

The DLVO Theory

(named after Boris Derjaguin and Lev Landau, Evert Verwey and Theodoor Overbeek).

Membranes are used to separate colloids and suspended solids from fluids. Colloids are typically in the size range of 0.003 micron to 3 microns. Suspended solids are typically in the range of 0.45 micron to 10 microns. The DLVO theory teaches us why solids/colloids in water will stay in suspension



DLVO Theory

This photograph shows a river that has natural fresh water from snow melt in the mountains. The water has a low ionic concentration and solids in suspension. The river enters the ocean where there is a high ionic environment due to the NaCl. As a result the solids separate from the water. When the solids are in suspension the Electrical Double Layer (EDL) around the colloid solid is strong and repulsion forces are strong. When the ionic strength of the local environment increases, the EDL collapses and attraction forces (van der Waal) become dominant

A good example of the DLVO Theory is a river with fresh water carrying a high concentration of suspended solids. The water, in the river, is from the snow melt and the ionic environment of the natural snow melt water is low so the solids stay suspended. The electric double layer (EDL) around the solids is strong causing the solids to repulse from each other. However once the river water reaches the ocean, the high ionic environment with the salt water and the electrolytes Na^+ and Cl^- , the suspended solids aggregate and settle thereby separating from the water. The water becomes clear. The DLVO theory also teaches us why colloidal and suspended solids repel from the surface of a RSL membranes™. **RSL Membranes™**

use an ionic powder on the surface of a membrane tube to simulate the DLVO theory. This intense ionic environment on the membrane surface keeps the solids in the wastewater repelled from the powder surface thereby facilitating high flux (flow rates) through the membrane. The solids continuously are rejected away from the membrane surface and concentrate in the housing. Eventually some of the solids penetrate the powder layer and the electric double layer around the solid collapses causing the solids to aggregate with each other and the powder. The membrane powder layer rapidly clogs and the pressure rises to 70 kpa. This latter phenomenon is similar to the solids entering the ocean where the sodium and chloride electrolytes cause the solids to aggregate and then settle. At the pressure differential of 70 kpa, the **RSL membrane™** and housing containing the membranes are backwashed. A new powder layer is added to the membrane tube and the filtration cycle repeats.

Let's look at the DLVO theory in more detail. In colloidal particle science, there are numerous forces that cause attachment and repulsion of colloidal solids. However, the DLVO theory assumes the dominant force of repulsion is the electric double layer (EDL) repulsion forces and attraction is due to van der Waals attractive forces.

Electric Double Layer

The EDL is cloud layer of ions that naturally concentrate on the surface of a colloid. There is the Stern layer where the opposite ion (counter ion) to the surface charge concentrates and then a mixture of co-ion and counterions is the diffuse layer

Electrical double layer

Stern model

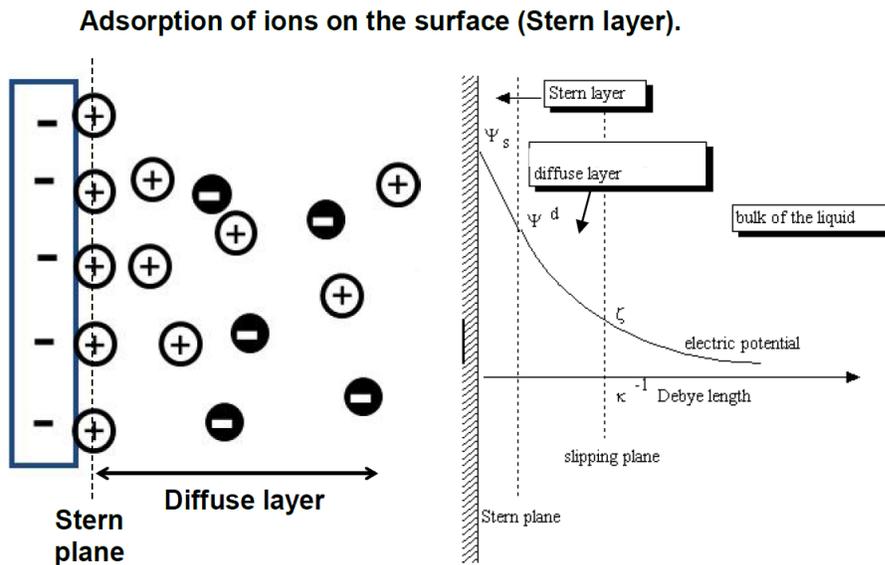
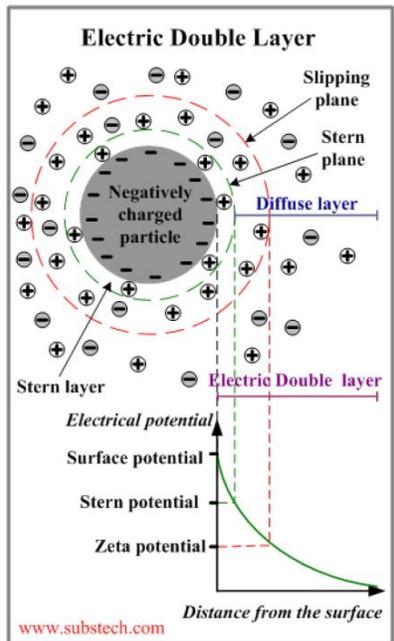


