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Emulsification and emulsion stability: the role of the interfacial properties

Francesca Ravera^{1,*} francesca.ravera@cnr.it, Katarzyna Dziza¹, Eva Santini¹, Luigi Cristofolini^{1,2}, Libero Liggieri¹

¹CNR - Institute of Condensed Matter Chemistry and Technologies for Energy Unit of Genoa, Italy

²Department of Mathematical Physical and Computer Sciences, University of Parma, Parma, Italy

*Corresponding author.

Abstract

In this review, we highlight and discuss the effects of interfacial properties on the major mechanisms governing the aging of emulsions: flocculation, coalescence and Ostwald ripening. The process of emulsification is also addressed, as it is well recognized that the adsorption properties of emulsifiers play an important role on it.

The consolidated background on these phenomena is briefly summarised based on selected literature, reporting relevant findings and results, and discussing some criticalities. The typical experimental approaches adopted to investigate the above effects are also summarised, underlining in particular the role of adsorption at the droplet interface. Attention is paid to different types of surface-active species involved with emulsion production, including solid particles. The latter being of increasing interest in a wide variety of emulsions-related products and technologies in various fields. The possibility to stop the long term aging caused by Ostwald ripening in emulsions is also discussed, quantifying under which conditions it may occur in practice.

Keywords: emulsion stability, coalescence, flocculation, Ostwald ripening, adsorption layer, dilational viscoelasticity

1. Introduction

Emulsions are systems of great interest for a large number of applied fields spanning from pharmaceuticals, cosmetics, foods to other practical applications like oil recovery or development of new nanostructured soft materials. Emulsions are water-oil dispersed systems, thermodynamically unstable, which tend to separate under the effect of external forces and/or perturbations. Such separation occurs in times that may differ of several order of magnitude. The prediction of these lifetimes, as well as the tailoring of the emulsion micro structure, are essential aspects in those technological fields where emulsions are produced and utilized.

In order to control emulsification and emulsion stability, appropriate components are employed such as low weight surfactants, biomolecules, polymers, proteins, solid

nanoparticles or more complex associations of surfactants and nanoparticles. Being these components generally amphiphilic, they adsorb at water-oil interfaces modifying their properties.

Several studies on the physico chemical mechanisms involved in the ageing process of emulsions have been carried out during the last years [1–6], some of them on how such mechanisms are influenced by the adsorption properties of the different additives used [2,3,5]. However, despite the huge number of studies dedicated to emulsions, most of the formulation adopted in the various application fields still rely on semi-empirical approaches, proving the need, not only of new advancements in this topic, but especially of a deepen analysis of the available literature in order to evidence the correlation between fundamental findings and practical applications.

This review addresses the relationship between the interfacial properties in liquid-liquid systems and the behaviour of the associated emulsions. The correlation between these properties is, in general, well recognized, even if some aspects, like for example the role of the rheological properties of the adsorbed layers on the emulsion stabilization, remain controversial issues because, although justified from the theoretical point of view, are only poorly supported by experimental evidences.

The often encountered difficulty in clarifying the correlation between interfacial properties and emulsion stability is mainly due to the fact that the ageing of emulsions is governed by several dynamic mechanisms, the importance of which depends on the nature of the emulsifiers and the oil phase. Thus, the role of the different interfacial features in the hindering of such destabilizing mechanisms may be of variable relevance and strongly dependent on the system.

The properties of emulsions present several similarities with those of foams which also are employed in a huge number of applied fields and, for this reason, widely investigated both theoretically and experimentally [7,8]. In particular, analogously to emulsions, the properties of foams have been investigated in relation to those of the adsorption layers at the water-air interface [9–11]. However, even if many of the investigation approaches and results concerning foams may be extended and adapted to emulsions, these latter present peculiarities that make them essentially different especially as concerns the destabilization rates and the morphology. This mostly originate from the density differences and viscosity of the fluid phases and from how interfaces and liquid films are modified by the surfactant transport phenomena: in particular, as related to the adsorption process and to the possible distribution between the two liquid phases.

Aim of this review is to highlight and discuss the results available in literature where the principal mechanisms governing the aging of emulsions are investigated in relation to the different features of the interfacial layers. To this purpose, the different mechanisms at the basis of the emulsion destabilisations such as flocculation, coalescence and Ostwald ripening, are discussed and their correlation with the emulsion stability pointed out. Concerning Ostwald ripening, a more deepen discussion on the possible effect of the surfactant adsorption is reported which allows the conditions for the hindering of this process to be better defined. A quantitative estimation based on literature data is also provided which further evidence the difference between emulsions and foams regarding this aspect.

The process of emulsification is also addressed as it is well recognized that also the adsorption of emulsifiers plays an important role on it. The typical experimental methodologies adopted to investigate the interfacial properties mostly involved in emulsion formation and stability are also briefly presented.

2. Emulsification

The process of emulsification consists in the fragmentation of one liquid phase inside the other one with the formation of a large number of small droplets. Emulsions in industrial or research fields may be produced adopting either high or low energy techniques, using different kind of mechanical devices such as shear mixers, high-pressure valve or membrane homogenizers, micro-fluidizers and sonicators. The choice of the method depends on the field of application as well as the kind of emulsifier employed [12,13].

The different factors influencing the emulsification process and the features of the emulsions obtained, have been widely investigated also considering the different emulsification techniques and emulsifiers [1,2,12,13]. However, some basic principles about the role of the adsorption properties of the emulsifiers and the dynamic processes occurring during emulsion formation are common to most systems and techniques.

In all cases, in fact, efficient emulsifiers present strong ability to lower the interfacial tension, short characteristic times of adsorption and high coverage degree of the water-oil interfaces once adsorbed. These characteristics have an important role in determining the initial morphology of the emulsions, i.e., the droplet average size and the size distribution and consequently their stability.

2.1 The role of the interfacial properties on the emulsification

Emulsification is associated to an important increase of the interfacial area ΔA which requires, from a thermodynamic point of view, a work on the system proportional to the interfacial tension, γ , that is $W = \gamma\Delta A$. Thus, we can say that the larger is the energy transferred to the system during emulsification, the larger may be this work and, therefore, the smaller the average drop radius in the emulsion. On the other side, for a given energy transferred to the liquid-liquid system, emulsification is favoured when the interfacial tension is low, that is smaller droplets are produced with emulsifiers more efficient to adsorb at the water-oil interface and to reduce the interfacial tension.

In addition, being emulsification a dynamic process where the water-oil interfaces are continuously renewed and submitted to stretching, it is very important that the adsorption of emulsifiers occurs in a relatively short time. In this case, in fact, the interfacial tension may reach the low equilibrium value in times comparable to those of the interfacial perturbation, favouring the droplet generation.

