EMULSIONS STABILITY

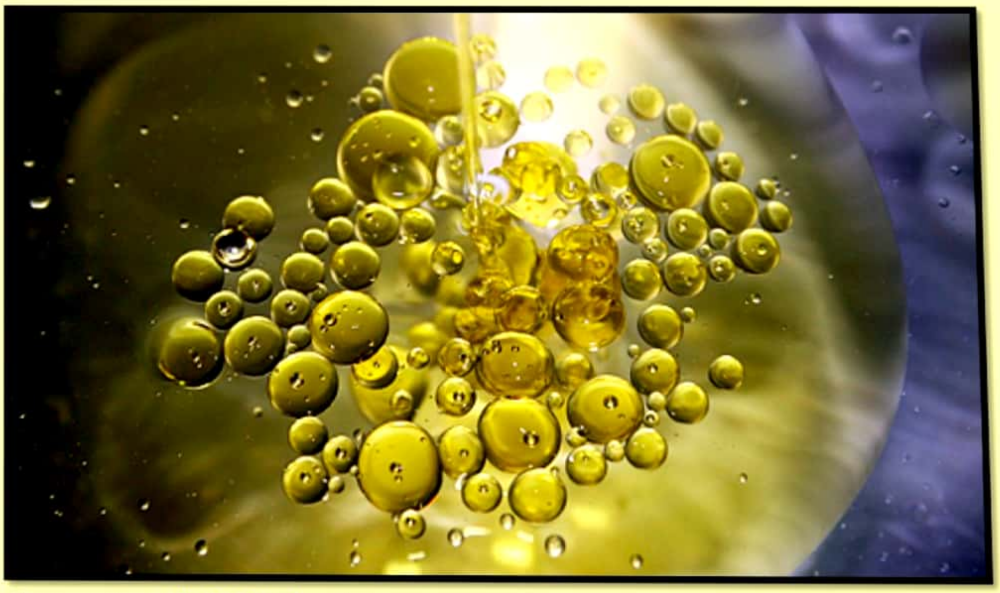


Photo courtesy of Beatriz Bonal on Flickr

Mechanisms of Emulsion Instability

- Emulsion stability – ability to resist changes in its physicochemical properties with time.

Mechanisms of emulsion breakdown:

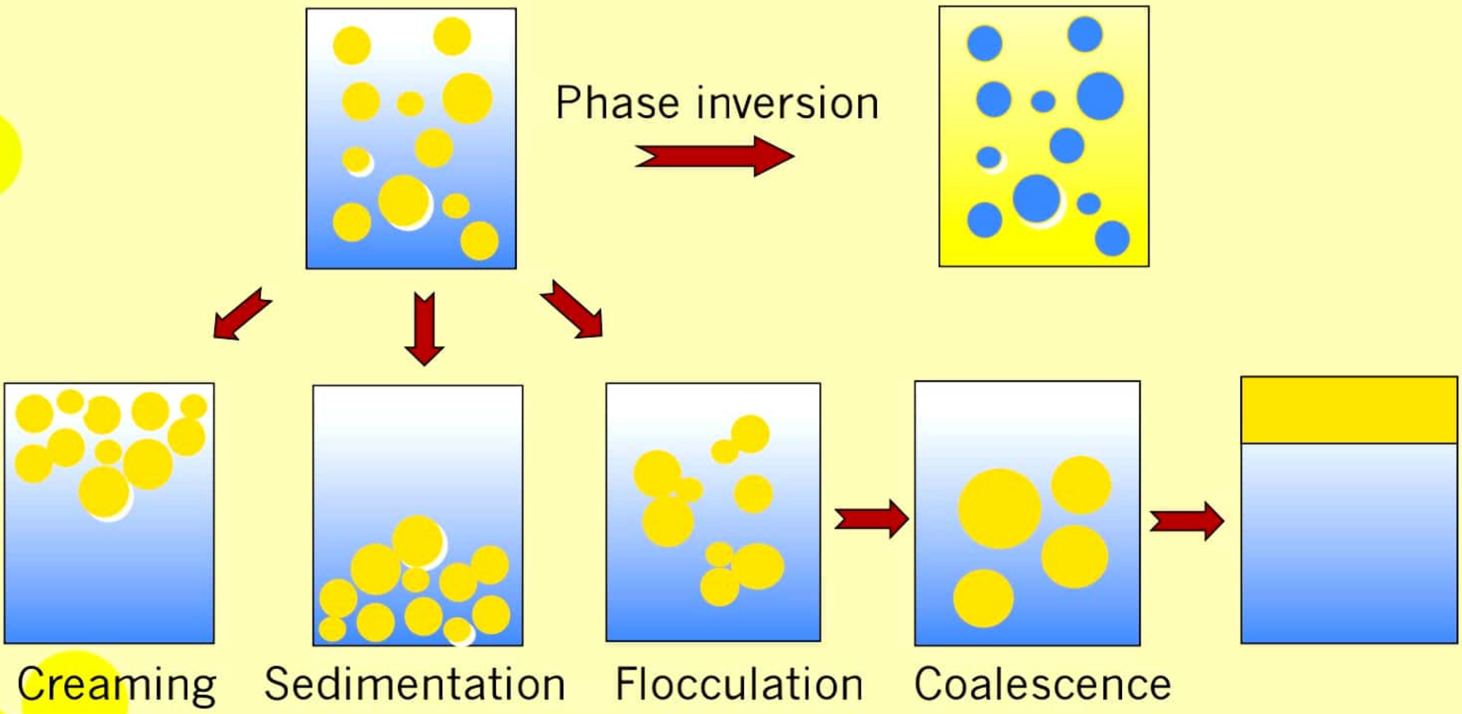
- Creaming – the process in which droplets move upwards (droplets density < density of continuous phase)
- Sedimentation - the process in which droplets move downwards (droplets density > density of continuous phase)

