Preparation and stability of emulsions

by Piero Baglioni, Debora Berti and Massimo Bonini

Emulsions are obtained by mixing at least two immiscible fluids. The emulsification process is achieved thanks to emulsifiers. Emulsions are important for several industrial applications as in pharmaceutical industry, food industry, in cosmetic, paints, plastic materials, for the petrochemical industry, etc. In this contribution are discussed at an introductory level the most relevant properties of emulsions. This article is addressed to readers with a poor knowledge of the subject, and reports the fundamental information on the emulsion properties.

Figure 1 - Diesel oil and Bio Crude Oil, obtained from pyrolysis of by-products of wood industry, are not miscible fluids (see left vial). However it is possible to obtain a stable emulsion by choosing one or several appropriate surfactants

Though emulsions are ubiquitous in everyday life, the study of these systems has been often carried on in empiric ways. Dispersions of two or more not miscible fluids are produced for many applications. Examples are abundant both among natural products (such as milk) and industrial products. Systems obtained from homogenization of two or more not miscible fluids are indicated as emulsions, miniemulsions or microemulsions (or swollen micelles) depending on the size of the particles dispersed in the continuous phase. These systems are produced using one or several additives (surfactants and cosurfactants) that are able to lower the surface energy at the interface of the produced droplets. The study of the properties of these systems dates at the end of 19th century and it developed in episodic ways, driven more by industrial requirements than by a systematic analysis. In this chapter we will focus our attention on emulsions. Rather than the above mentioned classification, based on the size of the dispersed droplets, the main difference between emulsions and microemulsions is that emulsions are not thermodynamically stable systems. So both academic and applied researches have focused their attention to metastability conditions of emulsions. It's not difficult to understand how the study of metastable systems shows peculiar difficulties. Moreover, the rationalization and the collection of the enormous amount of knowledge acquired in about a century of empirical use of emulsions are somewhat difficult to obtain.

Emulsions

Glossary

An emulsion is obtained from a dispersion of two immiscible fluids. The dispersion produces a continuous phase and a finely dispersed droplets phase. Most of the properties of emulsion systems (stability, viscosity, etc.) depend on the droplets size and size distribution, that usually cover a rather wide interval, i.e. from 300-400 nm to about 10 mm. In most of the case, stable emulsions are formed thanks to the presence of additives (emulsifying agents), and are typical multicomponent systems. Until some decades ago it was almost impossible to obtain a rigorous chemical-physical description of multicomponent systems. Emulsions formulation was practically carried on by the simple "trial and error" method.

A commonly used emulsion classification is based on the polarity of the continuous phase compared to the dispersed one. In almost all applications water is one of the two fluids, while the other fluid is characterized by a lower dielectric constant and is usually indicated as oil.

Dispersions of water droplets in oil or oil droplets in water are referred as water in oil emulsions (W/O) and oil in water emulsions (O/W) respectively. The simplest method to establish the nature of an emulsion (O/W o W/O) is to verify the miscibility with aqueous and apolar solvents. An emulsion constituted by a dispersion of oil droplets in water can be easily diluted with water, vice versa an emulsion constituted by water droplets in oil can be easily diluted with oil, without detectable phase separations on a sufficiently short time (Figure 1). This test can be easily executed with the aid of an optical microscope.

During the dilution of the emulsion, attention has to be paid to the possible phase inversion. This can occur when highly concentrated emulsions are consistently diluted and the emulsion can switch from O/W to W/O, or vice versa.

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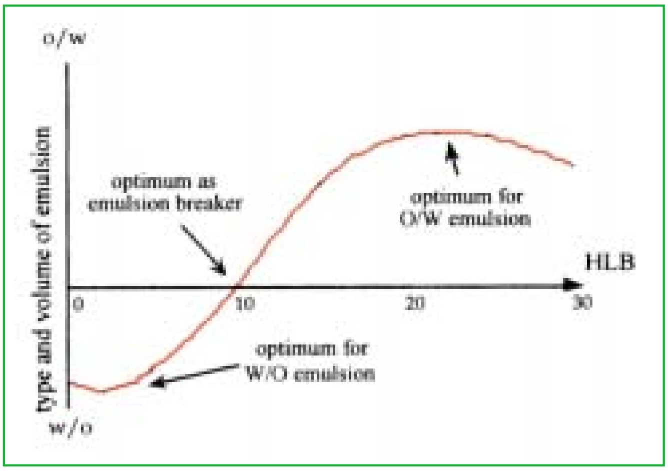

Figure 2 - Kind and volume of residual emulsion variation as a function of emulsifier HLB value

Bancroft rule

Bancroft has been the first researcher to understand that the structure of an emulsion, obtained using a surfactant, significantly depends from the nature of the surfactant. Bancroft established an empirical rule (without attempting further explanations) stating that the liquid in which the solubility of the surfactant is higher becomes the continuous phase of the emulsion. A classic example is the different behavior of sodium and calcium oleate. The first one is soluble in water and in fact it stabilizes O/W emulsions, while the second one is soluble in apolar solvents and it stabilizes W/O emulsions. Bancroft rule is generally valid.

