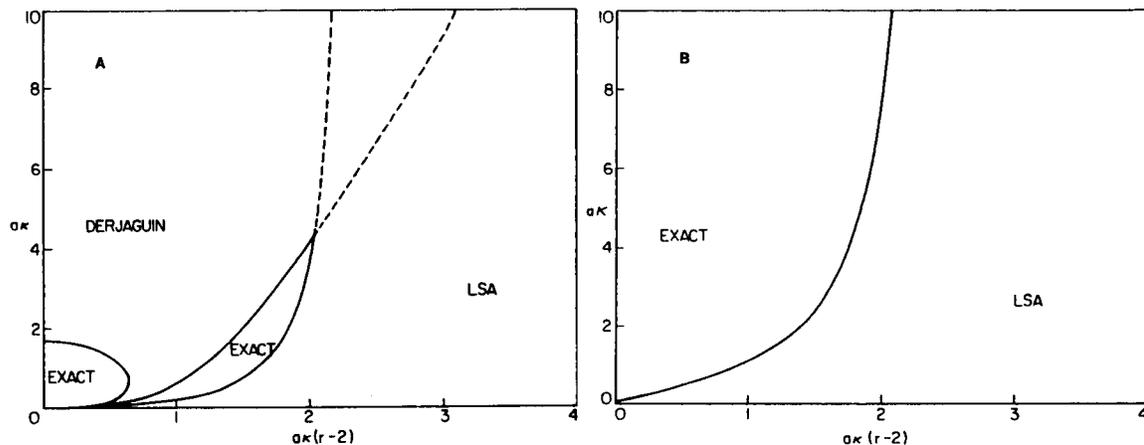


Fig. 2.30 Regions where the Derjaguin and Linear Superposition (LSA) Approximations are within 10% of the exact solution. Regions marked EXACT are where neither approximation is valid.

Horizontal axis is particle surface separation distance in multiples of Debye length, κ^{-1} .
(A) Constant surface potential conditions; (B) Constant surface charge conditions.

More recently Sader, et al. (32) presented a much improved set of approximation formulas which retain a fairly simple form while having a much increased range of applicability. This author will, and the reader is encouraged to, use the formulae presented in this reference in future calculations.

Although not discussed in depth here, there are two cases of the interaction of dissimilarly charged surfaces that should be mentioned here. (8) The first is the approach of two surfaces having constant surface potentials of the same polarity but different magnitudes. At long range there will be a repulsive electrostatic force between the particles, but at short range, to maintain constant surface potentials relative to the bulk of the solution, the sign of the surface charge on the surface with the lower potential will switch polarity creating an attractive electrostatic force between the surfaces. The second situation is that of two surfaces with constant surface charge of opposite polarity but with a large difference in surface charge density on each surface. At large separations the force between the particles will be attractive due to the opposite charges on each surface. At

short separation distances, less than the Debye length, the surface with a lower charge density will displace more charges from the diffuse layer of the surface with higher charge density than it brings due to charges on its surface. There is still an electrostatic attraction between the high charge density surface and counter ions dissolved in the solution, and therefore, an electrostatic force to keep a layer of solvent between the surfaces. This means that even if two surfaces are oppositely charged, if the charge density is significantly different there can be a short range repulsive force between the surfaces. This is one reason why particles with a steady positive charge can fail to deposit on a negatively charged electrode in spite of what would seem to be an inevitable electrostatic attraction.

2.6.3 Polymeric Stabilization

There are far too many possible types of interactions between particles, polymers and solvent to offer even a brief overview here. For example, Napper (17, p. 17) lists fourteen types of interaction for colloidal suspensions with non-ionic polymers. These fourteen could be further sub-divided by types of non-ionic polymers and added to by consideration of ionic polymers. What will be presented here are only a few cases which may be suitable for EPD, within the categories of steric, depletion and electrosteric stabilization.

Soluble Polymer in Solution — Understanding of polymer-steric stabilization requires first understanding the interaction of polymer and solvent. The most critical factor here is the solubility of the polymer in the solvent.

In free space the L-VdW force will always be attractive. This means that in free space polymer will stick to polymer, particle to particle and polymer to particle. Thus in free space, including in almost all gasses, steric stabilization is not possible. The critical role of solvent is in eliminating the *net* polymer-polymer (P-P) VdW attraction. Since the VdW is a fundamental property that cannot be eliminated, the attraction between the solvent and polymer should be at least as strong as the P-P interaction so that there is no net preference between a P-P and a polymer-solvent (P-S) interaction. In this case with no energetically favorable position, the polymer will diffuse by entropic/Brownian/osmotic forces until it is uniformly distributed throughout the solvent. In short — the polymer must be soluble in the solvent.

The next question is how the polymer will behave in solution. Here it is the simplest and most illuminating to analyse the case of a simple straight chain polymer. If

this polymer were completely straight rod its length would be simply $l_o \frac{M}{m_o} \text{Sin}\left(\frac{\tau}{2}\right)$; where l_o is the length per bond in the chain, M is the molecular weight, m_o is the molecular weight per chain bond, and τ is the bond angle in the chain. However, these molecules are flexible and Brownian motion will cause them to take the form of a tangle approximating a random walk. If each of the chain bonds of the polymer were perfectly flexible this would give a root-mean-square end-to-end distance $\langle r^2 \rangle^{\frac{1}{2}}$ of $[nl_o^2]^{\frac{1}{2}}$, where n is the number of repeat units in the chain. Of course, while the polymer is not stiff it is not completely flexible either. It is only over 4 to 10 bonds that the polymer will be completely flexible. Thus there is another factor added to the equation called the characteristic ratio, C_∞ , which accounts for this lack of flexibility. The larger the value the less flexible the polymer chain. Some experimentally determined values for the characteristic ratio are given in Table 2.2

Table 2.2 Values of the Characteristic Ratio (from (2&3)).

<u>Polymer</u>	<u>C_∞</u>
Poly-oxyethylene	3.9 - 4.0
Poly-dimethylsiloxane	5.2 - 6.4
Poly-12-hydroxystearic Acid	6.1
Poly-methylene	6.9
Poly-oxymethylene	8.5
Poly-styrene	9.5 - 10.0

Finally, there is the intermolecular expansion factor, α , which is a function of the P-S/P-P interaction energy ratio. In treating the polymer configuration as a random walk it was assumed that each segment of the chain is a volumeless line. A real polymer will, of course, have a volume, but the solvent surrounding the polymer will also have a volume. If the P-S/P-P interaction energy ratio is exactly one, then the polymer will in fact behave as a volumeless chain. This condition, where $\alpha = 1$, is referred to as the theta, θ , state and the solvent that produces this state as a θ -solvent. If the solvent is better than a θ -solvent, P-S interactions are energetically favored over P-P interactions. This causes the polymer to expand beyond a purely random walk ($\alpha > 1$). Values of α are generally between 1.0 and 1.5. Values of a less than one would occur in a worse than θ solvent and results in a contraction of the polymer chain, however, this is rarely seen since if P-P interactions are

avored, the polymer molecules will rapidly floc together and can no longer be considered dissolved in the solvent.