Mechanisms of Emulsion Instability

Mechanisms of emulsion breakdown (..cont'):

- **Flocculation**– the process in which two or more droplets "stick" together to form an aggregate (but the droplets still retain their individual integrity)
- **Coalescence** - the process in which two or more droplets merge together to form a single larger droplet.
- **Phase inversion** – the process in which o/w emulsion changes to w/o emulsion, or vice versa.

Mechanisms of Emulsion Instability



Phase inversion

Creaming

Sedimentation

Flocculation

Coalescence

Forces between colloidal particles

- Types of electrostatic (interactive/repulsive) forces
- DLVO theory
- Electrical double layer
- Zeta potential (what it is, its significance, how to measure)
- Effect of ionic strength & pH

INTERACTIONS BETWEEN DISPERSED DROPLETS

- The effects of the intermolecular forces on the stability of disperse systems can be described in terms of the forces between the colloidal particles determined by the summation of the intermolecular forces over many molecules.

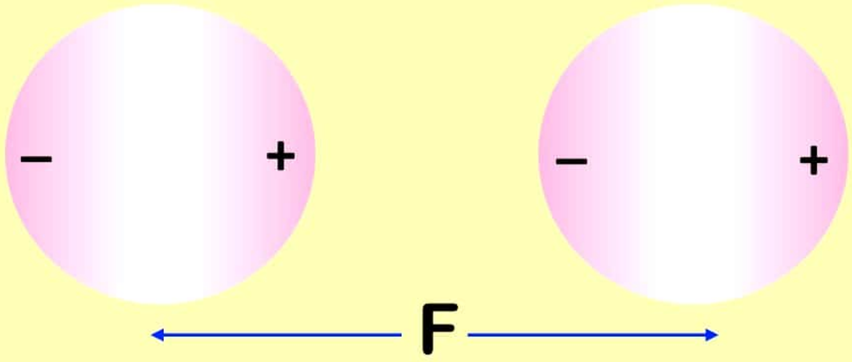
INTERACTIONS BETWEEN DISPERSED DROPLETS

- Two main interacting forces in affecting colloid systems: (1) van der Waals attractive forces and (2) electrostatic repulsive forces.
- Attractive forces tend to destabilise colloids whereas repulsive forces generally impart stability.

van der Waals Interactive Forces

- Originates from the dipole-dipole interactions.
- The force between two droplets arising from van der Waals interactions is always attractive for like droplets.
- The attractive force increases more and more rapidly as the droplets approach.