HLB scale (Hydrophilic Lipophilic Balance)

Table 1 - HLB numbers and appropriate applications

HLB	*Applications*
3-6	Emulsions w/o
7-9	Wetting agents
8-18	Emulsions o/w
13-16	Detergents
15-18	Solubilizers

Bancroft rule shows how formation and stability of emulsions are deeply connected to the emulsifier choice. In 1949 Griffin proposed a semi-quantitative explanation to this rule analyzing a consistent number of surfactants and grouping them into two classes: liposoluble surfactants (that form W/O emulsions) and hydrosoluble surfactants (that form O/W emulsions). He further established a continuous scale of solubility based on appropriate mixtures of oleic acid (100% lipophilic tendency, in his hypothesis) and sodium oleate (hydrophilic tendency). Mixtures of the two components in different proportions were used to define the hydrophobic/hydrophilic ratio. Griffin assigned the arbitrary values of 1 to the oleic acid and 20 to sodium oleate. Intermediate values were calculated with the following relationship:

$$HLB=1W_1+20W_2$$

where W_1 is the weight fraction of oleic acid and W_2 is that sodium oleate. Each mixture shows different polarity and therefore different emulsifying capability. Griffin verified that for HLB<10 water in oil emulsions (W/O) were obtained, while oil in water emulsions (O/W) were obtained for HLB>10 (Figure 2). The HLB number of commercial emulsifying agents are usually provided by the additives producers, and they can be used as an indication of the surfactant to be used for a specific emulsion formulation. In Table 1 the appropriate HLB values for different applications are shown. It has to be pointed out that the surfactant chemical structure is just sketched in its hydrophilic/lipophilic character. This approach is not useful in view of designing the synthesis of an emulsifying agent for a specific application. In fact, HLB scale, being disconnected from the chemical nature of the surfactant, is not useful for this purpose.

Nowadays it is generally accepted that the behavior of the interface between two immiscible fluids is characterized by a spontaneous curvature H_0 of the surfactant monolayer. Surfactants characterized by a mostly hydrophilic nature have a positive spontaneous curvature and they stabilize oil droplets in an aqueous continuous phase, while lipophilic surfactants produce W/O emulsions. Emulsifiers with HLB higher than 10 belong to the first class, while HLB lower than 10 corresponds to a negative spontaneous curvature. A useful and generally valid schematization is based on the surfactant packing parameter, formulated at the end of the seventies by Ninham and Israelachvili.

The packing parameter, defined as v/al (where v is the volume of the apolar chain, l is its length while a is the area occupied by the polar head at the interface), determines the curvature of the interface. This parameter has been widely used to relate steric hindrance, and then the chemical properties of the additive, to the curvature of the interface.

This approach is not always useful due to the dependence of the interfacial curvature of the surfactant on various factors. One of these factors can be, for example, the repulsion between hydrophilic charged portions of the additive. Here we just recall that aggregates with a positive curvature (spontaneous curvature $H_0>0$, i.e. O/W emulsion) have a packing parameter smaller than one. On the other hand, if, the surfactant with v/al >1 form aggregates characterized by a reverse curvature (spontaneous curvature $H_0<0$) i.e. W/O emulsion.

Determination of HLB number of surfactants

The original Griffin method is quite laborious and requires a tedious procedure based on the study of particular compositions of the emulsion systems that lead to phase separation. Later a simple equation was introduced to determine the HLB number of some non-ionic surfactants as fatty acid esters and alcohol ethoxylates ($R-(CH_2-CH_2-O)_n-OH$). The HLB number of polyfunctional fatty is given by

$$HLB=20(1-S/A)$$

where S is the saponification number of the ester and A the one of the acid. For example, a glyceryl-monostearate, with S=161 and A=198, has HLB=2.8. The HLB number of surfactants belonging to the alcohol ethoxylates family can be estimated from the weight percentage of oxyethylene (E) and of polyfunctional alcohol (P):

$$HLB=(E+P)/5$$

These empirical formulas are valid only for the classes of compounds here proposed.

Davies suggested a different method to calculate the HLB number directly from the chemical formula of the surfactant:

HLB=7+Σn°hydrophilic groups-Σn°lipophilic groups

The contribution of each group has been obtained empirically, (Table 2). Alternative methodologies to evaluate HLB numbers based, for example, on cloud point temperature and on gas-liquid chromatography have been proposed.