Examples of studies where the interfacial properties and the emulsification are compared can be found in refs [14] and [15], for water in oil emulsions stabilized by oil soluble surfactants, and for oil in water emulsions stabilised by non-ionic surfactants, respectively. In both cases, the correlation between the reduction of the emulsion droplet

size and the adsorption characteristic time decrease is evidenced. In ref. [16], the role of the surfactant head group in the emulsification process has been investigated, using water soluble surfactants with the same hydrocarbon tail length but different head groups. The results evidence a direct relation between the average droplet size of the oil in water emulsions and the interfacial tension at concentrations near the cmc, which is linked to the packing densities of surfactants at water-oil interfaces.

The adsorption properties of the emulsifiers play an important role not only for the lowering of the interfacial tension, but also as concerns the stabilization of the newly formed droplets against coalescence. In fact, during emulsification, the coalescence phenomenon is very important and contributes to determine the drop size distribution of the emulsion. Important results concerned with this specific aspect and focussing on drop-drop interaction during emulsification are reported in ref. [1] for oil in water emulsions stabilized by different ionic and non-ionic surfactants.

The interfacial properties involved in the stabilization against coalescence are analysed in more in detail in a next dedicated section. However, under the dynamic conditions addressed here, we can say that a relevant feature of the emulsifier, for the prevention of the droplet coalescence during the process of emulsion formation is the ability to reach high coverage degree at the surface of the dispersed drops. This property depends on the molecular structure of the surfactant and on the adsorption configuration that may assume at the water-oil interface, as already shown in some recent experimental studies [17][18]. Other interesting results on the relation between interfacial and emulsification properties are reported in some recent works about natural surfactants related to foods, cosmetics, and pharmaceutical products. For example in ref. [19] different natural surfactants, such as, saponins of different origin, are investigated and their ability as emulsifiers are correlated with their effects on interfacial tension features.

2.2 Other effects important during emulsification

The depletion of the surfactant solution during emulsification is an important phenomenon that must be considered for emulsion formulation because influencing the feature of the obtained final emulsion. This phenomenon is due to the huge increase of the available interfacial area associated to the fragmentation of the disperse phase. The consequent adsorption of surfactant may result in a significant impoverishment of the matrix phase, which, in turns, limits the adsorption process and the achievement of the high coverage degree necessary to stabilize droplets against coalescence.

This phenomenon has been purposely investigated for foams [20] but also taken into account for emulsions [1,17,18]. In particular, in the latter studies, it has been shown that, by knowing the adsorption properties of the emulsifier and, in particular, the thermodynamic parameters like surface activity and molecular area, it is possible to estimate the concentration of the depleted continuous phase from the drop sizes of the formed emulsion. In other words, a relation can be defined [18] between the initial concentration of the solution, the concentration of the depleted matrix phase of the emulsion, the droplet size distribution and their surface coverage, in a quasi-equilibrium condition achieved just after emulsification. From a practical point of view, such relation allows a better prediction of the feature of the emulsions, being possible to estimate,

through the knowledge of their adsorption properties, the minimum amount of emulsifiers necessary to obtain an emulsion with a given droplet size distribution. At large, such depletion become particularly significant as far as sub-micrometric emulsions or emulsions formulated with low surfactant concentrations (for example, sub-micellar concentrations) are considered. In these cases, the use of corrected concentrations allows for a better analysis of the correlation between emulsions features with the interfacial properties, which are usually estimated on single drops or bubbles.

The approach sketched above for the depletion of matrix surfactant concentration resulting from adsorption can be easily adapted [18] to account also for the depletion caused by surfactant partitioning in the droplet phase. In fact, partitioning of the emulsifier between water and oil is another important effect affecting the result of the emulsification. This is especially relevant when non-ionic surfactants are concerned. The transfer of the surfactant across the water-oil interfaces and the possible impoverishment of one phase with respect to the other one, may play an important role in the dynamics of the adsorption as well as in the features of the obtained emulsions. Partitioning of non-ionic surfactants and, in general, their solubility in both liquid phase has been widely investigated [21] and methods to quantify this property through the measurement of the partition coefficient have been developed [22,23]. Concerning the impact on the emulsion formation, partitioning has to be taken into account not only for its contribution to the impoverishment of the continuous phase or the reduction of the interfacial coverage, but also because of its possible role in the formation of complex emulsions, such as double or multiple emulsions. Such kind of disperse systems are commonly obtained, in various application, such as cosmetics and food technology, by using a combination of lipophilic and hydrophilic surfactants [24,25]. In fact, according to the empirical Bancroft rule the continuous phase in emulsions is commonly that where the emulsifier is predominantly soluble and such surfactant combination allows the generation of an emulsion where the disperse phase is an emulsion in turns. However, if the stabilizer presents comparable solubility in water and oil phases, the competition between the stabilization of water and oil droplets, may induce the coexistence of both water in oil and oil in water emulsions, or again the formation of double/multiple emulsions. This effect has been already observed in some experimental studies concerning non-ionic surfactants as emulsifiers [18].

3. Emulsion stability

As summarised in Fig. 1, the main mechanisms governing the aging of emulsions are: drainage and gravity driven separations, such as creaming and sedimentation, flocculation, coalescence, and Ostwald ripening or coarsening. While creaming and sedimentation are essentially governed by the density difference of the two liquid phases, the other phenomena are related, more or less directly, to the properties of the liquid-liquid interface.

Flocculation, which consists in the formation of droplets aggregates, is driven by the interaction of the adsorbed layers at the surface of the emulsion droplets. Coalescence is the merging of two droplets into a single one, related to the thinning and rupture of the liquid film between them and, for that, strongly influenced by the interfacial properties of the adsorbed layers. Coalescence in emulsions may occur when moving droplets get in

contact or as consequent to their flocculation. Ostwald ripening consists in a partial dissolution of the dispersed liquid phase induced by the capillary pressure, resulting in a mass transfer from small to big droplets. Though mainly driven by the solubility of the disperse liquid and strongly dependent on the size of the droplets, this phenomenon is also affected by the presence of surfactants and on the rheological properties of the interfacial layers.

The above destabilisation processes are all interconnected and may influence each other during the emulsion ageing. For example, creaming, as well as flocculation, does not modify the drop size distribution, which is instead affected by coalescence and Ostwald ripening, but tends to make more compact the droplet population and consequently may accelerate the processes of flocculation and coalescence. On the other side, both flocculation and the increase of the average droplet sizes induced by coalescence and Ostwald ripening, tend to quicken the creaming process and eventually the destabilisation of the emulsion.