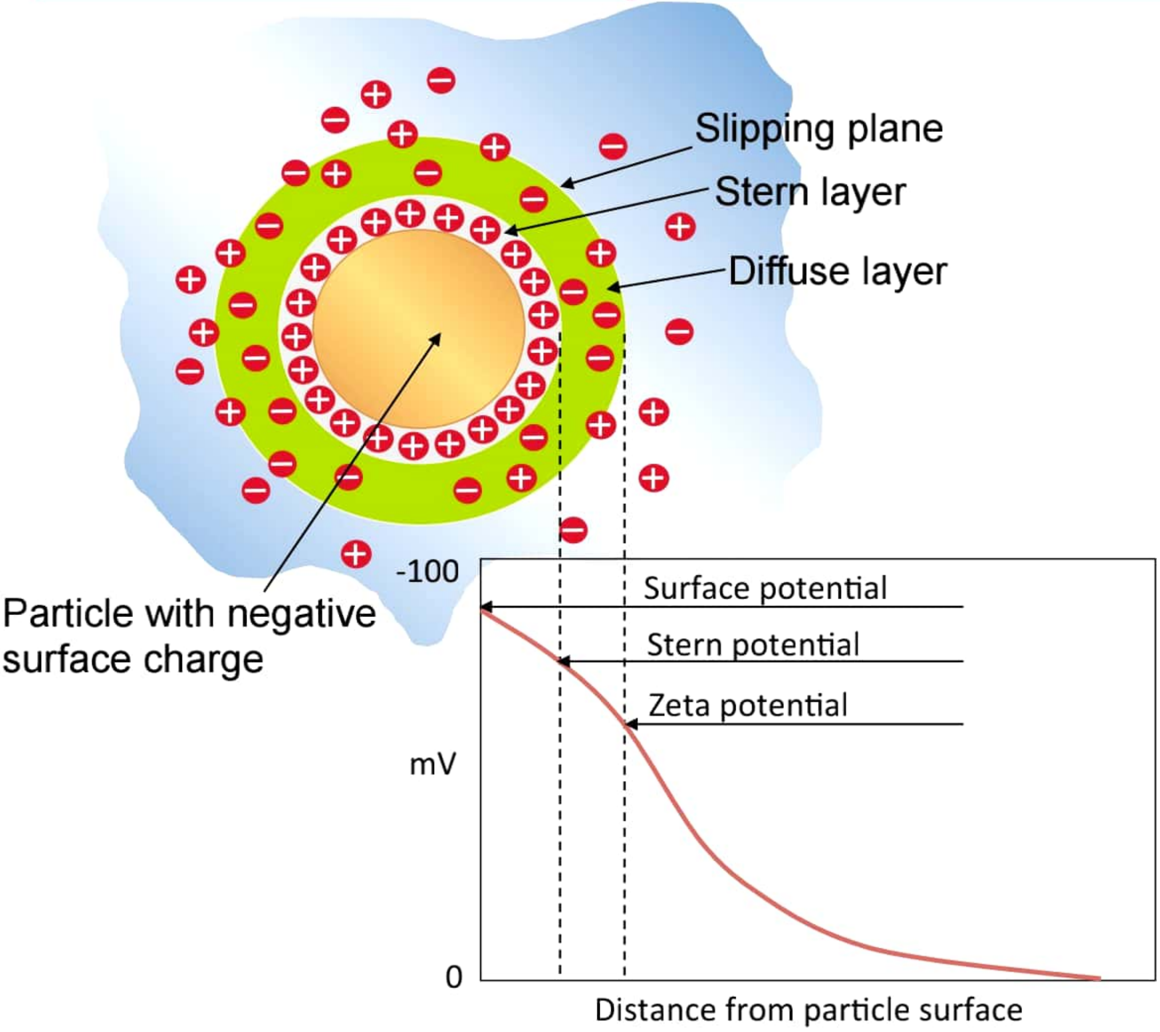
van der Waals Interactive Forces



$$F = -\beta/r^6$$

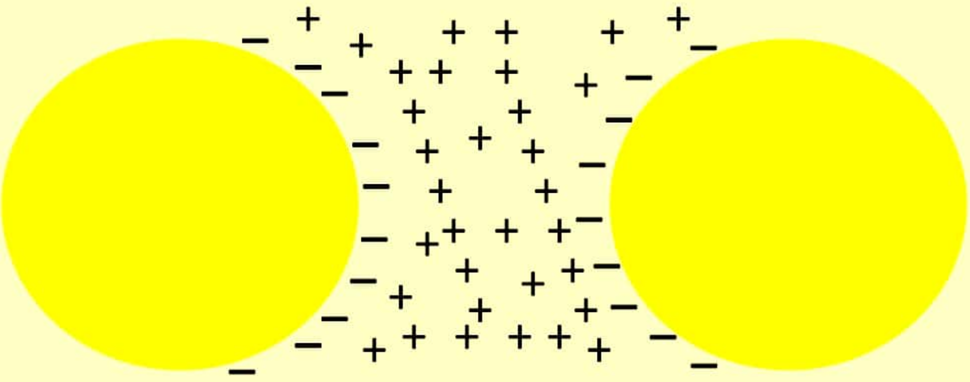
β = constant; r = distance in between

Electrical Double Layer & Zeta Potential



Abd Karim Alias, 2013©

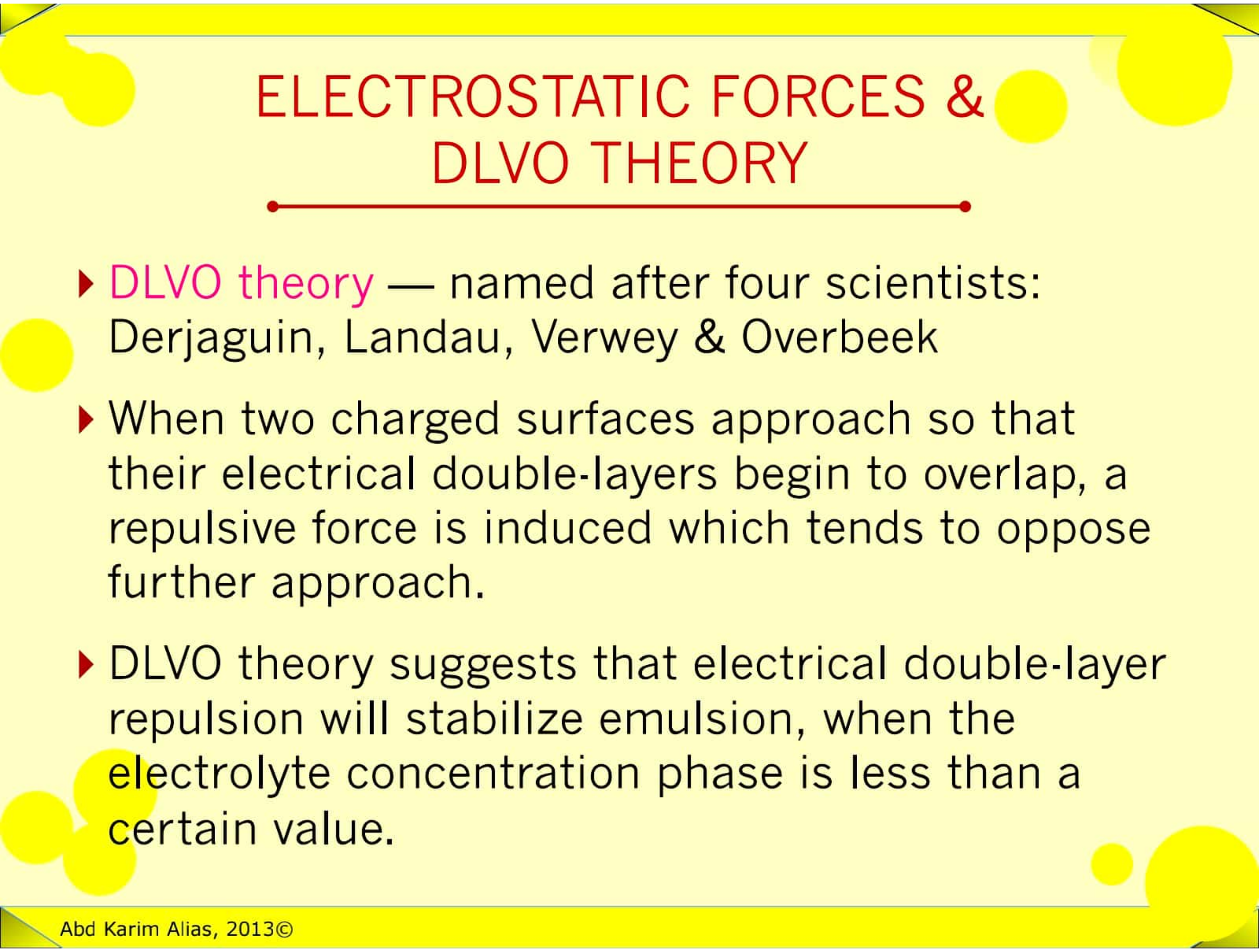
ELECTRICAL DOUBLE LAYER



- Oppositely charged ions (counterions) are preferentially attracted towards the surface, and ions of the same charge (coions) tend to be repelled away.
- The combination of the charged surface & the unequal distribution of coions & counterions near the surface is called the electrical double layer.