Figure 1: The Stern and Diffuse layer of the Electric Double Layer (EDL) showing a force of repulsion that diminishes over distance from the surface of the colloid



The right side of figure 1 shows the electric potential decreasing over distance from the surface. The electric potential defines the intensity and width of the EDL.

The Zeta potential (figure 2) is the mid potential of the electric potential curve. The zeta potential measurement provides an indicator of the potential strength. When colloids approach each other, the potential curves overlap as shown in figure 3. As the colloids become closer the potential increases and an osmotic pressure occurs from water naturally trying to dilute the potential between the colloids to a similar potential surrounding the individual colloid. The osmotic pressure causes the repulsion and is called electric double layer repulsion.

Zeta potential (ζ) is the electrical potential at the slipping plane.

Figure 2: Zeta Potential midpoint of potential curve

DLVO theory

Electrical double layer interaction

When two charged surfaces or particles approach, their corresponding electrical double layers overlap.

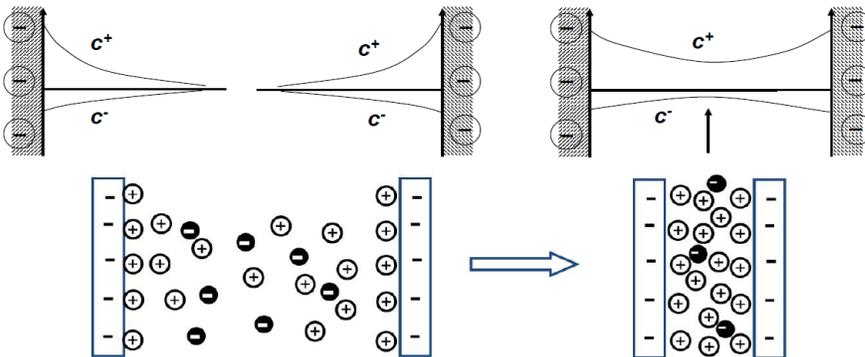


Figure 3: Osmotic Pressure causing repulsion

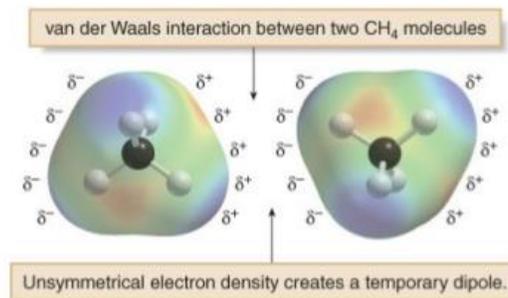
The accumulation of ions due to the overlap of the electrical double layers create an increase in osmotic pressure. Water from the bulk comes to dissolve the accumulation of ions, preventing the surfaces from approaching closer (**electrical double layer repulsion**).

Van der waal Forces

van der Waals Forces

- van der Waals forces are also known as London forces.
- They are weak interactions caused by momentary changes in electron density in a molecule.
- They are the only attractive forces present in nonpolar compounds.

Even though CH₄ has no net dipole, at any one instant its electron density may not be completely symmetrical, resulting in a temporary dipole. This can induce a temporary dipole in another molecule. The weak interaction of these temporary dipoles constitutes van der Waals forces.