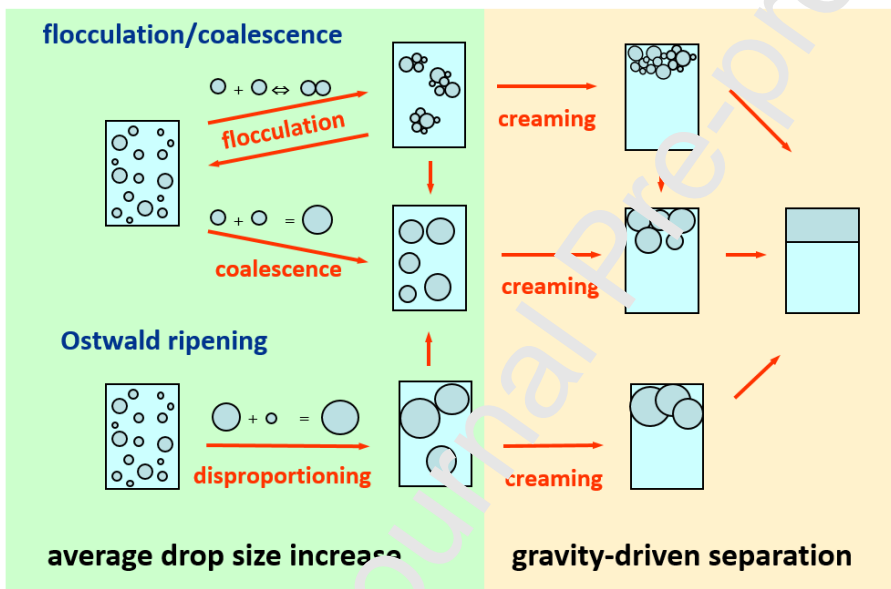


Fig. 1: Sketch of the main mechanisms involved in emulsion destabilisation

3.1 Role of the interfacial properties on flocculation and coalescence

When one emulsion droplet is pushed against another one, because of its movement or under the effect of long scale interaction, the deformable interfaces of two adjacent droplets are flattened forming a film of the continuous phase which drains till reaching a certain critical thickness (usually of the order on 50-100 nm). The stability of this films against further thinning and rupture determine the conditions for coalescence or the formation of droplet aggregates with longer life times, usually termed aggregation or flocculation depending on their degree of reversibility.

Thus, the phenomena of flocculation and coalescence during the emulsion ageing are recognized to be strictly connected to the stability properties of the corresponding liquid films [26,27], called foam films or emulsion films if limited by a gas phase or another immiscible liquid, respectively.

The properties of these films are commonly dealt on the basis of the DLVO theory [28], where the interaction potential between two approaching colloidal spheres is expressed as the combination of the van der Waals attraction and electrostatic repulsion. The experimental studies on liquid films are usually based on the measurement of the disjoining pressure, Π_d , or surface force between the two interfaces limiting the liquid film, as a function of their distance h , or film thickness. According to the DLVO theory, the disjoining pressure is the sum of long range repulsive electrostatic and attractive van der Waals forces. In most cases referring to liquid films in presence of surfactants, however, further terms have to be included in the expression of $\Pi_d(h)$ depending on the surfactant adsorption properties like, for example, short range repulsive steric forces [26,27]. This results in a theoretical feature of the disjoining pressure versus the film thickness [8] (or disjoining pressure isotherm) characterized by a minimum corresponding to irreversible aggregation. Reversible aggregation, or flocculation, is instead commonly associated to the presence of a secondary minimum at larger distances. Depending on the achieved equilibrium configuration. As sketched in figure 2, the aggregation in the primary minimum is associated to the formation of very thin films between the droplets, termed “Newton Black films”, because of their optical properties, with typical thickness of the order of 10 nm or less. The aggregation in the secondary minimum brings instead to thicker films, termed as “common black films”.

The steep increase of Π_d at the vanishing distances plays the role of a barrier against coalescence. The formation of the common black film, its transition to Newton black films and the possible drop coalescence are driven by complex physico-chemical fluid-dynamic phenomena as also by stochastic fluctuations [26].

The effect of the properties of the single interface on the feature of the disjoining pressure isotherm and, in particular, the presence of an adsorbed layer has been widely investigated especially for ionic and non-ionic surfactants [3] and proteins [4][29], and the results have been put in relation with the stability of the respective emulsions.

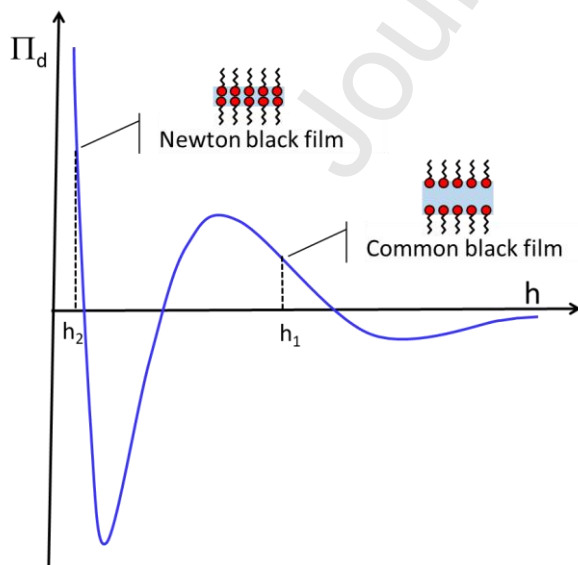


Fig. 2: Schematic representation of the disjoining pressure Π_d vs. the film thickness h .

The interfacial properties relevant for flocculation are definitely related to presence of surface charge. Non-ionic surfactants may be effective to stabilize emulsions against coalescence and Ostwald ripening, but not against flocculation because of insufficient electrostatic droplet repulsion. As shown in ref. [3], however, this drawback may be corrected adding a small amount of ionic surfactants and electrolytes in order to obtain a value of the maximum in the disjoining pressure which at least equals the capillary pressure of the drop.

The correlation between the feature of the disjoining pressure isotherm and the stability against flocculation and coalescence is particularly relevant for emulsions stabilized by macromolecules, like polymers, biomolecules and, in particular, proteins. Proteins are usually effective stabilizers of oil in water emulsions because of their ability to generate compact, resistant to ruptures, adsorption layers at the surface of the oil drops, providing repulsive steric and electrostatic interactions between droplets, which avoid their coalescence [29]. However, for these systems, the phenomenon of flocculation is rather common especially if emulsions are subjected to a long time storage with possible environmental perturbation, like in the cases of food applications [20]. In fact, an important peculiarity of proteins is their ability to undergo conformational changes once adsorbed at water-oil interfaces in order to maximize the favourable interactions with the two phases. This process occurs with a characteristic time that depends on the degree of flexibility and packing of the adsorbed molecules and implies the formation of robust interfacial layers, effective for the stabilization against coalescence. However, the change of environmental conditions, such as temperature, pH or ionic strength, may also influence the conformation of the adsorbed molecules inducing flocculation. This occurs, for example, in the case of oil in water emulsion stabilized by globular protein, where flocculation is promoted by the increasing hydrophobic attraction between proteins adsorbed onto different droplets [29].

In a recent work [4] the different effects inducing the appearance of flocculation in protein-stabilized oil in water emulsions, even when they are well stabilized against coalescence and OR, have been discussed. This analysis provides practical suggestions to contrast such phenomenon based, in general, on composition variations in order to increase the effect of the electrical repulsion with respect to the VDW attractions, increasing the surface charge, or the amount of ionic surfactants, or reducing the ionic strength in order to enlarge the effective thickness of the electrical double layer. Moreover, thicker adsorption layers may be obtained choosing emulsifiers with appropriate molecular size and structure, avoiding those that facilitate the bridging between adsorbed layers of different droplets.