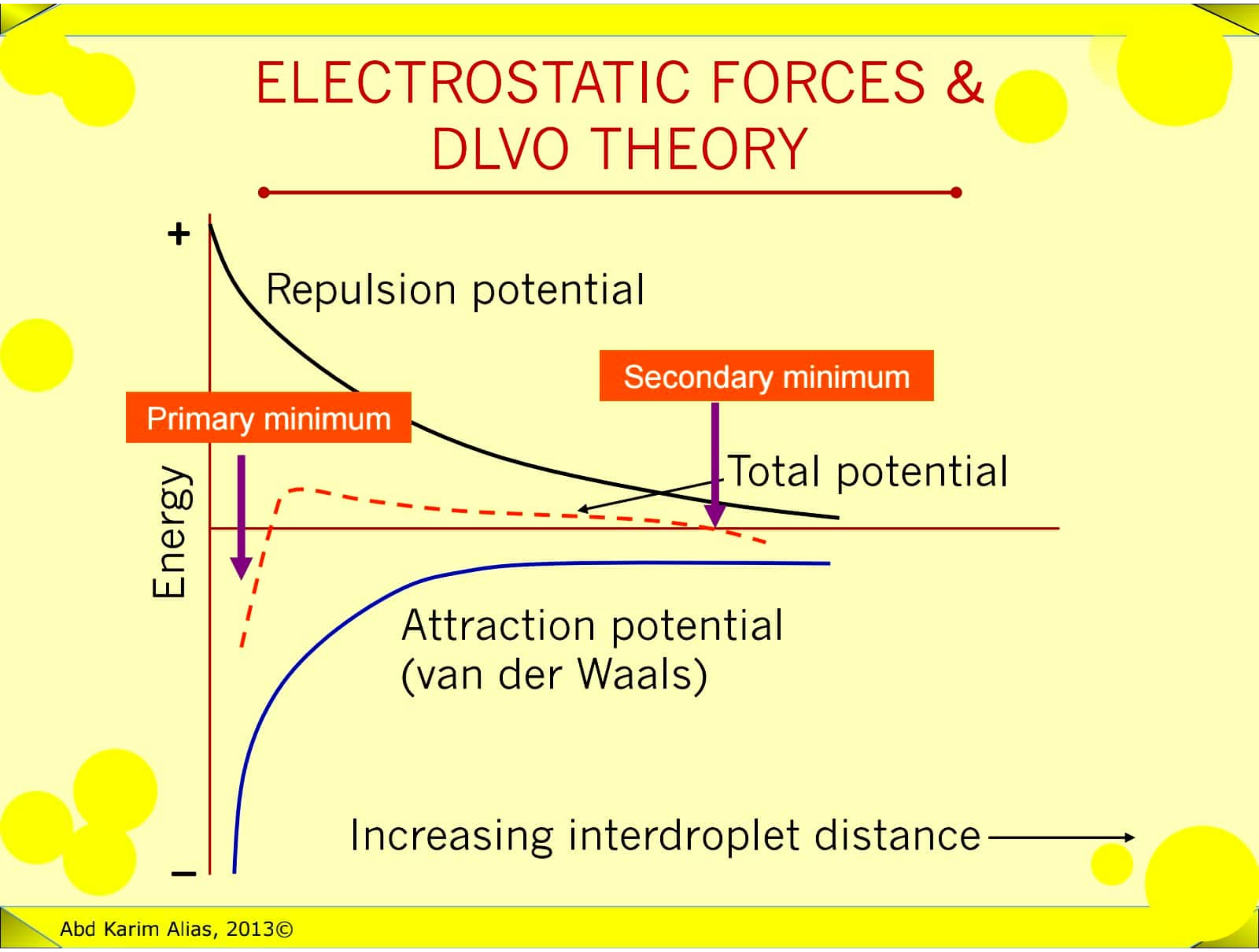
ELECTRICAL DOUBLE LAYER

- The formation of a double layer is very important for the stability of the colloid.
- The double layer is sensitive to electrolytes and also temperature.
- This means that the stability of the colloid may be manipulated by adding electrolytes or changing the temperature.



ELECTROSTATIC FORCES & DLVO THEORY

- DLVO theory — named after four scientists: Derjaguin, Landau, Verwey & Overbeek
- When two charged surfaces approach so that their electrical double-layers begin to overlap, a repulsive force is induced which tends to oppose further approach.
- DLVO theory suggests that electrical double-layer repulsion will stabilize emulsion, when the electrolyte concentration phase is less than a certain value.



ELECTROSTATIC FORCES & DLVO THEORY

ELECTROSTATIC FORCES & DLVO THEORY

- DLVO theory relates the stability of emulsified droplets to two independent potentials that come into action when two droplets approach each other.
- For small distances, the sum of the two energies is always negative (i.e., net attractive) ⇒ cause aggregation.
- When the sum of two energies is +ve ⇒ repulsive force

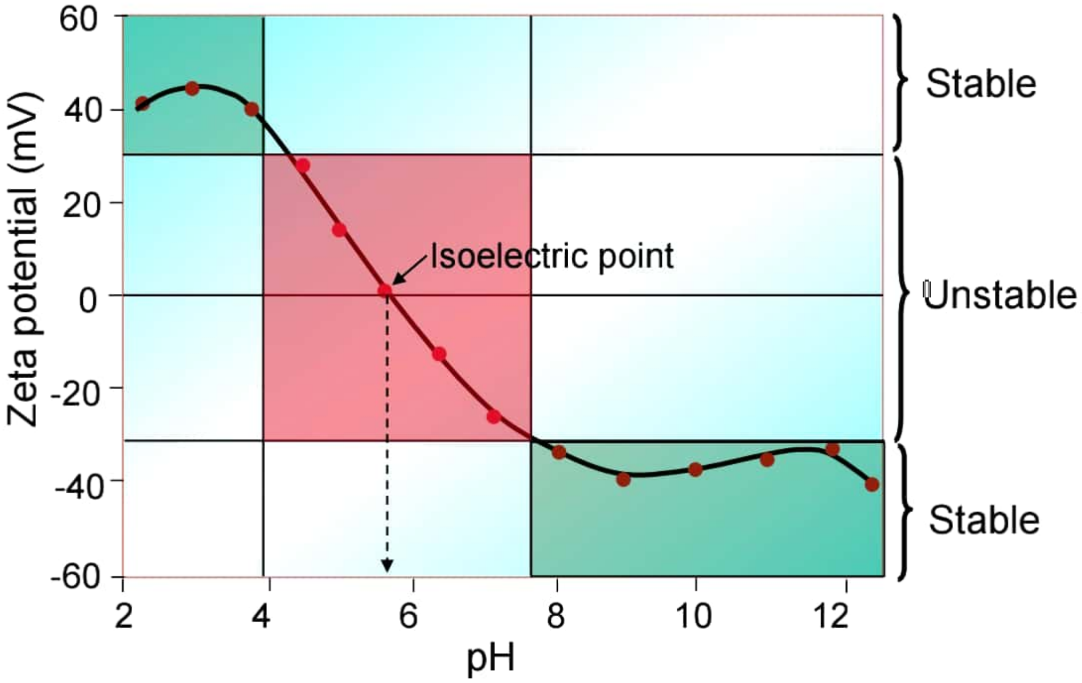
ZETA POTENTIAL

- Zeta potential is the electrical potential at the hydrodynamic plane of shear
- Particles interact according to the magnitude of the zeta potential, not their surface charge
- Zeta potential tells us the effectiveness of the surface charge
- For electrostatically stabilized dispersions, the higher the value of zeta potential, the more stable the dispersion is likely to be

