USE OF THE LIFSHITZ-SLYOSOV-WAGNER THEORY FOR THE PREDICTION OF THE DROP SIZE OF AN EMULSION SUBJECT TO FLOCCULATION AND COALESCENCE

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SUMMARY

A novel theoretical expression for the estimation of the temporal variation of the drop size of an oil-in-water (o/w) nanoemulsion subject to flocculation, coalescence and Ostwald ripening is proposed. It is based on the experimental evaluation of the mixed flocculation-coalescence rate. The predictions of the theory are contrasted with experimental results corresponding to a set of dodecane-in-water nanoemulsions stabilized with sodium dodecylsulfate. A satisfactory agreement is found whenever the size-dependence of the aggregates is conveniently represented.

Introduction

According to the Laplace equation (Evans and Wennerström, 1994), the internal pressure of a drop of oil suspended in water is directly proportional to its interfacial tension (γ), and inversely proportional to the radius of the drop (R_i). The excess pressure causes a difference between the chemical potential of the molecules of oil inside the drop and the ones belonging to an unbounded bulk oil phase. This difference (Δμ) is equal to (Kabalnov, 1991):

$$\Delta\mu = \frac{2\gamma V_M}{R_i} \tag{1}$$

where V_M: molar volume of the oil. According to Eq. 1, the excess chemical potential is positive, which means that a particle will be always dissolving when it is in contact with an aqueous phase. Furthermore, the derivative of the excess chemical potential is negative:

$$\frac{d\Delta\mu}{dR} = -\frac{2\gamma V_M}{R_i^2} \tag{2}$$

This means that an ensemble of particles of different sizes cannot be in equilibrium with each other (Kabalnov, 2001). As a result, larger particles grow at the expense of smaller particles by exchanging molecules of oil through the aqueous solution; a process referred to as Ostwald ripening. The theories of ripening start from the Kelvin equation:

$$\begin{aligned} C(R_i) &= C_\infty \exp\left(\left(\frac{1}{R_i}\right)\frac{2\gamma V_m}{\tilde{R}T}\right) = \\ & C_\infty \exp\left(\frac{\alpha}{R_i}\right) \approx C_\infty\left(1+\frac{\alpha}{R_i}\right) \end{aligned} \tag{3}$$

where $\tilde{R}$: universal gas constant, T: absolute temperature, R_i: radius of a drop, and C(∞): solubility of the oil molecules in the presence of a planar oil/water (R_i=∞). Thus, according to Eq. 3, the difference between the aqueous solubility of a slab of oil in contact with water (C(∞)) and the one of a drop of oil submerged in water ($C(R_i)$), depends on the quotient between the capillary length of the oil (α) defined as

$$\alpha = 2\gamma V_M / \tilde{R}T \tag{4}$$

and the radius of the particle. According to the theory of Lifthitz, Slyosov, and Wagner (LSW theory; Lifshitz and Slesov, 1959; Lifshitz and Slyosov, 1961; Wagner, 1961), the radius of a particle changes with time according to

$$\frac{dR_i}{dt} = \frac{D_m}{R_i}\left(\Delta - \frac{\alpha}{R_i}\right) \tag{5}$$

where D_m: diffusion coefficient of the oil, and Δ: supersaturation of the solution nearby the drop, Δ= $C(R_i)$-C(∞). For each value of Δ there exists a critical radius (R_c =α/Δ) at which a particle (or a monodisperse ensamble of suspended particles) is in equilibrium with the solution ($dR_i/dt=0$). Otherwise, the drop either grows ($R_i>R_c$, $dR_i/dt>0$) or dissolves ($R_i<R_c$, $dR_i/dt<0$). Eventually, a 'stationary regime' is attained, characterized by a self-similar drop size distribution. At this time, the ripening rate (V_{OR}) can be quantified in terms of a linear increase of the cube of the critical radius (R_c) of the colloid as a function of time:

$$\begin{aligned} V_{OR} &= dR_c^3/dt = \\ & 4\alpha D_m C(\infty)/9 \end{aligned} \tag{6}$$

Finsy (2004) demonstrated that the critical radius (R_c) of the dispersion is equal to its number average radius (R_a):

$$R_c = R_a = \frac{1}{N_T}\sum_k R_k \tag{7}$$

According to our simulations (Urbina-Villalba *et al.*, 2009b, 2012; Urbina-Villalba, 2014) the stationary regime results from two opposite processes: the exchange of oil molecules alone, which leads to a decrease of the average radius, and the elimination of particles (by dissolution or coalescence), which favors the increase of the average radius). The result is a saw-tooth variation of R_a superimposed to the average slope predicted by Eq. 6. This phenomena and its relation to the shape of the drop size distribution was recently studied experimentally by Nazarzadeh *et al.* (2013).