From the above considerations, it is clear that the principal characteristics of the adsorption layers ensuring the hindering of flocculation are related to the electrostatic repulsion between droplets, obtained by an adequate surface charge.

The electrical or steric repulsion between the adsorption layers also plays a fundamental role in the stabilization against coalescence. However, as shown in many theoretical and experimental works [17], the thinning and rupture of the liquid film between the emulsion droplets is a complex hydrodynamic process influenced by many factors related to the equilibrium and dynamic adsorption properties of the emulsifiers, i. e. the adsorption isotherm, the dynamic interfacial tension and the dilational rheology. Thus, while in case of ionic surfactants, the repulsive interaction is the most relevant effect and a

small amount of adsorbed molecules is sufficient to improve remarkably the stability of emulsions, for non-ionic surfactants a more important role is played by other factors. One of these is the ability to reach high values of surface coverage which, as already mentioned in the previous sections, depends on the size and configuration of the adsorbed emulsifier, which can be analysed by measurements of equilibrium interfacial tension versus concentration (adsorption isotherm). This property may influence the evolution of the droplet size during the emulsion aging. In fact, since the total area of the water oil interface decreases with droplet coalescence, the increase of the coverage is limited by a maximum value high enough to avoid coalescence.

An essential role in the fluidynamic contrast to the rupture of the liquid films between drops, or drop coalescence, is played by the interfacial rheology properties of the adsorbed layers and, in particular, by the dilational viscoelasticity E . This quantity is defined as the variation of the interfacial tension due to a compression/extension perturbation of the interfacial layer, that is

$$E = \frac{\delta\gamma}{\delta\ln A_0} \quad (1)$$

E is a key quantity to describe the effect of the surfactant adsorption on the mechanical dynamic properties of the liquid interfaces. According to classical approaches, E can be expressed in the field of frequency, ν , as a complex quantity,

$$E(\nu) = -\frac{\partial\gamma}{\partial\ln\Gamma}\kappa(\nu) = E_0\kappa(\nu) \quad (2)$$

where $E_0 = -\partial\gamma/\partial\ln\Gamma$ is the Gibbs elasticity, i.e. a thermodynamic quantity that can be easily calculated by knowing the adsorption isotherm. The complex character and the frequency dependence of the term κ expresses the viscoelastic behaviour of the adsorbed layer. Theoretical expressions for this factor can be found assuming different models for the adsorption dynamics [30]. For the present purpose, we can say that, excluding the adsorption from the film bulk (i.e. soluble surfactants) and the relaxation processes within the adsorption layer, κ is equal to 1.

The first effect of the resistance of the interfacial layers to dilational perturbation, expressed by the dilational elasticity, is the increase of the hydrodynamic rigidity of the interfaces which reduces the rate of drainage of the film. Another important effect concerns the response to mechanical perturbation of thin films when they are in a stable, or meta stable state, which can lead to their rupture. This is the case, for example, of films between flocculated drops. As schematically shown in Fig. 3, a small mechanical perturbation of the adsorbed layer may induce a local adsorption dilution associated, through the Gibbs elasticity, to a surface gradient of the interfacial tension. The induced surface flow, consequent to the restoring of the interfacial tension uniformity (Marangoni effect), drags a bulk flow in the film, contrasting its thinning and, consequently, the drop coalescence.

Nevertheless, it is important to underline that in case of soluble surfactants and relevant interfacial relaxation processes, the interfacial tension gradient induced by the local depletion of the adsorption layer may be not simply expressed by the Gibbs elasticity but more complicate models have to be applied taking into account such relaxation processes [31]. In case of soluble surfactants, for example, the adsorption flux from the

continuous phase tends to dampen the interfacial tension gradient induced by the area perturbation, in times depending on the adsorption-diffusion properties of surfactants, so that the effect of the Gibbs elasticity has to be considered as the maximum possible effect.

In most cases, however, the finiteness of the liquid volume of the film results in a limited possibility to restore the adsorption gradients by the transfer of surfactant molecules from the matrix phase to the interface. Such consideration constitutes a justification for the Bancroft rule and, in addition, allows saying that, in general, the systems characterized by high value of Gibbs elasticity present a better stability against coalescence.

It is also useful to underline that the presence of kinetic processes within the adsorbed layers, such as molecular reorientation or conformational changes, with characteristic times comparable with those of the perturbation, may imply values of the dilational elasticity larger than the Gibbs elasticity [30], resulting in an increased efficiency to contrast the film thinning.

The correlation between the value of the Gibbs elasticity and, in general, the feature of the dilational viscoelasticity versus frequency, with the stability of foams and emulsion films and the respective disperse systems have been widely investigated. In refs. [9] and [32], for example, the properties of foam films stabilized by non-ionic surfactants, investigated by disjoining pressure experiments, are put in relation with the rheological properties of the respective adsorption layers. The results demonstrate that the stability of such films cannot be explained solely in terms of repulsive electrical forces, but it is associated to the high values of the dilational viscoelasticity at high frequency, proving also the importance to investigate the dilational rheology properties in a wide frequency range. Even if these works have been performed for foams, the results have a rather general validity and similar correlations are expected to exist also for emulsion films and emulsions. In a number of studies, in fact, the stability against coalescence in emulsions is analysed in terms of the values of the dilational viscoelasticity of the adsorbed layers. In ref. [33], for example, such correlation was extensively investigated for oil in water emulsions stabilized by ionic and non-ionic surfactants. In ref. [34], Gemini surfactants with different hydrophobic chain length, for tuning the dilational viscoelasticity, are systematically investigated and a reduction of the coalescence rate is observed while increasing the rheological modulus. In other recent works [35], [36] this correlation is found for systems of practical interest in the field of fuels treatment.

The effect of the interfacial properties on the coalescence mechanism is particularly important also for emulsions stabilized by solid particles also called "Pickering emulsions". This kind of emulsions is of increasing interest in a wide variety of applied fields, from foods and cosmetics to the field of the development of new nanostructured materials [37–40], especially for their unique efficiency in the control of stability, morphology and droplet size distribution of the emulsions [10,13]. Many experimental studies rely on nanoparticles associated to ionic surfactants, allowing the tuning of their partial hydrophilicity and, consequently, their degree of adsorption at water – oil interfaces [41–43].

The principal reason of the good stabilizing effect against coalescence of nanoparticles or composite nanoparticles-surfactant complexes is the fact that such systems form rigid quasi-solid membranes at the drop surfaces which hinders coalescence

mainly for steric or electrostatic repulsion [44]. The surface coverage is very important for these systems, in fact, as in most cases nanoparticles adsorb irreversibly to the liquid – liquid interface, coalescence is stopped with the achievement of the surface saturation. This mechanism is at the origin of the monodisperse character typical of Pickering emulsions.