ZETA POTENTIAL

- Stability dividing line is generally considered to be ±30mV
- Particles with zeta potential more positive than +30 mV or more negative than -30 mV are formed a stable dispersion.
- Small changes in the pH or concentration of ions (ionic strength) can lead to dramatic changes in the zeta potential

Effect of pH on Zeta Potential



Emulsion Stabilization

Ionic (Electrostatic) Stabilization

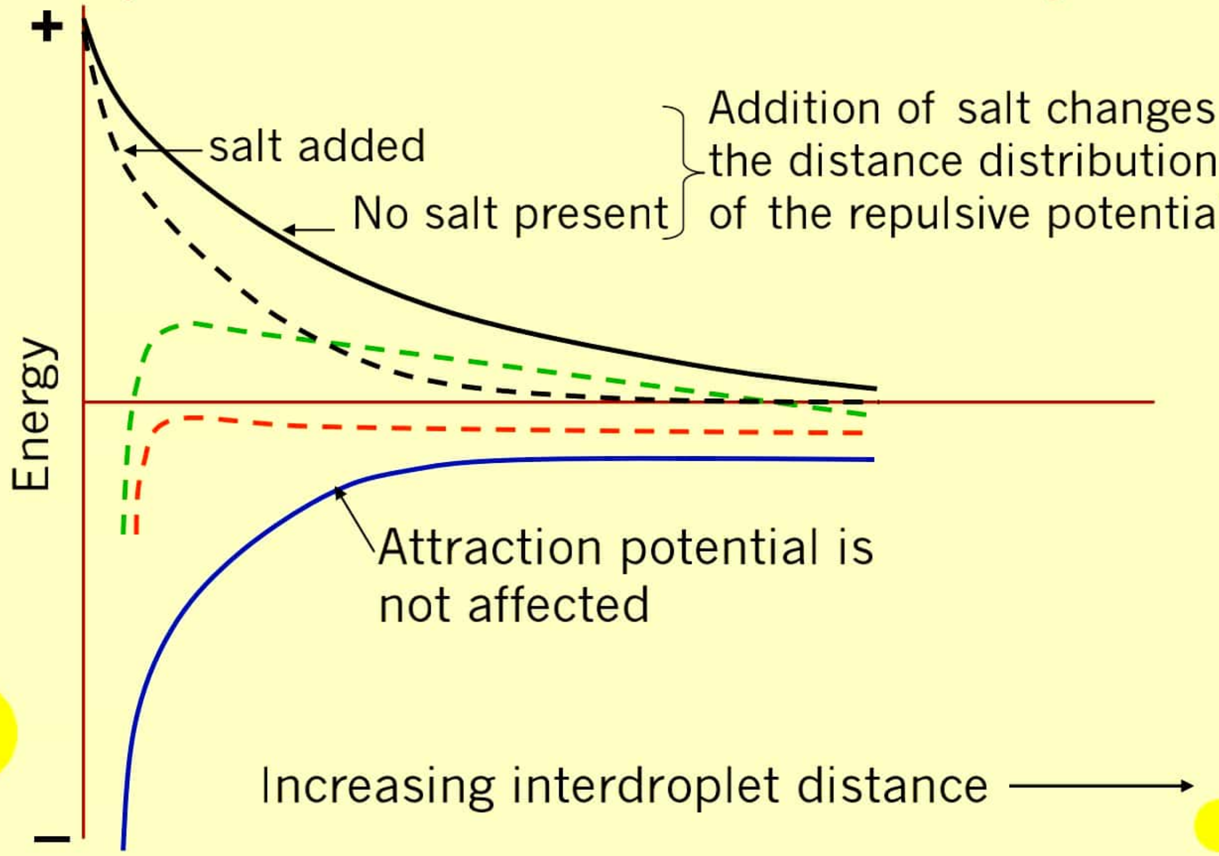
- The introduction of charged groups on the surface of the emulsion droplets increases the repulsive forces.
- Ionic emulsifiers will form an electrically charge double layer in the aqueous solution surrounding each oil droplet.

Emulsion Stabilization – Functions of Emulsifiers

Ionic Stabilization

- The thickness of the electrical double layer is affected by ionic strength. As long as ionic strength is low, electrical repulsion is > van de Waals attraction ⇒ the droplets remain suspended.
- With ionic emulsifiers, low [salt] enhances stability, while high [salt] conc increase flocculation and/or coalescence.