Thus we obtain a rough but useful model of the length of a dissolved polymer molecule:

$$\langle r^2 \rangle^{\frac{1}{2}} = [\alpha C_{\infty} n l_0^2]^{\frac{1}{2}} \quad [2.71]$$

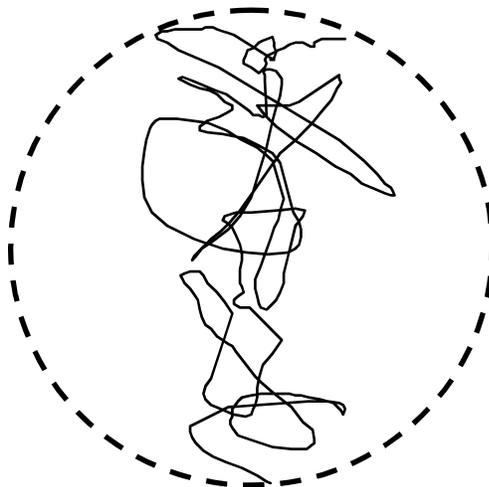


Fig. 2.31 Polymer random walk will not have a spherical shape, however, due to rotational motion a completely unconstrained polymer can be considered to occupy a spherical space.

Although the polymer is almost never spherical at any single moment in time, because it can rotate freely in the solvent the above rms end-to-end length can be used to define a spherical volume for the polymer. Anytime this sphere is compressed, such as by the surfaces of two approaching particles, the number of configurations available to the polymer is reduced and the total energy of the system is increased. As particles approach more closely solvent is forced out from the loops of the polymer increasing the energy further.

In the classic physical sense the steric force is the repulsion which prevents one atom from interpenetrating another and is based on the Pauli exclusion principle. In colloidal science the steric repulsion force is primarily an entropic/osmotic pressure force. Only when the polymer is fully compressed does the repulsion become steric in the classical sense. A soluble polymer will act as a linear spring extended by osmotic/entropic forces. This polymer-steric repulsion has a much different force-distance curve than the classic steric repulsion force and is able to act over the much longer distances necessary to keep particles out of range of their mutual VdW attraction.

Polymer at a Solid Surface – When a solid surface is introduced to the polymer solution the polymer can exhibit a range of adsorptions from zero to very strong.

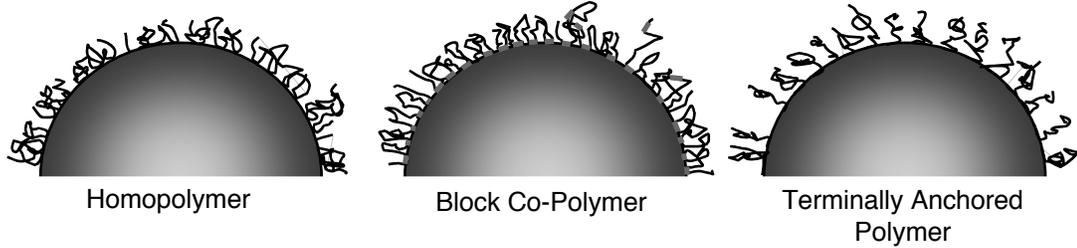


Fig. 2.32 Behavior of Various Polymers at a Surface

In the case of non-adsorbing polymer the polymer molecules near the surface will try to retain their time averaged spherical shape. This means that immediately adjacent to the surface there will be a layer of about $\frac{1}{4}\langle r^2 \rangle^{1/2}$ thick which will have a significantly lower average concentration of polymer chain segments than the bulk solution. In a good solvent for the polymer, i. e. a negative free energy of dissolution, this depleted layer will have a higher energy than the bulk solution. From the standpoint of osmotic pressure, the lower concentration of dissolved polymer at the surface than in the bulk means that the hydrostatic pressure in this surface layer is lower than in the bulk.

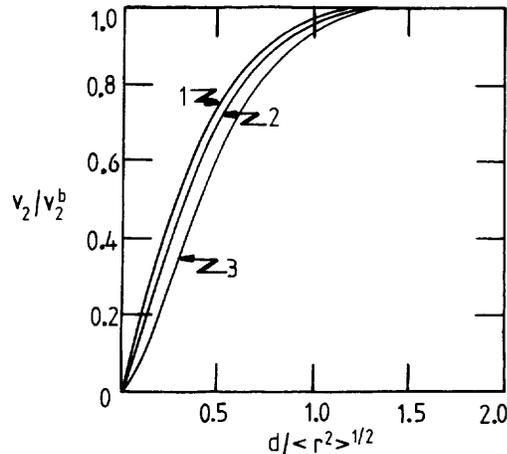


Fig. 2.33 Density of dissolved polymer near a surface. 1.0 = density in solution. (1) poly(oxethylene) MW. 400, (2) poly(oxethylene) MW. 4,000, (3) random flight chain of 4,000 bonds. Napper (17, p. 387)

A polymer made up of the same repeat unit, a homopolymer, can also weakly adsorb to the surface. If this polymer adsorbs too strongly it will collapse entirely onto the surface. If the polymer is only weakly adsorbed then segments will be dynamically adsorbing and desorbing to the surface. This leaves loops of the polymer extending out into the solvent.

There are also polymers that have specific adsorbing groups. These can be either terminally anchored polymers or block co-polymers. These have groups that will attach to

the solid surface either because they are insoluble in the solvent or due to specific adsorption interactions. Terminally anchored polymers at low coverage will extend out into the solvent by the same rms. distance, $\langle r^2 \rangle^{\frac{1}{2}}$, as the polymer in free solution. As the coverage increases the polymer tails will extend much further away from the surface as the scaling law exponent of number of repeat units changes from 1/2 to almost 1 as the polymers crowd each other laterally, forcing each other out into straighter and straighter lines. The extension of block co-polymers is more complex but follows the general rules with increased coverage leading to a thicker layer.

Finally there are the polyelectrolytes. These polymers have ionic groups along their length. These ionic groups will create a strong self repulsion extending the molecules well beyond the $\langle r^2 \rangle^{\frac{1}{2}}$ of an uncharged polymer. This molecule can adsorb to charged or ionizable sites on the surface. The coverage and extension of these charged polymers into the solvent is a complex function of site density on the surface, and, in the solvent, the polymer concentration, chemical activities, and the ionic strength.