Table 2 - Group contribution to HLB number using Davies equation

Group	*Contribution*	*Group*	*Contribution*
Hydrophilic		*Lipophilic*	
$-SO_4^-Na^+$	30.7	-CH-	0.475
$-COO^-H^+$	21.2	$-CH_2-$	0.475
$-COO^-Na^+$	19.1	$-CH_3$	0.475
-N (tertiary amine)	*9.4*	*Derivatives*	
Ester (sorbithol)	6.8	$-CH_2-CH_2-O-$	0.33
Ester (free)	2.4	$-CH_2-CH_2-CH_2-O-$	-0.15
-COOH (not dissociated)	2.1		
-O-	1.3		
-CH- (sorbithol)	0.5		

Phase Inversion Temperature (PIT)

The HLB number of an emulsifier indicates the type of emulsions (W/O and O/W) and it is connected to the emulsifier solubility according to the Bancroft rule. This number, related to the solubility of the surfactant hydrophilic and hydrophobic portions, has temperature dependence. The solubility of non-ionic surfactants strongly decreases as temperature increases, until a phase separation is reached. The temperature at which this separation occurs is named consolution temperature or cloud point temperature. Therefore, many surfactants, soluble in water, stabilize O/W emulsions at low temperatures, while at high temperatures their affinity for water strongly decreases and they are able to stabilize W/O emulsions.
Shinoda was the first to describe this phenomenon. He defined PIT as the temperature at which an O/W emulsion became a W/O emulsion. Therefore, PIT can be considered as the temperature at which hydrophilic and lipophilic tendencies of a surfactant are perfectly balanced. Furthermore, Shinoda underlined how emulsion stability with respect to the coalescence strongly depends on PIT proximity. In fact, O/W emulsions are relatively stable when PIT is from 20 to 60 °C higher than the storage temperature of the emulsion. Emulsions prepared with non-ionic surfactants show an enhanced stability (with respect to coalescence) for surfactants with a consistent number of hydrophilic groups (Figure 3).

Preparation of emulsions

The emulsification process is related to a consistent increase of the interface between oil and water phase. This process is not energetically favored. The Gibbs free energy of emulsions contain a term γA (where γ is the interfacial tension and A is the total extension of the emulsion interface) that accounts for the surface contribution. It is useful to express the emulsification free energy, ΔG_{em}, as a function of droplet dimensions:

$$\Delta G_{em}=-\gamma 3v/d$$

where d is the droplet diameter and v its volume. This relationship shows that the formation of a dispersion formed by droplets with a diameter d=100nm (g=50mN/m), requires an energy of about 27 J/mole. From a chemical point of view this is not a prohibitive amount of energy. ΔG_{em} value can be further decreased by adding to the emulsion a surfactant that lowers the emulsion interfacial tension g.
There are two ways to lower (at constant volume) the energy amount necessary for the emulsion production. The first one is to decrease the interfacial tension; the second one is to favor the formation of very large droplets, i.e. to decrease the extension of the interface. While the first approach is easy to be carried on (for example, in the case of microemulsions g is about zero and formation of microdroplets is spontaneous, and the system is thermodynamically stable), the second approach is not practicable because of the dependence of the emulsion stability from the droplets size.
We should notice that the formation of emulsions requires an amount of energy higher than that calculated according to the previous formula for two reasons:

- a direct introduction of energy is technically difficult: in fact the stirring of an emulsion converts most of the energy into heat because of the viscous friction;
- the stabilization of droplets with respect to the coalescence implies the existence of an energy barrier that avoids the splitting of one droplet into two smaller ones, and the emulsion formation requires that the amount of energy introduced in the system exceeds this barrier.

As already pointed out, emulsions are systems far from the thermodynamic equilibrium. Therefore, their properties do not depend only from state variables, as temperature and composition, but also from the method used for the emulsion preparation. It is not possible to establish general rules, however it's possible to underline some important factors, controlling the emulsions preparation and the stability.

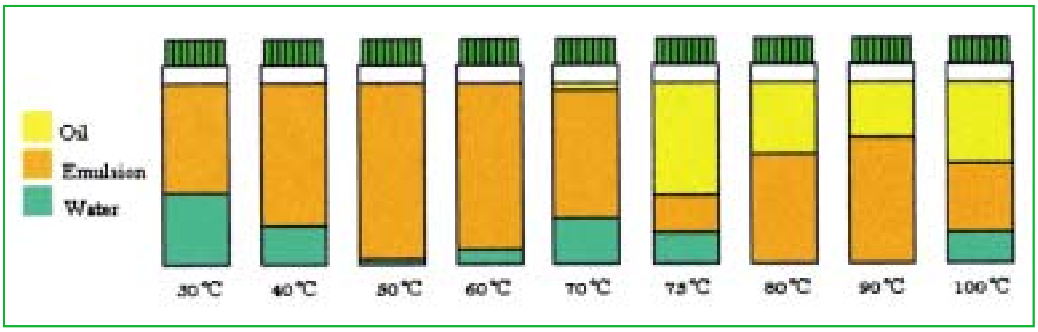

Figure 3 - Emulsion stability according to results obtained by Shinoda. PIT is equal to 75 °C. At lower temperature oil in water emulsions are obtained, at higher temperature water in oil emulsions