On the other hand, experimental studies on the rheological properties of composite nanoparticle-surfactant layers [42,45,46] suggest that also for these systems when they are rather far from saturation, a mechanical stabilizing effect may arise from the dilational viscoelastic properties of the interfacial layers, like discussed above for common surfactants stabilized emulsion. Characterizing these systems with measurements of dilational viscoelasticity versus frequency is an effective method to assess the dynamic processes occurring in the interfacial layer and to correlate these properties with the stability of emulsions. This kind of investigation are promising in view of new formulation of Pickering emulsions at low content of solid emulsifier but still require further investigations.

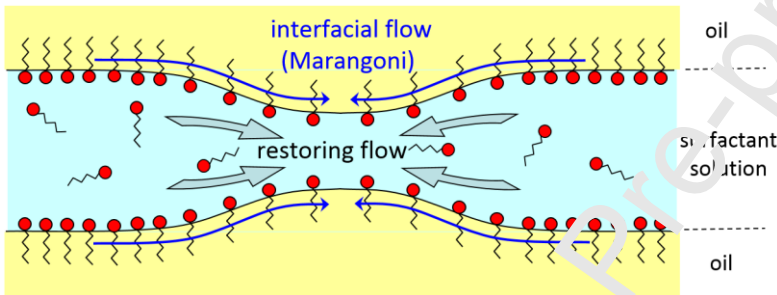


Fig. 3: Mechanism of coalescence stabilisation by Marangoni flow.

3.2 Role of interfacial properties on Ostwald ripening

In emulsion, Ostwald ripening is the process of growth of large droplets at the expenses of the smaller ones. This is a non-equilibrium process involving both thermodynamic and transport effects. Because of their smaller radii, smaller droplets experience in fact a larger capillary pressure and have therefore a larger solvability.

The Lifshitz, Slyozov and Wagner (LSW) theory [47–49] firstly approached the problem of OR, accounting for a size distribution. The theory holds for emulsions within simplified assumptions: in particular, for pure liquids (no surfactant and constant surface tension), in the limit of very dilute emulsion and for purely diffusive transport. As summarised in [50], under these assumptions, the theory predicts the existence of a critical radii, r_c , setting the border between growing and shrinking droplets and that, at sufficiently large time (asymptotic solution), the cube of such radius grows linearly with time

$$\frac{d(r_c^3)}{dt} = \frac{8D\gamma Mc}{9RT\rho^2} = \Omega \quad (3)$$

where M is the molar mass and ρ the density of disperse liquid; D , c and γ are respectively the diffusion coefficient, the interfacial tension and the solubility of the disperse liquid with respect to the matrix liquid; R is the gas constant and T the absolute temperature.

The same asymptotic solution predicts also the achievement of a specific stationary frequency distribution, $\phi(u)$, for the scaled radii, $u=r/r_c$:

$$\left\{ \begin{array}{l} \phi(u) = \frac{81e}{\sqrt{32}} u^2 (3+u)^{-7/3} \left(\frac{3}{2}-u\right)^{-11/3} \exp\left[\left(\frac{2}{3}u-1\right)^{-1}\right] \quad \text{for } u < \frac{3}{2} \\ \phi(u) = 0 \quad \text{for } u \geq \frac{3}{2} \end{array} \right. \quad (4)$$

Since the average u in the above distribution is about 1.14, the cube of the average radius grows with a rate of about $1.5 \cdot \Omega$.

The LWS theory has been shown to be sufficiently accurate in the prediction of the OR growth rates in emulsions with volume ratio below 0.05, even in the presence of surfactant, which in fact show a linear growth trend of the cube of the average drop size. The same trend is in most cases found for more concentrated emulsions, but with values of Ω that tends to be larger of the LSW estimation. This can be easily rationalised considering that the presence of a number of droplets, moving under the effect of gravity (large droplets) or of Brownian forces (small droplets), provides some mixing of the emulsion and therefore a more efficient transport of solutes, as compared to pure molecular diffusion.

During the last 4 decades, the effect of surfactants on OR has been the subject of speculations, theories, simulations and experimental investigations. In spite of that, the experimental findings and theoretical approaches still do not provide a clear picture of the phenomena, in particular for more concentrate emulsions and foams.

Experimental investigations on OR in dilute oil in water emulsions for surfactant concentrations below and slightly above the micellar surfactant solutions [51–55] provide values of Ω decreasing with the increase of surfactant concentration and with the decrease of the oil solubility, in agreement with the prediction of LWS theory (see eq. 3) for decreasing interfacial tensions. However, significant differences are found for the absolute values, even if not very large. Such differences can be ascribed to the simplified assumptions of the LWS theory, which considers a constant surface tension and neglects any possible role of micelles as means of mass transport for the dispersed phase between droplets. On the other side, these differences could also result from the techniques utilised to measure the size evolution of drops in the sub-micrometric range. In fact, in an emulsion, the characterization of drop size distribution relies on nontrivial methodologies and simplifications. This is e.g. the case of Dynamic Light Scattering [56], that requires sample dilution in order to achieve the single scattering regime, or of Diffusing Wave Spectroscopy [57], Ultrasonic Spectroscopy [52] which requires by themselves complicate modelling and simplifications, that may result in significant inaccuracies.

Owing to its relevance for applications, OR in emulsions concerned with micellar solutions has been largely investigated, focussing in particular on the role of micelles in the transport of the disperse phase. Surprisingly the growth rate resulted to be much smaller

than initially speculated, considering the capability of micelles to act as efficient carriers for oil molecules [50], as for the common understanding in detergency. Such apparent anomaly was ascribed to different effects, among them, the repulsive interactions or barriers between micelles and droplet interface, in particular, for ionic surfactants [51].

The possibility for interfacial layers to stabilise OR of drops/bubbles has been speculated on the basis of the so-called Gibbs principle [58],[59]. In fact, since the driving force for OR disappears when $dP/dr \geq 0$, that leads, using Eq. (1), to the condition $E \geq \gamma/2$ for the stop of OR.

Modifications of such criterion have been proposed, based on simulations and models accounting for the variation of interfacial tension and dilation elasticity/viscosity caused by the shrinking process [5,50,60]. These models, however, mostly consider situations concerned with purely elastic interfaces, and apply therefore only to insoluble surfactants, or irreversibly adsorbed surface-active species such as particles or proteins. In this case, the amount of adsorbed molecules remains constant during the shrinking process. Therefore, in the absence of relaxation processes within the adsorption layer, according to its definition, is $\kappa=1$. Thus, the dilational viscoelasticity equals E_0 and the application of the Gibbs criterion do not require considerations about the kinetics aspects related to the droplet area variation. These are in fact the conditions concerned with several experimental studies, proposing the use of irreversibly adsorbed species to control OR in foams and emulsions. Among them particularly relevant are the studies related to OR in protein-stabilised [11] and Pickering emulsions [60,61]. For these latter, the stabilisation against OR is also related to the reduction of the droplet interfacial area effectively subject to the molecule dissolution, which is obviously reduced by the particle layer.