Integration of Eq. 6 between t_0 and t leads to

$$\begin{aligned} R_c^3(t) &= \\ & V_{OR}\left[t - t_0\right] + R_c^3(t_0) \end{aligned} \tag{8}$$

where t_0 is the initial time of the measurements. Eq. 8 is invariably used for the

KEYWORDS / LSW / Coalescence / Drop Size / Emulsion / Ostwald / Ripening /

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USO DE LA TEORÍA DE LIFSHITZ-SLYOSOV-WAGNER PARA LA PREDICCIÓN DEL TAMAÑO DE GOTA DE UNA EMULSIÓN SUJETA A FLOCULACIÓN Y COALESCENCIA

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RESUMEN

Se propone una nueva expresión para la estimación de la variación temporal del tamaño de gota de una nanoemulsión de aceite-en-agua (o/w) sujeta a floculación, coalescencia y maduración de Ostwald. La expresión está basada en la evaluación experimental de la tasa de floculación y coalescencia. Las predicciones de la teoría se contrastan con resultados experimentales correspondientes a un conjunto de nanoemulsiones de dodecano en agua estabilizadas con dodecil sulfato de sodio. Se encuentra un acuerdo satisfactorio siempre que la dependencia de tamaño de los agregados sea convenientemente representada.

USO CORRECTO DA EXPRESSÃO LIFSHITZ-SLYOSOV-WAGNER PARA OVCÁLCULO DO RAIO MÉDIO DE UMA EMULSÃO ÓLEO-EM-ÁGUA (O /A) SUJEITA A FLOCULAÇÃO E COALESCÊNCIA

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RESUMO

Propõe-se uma nova expressão para a estimação da variação temporal do tamanho de gota de uma nanoemulsão de óleo-em-água (o/a) sujeita a floculação, coalescência e maturação de Ostwald. A expressão está baseada na avaliação experimental da taxa de floculação e coalescência. As predições da teoria se contrastam com resultados experimentais correspondentes a um conjunto de nanoemulsões de dodecano/água estabilizadas com dodecil sulfato de sódio. Encontra-se um acordo satisfatório sempre que a dependência de tamanho dos agregados seja convenientemente representada.

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experimental evaluation of the Ostwald ripening rate (see for example Kabalnov *et al*., 1990; Taylor, 1995; Weiss *et al*., 1999; Izquierdo *et al*., 2002; Tadros *et al*., 2004; Sole *et al*., 2006, 2012; Nazarzadeh *et al*., 2013). However, the average radius weighted in volume, area, intensity or mass is commonly used for this purpose. Moreover, the vast majority of the equipment available for static and dynamic light scattering measures the hydrodynamic radius of the 'particles'. Hence, they are unable to distinguish between the radius of a big drop and the hydrodynamic radius of an aggregate of drops. This creates an uncertainty regarding the effect of flocculation and coalescence on the increase of the average radius of the emulsion. If aggregation occurs, the slope dR_e^3/dt will not be the product of ripening alone, and yet it will be usually contrasted with Eq. 6.

Average Radius of an Emulsion Subject to Flocculation and Coalescence

Recently, a novel theoretical expression for the turbidity of an emulsion (τ) as a function of time was deduced (Rahn-Chique *et al*., 2012a, b, c). According to this equation, and in the absence of mixed aggregates (Rahn-Chique *et al*., 2012a), the scattering of light results from the original drops of the emulsion (primary drops), aggregates of primary drops, and larger spherical (secondary) drops:

$$\tau = n_1\sigma_1 + \sum_{k=2}^{k_{max}} n_k \left[x_a\sigma_{k,a} + \left(1 - x_a\right)\sigma_{k,s} \right] \quad (9)$$

where $\sigma_{k,a}$ and $\sigma_{k,s}$ represent the optical cross sections of an aggregate of size k and that of a spherical drop of the same volume. According to recent studies (Mendoza *et al*., 2015), x_a is related to the non-globularity of the aggregates. The term inside the brackets stands for the average cross section of an aggregate of size k, and n_k is the number density of aggregates of size k existing in the dispersion at time t (Smoluchowski, 1917):

$$n_k\left(t\right) = \frac{n_0\left(k_{FC}n_0t\right)^{k-1}}{\left(1+k_{FC}n_0t\right)^{k+1}} \quad (10)$$

In Eq. 10 n_0 is the total number of aggregates at time t= 0 $\left(n_0 = \sum n_k\left(t=0\right)\right)$ and k_{FC} is an average aggregation-coalescence rate. The values of k_{FC} and x_a are obtained fitting Eq. 9 to the experimental variation of the turbidity as a function of time.