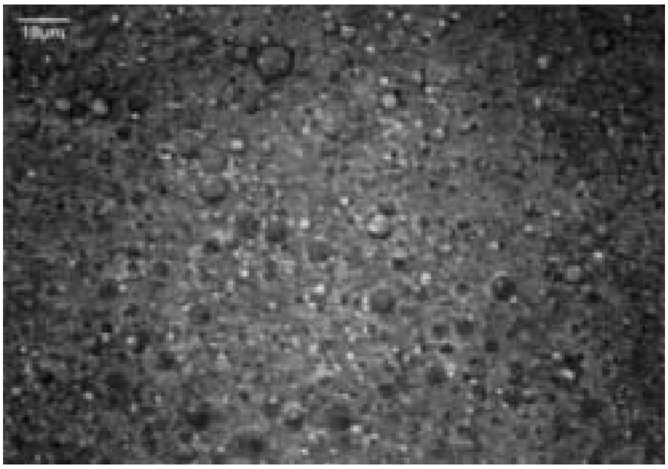

Figure 4 - Typical aspect of an emulsion observed with an optical microscope

What does it determine the O/W or W/O structure of the final emulsion? The formation and stability of droplets depends on two competitive factors:

i) the migration of the surfactant at the droplets interface (stabilization process);
ii) the droplets coalescence (destabilization process). The phase characterized by the highest coalescence rate will become the continuous phase.

Emulsions formation and stability are also affected by the sequence and the methodology used to mix together the emulsion components. For example, we can dissolve the emulsifier either in the oil and in the water phase; the emulsification can be carried on simply by mixing all the components together or by adding slowly a fluid to the other one, etc. Moreover, the mean droplet diameter depends on the intensity and amount of the introduced energy for the particular preparation technique.

Chemical energy can be used to obtain emulsions. There are several ways to do it, like, for example, using gradients of concentration or of osmotic pressure to form little droplets at the interfacial region.

We will review in the following paragraph the mostly used methods to produce emulsions.

Micronization methods

The simplest way to obtain an emulsion is to provide mechanical energy to the system. This purpose can be easily reached using mechanical stirrers, homogenizes, or by cavitation effects obtained with ultrasounds. Mechanical dispersion can become difficult when the fluids to be emulsified have very different viscosity. It has been observed that it is not possible to disperse a liquid A into a liquid B when viscosity of A is about four times the viscosity of B, as it occurs with resinous substances in water. In this case an alternative methodology is the production of a B/A emulsion followed by the inversion into the A/B emulsion.

An emulsion can be obtained simply by stirring the two fluids and the emulsifier together (Figures 4, 5). Anyway, the mechanism of formation of emulsions is not yet completely understood. For example, an emulsion constituted by 60% of benzene and a 1% sodium oleate water solution can be obtained simply by hand shaking 5 times at 20-25 seconds intervals. For the same system, mechanically stirred, more than 3000 shakings are necessary.

Ultrasound emulsification process uses the sudden production and the subsequent collapse of cavities into the liquid. This collapse, producing a big increase of local pressure, is able to destroy a droplet. The emulsification by "sonication" presents problems in terms of reproducibility due to the difficulty of controlling the cavitation nucleus (domains where the pressure of the liquid is lower than the pressure of the vapor). Laplace law regulates the shape of the droplets. This law establishes that the pressure at the interface, directed towards the droplet center, can be calculated according to the following equation:

$$P_{Laplace}=2\gamma Ad$$

A pressure in the order of $\Delta p/\Delta x=2\gamma A$ is necessary to divide a droplet into two smaller ones (higher pressures are necessary to obtain smaller droplets).

It is possible to demonstrate that the mean radius of the droplet depends on the energy introduced per volume unit according to the scalar law: $d \approx P^{0.4}$

Phase inversion method

In this strategy, an O/W emulsion is prepared from a W/O emulsion and a phase inversion is obtained using a mechanism similar to that leading to bicontinuous microemulsions. At low water content (depending on the surfactant) the W/O emulsion is not conductive and the system is formed by water droplets in oil.

By titration of this emulsion with water, conductivity increases, it reaches a maximum and it finally decreases. Water addition creates a continuous network that evolves to the formation of a dispersion of oil droplets in water.

In this procedure, the surfactant should stabilize, even temporarily, both the direct and inverse emulsion. Generally speaking, the amphiphilic nature of the surfactant makes this transient stabilization possible. The "driving force" for the whole inversion process is connected to the massive migration of the surfactant from the oil to the water phase. The main advantage of this methodology is that emulsion can be obtained without mechanical work.

To produce an O/W emulsion the emulsifier is solubilized in oil and water is slowly added under continuous stirring. In this way a W/O emulsion is obtained. Keeping on adding water, the viscosity of the system increases until water concentration reaches 50-70% wt. With a further addition of water, the emulsion goes through the phase inversion (from W/O to O/W) accompanied to a strong viscosity decrease.