For soluble surfactants, the increase of Γ caused by the compression of the Gibbs adsorption layer during bubble/drop dissolution competes with the rejection of surfactant molecules from the interface. In these cases, the application of the Gibbs criterion to OR is not straightforward, since the dilational elasticity is dependent not only on equilibrium features (isotherm), but also on the time-characteristics of the area perturbation and of the relaxation processes. Models have been proposed to describe E in presence of different time-dependent processes regulating the kinetics of the adsorption [30], [31]. For the sake of simplicity, we can limit the present discussion to diffusion-controlled adsorption [62]. In this case, the value of κ varies from 0 to 1, depending on the relative importance of the characteristic times of the area perturbation and of the surfactant diffusion process. If the area perturbation is much faster than diffusion, the latter does not efficiently transport the surfactant molecules out of the interface during the drop shrinking. The adsorption layer behaves in this case as an insoluble one, and κ will be close to 1. Vice versa, if the area perturbation is much slower than diffusion, the latter is quickly and efficiently restoring the equilibrium between the adsorption layer and the surrounding bulk, so that the surface tension remains constant and E will be vanishing. This latter appears to be likely the case for most emulsions. In fact, the rate of growth in OR is strongly influenced by the disperse phase solubility, which for the majority of oils is rather small [6,52,55]. Therefore, the area perturbation imposed by the OR process in emulsions is usually much slower than the diffusion process, so that the elasticity is vanishing and the Gibbs condition is hardly satisfied. Of course this does not exclude this possibility for very special systems where,

interfacial tensions, high oil solubility, low surfactant concentrations, may properly combine to provide sufficiently large OR growth rate to compete with the diffusion process and may satisfy the Gibbs criterion.

An estimation of the characteristic time, τ_A^{OR} , for the increase of the droplet area, A , caused by the OR process is given by $(d\ln A/dt)^{-1}$. By introducing the growth rate, after making explicit the area, for a spherical drop with radius, r , it is

$$\tau_A^{OR} = \frac{3r^3}{2\Omega} \quad (5)$$

As expected, τ_A^{OR} is obviously an increasing function of the drop size. The characteristic time for the diffusion process is instead given by:

$$\tau_D = \frac{1}{D_s} \left(\frac{d\Gamma}{dc_s} \right)^2 \quad (6)$$

where D_s and c_s are respectively the diffusion coefficient and the concentration of the surfactant.

Following the above discussion, for a soluble surfactant, the possibility to have non vanishing values of E exists only for τ_A^{OR} comparable with, or smaller than τ_D . That means that also the drop size has implications in the effects of dilational elasticity on the OR process. In fact, equating the two characteristic times provides a critical value, r^* , for the radius,

$$r^* = \left(\frac{2\Omega}{3D_s} \left(\frac{d\Gamma}{dc_s} \right)^2 \right)^{\frac{1}{3}} \quad (7)$$

such that, E will be always vanishing for drops with radii much larger than this critical value. For these drops therefore the OR process cannot be stopped on the basis of the Gibbs principle, unless ultralow interfacial tensions are concerned. In that case however, according to the LWS theory, a so Ω would be small. The possibility to stabilise OR based on the Gibbs principle remains instead for drops with radii comparable or smaller than r^* that in fact presents non-zero dilational elasticity.

It is worth noticing that the value of $d\Gamma/dc_s$ is capped by its value at vanishing c_s - the so called adsorption constant, α , - while it vanishes approaching the saturation adsorption, Γ_{sat} . r^* will be then vanishing at large c_s concentrations, i.e. close to the CMC. The largest value of r^* for a given Ω and D_s is therefore given by

$$r^* = \left(\frac{2\Omega\alpha^2}{3D_s} \right)^{\frac{1}{3}} \quad (8)$$

For most utilised models, such as, Langmuir, Frumkin, reorientation, it is $\alpha = \Gamma_{sat}/a$, where Γ_{sat} is the saturation adsorption and a is the Langmuir-Szyszkowski constant.

As an example, using values comparable to those found for emulsions of dodecane in aqueous solutions of SDS [8] ($\Omega = 3.2 \cdot 10^{-26}$ m³/s, $D_s = 1 \cdot 10^{-10}$ m²/s, $\Gamma_{sat} = 5.6 \cdot 10^{-6}$ mol/m², $a = 1.9$ mol/m³), such maximum value for r^* can be estimated as 1.2 nm. This size is below what could be expected for an ordinary emulsion, meaning that the possibility to stabilise these emulsions against OR, according to the Gibbs principle hardly exists in practice.

It is worth noticing that the above values for D_s and Γ_{sat} are typical for low molecular weight surfactants. Ω and α can instead vary by orders of magnitude, depending on the type of disperse phase and of surfactant. α in particular decreases with the increase of the HLB. Therefore, drops with more reasonable sizes and non-vanishing E can more likely exist for the more surface-active molecules. According to the expression of r^* , also surfactants with smaller hydrophilic heads (i.e. larger Γ_{sat}) increase its maximum values.

Based on the dependence of r^* on the cubic root of Ω , it is however difficult to speculate about the existence of emulsions where the maximum value of r^* could be in the order of hundreds nanometers. As an example, extrapolating the values the growth rate reported [52] for emulsions of higher alkanes, one can estimate Ω for emulsions of hexane to decrease by 4 orders of magnitude ($\Omega \approx 10^{-22} \text{ m}^3/\text{s}$) with respect to dodecane in SDS solution: that however increases the maximum value of r^* only to about 25 nm.

In summary, applying the above consideration to an emulsion with a given size distribution, we conclude that there will be little chance to use soluble surfactants to stabilise OR for the drops larger than a given size. On the contrary, the Gibbs principle may be effective in stabilising the smaller droplets of the distribution. If this subset of drops is actually stabilised, we could expect that a bimodal distribution may emerge from the OR process. In such distribution, the peak at the smaller size will be time-invariant, since related to the drops stable against OR, while the other, related to the drops prone to OR, is moving with time towards the larger sizes showing features similar to those predicted by the LWS theory.

It is worth to recall that the shift of the size distribution toward larger sizes results in a general increase of the surfactant concentration in the matrix liquid, caused by the decrease of the total interfacial area in the system, as the size of the drops/bubbles increases. According to the dependence on $d\Gamma/dc_s$, the value of r^* will therefore decrease with the progress of OR. Therefore, on long time it is even possible that also initially stable droplets may eventually become unstable against OR. However, most experimental works show that for any given area perturbation, the dilational elasticity passes through a maximum when the surfactant concentration increases. That introduces a further complexity in the above analysis.

As far as gas bubbles (for example air) are considered, because of the large solubility and diffusion coefficients in water of the of gas molecules, the values of Ω may become very large, and r^* may easily increase by 2-3 orders of magnitude for insulated bubbles and even more in foams, owing to the gas permeability in the liquid film. Thus for foams it is more likely that OR could be stopped by soluble surfactants.

4. Methods for investigating the role of interfacial properties in emulsions

As evidenced in the previous sections, the equilibrium and dynamic adsorption properties of the various surfactant species used to stabilize emulsions, contribute to determine the mechanical properties of liquid interfaces and films, which have a role in the mechanisms of destabilization of emulsions, in particular, for drop coalescence and Ostwald ripening.