Emulsion Stabilization – Effect of ionic strength



Abd Karim Alias, 2013©

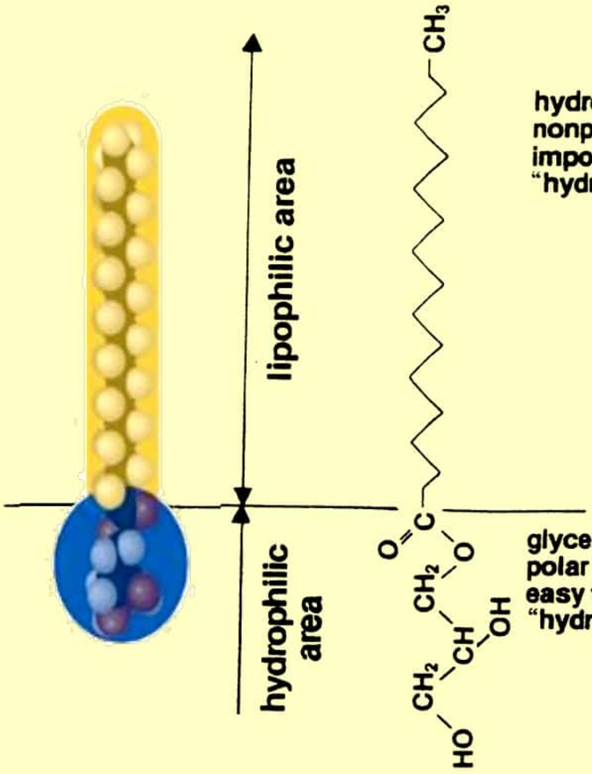
Scanned with CamScanner

Emulsion Stabilization

Emulsion stability can be achieved by using emulsifiers (surfactants) and/or stabilizers:

- Emulsifiers – compounds that facilitate the formation of emulsion by lowering the oil/ water interfacial tension & imparting short-term stability by forming a protective film around the droplets.
- Stabilizers – compounds that are not (or only slightly) surface active but impart long-term stability to emulsions by restricting interfacial interactions.

Emulsion Stabilization – Functions of Emulsifiers



hydrocarbon chain
nonpolar group
impossible or hard to hydrate
"hydrophobic tail"

glycerol-residue
polar group
easy to hydrate
"hydrophilic head"

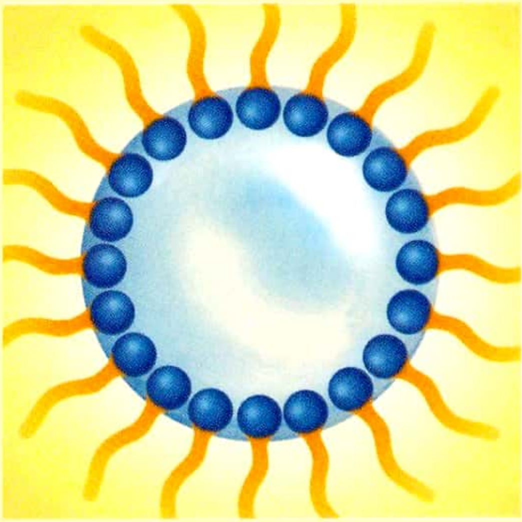
Emulsion Stabilization – Functions of Emulsifiers

Adsorption at Interface

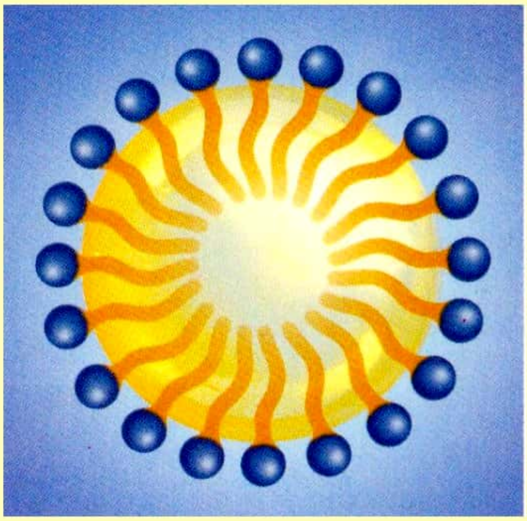
- Emulsifiers, because of their amphiphilic nature, adsorb at the interface between oil & water & form an interfacial film ⇒ reduction of interfacial tension.
- The reduction of interfacial tension through addition of emulsifiers allows emulsion formation with considerably less energy input.