Polymer Between Two Surfaces – For two surfaces approaching in a solution of completely dissolved polymer there is first a repulsive force as polymer molecules are compressed between the surfaces. Then as polymer molecules are forced out of the gap an 'attractive' force as solvent diffuses out into the bulk solution. When the gap between surfaces approaches the size of the dissolved polymer, the polymer is compressed, increasing the osmotic pressure between the surfaces and driving polymer out of the gap between the surfaces into the bulk solution. When the surfaces get close enough, so much polymer is forced out of the gap that the concentration drops below the bulk and the osmotic pressure in the bulk is higher than between the surfaces. This causes a 'suction' between the surfaces pulling them together. This final stage can also be considered as an overlap of the depleted layers described in Fig. 2.33 above.

Figure 2.34 below shows the equilibrium energy of approach of two 155nm particles calculated by Feigin and Napper (21) for three polymer concentrations. The particles will experience no net force until the surfaces approach to less than $2\langle r^2 \rangle^{\frac{1}{2}}$ of the dissolved polymer. At this point the number of possible conformations for the polymer chains begins to be constricted. The concentration of polymer segments per unit volume goes up and therefore the osmotic pressure in the gap rises. This rise continues until at about $\langle r^2 \rangle^{\frac{1}{2}}$ the increased concentration of polymer in the gap causes polymer to diffuse out of the gap faster than it is compressed and the pressure begins to decline again. At

about $\frac{1}{2}\langle r^2 \rangle^{\frac{1}{2}}$ the concentration of polymer has dropped to the same as in the bulk and there is no net force between the surfaces. Below $\frac{1}{2}\langle r^2 \rangle^{\frac{1}{2}}$ the polymer concentration drops below the bulk and the osmotic pressure drops below that of the bulk. The surfaces experience a "suction" force which can cause the particles to floc together independent of the van der Waals force.

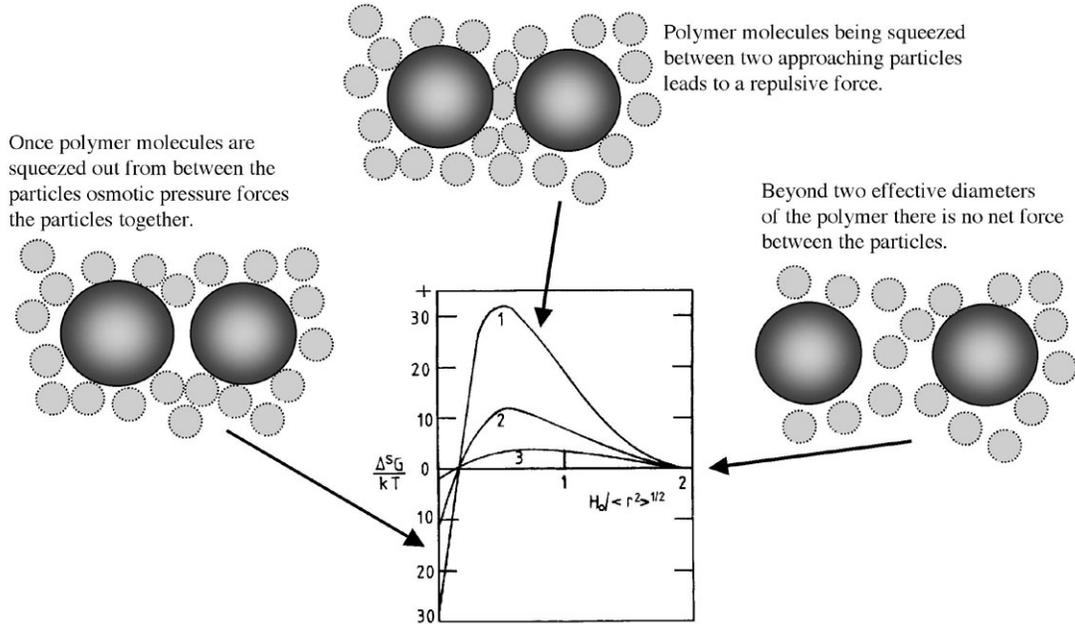


Fig. 2.34 Interaction energy chart for depletion stabilization. (adapted from Napper 17, p. 387)

In the cases where the polymer is adsorbed to the surfaces the behavior is initially the same. As the surfaces approach to less than two times the thickness of the soluble portion of the adsorbed polymer layers, these layers are compressed driving out solvent and increasing pressure between the surfaces. As long as the polymer remains adsorbed, the force between the surfaces is uniformly repulsive.

However, for different types of molecules varying adhesion can lead to different long term behavior. A homopolymer coating which is only weakly adsorbed will diffuse out from between the two surfaces, in the same manner as the non-adsorbed polymer but more slowly. This also applies to terminally anchored chains at less than complete coverage where the chains can be forced across the surface away from particle contact points. For block co-polymers, also at less than full coverage, an adsorbing block on one surface can desorb and adsorb to the opposite surface creating a bridge holding the surfaces together. Thus adsorbed polymers can have a time dependent hysteretic effects on the forces between particles.

2.7 Application to EPD

What makes suspension development for EPD unique is that whatever mechanism is used to keep the particles separate in the suspension, something must change to allow the particles to be bound together at the deposition electrode. Therefore the suspension must be designed for stability or quasi-stability in the bulk and instability at the deposition electrode. Therefore, before discussing deposition methods, it will be useful to list briefly some of the differences that can exist between the bulk solution and the immediate vicinity of the deposition electrode.

1. Density – With electrophoresis particles will accumulate at the deposition electrode causing the particle volume fraction and number density to go up by an order of magnitude or more. Frequently, this alone can change the stability of the system.
2. Electrostatic and Electrohydrodynamic (EHD) Forces – In the bulk, charged particles will move by electrophoresis toward the oppositely charged electrode with an EHD flow around the particles going the opposite direction. When the particle motion stops either at the electrode or against other particles stopped by the electrode the balance of the electrostatic and EHD forces will change.
3. Electrodeposition – In EPD particles can rarely be considered alone. The force on a particle will include the sum of the forces on the particles behind it relative to the deposition electrode. This is the same as for gravitational sedimentation where the force on a layer is the sum of the forces on all of the layers above it.
4. Electrochemical Gradients – It is important to recognize that EPD is always an electrodynamic process. Current must flow through the deposition cell, which means that electrochemical reactions will be occurring at each of the electrodes. This leads to the formation of an electrode boundary layer that can have either an increased or decreased ionic strength, changed acid/base equilibrium, as well as a change in the ionic species present.

It is these differences at the deposition electrode that must be managed and used to take freely moving particles from the bulk suspension and bind them together in a rigid mass with the desired thickness, density and adhesion.