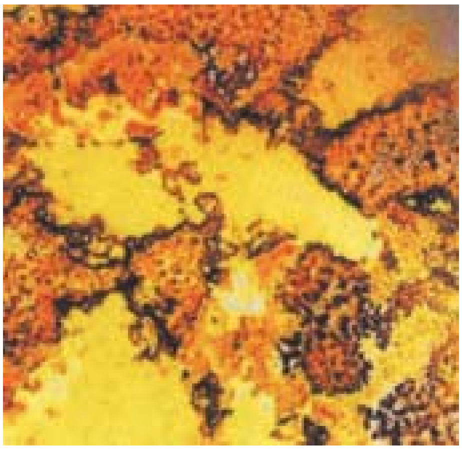

Figure 5 - Emulsions are widely used in the photographic industry. Here is reported the image of a photographic film

Phase Inversion Temperature method

Small droplets can be obtained by emulsifying two fluids at a temperature a few degrees under the surfactant PIT. At a temperature few degrees over the PIT, the interfacial tension decrease making possible the formation of smaller droplets. Once terminated the "fragmentation" process the temperature is quickly lowered. These emulsions are usually very stable.

Breaking of emulsions

Sometimes it is necessary to separate emulsified fluids. The breaking of the emulsion is spontaneous for droplets bigger than 1mm. Creaming (see below) can take place in concentrated systems. However, the breaking process requires coalescence subsequent to creaming. If coalescence doesn't take place, a further amount of energy is necessary to exceed the gap of potential energy that avoids aggregation of droplets. This energy, like for the reverse process (i.e. the emulsification process), can be provided in various ways depending on the system and on the working conditions.

Stability of emulsions

Since emulsions are not thermodynamically stable, it is obvious that the control of the stability of the emulsions is limited to the kinetic control of the separation of the constituents (oil and water). Many methodologies can be used to increase or decrease stability of emulsions, as, for example, mechanical dispersants and/or chemical additives that can change both the interfacial properties of the emulsion droplets and the viscous properties of the continuous medium. Stability of emulsions can be described by DLVO theory and its implementations that take into account different kind of interactions, like Van der Waals interactions, electrostatic interactions, steric, hydration, etc. Before analyzing how it is possible to stabilize an emulsion, we summarize the main mechanisms of emulsions breaking:

- creaming, i.e. the formation of an upper phase made of emulsion droplets. Clearly the density of this phase is lower than that of the continuous medium.
- flocculation, i.e. aggregation of droplets. Flocculation occurs when, following to the collision of droplets, the interfacial repulsive forces are not able to avoid the interpenetration of the interfacial region of the droplets, and the droplets are no longer able to split themselves.
- coalescence, i.e. similar to flocculation but, because of the collisions, the content of droplets is exchanged producing larger droplets
- Ostwald ripening, i.e. the diffusion of smaller droplets to the surface of the bigger ones. It is connected to the decrease of the chemical potential when droplets become larger.

Therefore, the stability of the emulsions is deeply connected to the concentration (volume fraction) and the dimensions of the droplets. The mechanisms of emulsions breaking are shown in Figure 6.

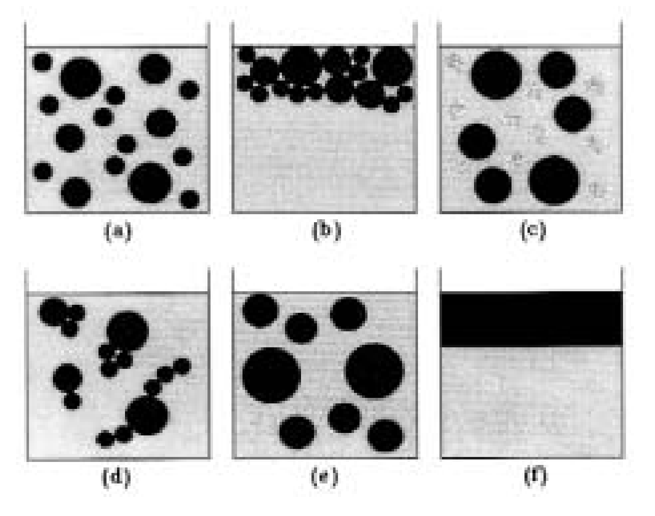

Figure 6 - Most important mechanisms of emulsion breaking: a) stable emulsion, b) creaming, c) Ostwald ripening, d) flocculation, e) coalescence, f) breaking

Determination of emulsions stability

The most important index of emulsions stability is the variation of total surface (interface) in time. After some time, emulsions destabilize as a result of the aging effect, and the total area of the system decreases. For example, the total area of 2 nm emulsion droplets is equal to 30.000 cm^2/cm^3. If droplets coalesce and the radius becomes 3 nm the total area decreases to 20.000 cm^2/cm^3. The total area determination gives important information about aging processes. However, the measurement of the surface of an emulsion is not simple. Usually, the total surface area is calculated from the particles size distribution. Several methodologies can be used for this purpose. For example, the surface area can be measured with a good optical microscope when the size of the droplets is >1μm. Unfortunately, the statistic that can be obtained with microscopic images is usually poor, unless a consistent number of images are analyzed.