Depending on the kind and concentration of the emulsifier, these properties may be only marginal, like in the case of certain macromolecules, charged solid particles or concentrated ionic surfactants, presenting predominant electrical and steric repulsions. For other systems, instead, they are expected to play a fundamental role because governing the hydrodynamic response to mechanical perturbation. This is the case, for example, of emulsions stabilized by non-ionic surfactants, but also more complicated systems like mixtures of nanoparticles and surfactants at moderate or low concentrations.

Thus, studies on adsorption kinetics and thermodynamics of emulsifiers are required to assess the adsorption properties relevant for emulsion stabilisation. These studies are commonly based on dynamic and equilibrium interfacial tension measurements against concentration, as well as dilational rheology investigations which also allow the intrinsic dynamic properties of the adsorbed layers to be accessed.

In recent literature studies, complementary techniques are applied to compare the adsorption properties on a single interface with the feature of the corresponding disperse systems. Some of these studies, even if concerning foams [8,63,64] report methodologies and results, useful also for the comprehension of similar mechanisms in emulsions. In other works concerning emulsions, similar multi-technique methodologies are applied [17–19,33,35] paying also attention on some aspects, typically relevant for emulsions, such as partitioning of the surfactant in the two liquid phases, low values of interfacial tensions and, in some cases, more complex adsorption mechanisms [17,18].

In most of these studies the adsorption properties of the surfactant system at water-oil interface is carried out measuring the dynamic and equilibrium interfacial tension, and dilational viscoelasticity. Drop tensiometers have been widely used for this kind of measurements and, among them those based on the acquisition of the drop profile, or drop shape tensiometer [65] have been shown to be particularly appropriate. The measurement of the dynamic interfacial tension, from the formation of a fresh drop, until the achievement of the adsorption equilibrium allows the adsorption characteristic time to be assessed, that is a key parameter especially relevant for the process of emulsification.

The evaluation of the adsorption isotherm, or the equilibrium interfacial tension versus the surfactant concentration, based on appropriate models, allows the parameters characterizing the adsorption properties to be assessed. These are the surface activity, the interaction parameters between the adsorbed molecules and their occupational area, which give information about the coverage degree obtainable with that surfactant. The knowledge of these thermodynamic characteristics is very important because allows the prediction of the efficiency of the surfactant in emulsion formation and stabilization, especially as concerns the hindering of coalescence.

Drop tensiometer are commonly employed also for dilational rheology studies [66], that is for the measurement of the dilational viscoelastic modulus versus frequency, according to the oscillating drop method [67]. Due to the limitation in the frequency range imposed by the drop shape technique (the condition of mechanical quasi-equilibrium is required) [68], capillary pressure drop tensiometers are, in some cases, more appropriate, as explained in details in ref.[69].

For optimizing the information acquired from the dilational rheology characterization, it is important to adopt appropriate theoretical models to analyse the experimental data,

which take into account both the thermodynamic adsorption properties of the surfactants and the possible relaxation processes occurring in the interfacial layers [30], [31]. In this way, a deeper knowledge of the dynamic response of the interfaces and films to mechanical perturbations can be obtained contributing, consequently, to the prediction of coalescence stability in emulsions.

In order to correlate these results on the interfacial properties with the behaviour of emulsions obtained with the same systems, several investigation methods are adopted. The monitoring of the emulsion volume during its aging till the complete separation of the two phases, is a very simple method allowing comparative studies between different emulsifiers and/or their concentrations [17,18]. Other methods to characterize the emulsion stability and also the efficiency of emulsification rely on microscopy techniques and/or optical scattering techniques like the classical Dynamic Light Scattering (DLS) [56] or the Diffusing Wave Scattering (DWS) [57,70–72]. The drop size distributions can be assessed within some approximations by the former two methods. Given the complexity of the problem, all the techniques suffer of some limitations, and a combination of more than one technique is often employed to obtain reliable results. By optical microscopy in dense emulsions one often observes drops close to the container walls, assuming that these are representative of the population in bulk. On the contrary, by DLS drops are characterized in the bulk of the volume, but the technique is only applicable in extremely diluted emulsions fulfilling the assumption of optical single scattering. On the contrary DWS allows analysing optically dense emulsion and obtaining the evolution of the average drop size and the droplet dynamics. However in its common implementation DWS does not go beyond average values, accessing only the average and not the width of the drop size distribution. However in some cases, and with some additional modelling, DWS could access heterogeneities and also allow to discriminate different regimes in the destabilization, such as creaming or coalescence [73].

In the experimental studies reported in refs. [17,18] the above approach has been applied to investigate oil-in-water emulsions stabilised by ionic (SDS) and non-ionic and ionic synthetic surfactants - Tween 80, and SDS, respectively - , and by surfactants derived from vegetable sources, such as Saponin and Citronella Glucoside (CG). Dynamic and equilibrium interfacial tension, dilational viscoelasticity were measured by Drop Shape tensiometry. The integrated analysis of these data allowed assessing the appropriate interfacial model for the description of the adsorption layer. The droplet size distribution of the freshly formed emulsions, containing different amounts of surfactant, was determined by direct microscopy analysis, or by DLS and DWS.

The actual surfactant concentration in the continuous phase, c , after the depletion resulting from the adsorption of the surfactant at the droplets interface can be estimated from the droplet size distribution and from the adsorption isotherm, $c = c(\Gamma)$, as the solution of the set of equations

$$\begin{cases} c = c_0 - 3 \frac{\sum_i f_i r_i^2}{\sum_i f_i r_i^3} \phi \Gamma \\ c = c(\Gamma) \end{cases} \quad (9)$$

where c_0 is the concentration of the continuous phase before emulsification, ϕ is the volume ratio of the disperse phase, f_i are the frequencies corresponding to the radii r_i of the distribution.

For narrow size distributions, the first equation of the set can be approximated by introducing the average radius, r_{av} , as

The results of this calculation for 1:1 emulsions of Medium Chain Triglyceride (MCT) in aqueous solutions of Tween 80, Saponin and CG, are summarised in Fig. 4, reporting the depletion ratio $K=c/c_0$ and the actual coverage, Γ/Γ_{sat} , versus c_0 .

For SDS – as also for other ionic surfactants - it is possible to infer with a remarkable accuracy the concentration in water by electrical conductivity measurements. Such principle has been applied in ref [17] to estimate the concentration after depletion, without knowing the droplet size distribution. The results concerned with 1:1 dodecane in SDS aqueous solutions emulsions are also reported in Fig. 4. The surface isotherm, in this case can be instead utilised to evaluate the total area of the droplets in the emulsion, and therefore, in the case of narrow size distributions, to obtain a reasonable estimation of r_{av} .

The data in Fig. 4 show for all surfactants a significant reduction of the concentration in the continuous phase: by 1 to 4 orders of magnitude, depending on the initial concentration. Accounting for these actual concentrations is very important in order to investigate correlations between the different properties and phenomena concerned with emulsion aging. In fact, the vanishing actual coverages allowed us to explain the lack of stability for emulsions formulated with Tween80 and with the lower concentrations of CG and Saponin [18]. For these latter surfactants, coverages above 0.15 and up to 0.6 resulted instead already effective in stabilising the corresponding emulsions, by stopping the coalescence process.