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The other force that needs to be understood is Van der Waals force, named after Dutch scientist Johannes Diderik van der Waals. This force is a distance-dependent interaction between atoms or molecules. Van der Waals forces are random forces that occur from electrostatic attraction because of a random dissymmetry of the positive and negative ions on the Stern layer of

a colloid (See figure 2 and figure 4)

Figure 4: Van der Waal forces- Random

condition

Van der Waals forces are the sum of the attractive and repulsive electrical forces between atoms and molecules. These forces differ from covalent and ionic chemical bonding because they result from fluctuations in charge density of particles. Examples of van der Waals forces include hydrogen bonding, dispersion forces, and dipole-dipole interactions.

www.thoughtco.com/definition-of-van-der-waals-forces-604681

As shown in figure 5, the energy barrier is the sum of the repulsive EDL forces and the attractive Vander Waal forces. In very close proximity to the contact surface the repulsive forces are very strong. There is also a primary attractive force and then a secondary repulsive force followed by a secondary attractive force.

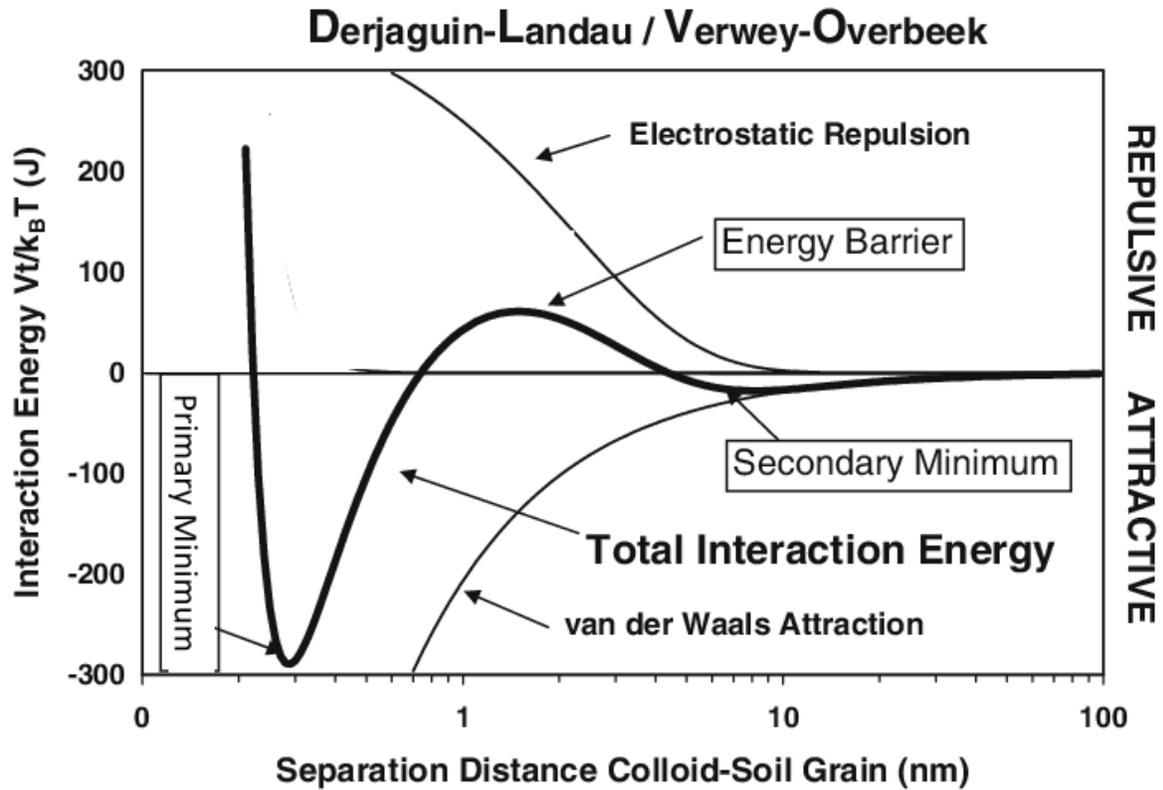


Figure 5 – Sum of Van der waal and EDL Forces = Energy or Force Barrier

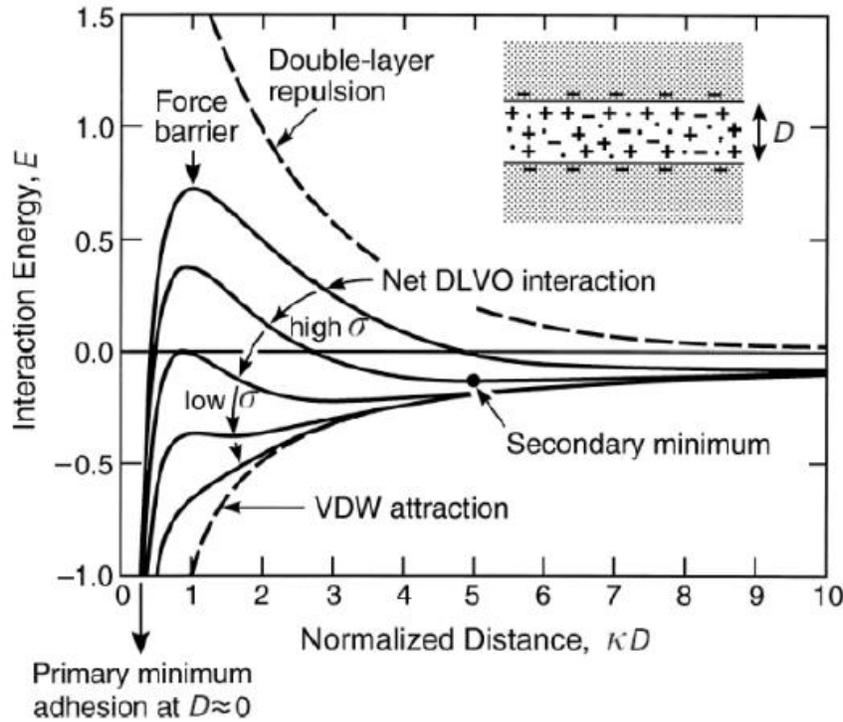
Electrolytes Impact

The energy or force barrier can change depending on the ionic strength of electrolytes in the water. The following ions are electrolytes

- Sodium (Na⁺)
- Chloride (Cl⁻)
- Potassium (K⁺)
- Magnesium (Mg⁺⁺)
- Calcium (Ca⁺⁺)
- Phosphate (HPO₄⁻)
- Bicarbonate (HCO₃⁻)

Figure 6 shows how the increase in electrolytes cause a reduction in the force barrier between solids to the point that the van der waal attraction forces become dominant.

The high concentration of electrolytes in the water reverses the osmotic pressure as displayed in figure 3.



The high electrolyte environment in the bulk water cause the water between the colloids to move to the bulk solution to dissolve the accumulation of ions from the electrolytes.