The most appropriate technique for size determinations of emulsions with particles smaller than 1μm is Quasi Elastic Light Scattering (especially in the back-scattering configuration) and, with particles >1μm, PFG-NMR. For systems with droplets dimension of 10-100 nm, neutron and X-ray scattering can be used. These techniques allow a more refined analysis than optical methods. Coalescence process is really slow in stable emulsions, making difficult and tedious the determination of the aging rate. Centrifugation of emulsions (from 1000 to 25000 g) strongly speeds up the aging process, making possible, on acceptable time scale, the determination of emulsion stability.

DLVO Theory

This theory has been formulated separately by Derjaguin, Landau, Vervey e Overbeek. The complete theory formulation has taken about 60 years. The idea is very simple. Two opposite forces contribute to the stability of a colloidal system: dispersion or Van der Waals forces, that are attractive, and repulsive electrostatic forces. The balance of these opposite forces determines the stability of the system. We will discuss separately these contributions.

Van der Waals interactions

In 1937 Hamaker demonstrated that the attraction in the vacuum between two spherical particles with radius a_1 and a_2 separated by a distance R is given by the relation:

$$G_{att} = -\frac{A}{12}\left[\frac{y}{x^2+xy+x}+\frac{x}{x^2+xy+x+y}+2ln\left(\frac{x^2+xy+y}{x^2+xy+x+y}\right)\right]$$ London energy

where: $x=R/(a_1+a_2)$, $y=a_1/a_2$ and A is the Hamaker constant. If the particles have the same radius: $a_1=a_2=a$, then $(R/2a)=x$, $y=1$, and the previous equation becomes:

$$G_{att} = -\frac{A}{12}\left[\frac{1}{x(x+2)}+\frac{1}{(x+1)^2}+2\ln\left(\frac{x(x+2)}{(x+1)^2}\right)\right]$$

In the presence of a coagulation process R<<a, i.e. the interparticle distance is smaller than the particle radius. This approximation is possible since usually colloidal particles have a radius 1000<a<10000 nm and the approaching distance is £10-20 Angstrom. Within this hypothesis $x=H/(a_1+a_2)<<1$ and the preceding equation becomes:

$$G_{att} = -\frac{A}{12}\frac{a}{H}$$

This relation, valid in vacuum, shows that Van der Waals forces are always attractive and they depend on the Hamaker constant, on the size of particles and on their distance. Ottewill has proposed a relationship for particles in an aqueous phase and in the presence of a surfactant layer of thickness d:

$$G_A = -\frac{1}{12}\left[\left(A_{22}^{\frac{1}{2}}-A_{33}^{\frac{1}{2}}\right)^2\left(\frac{a+\delta}{a}\right)+\left(A_{33}^{\frac{1}{2}}-A_{11}^{\frac{1}{2}}\right)^2\left(\frac{a+\delta}{\Delta+2\delta}\right)+\frac{4a\left(A_{22}^{\frac{1}{2}}-A_{33}^{\frac{1}{2}}\right)\left(A_{33}^{\frac{1}{2}}-A_{11}^{\frac{1}{2}}\right)(a+\delta)}{(\Delta+\delta)(2a+\delta)}\right]$$

where: A_{11} is the Hamaker constant for the aqueous phase; A_{22} is the Hamaker constant for the particles; A_{33} is the Hamaker constant for the surfactant. This equation shows that G_A depends on A_{ii} values. Since usually $A_{11}>>A_{22}$ the trend of G_A depends on the value of A_{22} and $A_{33.}$ In particular, G_A decreases for $A_{22}<<A_{33,}$ and increases for $A_{22}>A_{33}$.

Other considerations are:

- small particles (a<10nm) can be stabilized just by the solvating layer;
- an absorbed layer can reduce G_A better than the solvent alone;
- point 2 depends on the thickness δ of the absorbed layer. Particles with a radius of about 1μm are stabilized with δ≅10nm.

Electrostatic interactions

Electrostatic repulsion in an aqueous medium is due to the presence of a dielectric discontinuity at the interface and of surface charges, due to ions dissociation and adsorption. The result of this process is the formation of an electric layer, named Stern layer, and of a counter-ion layer, the Gouy-Chapman layer, that are both located at the surface of the dispersed system.

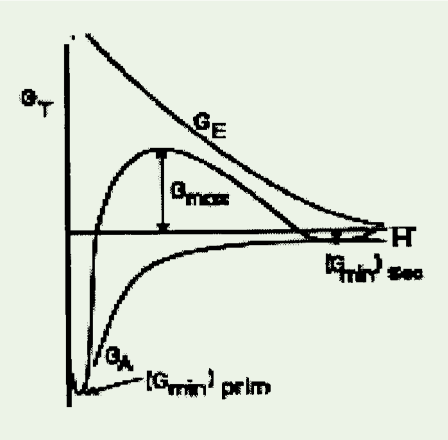

Figure 7 - Behavior of the total interaction energy according to DLVO theory

Derjaguin derived an expression valid for spherical particles when a<<R. Within this hypothesis:

$$G_E = 2\pi a\, \varepsilon_\gamma \varepsilon_0 \psi_0^2 \ln[1+e^{-KH}]$$

where ε_g is the dielectric constant of the medium, ε_0 is the vacuum permittivity, ψ_0 the surface potential and H the smallest approaching distance.

