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Article

Emulsions and Microemulsions Stabilization Comprehension by Helmholtz Free Energy

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ABSTRACT

Emulsions and microemulsions are presented in this review article, in which we give the differences between these two mixtures and we give the energy stability dependency for both of them. We show that the emulsifiers adding facilitate the generation of small droplets during homogenization by lowering the interfacial tension. The energy stability is obtained when the surfactant concentration is augmented. Using the Helmholtz free energy, we show that microemulsion's stability increases with the increasing of entropy disorder. The promise of microemulsions under certain conditions offers great potential for liposome and vesicle comprehension. Then it also offers a beginning for cell membrane comprehension.

Keywords: Emulsions, Microemulsions, Emulsifier, Surfactant, Micelle, Lamellar Phase

Introduction

Since their discovery[1] microemulsions arouse an increasing interest in both the fundamental research and industrial field. This is due to their specified properties, such as low interfacial tension, thermodynamic stability, and ability to solubilize aqueous or lipid compounds.[2-6]

Emulsions and microemulsions are formed by the dispersion of two mutually immiscible liquids. To obtain this type of stabilized system, the mechanical agitation alone proves useless, because the two liquids separate into two phases as soon as we stop steering. To stabilize the mixture, we add particular molecules called surfactants or emulsifiers. The difference between emulsion and microemulsion manifests essentially on the size of the micro droplets, and the microemulsion thermodynamic stability.

In this work, we first give the differences between the emulsions and microemulsions. Then we introduce the structures of both mixtures, in which the notions of micelle and inverse micelle are explained for the aqueous phase and lipid phase dominances. Finally, we give the concept of free energy to explain the microemulsions stability.

Emulsions and Microemulsions

Emulsions

Definition

We are talking about emulsion when the liquid droplets – water for example – are dispersed in another liquid (oil for example). Both liquids are immiscible in each other. This mixture stays stable in case we add a third element known as emulsifier or surfactant.

Emulsion systems can be considered as a subcategory of hydrophobic colloids – like solid – liquid dispersions, their preparation requires an energy input, such as ultrasonication, homogenization, or high speed stirring.[3,16]

Surfactants

They are amphiphilic[2] molecules, i.e., they are formed by two parts, which present different polarities. The first part is composed by a hydrophilic polar head, and the second part is composed by a lipophilic carbon chain, as shown in Figure 1.

There are different types of surfactants[14] as shown in Figure 2, the anionic surfactants, which have a negative polar head,

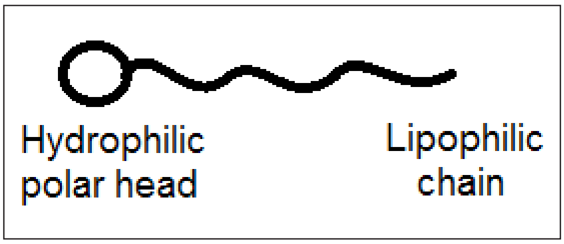

Figure 1.A schematic surfactant representation

the cationic surfactants, which have a positive polar head, the nonionic surfactants, in which the polar head can't be ionized, the amphoteric molecules, which are formed by a dipolar union.

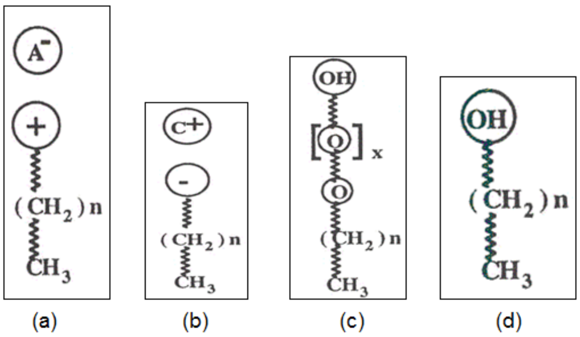

Figure 2.Surfactants types: (a) cationic, (b) anionic, (c) nonionic, (d) amphoteric molecules

There are also another surfactants called emulsifiers, which are used in food industry like amphiphilic proteins, polysaccharides, phospholipids, and small molecule surfactants.[7,8,18,19]

Amphipatic molecules consist of two parts, one of which has a high affinity for the medium (liophobic).[3] They tend to adsorb at interfaces to reduce the interfacial energy between the liophobic portion of the molecule and the medium.[3]

Emulsions Structures

- The Micelle

It appears that a charged, a zwitterionic, or a bulky oxygen-containing hydrophilic group is required to form micelles in an aqueous medium.[3,14] The oil droplets are dispersed in the aqueous phase, or the water droplets are dispersed in the lipid phase. The stabilization is obtained by the surfactant molecules, which are localized in the droplets surface. Micellar shape is dependent on surfactant concentration as shown in Figure 3. At low concentration, the micelles are spherical, have well defined aggregation numbers, and therefore are monodisperse. As the value is increased above the critical micelle concentration, micellar shape becomes distorded, forming cylindrical rods or flattened discs.[3]

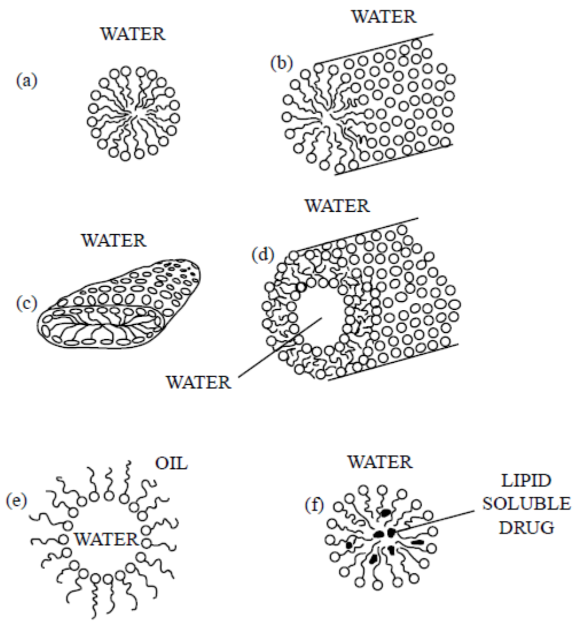

Figure 3.Association colloids: (a) spherical micelle, (b) cylindrical micelle, (c) flattened disc-shaped micelle, (d) microtubular micelle, (e) inverted micelle, (f) micelle swollen by the presence of solubilized lipid soluble drug.[3]