Figure 6: Impact of Electrolyte concentration on reducing repulsion from EDL
 Note: Electrolyte concentration has to be very high

A good example of this phenomenon can be viewed in the treatment of produced water. Below is a typical oil and gas produced water from the Texas Permian zone. The Na and Cl in this water totalled 60000 to 80000 ppm.



Figure 7: (Left) Permeate from **RSL Membrane™**, (Center) Feed water, (Right) Top View of Feed



As shown the, the RSL membrane removes all suspended solids in the permeate. The removal of the solids, results in an increased concentration of solids in the housing. As the solids increase, they become closer in contact. With the high electrolyte concentration, the solids start to aggregate as a floc. Figure 8 displays the floc forming in the housing after 2 hours of filtration of the feed water in Figure 7. No chemicals have been added. Flocculation is naturally occurring. The photograph shows two tubes that have the RSL powder layer on the tube and a mat of solids up close to the tube but separated from the RSL powder. The separation/repulsion from the RSL powder is due to the EDL repulsion forces. This observation is supported by the pressure data. Two hours into the filtration cycle the pressure across the membrane is registering zero.

Figure 8 Coagulated solids – No Chemicals added

Temperature Impact

Temperature has a significant impact on the Electric Double Layer. The impact of the temperature is based on the square root of the temperature value. The higher the temperature the stronger the Electric Double Layer.

Research and Development Objectives

The R and D objectives with regards to the DLVO theory are extensive. We continue to focus on the

1. Enhancement of the powder and the membrane materials to further advance the strength of the electric double layer (EDL) to create longer filtration cycles.
2. Use of pressure and the impact of trans membrane pressure
3. Identification of other parameters that effect the EDL