K, the inverse Debye length, is given by:

$$K=(2Ze^2c^2)/(\varepsilon_\gamma \varepsilon_0\, KT)$$

where Z is the counter-ion valence, c is the ionic concentration ($c=c_+=c_-$), and e is the electron charge. This equation is valid only at low values of surface potential, that is when $Z\psi_0<25mV$, and for spherical particles with a radius a larger than the Debye length (1/K<<a) and for weak interactions between the spheres (KH>>1). It is clear that G_E depends on both ψ_0 and K. This energy can be changed in two ways:

- an increase of the surface potential, $\psi_{0,}$ (by adsorption of ions, surfactants or polyelectrolites), produces an increase of G_E;
- an increase of K (associated to an ionic concentration increase of the solution) produces a decrease of G_E.

We recall that G_E is repulsive until the particles have the same charge sign. For example, systems stabilized by anionic and cationic surfactants coagulate if mixed. The shape of $G_{tot}=G_A+G_E$ is reported in Figure 7. The curve is characterized by three main parameters: G_{min} (primary); G_{min} (secondary); G_{max}. The values of these parameters change on the basis of the system and the experimental conditions. Three important cases are:

- $G_{max}>>100kT$ and $G_{min}<1kT$: the surface charge is high (for example a surfactant is absorbed at the droplet interface). In this case a stable emulsion is obtained.
- $G_{max}<10kT$ or not present: emulsion coagulates because the particles easily exceed the gap of potential energy. This is the case of a surfactant lightly absorbed at high electrolytic concentration.
- $10kT<G_{max}<100kT$, $1kT<G_{min}<5kT$. Emulsion is lightly flocculated. At particular electrolytic concentrations the system is in a gel state.

Steric interactions

Emulsions stability can't be explained only in terms of Van der Waals and electrostatic interactions. This occurs when the colloidal particles are coated by adsorbed substances as polyelectrolytes or non-ionic surfactants (for example: $R–(CH_2–CH_2–O)_n–OH$) or macromolecular surfactants containing blocks A-B, A-B-A, as $(CH_2\text{-}CH_2\text{-}O)_x–(CH_2CRH–O)_y–(CH_2\text{-}CH_2O)_x$). If the surfactant chain is sufficiently flexible a portion of the surfactant is anchored to the particle surface and the other into the solvent. In this case there are two additional stabilizing contributions:

$G_{steric}=G_M+G_{VR}$

where G_M is the osmotic and mixing contribution to the free energy and G_{VR} is the restrictive volume contribution.

G_M contribution

A remarkable macromolecular gradient concentration is present at the particle interface, when a macromolecular layer is absorbed onto the particle. The layer gradient depends on the concentration, on the length and flexibility of the absorbed chain, on the particles covering ratio, etc. If two identical particles collide, the polymeric chains will overlap in a volume dV. The increase of the local concentration present in this region leads to a chemical potential excess that can be calculated as the difference between the interacting particles system and the non interacting particles system, $\Delta\mu_E=\Delta\mu-(\Delta\mu)_{ideal}$. It can be demonstrated that*:

$$\Delta G_M/RT = (4/3)\ [(\pi N_A C^2)/(V_1\rho_2^2)]\ (1/2-\chi)\ (\delta-H/2)^2\ (3a+2\delta+H/2)$$

where V_1 is the partial molar volume of the solute and C is its concentration. In the case of polymers, the second virial coefficient is connected to polymer-solvent interactions by the relation:

$$B=RT(\psi_1-\chi_1)/(V_1 x\rho_2^2)$$

(remember that B α 1-θ/T) where ρ_2 is the density of the absorbed layer and ψ_1 is an entropy parameter equal to 0.5. As we can see from the preceding relations, the sign of G_M depends on the term (1/2-χ)**.
There are three different cases:

$\chi>1/2$	$G_M<0$	attraction → coagulation
$\chi=1/2$	$G_M=0$	no effects
$\chi<1/2$	$G_M>0$	stabilization

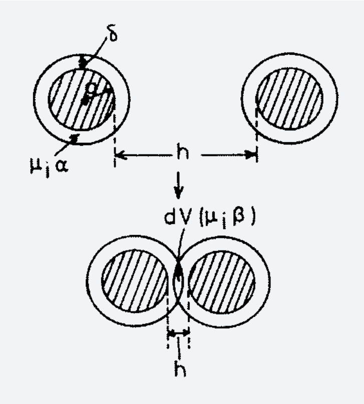

Figure 8 - The volume of a spherical cap is given by: (π/3)[x²(3r-x)]; for emulsion droplets:V_s=(π/3) (δ-H/2)²(3a+2δ+H/2), $V_{tot}=2V_s$