2.7.1 Deposition from Electrostatically Stabilized Suspensions

The question then becomes how these near electrode effects can be used to convert freely moving particles in the suspension to mutually adherent components of a stable, rigid deposition. To answer this, each of the above enumerated effects will be considered in turn as they relate to an electrostatically stabilized suspension.

Density — Increased density alone will be a relatively ineffective means of depositing particles. Electrophoresis can raise the density of particles by one or two orders of magnitude at the electrode, however, density alone does not change the stabilizing force between the particles. Only for suspensions with little or no stabilizing force where particles are already floccing in the bulk suspension will the increase in density lead to the formation of a deposit. Moreover, in this case since the particles will ultimately come into contact due to the random Brownian motion superimposed on their electrophoretic velocity, the deposition will likely be a very weak, low density structure with a very low average number of interparticle contact points.

Electrostatic Force — The externally applied electric fields commonly used in EPD range from a few volts to several hundred volts per centimeter. This electric field causes the electrophoretic motion of the particles toward the deposition electrode, however, in most cases where there is a sufficient electrostatic repulsion to stabilize the particles from floccing in suspension, the electrostatic force due to the average electric field is insufficient to overcome the interparticle repulsion.

Figure 2.35 below gives the total interaction energy for alumina particles in ethanol at one condition where EPD was successfully performed. The ionic concentration of the suspension was 0.4 millimolar and particle zeta potential was 42mV. The interaction energy was calculated using the Derjaguin approximation for constant potential and the Van der Waals interaction calculated using Eq. [60]. This gives an energy barrier to flocculation of 53 kT units; a maximum interparticle repulsion force of 13.4 picoNewtons at a 7 nm separation; and a total charge on one particle of 0.29 femtoCoulombs (10^{-15}). To produce an electrostatic force on a single particle equal to the maximum repulsive force would require an imposed electrostatic field of 460 V/cm. Given that the average applied electric field is only ≈ 10 V/cm, it is clear that more than simple electrostatic force must be involved here. (More details of this type of deposition are given in Ch. 4.)

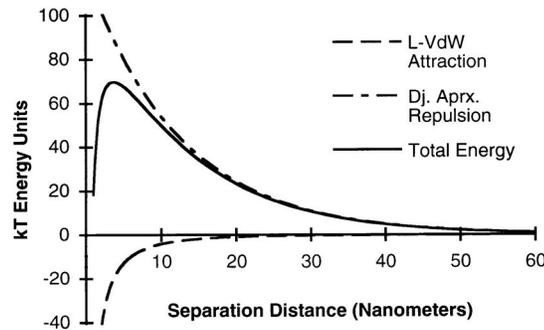


Fig. 2.35 Energy potential of two approaching 270nm dia. alumina particles with a Debye length of 12.5 nm and surface potential of 51 mV.

However, this does not mean that electrostatic force cannot be used to drive deposition from a stable suspension. Table 2.3 below shows the calculated surface potential necessary to create an energy barrier of 15 kT between two 270 nm dia. alumina spheres in ethanol. This is an energy barrier sufficient to provide long term stability against flocculation in the bulk suspension. The voltage fields necessary to overcome the interparticle repulsion at these conditions are given in the last column. These voltage gradients are not unreasonable and are frequently used in very low conductivity suspensions. In higher conductivity suspensions continuous use of these voltages would lead to vigorous convection and heating of the suspension, however, this would not preclude their use in brief pulses.

Table 2.3

Surface potential necessary to provide a 15 kT electrostatic energy barrier to flocculation for two 270 nm diameter alumina particles in ethanol at several ionic strengths; maximum repulsive force between the particles (picoNewtons); separation distance at which maximum force occurs (nanometers); total surface charge for one particle (attoCoulombs); and electric field necessary to produce a force on the charged particle equal to maximum interparticle repulsion force.

κa	κ^{-1} (nm)	mMol	mV for 15kT	pN	@ nm	attoC ($\times 10^{-18}$)	V/cm
4	34.0	0.026	26	1.27	23	51	250
6	22.5	0.059	28	1.84	18	77	240
8	16.9	0.105	30	2.45	15	108	230
10	13.5	0.165	32	3.13	13	142	220
12	11.3	0.235	33	3.5	11	172	200
16	8.4	0.42	36	4.8	9	250	190
20	6.7	0.66	39	6.2	8	340	180

This deterministic approach, however, ignores Brownian motion. The most likely scenario for the formation of a deposition is that the electrostatic force will reduce the

effective interparticle force to a certain point and then this final energy barrier is overcome by thermal motion of the particle. The superposition of the Brownian motion on the electrophoretic motion of the particle introduces a time/probability function to the problem of particle contact. This can affect the density of the deposition, with faster deposition rates leaving less time for particle re-arrangement in the depositing layer and thus lower deposition densities.

Electrohydrodynamic (EHD) Forces — Given that there is a net charge balance in the suspension, there will be a net electrostatic force balance due to the applied electric field as well. In the suspension this means that as particles are pulled toward the deposition electrode, the charged solvent around them is pushed in the opposite direction. The effect of this EHD flow in the opposite direction on electrophoresis of a single particle is discussed in § 2.4. There have been some studies on EHD flows around single or paired particles in the vicinity of an electrode (**22,23**). These show the mechanism by which particles at less than a single layer coverage can be made to aggregate into one dimensional colloidal crystal arrays on an electrode. However, how these EHD flows affect the approach of a particle to an existing layer of particles, how they affect particle re-arrangement prior to deposition, and finally their effect on the deposition of has not been determined. Some speculation on this topic is presented in Ch. 4.

Electrosedimentary Force — That the electrostatic force on a single particle alone was insufficient to cause deposition became apparent very early on in the compilation of the theory electrostatic repulsion (**24**). A simple solution to this inconsistency was proposed by Hamaker and Verwey in 1940 (**25**). Rather than the electrostatic force on a single particle this deposition mechanism relies on the force on a layer of undeposited particles to provide the force necessary to overcome the repulsion on the innermost layer. Because this mimics gravitational sedimentation with electrostatic force replacing gravity, this is referred to as electrosedimentary deposition. Below is the original chart from Hamaker and Verwey showing the effect of a superposition of the linear compaction force on the interparticle energy barrier.