- Oil in Water Emulsion (Spherical Micelle)

When the dispersed phase is formed by oil droplets, and the continuous phase is formed by the aqueous phase, then we are talking about oil in water micelle, or spherical micelle, Figure 3 (a). Anionic surfactants and hydrophilic surfactants are suitable for producing oil-in-water emulsions.[5,9,11,17]

The mixture stays stable, because the surface surfactants effect, which decrease the interfacial tension γ. The hydrophilic heads are oriented to the aqueous phase, and the lipophilic chains are immersed into the oil droplets.

- Water in Oil Emulsion (Inverted Micelle)

If the dispersed phase is formed by water droplets, and the continuous phase is formed by the lipid phase, then we are talking about water in oil inverted micelle, Figure 3 (e). Hydrophobic surfactants are suitable for producing water-in-oil emulsions.[5,17]

The surfactants – being in the surface between oil and water phases – decrease the interfacial tension γ. The lipophilic chains are oriented to the continuous oil phase, and the hydrophilic heads are immersed into the water droplets.

Stabilization

It is clear that when two immiscible liquids are in contact, a surface tension γ appears in the interface between these mediums. This tension is correlated to the electrostatic forces between molecules. The emulsifiers adding – which are surface active ingredients – facilitates the generation of small droplets during homogenization by lowering the interfacial tension, and that improve emulsion stability by forming protective membranes around droplets, that may help protect them from aggregation by generating repulsive forces between droplets.[7,8,18-21] But, the system is not thermodynamically stable in long term. Because the system energy tends to minimize, the emulsion tends to form two distinct separated phases.

To solve this problem, scientists made emulsions more stable in energetic point of view by the creation of the microemulsions.

Microemulsions

Definition

A microemulsion differs from an emulsion in that it forms spontaneously, is in equilibrium, and contains small, sub-micron droplets. High fractions of surfactant are required to coat the extensive interfacial surface of a microemulsion.[12] Microemulsions have fine droplets, they are transparent, and are more stable. This exceptional stability is due to the system entropy, which account the disorder degree. The free energy is given by Helmholtz,[3]

$$G = \gamma A - TS, \quad (1)$$

where,

ΔG, Gibbs free energy,

. ΔA, interfacial area,

γ, interfacial tension,

T, absolute temperature,

ΔS, entropy of the system.

The γA term specifies the energy of the system, which is in competition with the entropy disorder. Then, more the entropy increase, more the free energy decrease and the system is more stable. The microemulsions in which the entropies are higher will be more stable thermodynamically than emulsions.

Cosurfactants

We note that, to have more stability and in addition to the surfactant concentration elevation, we have to add a second surfactant known as cosurfactant. This cosurfactant permits the interfacial tension γ decreasing.

Microemulsions Structures

- Micelles Forms

Micelles are the smallest assemblage of surfactants in a liquid. It is a colloidal assemblage of a few nanometers as shown in Figure 3 (a) and (e). The lower size limit is at approximately 1nm and the upper limit at approximately 1µm. To qualify as a colloid, only one of the dimensions of the particle must be within this size range.[3]

- Other Microemulsions Forms

Addition of surfactant beyond the amount required for a single microemulsion phase eventually results in a lamellar phase with alternating sheets of oil and water coated with surfactant.[12,23] At very high concentrations, liquid crystals forms.[3,15] Under specific conditions, surfactants can form 2-D membranes,[10] or bilayers separating two aqueous regions (similar to biological membranes). If this bilayer is continuous and encloses an aqueous region, then a vesicle results (liposome).[3]

Liposomes can be subcategorized into, Small unilamellar vesicles (SUV), 25 – 70nm in size that consist of a single lipid bilayer, large unilamellar vesicles (LUV), 100 – 400nm in size, that consist of a single lipid bilayer, multilamellar vesicles (MLV), 200nm to several microns that consist of two or more concentric bilayers.[3]

Finally, given the right circumstances, membranes could constitute a 2-D microemulsion.[12,13,22,23]

Conclusion

We have given a short review about the differences between emulsions and microemulsions. We have also given the definition of the emulsifiers, surfactants and their role. We have done the definition of the direct and inversed micelles, the structures of emulsions and microemulsions. We have shown that a microemulsion's droplet is a colloid, with a size comprised between 1nm to 1000nm. Colloid systems are composed by at leaste two components. These later are dispersed in each other and can be large molecules or small particles. Finally, in relation with the surfactant concentration elevation in a microemulsion, we can obtain different structures: starting by lamellar phase, and ending by a vesicle or liposome which is similar to a biological membrane. Characteristic properties related to these systems are unique and are influenced by the dimensions of the dispersed units.

This review of emulsions and microemulsions has massive potential in applications as diverse as material science, nanotechnology and biomedicine. Small emulsion droplets can be used in drug delivery or drug solubility purposes.

Large emulsion droplets can be used in food processes, and then to stabilize liquids and colloidal solutions. These emulsions are very stable in time and can be stored for two years a t room temperature.

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