Emulsion Stabilization – Functions of Emulsifiers

W/O emulsion



O/W emulsion



Emulsion Stabilization – Functions of Emulsifiers

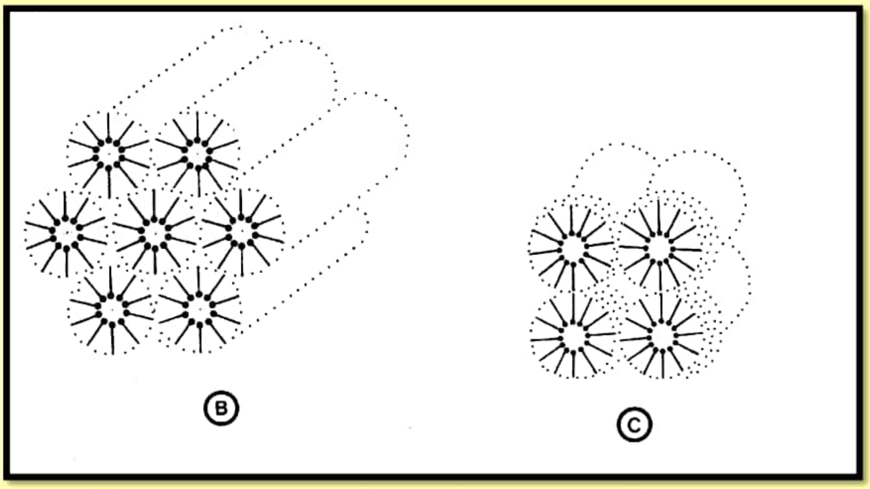
Liquid Crystal Stabilization

- Mixtures of emulsifier & water form a "liquid crystals" or mesophase structures.
- Liquid crystalline phases may form on the surface of oil droplets in o/w emulsions & reduces the rate of coalescence, even if flocculation occurs.

Emulsion Stabilization – Functions of Emulsifiers

Liquid Crystal Stabilization

A micelle is an aggregation of the emulsifier molecules, oriented with the hydrophobic chains to the inside & the hydrophilic groups on the surface.



Some examples of mesophase structures

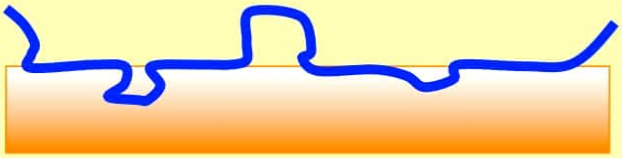
Emulsion Stabilization – Functions of Emulsifiers

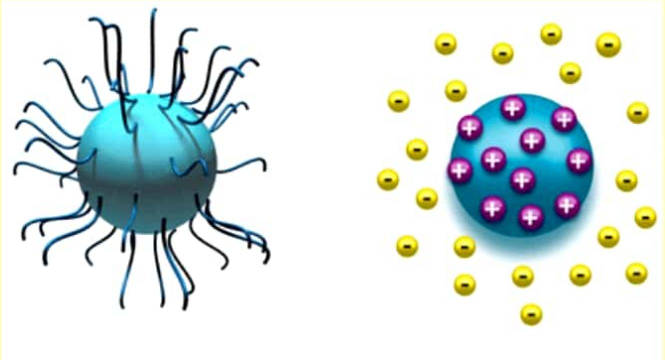
Stabilization via Steric Hindrance (also known as steric stabilization)

- Hydrocolloids such as xanthan gum, arabic gum, CMC, guar gum, etc., significantly increase emulsion stability (function as stabilizers).
- The macromolecules act by either increasing the viscosity or partitioning into the o/w interface as a physical barrier to coalescence.

Emulsion Stabilization

Steric Stabilization





Steric stabilization

Electrostatic stabilization

Emulsion Stabilization

Gravitational Separation

- Droplets in an emulsion have a different density to that of liquid which surrounds them ⇒ a net gravitational force acts upon them ⇒ cause creaming or sedimentation.
- Droplets in an o/w emulsion tend to cream (e.g. milk), whereas those in a w/o emulsion tend to sediment.

Emulsion Stabilization

Gravitational Separation

- Creaming rate of an isolated spherical particle can be predicted by Stokes's equation:

$$v_{Stokes} = -\frac{2gr^2(\rho_d - \rho_c)}{9\,\eta_1}$$

- In general, if creaming rate < 1 mm/day, the emulsion is considered stable toward creaming.

Emulsion Stabilization

Methods of Controlling Gravitational Separation

(1) Minimize Density Difference

- Matching the densities of the oil & aqueous phases
- Density matching can be achieved by mixing natural oils with brominated vegetable oils (which have a higher density than water).

“Ring”in beverage emulsion

- The driving force for gravitational separation is the density difference between the droplets and the surrounding liquid: $\Delta r = (r_2 - r_1)$
- Therefore possible to prevent gravitational separation by “matching” the densities of the oil and aqueous phases

“Ring” in beverage emulsion

- This approach is commonly used for stabilizing beverage emulsion whereby the “ring” phenomenon due to creaming of the flavor oil is sometimes observed.
- Density matching can be achieved by mixing natural oils with *brominated vegetable oils* (which have a higher density than water), so that the overall density of the oil droplets is similar to that of aqueous phase.

Emulsion Stabilization

Methods of Controlling Gravitational Separation

(2) Reduce droplet size

- The velocity at which a droplet moves is proportional to r^2 (Stoke's law).
- Stability of an emulsion to gravitational separation will increase by reducing the size of droplets.
- High pressure homogenization

Emulsion Stabilization

Methods of Controlling Gravitational Separation

(2) Modify rheology of continuous phase

- Increasing the viscosity of continuous phase surrounding the droplets decreases the velocity at which droplet moves.
- Add thickening agent, e.g. hydrocolloids such as arabic gum, xanthan gum, etc.

Emulsion Stability Index

- To predict long term stability of an emulsion
- Simple test using centrifuge at a given speed & time – observed degree of creaming.
- Measure the change in particle size distribution (PSD) of an emulsion with time (a good emulsifier does not change PSD with time, and vice versa).

Changes in droplet size distribution