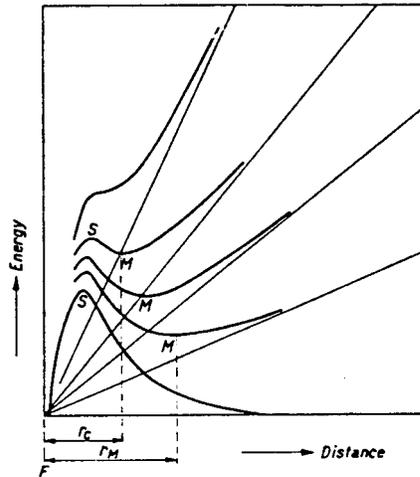


Fig. 2.36 Superposition of an electrostatic compaction force on the interparticle energy barrier, from Hamaker and Verwey, 1940 (25)

Electrochemical Changes — Finally, there are the electrochemical changes that can occur due to conduction at the deposition electrode. These changes can go in any direction, either an increase or decrease in ionic strength, proton activity or a change in ionic composition.

— *Ion Depletion Enhanced Electrostatic* — The first electrochemical change is the decrease of the ionic strength in the deposition layer. If an ion in solution is consumed at the deposition electrode there will be a decrease in the total ionic concentration at that electrode due to the outward migration of the counter ion. This is source of the limit current behavior discussed in Section 2.2. The important difference between the formation of this charge depleted layer in a solution and during EPD is the presence of the growing deposit on the electrode surface. The ion depleted layer is very unstable and in the free solution quickly transitions to convective flow. This improves mass transport of ions and eliminates the charge depleted region. However, the presence of an electrophoretically deposited layer of particles on the electrode can act as a strong damper to the initiation of convective flow as will be shown in Ch. 4. This damping allows the charge depleted layer to grow, and voltage gradients can rise to levels on the order of 10,000 V/cm. If the particles retain their surface charge, the electrostatic force on the particles is both sufficient to overcome interparticle repulsion and to provide a significant compressive force to compact the deposition.

— *Salting Out*— In some cases the exact opposite will occur and electrochemical reactions at the deposition electrode will lead to an increase in the ionic strength of the solution at the electrode. This can occur when the current through an electrode-solvent interface is due to electrolysis of the solvent or dissolution of the electrode material. This is illustrated in the left part of the diagram in Fig. 2.11.

This increase in ionic strength in the vicinity of the electrode will reduce the thickness of the diffuse layer around the particles. This can reduce or eliminate the electrostatic stabilizing force around the particles allowing them to deposit. This flocculation by increased ionic (salt) concentration is commonly referred to as 'salting out'.

What will be critical for this type of deposition is the ratio of the growth of the ion enriched layer to the growth of the deposition layer. If the ion enriched layer grows faster than the deposition layer particles can be destabilized and begin to floc before entering the deposition. If the ion enriched layer grows slowly through a dense suspension of particles held in place by electrophoresis, the gradual thinning of the repulsion layers around the particles should allow the layer to gradually compact as the particles move toward each other resulting in a fairly dense deposition. If particles arrive at the deposition electrode much faster than the growth of the ion enriched layer then deposition may occur by electrosedimentation and the growth of the ion enriched layer will be irrelevant.

— *Charge Reduction/Neutralization* — The final case where electrochemical reactions at the deposition electrode cause electrostatically stabilized particles to deposit is where the ionic strength changes relatively little but there are critical changes in the composition. This can occur when the electrochemical reactions produce ions of opposite charge to the particle surfaces, which then adsorb to the particles eliminating the surface charge. Conversely, if the particle surface charge is produced by the equilibrium adsorption of one ionic species, if that species is consumed at the electrode the concentration near the electrode will drop, causing desorption of the charging species from the particle surface. This again reduces the particle surface charge and therefore the electrostatic stabilizing force, allowing the particles to deposit.

2.7.2 Deposition from Polymerically Stabilized Suspensions

One of the great attractions of steric stabilization for the creation of colloidal suspensions is the ability to create dispersions which are thermodynamically stable. At all distances the force between particles are repulsive. Even particles that are brought into intimate contact, such as by drying, will spontaneously redisperse with the addition of solvent.

This is, of course, not the behavior we need for EPD. Deposited particles must adhere to each other so that the deposition will remain after the deposition voltage is turned off and the deposition is removed from the deposition bath. To do this the soluble polymer must either be removed from the contact points between the particles so they can adhere due to VdW forces, or the polymer must itself become a binder holding the particles together. There are three ways that this destabilization can take place: squeezing out of the polymer from particle contact points, bridging flocculation between particles, and a change in the solubility of the polymer. The first two rely only on the electrostatic and electrosedimentary forces slowly pulling the particles together. Change in solubility will depend on electrochemical changes in the depositing layer.

The simplest polymer to squeeze out, naturally, is the non-adsorbed polymer used in depletion stabilization. The combination of viscous and depletion stabilization in the bulk can be used to create exactly the sort of slowly floccing suspension which is stable long enough to perform EPD but where the stabilizing force can easily be overcome in the depositing layer. This is particularly true for the viscous component of stabilization. Viscous forces will preferentially damp the Brownian motion of one particle toward another. With a steady unidirectional force the additional viscosity of the dissolved polymer will only slow the final approach of one particle to another without creating a repulsive energy barrier.

The greatest advantage of this stabilization scheme is that it does not require any specific interaction with the particle surface. There is no need to find a match between the adsorbing groups of a polymer and the particle surface. One polymer/solvent pair could potentially stabilize many types of particles. Furthermore, none of the active surface sites on the particle will be covered by adsorbed polymer. So if particles only develop a modest surface charge it will not be reduced or eliminated by polymer adsorption.

This appears to be the mechanism used by Bouyer, et al. (26) to stabilize their suspensions of silicon carbide for deposition. They added AlCl_3 to their suspension to create a positive surface charge on the particles by preferential adsorption of Al^{+3} ions. However, the charge was too low to significantly stabilize the suspension. They then added 2 wt. % polyvinylbutyral (PVB) which significantly improved the stability of their suspension without any indication of significant adsorption to the particle surfaces.

Unfortunately, the authors did not report the molecular weight of their polymer, so it is not possible to say for certain, but depletion stabilization seems the most reasonable explanation of their reported data. While they had difficulties in deposition due to electrochemical reactions at the deposition electrode, there was no indication that the stabilization scheme created any difficulty in producing adherent depositions of the particles.

This squeezing out process can also work with either weakly adherent homopolymer or terminally anchored polymer stabilized suspensions at less than complete coverage. In these cases the diffusion outward will be driven by the same osmotic forces as drive out the non-adsorbed polymer. The homopolymer is by its nature constantly desorbing and re-adsorbing loops onto the surface. The homopolymer can effectively 'roll' across the surface away from particle contacts points. At less than complete adsorption the anchor group on terminally anchored polymer chains can 'walk' from site to site across the surface.

The drawback with using this scheme of stabilization/destabilization is the very slow speed at which this squeezing out of adsorbed polymer can occur.