As evident from Fig. 4, SDS presents extremely large values of the coverage already at concentrations 2 orders of magnitude below the cmc. Together to the high surface charge, this confers an excellent stability against coalescence and these emulsions resulted to be stable over months. DSL measurements of the drop size distributions showed instead [17] a linear increase of r_{av}^3 with time - compatible therefore with a Ostwald Ripening process -, with a growth rate of $3.2 \times 10^{-8} \mu\text{m}^3/\text{s}$, in reasonable agreement with what reported in [52].

In other studies the results about interfacial properties are correlated with the behavior of the liquid films, using film balance techniques [9] or with the results of droplet coalescence experiments, performed using appropriate drop-drop interaction techniques [8] [74]. In fact, this latter is an indirect way to investigate the effect of the interfacial properties on the emulsion stability.

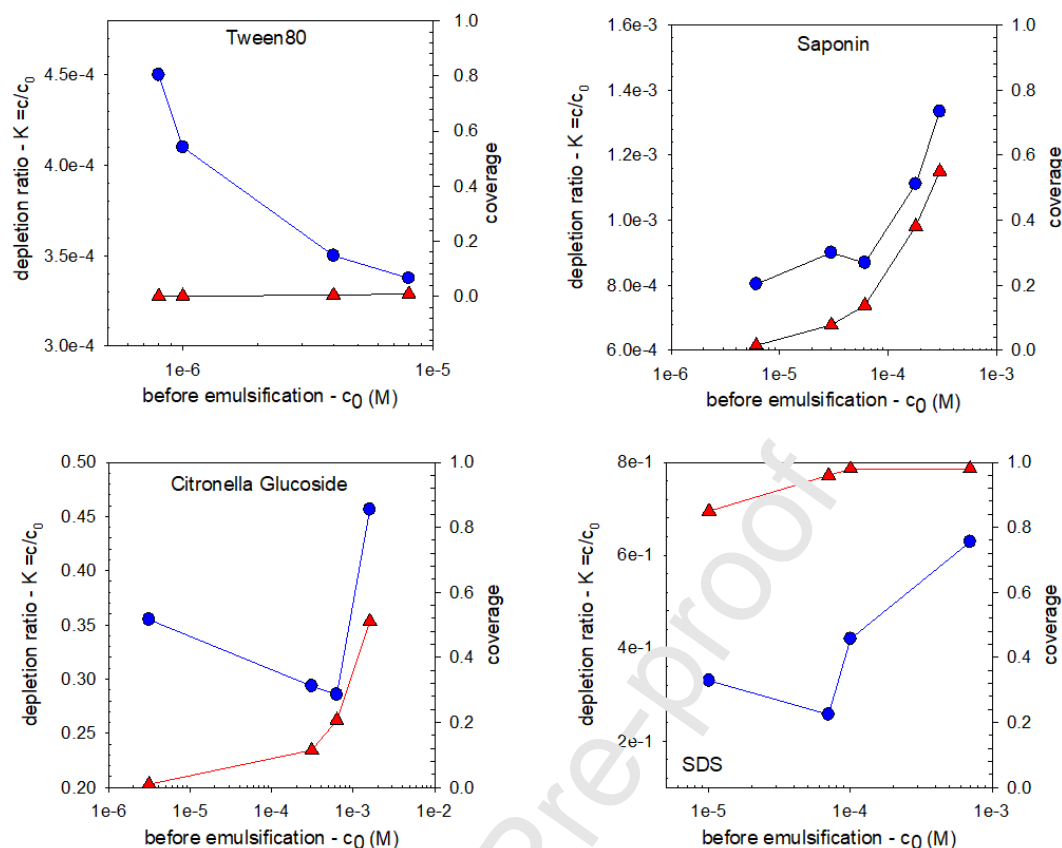


Fig. 4: Depletion ratio (circles) and actual coverage (triangles) after the depletion of the surfactant concentration in the continuous phase caused by the adsorption of surfactant at the droplet interface, in various types of emulsions (see text for details).

5. Conclusions and perspectives

Nowadays, the development of technology in the various production fields is facing important challenges related with the rising awareness of society about issues related to sustainable development, environment and health. Specifically, for emulsions-related technologies and products that means: i) the development of more efficient, energy and resource-saving processes in emulsification and emulsion breaking; ii) the reduction of emulsifiers - in particular of surface active species – and their substitution with compounds with a milder impact for environment and health; iii) the increase of shelf-life and, more generally, of the performance of emulsified products for consumers and industry.

As also shown by this review, we have gained a general understanding of the role that the interfacial properties play in the different processes concerned with the production, processing and stability of emulsions. The mentioned technology challenges however require pushing our knowledge to a new level of detail, in order to foster the development of methodologies and modelling tools for an on-design approach to emulsions and emulsifiers formulation. In fact, at present, emulsion technology is still relying on semi-empirical approaches and concepts, which lead, for example, to formulations utilising overabundant amounts of emulsifiers. Particularly important appears therefore the possibility to obtain significant reductions in the utilised amounts of surface active species,

which, mostly in developing countries, represent an important contribution to pollution of waters. In that respect, an important challenge is represented by the targeting of emulsion stability in the sub-micellar concentration range, where according to the general concepts given here, the adsorption layers play a predominant physico-chemical role in relation to droplet interaction, coalescence and ripening. For these aims, experimental techniques need to be revisited, implemented and developed for the various levels of details and scales concerned with emulsions: interfacial adsorption layers, liquid films and droplet interaction, Ostwald ripening and collective dynamics. The knowledge developed for these single components must be integrated as much as possible in tools of increased complexity, which may include both chemo-fluid-dynamics models and simulation tools. Particularly welcome in this context is the development of methods for the accurate characterisation of collective features of the emulsions, such as, the evolution of the droplet size distribution, the rate of coalescence and aggregation events, and of their effects on the droplet dynamics. Optical scattering techniques, such as DLS, DWS and their modification, or other emerging optical methodologies, such as Differential Dynamic Microscopy (DDM) [75] [76], seem appropriate to these aims, provided new and more accurate modelling are developed [77][78][79]. New methodologies are also needed for interfacial properties, in particular for dilational rheology on a wide time scale, which results a key property to understand the dynamic behaviour of interacting droplets and therefore the problem of the stability of the emulsion.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Graphical abstract

Highlights:

- The effects of interfacial properties on the main mechanisms underlying the aging of emulsions are reviewed.
- Suitable methodological approaches for the investigations of these effects are discussed.
- Procedures to account for the surfactant depletion of the continuous emulsion phase, caused by the adsorption at the droplet interface, are reported. The necessity to apply these corrections is discussed on the basis of previous experimental studies.
- A criterion to assess the practical possibility to stabilise Ostwald ripening in emulsions, based on the sole dilational rheology is derived.