DLVO Theory Diagram from Martin's Physical Pharmacy

V_{max} > thermal energy → repulsion

V_{sec} > thermal energy → flocculation

V_{sec} < thermal energy < V_{max} → repulsion

Blue line indicates decline in electrostatic repulsive forces with distance between particles

Red line indicates decline in van der Waals attractive forces with distance between particles

Black line indicates the sum of the attractive and repulsive forces (ie red plus blue)

VdW forces are effective over a longer distance than electrical repulsion leading to a secondary minimum in the plot.

X-axis is the distance between the two particles

Y-axis is the total potential energy, top part=repulsive forces + bottom part=attractive forces

Blue line= indicates decline in electrostatic repulsive forces with distance between particles

Red line= decline in Van der Waals attractive forces with distance between particles

Black line= indicates the sum of the attractive and repulsive forces (red plus blue lines)

V_{max} > thermal energy → repulsion

V_{sec} > thermal energy → flocculation

V_{sec} < thermal energy < V_{max} → repulsion

➢ If the curve is high, then repulsive forces are greater than the attractive forces
➢ Red curve= when the particles are very close, the attractive forces are very large, the particles will have permanent contact. Only when they have a charge, they will have repulsive forces
➢ Vmax= net force between the repulsive and attractive forces
➢ When the particles are a small distance away from each other, the electrostatic repulsive forces are very large (bigger than the attractive forces). However when the distance between particles gets larger, the electrostatic repulsive forces drop becomes greater than the Van der Waals attractive forces drop.
➢ The attractive forces are also getting smaller, however are slower than the reduction of the repulsive forces.
➢ When you particles are a fair distance away, the dip occurs in the graph which indicates the attractive forces overpower the repulsive forces – this is where flocculation occurs
➢ Reducing V_{sec} induce flocculation, reducing the charge in the Zeta potential (provides repulsive forces)
➢ For example whilst making a suspension, we don't want the particles to be close together hence we add a flocculating agent to let it make an open structure

➢ The size of V_{max}, depends on the Zeta potential which is dependent on ψ0 (Ernst potential) and electrolyte concentration (which affects the length of EDL and magnitude of zeta potential
➢ Reduction of V_{max} leads to instability and coagulation of hydrophobic colloid

Controlled flocculation can be done by;
- ➢ Addition of electrolytes (compress the EDL, reduce Zeta potential)
  This lowers the primary maximum and deepens the secondary minimum, resulting in an increased tendency for particles to flocculate in the secondary minimum
- ➢ Specific adsorption of ionic surfactants reduces zeta potential but does not compress the electric double layer

Lyophobic colloids are stabilised entirely by electric charges on their surfaces
- Very sensitive to addition of electrolytes (has an impact on the Zeta potential)
- Schulze-Hardy Rule: when valencies increase, precipitation power also increases
- Concentration of electrolytes: at a particular concentration, accumulation of opposite ions will cause the Zeta potential to get too low, resulting in aggregation

Stability of Lyophilic Colloids
Stabilised by the combination of electrical double layer interaction and solvation
- ➢ Adding small amounts of electrolytes, will have no impact. Large amounts of electrolytes added, will cause 'salting out' to occur
- ➢ Salting out powder ranked by Lyotropic series; if the charge of the compound is high, will mean it has a higher power of salting out
- ➢ Salting out effect: colloidal material loses its water of solvation to those electrolytes or ions which have strong hydration capacity/power, resulting in coacervation

- ➢ Mixing hydrophilic colloids with solvents such as acetone and alcohol, will turn hydrophilic colloid into hydrophobic colloid, therefore making it very sensitive to electrolytes → coagulation
- ➢ Coacervation: the separation of lyophilic colloid into two liquid layers on addition of another substance indicating physical incompatibility
  Bottom layer: colloid-rich layer also known as coacervate
  Upper layer: colloid-poor layer with low viscosity
- ➢ Can be induced by addition of electrolytes, non-solvent or oppositely charged lyophilic colloids
- ➢ Applications: gelation, microencapsulation

Effect of addition of hydrophilic macromolecular material to lyophobic colloidal systems
- ➢ When moderate amounts of polyelectrolyte or polymer are added (not enough to cover the whole surface), a structured floc forms
  Application: removal of colloidal materials, water purification
- ➢ When large amounts of polymer are added lyophobic colloids will be stabilised by steric stabilization or protective colloid effect. Turns lyophobic colloids into lyophilic colloid

Modified DLVO Theory: $V_T = V_A + V_R + V_S$
Vs: potential energy for steric stabilisation
- Large amount of hydrophilic polymer on the surface, we can provide steric stabilisation to the lyophobic colloid

(a): in the absence of electrostatic repulsion

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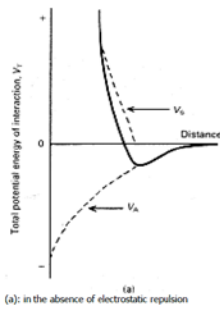
If the hydrophilic polymer which attaches onto the surface of colloid, doesn't contain a charge (not ionisable), there is no electrostatic repulsion.

(b): in the presence of electrostatic repulsion: $V_T = V_R + V_A$. V_S
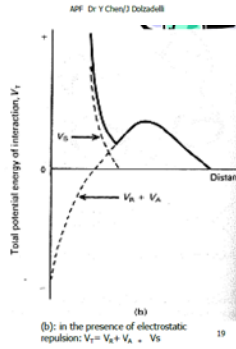
If there is electric charge, added repulsion forces (energy curve goes into the repulsive forces)