"... a distinctive feature of polymer interactions — one that has often been noted by experimentalists — is the extreme sluggishness with which equilibrium is attained once polymer molecules are confined within a narrow space ... Most of these processes involve the concerted motions of many entangled molecules which may require many hours or days even though the rate of similar molecular motions of isolated coils in the bulk may take less than 10^{-6} sec."

Israelachvili (3, p. 303)

For block co-polymers at less than full coverage the polymer can be used to make the particles adhere to one another. A block co-polymer will likely adhere too well to the surface to be squeezed away from the particle contact points. However, not all of the adsorbing groups on the polymer chain will necessarily be adsorbed or remain adsorbed to the particle surface. If another particle which has free surface area is brought within the polymer's effective radius some of these free groups will adsorb to the other particle. One polymer molecule then has groups adsorbed to both particles and forms a bridge between them. This is very attractive because this type of polymer bonding between particles in a deposition would create a green body which would be much stronger and more damage resistant than a compact held together only by VdW forces. It would also do this with relatively little polymer that would not close off the porosity in the deposition.

However, it is not known whether block co-polymer stabilization will work for EPD. At low surface coverages this bridging flocculation will be the only interaction

between the particles and there will be no stabilizing mechanism preventing flocculation prior to deposition. At full coverage the interaction between particles will be purely repulsive, the dispersed condition will be thermodynamically stable, and it will be impossible to electrophoretically deposit the particles. It is not obvious whether there is a transition region where there can be a repulsive interaction in the bulk with bridging flocculation occurring an electrophoretically formed compact.

Finally, there are changes in the chemistry of the solvent in the deposition layer that can be used to cause the polymer to either desorb from the particle surface or to cause the polymer to collapse into a much more compact configuration allowing particles to approach within range of their L-VdW attraction. Using chemical changes to manipulate the stability of a suspension will most like require that the stabilizing element be a polyelectrolytic polymer. Non-ionic polymers which adsorb by combining soluble and insoluble segments can be manipulated by composition or temperature changes in the solvent but will be relatively unaffected by changes in ionic strength or ionic composition. Ionic polymers, on the other hand, have the potential to be changed from adsorbing to non-adsorbing and from soluble to insoluble by changes in the ionic composition of the solvent around them.

Table 2.4 Mechanisms of Electrophoretic Deposition

<u>Stabilization Type</u>	<u>Deposition Mechanism</u>	<u>Examples</u>
Kinetic/Density	Densification	R. Bagwell - BaTiO ₃ (Unpublished)
Electrostatic	Electrostatic Force	Here - PZT, Ag/Pd
"	Electrosedimentary	Here - Alumina
"	Ion Depletion Augmented Electrostatic	Here- Alumina Sarkar & Nicholson-Alumina
"	Salting Out	Overbeek - MgO (27)
"	Charge Reduction/ Neutralization	<i>Unknown</i>
Polymer Depletion	Squeezing Out	Bouyer & Foissy - SiC (26)
Homopolymer	Squeezing Out	<i>Unknown</i>
Terminally Anchored at less than full coverage	Squeezing Out	<i>Unknown</i>
Block Co-Polymer at less than full coverage	Bridging Flocculation	<i>Unknown</i>
Homo-, Terminal-, or Block Polymer	Desorption of Neutral Polymer	<i>Unknown</i>
Terminal polymer, Block or Simple Polyelectrolyte	Desorption of Charged Polymer	H. Saita, (Unpublished) Polyethyleneimine (PEI)
Polyelectrolyte Electrosteric	Polymer Neutralization	PEI

2.8 Post-Deposition Effects

The floccing of particles at a deposition electrode to form an adherent coating is not the end of the evolution of the deposition. There are several changes that can occur in the deposited layer — while the deposition voltage/current is still applied, — when the voltage/current is turned off, — and when the deposition is removed from the deposition bath for further processing.

2.8.1 Electrosedimentary Collapse

When particles are deposited from an electrostatically stabilized suspension with a low interparticle repulsion energy they can form a very soft, low density deposition. As the deposition grows the electrosedimentary force from the accumulating outer layers will increase the pressure on the loosely flocced inner layers. At some point this pressure will exceed the shear strength of the inner layers. This can trigger a collapse in one area of the deposition, transferring additional stress to the areas around it. This can cause an avalanching collapse of the deposition inner layer with the layer temporarily fluidizing then resetting in a denser configuration. The extent of the densification will be limited by the viscosity of the solvent which must be forced out of the consolidating deposition before it rigidifies again.

This is the same behavior that is seen in natural sediments consolidated by gravity. The consolidating sediment behaves as a pseudoplastic solid, compressing elastically to a critical stress at which point the structure breaks and the sediment densifies plastically until it reaches a new stable equilibrium. The sediment compacts through a series of these discrete events, with density increasing non-linearly with distance from the surface. **(28)**

In the case of EPD this behavior manifests itself as a deposition which, when first pulled out of the deposition bath, has a surface marked by plateaus and flat bottomed craters. If the deposition remains adherent and does not crack as it dries, the thicker areas will be consolidated by drying so that the final layer has a uniform thickness. This is because the deposition rate over the electrode area will remain essentially constant, therefore the amount of powder per unit area will be constant as well. Drying (§ 2.8.6 below) is a much stronger force than electrosedimentary compaction and so will compact the deposition to a uniform density. However, density gradients in the deposition layer will lead to a strong curling force during drying. If the deposition is on a flexible substrate it will curl up and if the deposition cracks it will curl up away from the substrate.

2.8.2 Ion Depletion Enhanced Compaction

In some depositions where an ion depletion layer forms, it is possible for this layer to grow more slowly than the growth of the deposition. This is shown very clearly in Ch. 4. This means that outer portions of the deposition will only be exposed to the average electric field of the deposition bath while the inner portions of the deposition are consolidated by the very high fields in the ion depletion region. This can lead to a deposition with a bi-modal density distribution which can lead to a strong tendency to curl up from the substrate during drying or sintering.

2.8.3 Convective Lumping, Cratering & Flaking

While the presence of a deposition on a surface can retard the initiation of EHD convection, at some voltage-thickness level the driving force for convection will exceed the damping of the deposition and relatively large scale convection will begin through the deposited layer. Given that the velocity of this convection will be orders of magnitude higher than the electrophoretic velocity of the particles, particle transport will now be almost exclusively by convection. Where a convective flow enters a deposition layer particles will be deposited by filtration of the flow, leading to a lump on the surface. Flows out of the deposition away from the electrode will carry particles away from the deposition surface and stop the growth of the deposition in this area. This outward flow can also erode the existing deposition leaving craters that extend down to the electrode surface. Another phenomenon which has frequently been observed here is the flaking off of portions of a dense deposition formed prior to the initiation of convection. Where the convection flows inward the flow will press the deposition more firmly onto the electrode. Where this convective flow moves away from the electrode the hydrostatic pressure necessary to force the flow through the deposited layer can grow to the point that it will pop flakes of the deposition off the electrode.