If the average radius of an emulsion is solely the result of flocculation it can be calculated as

$$R_a = R_{FC} = \sum_{k=1}^{k_{max}} \left[\frac{n_k}{n}\right] R_k \quad (11)$$

where R_k: average radius of an aggregate composed of k primary particles, and n: total number of aggregates per unit volume. The term in parenthesis corresponds to the probability of occurrence of an aggregate of size k at a given time. The value of n is equal to

$$n(t) = \sum_{k=1}^{k_{max}} n_k\left(t\right) = \frac{n_0}{1 + k_{FC}\,n_0\,t} \quad (12)$$

where $k_{FC} = k_F$ in the absence of coalescence. If an emulsion is subject to both flocculation and coalescence (FC), the average size of the aggregates results from the contributions of the 'true' aggregates of the particles, and the bigger drops resulting from coalescence. According to our simulations (Urbina-Villalba *et al*., 2005, 2009a) Eq. 12 also applies to the mixed process of flocculation and coalescence whenever coalescence is much faster than flocculation.

Every time Eq. 9 is valid, Eq. 11 could be recast in the form

$$R_{FC} = \left[\frac{n_1}{n}\right] R_1 + \sum_{k=2}^{k_{max}} \left[\frac{n_k}{n}\right] \left[x_a R_{k,a} + \left(1 - x_a\right) R_{k,s} \right] \quad (13)$$

where: $R_{k,a}$: average radius of the aggregates with k primary particles, and $R_{k,s}$: radius of a drop resulting from the coalescence of k primary particles $\left(R_{k,s} = \sqrt[3]{k}\,R_0\right)$. Only in the case in which $R_{k,a} \approx R_{k,s}$ Eq. 13 can be easily evaluated as

$$R_{FC} = \left[\frac{n_1}{n}\right] R_1 + \sum_{k=2}^{k_{max}} \left[\frac{n_k}{n}\right] R_{k,a} \left[x_a + \left(1 - x_a\right) \right] = \sum_{k=1}^{k_{max}} \left[\frac{n_k}{n}\right] R_k \quad (14)$$

In general, the dependence of $R_{k,a}$ on k is unknown due to the variety of conformations available for each aggregate size. Alternative approximate

$$R_{FC}=n_1\left(\sigma_1/Q_s\pi\right)^{1/2}+\sum_{k=2}^{k_{max}}n_k\left[x_a\left(\sigma_{k,a}/Q_a\pi\right)^{1/2}+\left(1-x_a\right)\left(\sigma_{k,s}/Q_s\pi\right)^{1/2}\right] \quad (15)$$

expressions can be formulated based on Eq. 9 and the connection between the optical cross section of a spherical particle (σ) and its radius ($\sigma = Q_s \pi R^2$) as where Q is the scattering coefficient (Gregory, 2009). The value of Q for a spherical particle, Q_s, can be estimated using the program Mieplot (www.philiplaven.com). Alternatively, a k-dependence of the average radius of an aggregate composed of k primary drops of size R_0 can be extrapolated based on the variation of the average radius of the coalescing drops ($R_{k,s}=k^{1/3}R_0$):

$$R_{FC}=n_1R_0+\sum_{k=2}^{k_{max}}n_k\left[x_ak^m+\left(1-x_a\right)k^n\right]R_0 \quad (16)$$

where m and n are rational numbers. Hence: it is possible to calculate the variation of the average radius of an emulsion due to flocculation and coalescence, if the value of k_{FC} can be obtained by adjusting Eq. 9 to the experimental data.

Number Average Radius of an Emulsion Subject to Flocculation, Coalescence and Ostwald Ripening

From the previous sections it is clear that once the value of k_{FC} has been evaluated by means of Eq. 9, equations 14, 15 or 16 can be employed to predict the effect of flocculation and coalescence on the temporal variation of the average radius. Instead, Eq 8 can be used to predict the sole influence of Ostwald ripening according to LSW. In fact, the change of the average number of drops (n_d) due to Ostwald ripening has the same mathematical structure of Eq. 12 (Weers 1999; Urbina-Villalba *et al.*, 2014):

$$n_d=\frac{n_0}{1+k_{OR}\,n_0\,t} \quad (17)$$

where

$$k_{OR}=\frac{16\,\pi\alpha D_m C_\infty}{27\,\varphi} \quad (18)$$

where φ is the volume fraction of oil. Eq. 17 is similar to Eq. 12 and, therefore, the evaluation of the rate constant by means of the change in the number of aggregates as a function of time does not identify the process of destabilization.