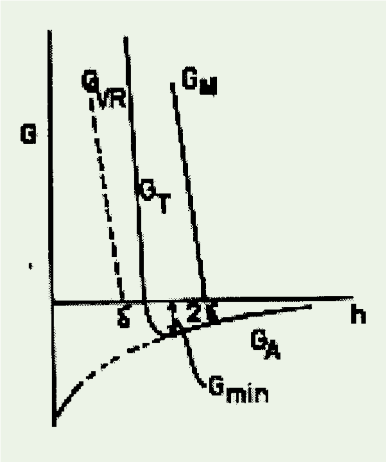

Figure 9 - Behavior of G_M and G_{VR} as a function of H

The last important contribution to dispersion stability becomes important when the superimposition between hydrophobic chains is really high, i.e. when H<<δ. This contribution is named as volume restriction or elastic contribution (G_{VR}). Markov demonstrated that the chains of a surfactant loose a certain number of degrees of freedom when the chains are adsorbed and show side interactions. This contribution is given by:

$$G_{VR}=N_S RT\theta_\infty\ (1-H/\delta)$$

where N_S is the number of absorbed chains per area unit and θ_∞ is the fraction of surface of a single particle covered by the absorbed layer. Steric interactions contribute only when H<2δ o <δ.Therefore:

$$G_{steric}=G_M+G_{VR}=(4/3)[(\pi RTN_A C^2)/(V_1\rho_2^2)](1/2-\chi)\ (\delta-H/2)^2(3a+2\delta+H/2)+N_S RT\theta_\infty(1-H/\delta)$$

Qualitatively the energetic diagram shown in Figure 9 describes this contribution. In all the above relationships containing G_M and G_{VR}, a term connected to molecule-molecule interaction (2° virial coefficient) is present. The second virial coefficient for polymer solutions is proportional to (1-θ/T), that is temperature depending.
This term is equal to zero when θ=T, i.e. at the θ temperature of the polymer-solvent the system. Therefore, a system stabilized only in a steric way easily coagulates when the temperature is higher than the θ temperature of the polymer (T>θ). Napper found that, in the case of certain systems stabilized with non-ionic surfactant, there is an incipient system coagulation when T>θ (Figure 10).

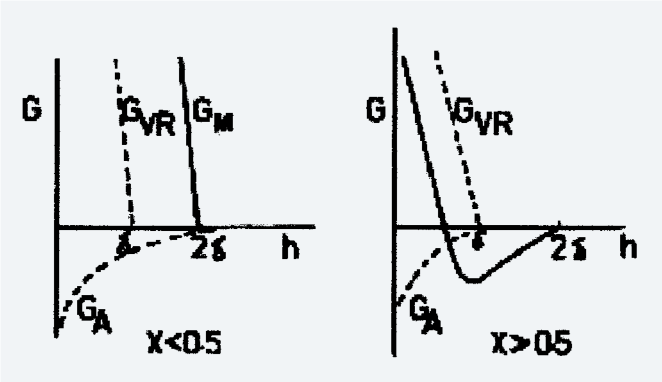

Figure 10 - Free energy contribution behavior as a function of the solvent. In particular, in the left case the solvent is better than the θ solvent, while in the right case it is worst than the θ solvent

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*Following Ottwill theory (1967) we can intuitively consider that: $(\Delta\mu_i)_E=-RTBV_1C^2=-\Pi_E V_1$ and $\Pi_E=RTBC^2$ where Π_E is the excess of osmotic pressure arising from the increase of the local concentration of macromolecular chains. Therefore, the energy variation for two particles is given by:

$$\Delta G_M = 2\int_0^V \Pi e dV = 2\Pi eV$$

Considering the superimposition volume we have: $\Delta G_M=2\pi e(2\pi/3)(\delta-H/2)^2(3a+2\delta+H/2)$ substituting now the value $\Pi_E=RTBC^2$ we obtain: $\Delta G_M=2RTBC^2(2\pi/3)\ (\delta-H/2)^2(3a+ 2\delta+H/2)$ that is:$\Delta G_M=RTC^2B(4/3\pi)\ (\delta-H/2)^2(3a+2\delta+H/2)$

**From Flory-Huggins: (1/2-χ)=ψ(1-θ/T)

The total energy contribution is summarized by: $G_{tot} = G_A+G_E+(G_{VR}+ G_M)$. It follows that for a sterically stabilized system it is really difficult to reach the primary minimum and therefore to destabilize the system. An emulsion sterically stabilized can be destabilized by desorbing the surfactant or changing its solubility, i.e. changing is θ temperature.

In conclusion, DLVO, including steric interactions, is really useful in the understanding of stabilization process, and in the emulsion formulation.

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Preparazione e stabilità di emulsioni

Le emulsioni sono formate dal miscelamento di due o più fluidi immiscibili. Questi sistemi sono importanti per la formulazione di un numero sempre maggiore di applicazioni industriali, come ad esempio in campo farmaceutico, alimentare, nella cosmesi, nella formulazione di vernici, materiali plastici, in campo petrolchimico, ecc. In questo contributo sono discusse a livello elementare le principali proprietà delle emulsioni. L'articolo è strutturato in modo da fornire a lettori con una scarsa conoscenza dell'argomento le nozioni di base necessarie per la realizzazione di sistemi emulsivi.