2.8.4 Electrolytic Gas Termination

This effect occurs while the deposition current-voltage is still applied but acts very quickly to terminate the deposition process. In a conductive EPD bath the reactions at the electrodes frequently produce a gas. In low conductivity solutions the amount of gas produced is small enough that it is able to dissolve in the solution and diffuse away from the electrode surface without forming bubbles. However, as a deposition builds up on an electrode surface the diffusion path will get longer and longer. At some point the gas concentration in solution at the electrode will reach a critical point and a gas bubble will

form. The bubble will spread along the electrode/deposition interface stopping conduction in that area. This increases the current density in the areas where there is still liquid contact with the electrode, increasing the generation of gas in these areas. Since these areas are also likely to be close to the critical concentration of dissolved gas, they will form gas bubbles as well, decreasing the conductive area further. Thus the electrode/deposition interface will flood with gas at an exponential rate until conduction and therefore deposition are terminated.

2.8.5 Electrostatic Pop-Off

In the case where the ion depletion effect is used for deposition or for consolidating a deposition, a significant unbalanced electrostatic charge can build up. This can cause flakes of a deposition to pop off when the voltage is turned off. This is especially noticeable when the deposition is transferred to clear solvent for rinsing of the deposition. Flakes popping off of the deposition electrode can be seen to move several millimeters away from the deposition electrode in a fraction of a second.

2.8.6 Repulsive Decomposition

If particles are electrostatically stabilized in the bulk suspension, after the deposition current is turned off the same repulsive force will exist between the particles in the deposition. If the particle diffuse layer thicknesses approach the scale of the pores in the deposition this can create a higher osmotic pressure inside the deposited layer.

If the deposition is dense, with a high average number of interparticle contacts, then the L-VdW forces will be sufficient to hold the deposition together. If the deposition is slightly less dense, the internal pressure can be sufficient to break flocs off of the outer surface of the deposition. Rinsing in pure solvent will maximize the osmotic pressure differential within the deposition. It was observed that an alumina deposition when rinsed briefly in pure ethanol would lose very little mass. However, if the deposition was held vertically without motion in the ethanol a small but continuous cascade of alumina flocs was seen to flow down off of the surface as the surface slowly decomposed due to the internal osmotic pressure.

2.8.7 Drying and Sintering

The final stage of the process is drying the solvent from the deposition. Even though the particles can be well packed by the EPD process, some particle re-arrangement

and a slight additional densification is possible. The following example illustrates the relative magnitudes of the forces generated by EPD and drying respectively.

A $7\mu\text{m}$ deposition of Al_2O_3 powder was made from ethanol using a constant current. During the course of the deposition the voltage across the cell increased from 20 to 64 volts. If we assume that this entire additional 44 volt field drop occurs across the deposited layer we can calculate a pressure due to electric field $P = \epsilon_r \epsilon_o \frac{V^2}{d^2}$. For a voltage drop of 44V across a $7\mu\text{m}$ deposition layer the Maxwell pressure is ≈ 8 kPa. This is an oversimplification of what is occurring in the deposition layer, but gives an idea of the relative forces involved.

During drying, a capillary tension is created in the particle compact as the solvent/vapor interface moves into the pores in the final phase of drying. (32,33) The capillary tension is a function of the surface energies of the solvent/vapor and solvent/particle interfaces and pore diameter in the compact. This capillary pressure can be estimated by

$$P = \gamma_{LV} \cos(\theta) \frac{S_V}{V_{P_V}} \quad [2.72]$$

Given: γ_{LV} surface energy of ethanol = 2.197 N/m, θ liquid/solid contact angle $\approx 40^\circ$, S_V the surface area/unit volume calculated using; powder surface area = $9.9\text{m}^2/\text{g}$, α -alumina theoretical density 4 g/cc, deposition packing density 60%, and V_{P_V} the volume fraction porosity, the estimated capillary tension is $\approx -100\text{MPa}$. As can be seen from the formula above, the most significant variable affecting the drying stresses is the surface to volume ratio, which is inversely related to the particle size. While the liquid-vapor surface energy would be eliminated by supercritical drying which can eliminate the drying stresses, at normal pressures and temperatures it is difficult to have a significant impact on this variable. Frequently something that reduces this energy will also reduce the wetting angle, negating the effect. However, each step going from micron to sub-micron to nano scale powders involves an order of magnitude increase in the capillary tension.

A dense electrophoretically deposited layer will behave as a brittle solid, with the probability of cracking during drying a function of defect size and volume under stress. Remarkably enough, despite the order of magnitude higher stress during drying compared to deposition of the sub-micron scale Al_2O_3 powder in the above example, cracking is not a problem on continuous deposited layers up to 0.1 mm dried on a flat, rigid substrate. Cracking in thinner coatings is usually an indication of a low density deposition and can be eliminated by improving the stability of the deposition suspension. In moving to nano-

scale particles, the drying stresses will jump another order of magnitude. However, given that one of the primary reasons for depositing nano-particulate materials will be to form layer thicknesses in the low sub-micron region, these stresses should not be a problem so long as dense, uniform, and defect free particulate depositions can be formed.

Constrained sintering is a problem very similar to constrained drying. The film is constrained in the two in-plane dimensions and sintering shrinkage can only occur in the thickness direction. However, these sintering stresses are an order of magnitude lower than the drying stresses (29). If the deposition is not cracked by drying stresses it will likely remain intact through sintering as well.

2.9 Summary

EPD is not simple, and to look at it from any one point of view will miss many important aspects of the process. This chapter is intended to be an introduction to the four areas of science that bear on aspects of EPD: electrochemistry, colloidal chemistry, surface chemistry and electrohydrodynamics. Space and time are too limited to discuss fully how each of these fields relate to EPD, and, in general, most of the relations between these fields of study and EPD awaits future study and analysis. However, just by considering each of these aspects of the operation of an EPD cell, a list of near-electrode effects was generated. This list was then compared with a list of means by which a colloid suspension can be stabilized. The result is a matrix of stabilization mechanisms vs. near electrode effects. From this matrix a list of combinations that may lead to deposition of the particles on or next to the deposition electrode was compiled.

This list, to the current knowledge of the author, is the first comprehensive list of mechanisms of EPD ever compiled. Some of the mechanisms are speculative and there are no clear demonstrations of deposition by that mechanism in the literature reviewed for this thesis. Other mechanisms have been established in previous work.

The next two chapters here will be devoted to clearly demonstrating one of the most interesting of these mechanisms, ion depletion enhanced electrostatic deposition. A vital part of demonstrating this clearly is developing an accurate, quantitative description of the surface and colloidal chemistry of the deposition suspension. This is done in Ch. 3. This information is then used to complete a quantitative analysis of a series of depositions in Ch. 4. This chapter then clearly demonstrates the formation and stabilization of an ion depleted conduction layer and its role in the EPD of alumina particles. Future studies can then be devoted to attempting to demonstrate clearly each of the other mechanisms to fill out this table.

References

Chapter 2

1. Russel, W.B., Saville, D.A. and Schowalter, W.R. , *Colloidal Dispersions*, Cambridge University Press, Cambridge, (1989)
2. Hunter, R. J., *Zeta Potential in Colloid Science, Principles and Applications*, Academic Press, New York, (1981)
3. Israelachvili, J.N., *Intermolecular and Surface Forces*, Academic Press, New York (1992)
4. Heisinger, Karl, "Molecular Dynamics of Water at Interfaces", in *Structure of Electrified Interfaces* (eds. Lipkovski, Jacek and Ross, P.N.) VCH Publishers, New York (1993) 239-276
5. Frumkin, A.N., "2. Hydrogen Overvoltage and Adsorption Phenomena: Part I. Mercury", In *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 1 (ed. Delahay, Paul) Interscience, New York (1961) 65-138
6. Newmann, John S., *Electrochemical Systems*, 2nd Ed. Prentice Hall, Englewood Cliffs, NJ, (1991)
7. Wang, Joseph, *Analytical electrochemistry*, 2nd ed., Wiley, New York , (2000).
8. Hogg, R., Healy, T.W. and Fuerstenau, "Mutual Coagulation of Colloidal Dispersions", *Far. Soc. Trans.* **62**, (1966) 1638-1651
9. Levich, Veniamin G., *Physicochemical Hydrodynamics*, Prentice-Hall, Englewood Cliffs, NJ (1962)
10. Chazviel, J.-N., "Electrochemical Aspects of the Generation of Ramified Metallic Electrodeposits", *Phys. Rev. A*, **42**[12], (1990) 7355-7367
11. Van Tassel, J. and Randall, C.A., "Surface Chemistry and Surface Charge Formation for an Alumina Powder in Ethanol with the Addition of HCl and KOH", *J. Colloid and Interface Sci.*, **241** (2001) 302-316
12. Hooton, John A. and Merz, Walter J., "Etch Patterns and Ferroelectric Domains in BaTiO₃ Single Crystals", *Phys. Rev.*, **98**[2], (1955) 409-413
13. Smoluchowsky, M. von, "Contribution à la théorie de l'endosmose électrique at de quelques phénomènes corrélatifs", *Bulletin International de l'Académie des Sciences de Cracovie*, 8 (1903) 182-200
14. Henry, D.C., "Cataphoresis of Suspended Particles", *Proc. Roy. Soc. A.* **133**, (1931) 106-129
15. O'Brien, R. W., and White, L. R., "Electrophoretic Mobility of a Spherical Colloidal Particle", *J. Chem. Soc. Faraday II*, **74**, (1978) 1607
16. Auzeais, F.M., Jackson, R., and Russel, W.B., "The Resolution of Shocks and the Effects of Compressible Sediments in Transient Settling", *J. Fluid Mech.*, **195** (1988) 437-462

17. Napper, D. H., *Polymeric Stabilization of Colloidal Suspensions*, Academic Press, London (1983)
18. Weitz, D.A. and Huang, J.S., Self-similar structures and the kinetics of aggregation of gold colloids. In *Kinetics of Aggregation and Gelation* (eds. Family, p. and Landau, D.P.), Elsevier 1984
19. Smoluchowski, M. von, "Versuch einer mathematischen Theorie der Koagulationskinetik kolloider Lösungen", *Z. Phys. Chem.* **92**, 129-68 (1917)
20. Glendinning, A.B. and Russel, W.B., "The Electrostatic Repulsion between Charged Spheres from Exact Solutions to the Linearized Poisson-Boltzmann Equation", *J. Colloid and Interface Sci.*, **93** [1], (1983) 95-104
21. Feigin, R.I. and Napper, D.H., "Depletion Stabilization and Depletion Flocculation", *J. Colloid and Interface Sci.*, **75** (2), 525-42 (1980)
22. Solomentsev, Y., Böhmer, M. and Anderson, J.L., "Particle Clustering and Pattern Formation during Electrophoretic Deposition: A Hydrodynamic Model", *Langmuir*, **13** (1997) 6058-6068
23. Solomentsev, Y., Guelcher, S.A., Bevan, M., and Anderson, J.L., "Aggregation Dynamics for Two Particles during Electrophoretic Deposition under Steady Fields", *Langmuir*, **16** (2000), 9208-9216
24. Verwey, E.J.W. and Overbeek, J.Th.G., *Theory of the Stability of Lyophobic Colloids*, Elsevier Publishing Company, New York (1948)
25. Hamaker, H.C., and Verwey, E.J.W., "The Role of the Forces Between the Particles in Electrodeposition and Other Phenomena", *Trans. Faraday Soc.*, **36**, (1940) 180-185
26. Bouyer, F. and Foissy, A., "Electrophoretic Deposition of Silicon Carbide", *J. Am. Ceram. Soc.*, **82**[8], (1999) 2001-10
27. Koelmans, H. and Overbeek, J.Th.G., "Stability and Electrophoretic Deposition of Suspensions in Non-Aqueous Media", *Disc. Faraday Soc.*, **18** (1954) 52-63
28. Buscall, R., and White, L.R., "The Consolidation of Concentrated Suspensions, Part 1. The Theory of Sedimentation", *J. Chem. Soc., Faraday Trans. 1*, **83** (1987) 873-891
29. Bordia, R.K. and Jagota, A., "Crack Growth and Damage in Constrained Sintering Films", *J. Am. Ceram. Soc.*, 76[10], (1993) 2475-2485
30. Hackley, V. A., and Ferraris, C.F., *The Use of Nomenclature in Dispersion Science and Technology*, NIST Recommended Practice Guide, Special Publication 960-3, U.S. Government Printing Office, Washington, D.C., August 2001
31. Healy, T.W., and White, L.R., "Ionizable surface Group Models of Aqueous Interfaces", *Adv. Colloid and Interface Sci.*, **9** (1978) 303-345
32. Scherer, G.W., "Theory of Drying", *J. Am. Ceram. Soc.*, **73**[1] (1990) 3-14
33. Scherer, G.W., "Physics of Drying", in *Ceramic Powder Science III*, Eds.: Messing, G.L., and Hirano, S., American Ceramic Society, Westerville, Ohio (1990)