It is evident that flocculation, coalescence and ripening are not independent processes. This situation is clearly illustrated in the algorithm proposed De Smet *et al.* (1997) to simulate the process of Ostwald ripening. Starting from Fick's law, using the Kelvin's equation, and assuming that the capillary length of the oil is substantially lower than the radii of the drops ($\alpha \ll R_i$), these authors demonstrated that the number of molecules of a drop of oil (i) suspended in water (m_i), changes in time according to

$$\frac{dm_i}{dt}=4\pi D_m C_\infty \alpha\left(\frac{R_i\left(t\right)}{R_c\left(t\right)}-1\right) \quad (19)$$

According to Eq. 19 the drops can increase or decrease their volume depending on the quotient between their particular radius and the critical radius of the emulsion. The amount of molecules transferred to/from a particle depends on the referred quotient. Hence, if the average (critical) radius of the emulsion increases due to a mechanism different from Ostwald ripening, the process of ripening should also be affected. As previously noted, the simulations suggest that the average radius of the emulsion only increases due to ripening when the total number of drops decreases by complete dissolution. Hence, if the average radius of the emulsion increases faster than predicted by LSW, the number of drops whose size ($R_i(t)$) fall below the critical radius at time t ($R_c(t)$) increases. Consequently, the number of drops subject to dissolution can be substantially larger than the one predicted by LSW. This should promote a further increase in the average radius, and a ripening rate that might be substantially larger than predicted by Eq. 6.

In this paper we only consider the simplest scenario in which Oswald ripening occurs independently of flocculation and coalescence. In this case the average radius of the emulsion at time t should be equal to

$$R\left(t\right)=R\left(t_0\right)+\left(\Delta R\right)_{OR}+\left(\Delta R\right)_{FC} \quad (20)$$

Here the symbol $(\Delta R)_p$ stands for the change of the average radius due to process 'p':

$$\left(\Delta R\right)_p=R_p\left(t\right)-R_p\left(t_0\right) \quad (21)$$

We had previously deduced an explicit expression for flocculation and coalescence (FC) which allows the evaluation of $(\Delta R)_{FC}$ (Eqs. 11, and 14-16). In the case of Ostwald ripening (OR), Eq. 8 leads to

$$R_{OR}\left(t\right)=\sqrt[3]{V_{OR}\left[t-t_0\right]+R_{OR}^3\left(t_0\right)} \quad (22)$$

Notice that

$$R\left(t_0\right)=R_{FC}\left(t_0\right)=R_{OR}\left(t_0\right)=R_0 \quad (23)$$

hence

$$R\left(t\right)=R_0+\left(\sqrt[3]{V_{OR}\left[t-t_0\right]+R_0^3}-R_0\right)+\left(R_{FC}\left(t\right)-R_0\right) \quad (24)$$

$$R\left(t\right)=\sqrt[3]{V_{OR}\left[t-t_0\right]+R_0^3}+R_{FC}\left(t\right)-R_0 \quad (25)$$

Eq. 25 has the correct limit (R_0) for $t= t_0$. Moreover, it is the most accurate expression that can be derived with the classical theories, assuming that FC and OR occur simultaneously but independently.

An interesting expression results if Eq. 6 is integrated between t-Δt and t, and it is assumed that the process of flocculation and coalescence occurs much faster than the one of Ostwald ripening $\left(R_{OR}^3\left(t-\Delta t\right)=R_{FC}^3\left(t-\Delta t\right)\right)$:

$$R_c\left(t\right)=\sqrt[3]{V_{OR}\Delta t+R_{FC}^3\left(t-\Delta t\right)} \quad (26)$$

Using Eq. 26 recursively in order to reproduce the total time elapsed (see Eq. A.6 in Appendix), and assuming that the FC contribution is independent from the one of OR:

$$R_a\left(t\right)=R_{FC}\left(t\right)+R_c\left(t\right) \quad (27)$$

one obtains a very good approximation to all the experimental data of the systems with the stronger variation of the average radius. However, while Eq. 26 is a reasonable approximation to the critical radius, Eq. 27 is incorrect, since it obliterates the fact that there is only one average radius for the system ($R_a(t) = R_c(t)$), and therefore, Eq. 26 already contains the effects of both OR and FC (see Appendix).

Experimental Details

Materials

N-dodecane (C_{12}; Merck 98%) was eluted twice through an alumina column prior to use. Sodium dodecylsulfate (SDS; Merck) was recrystallized from ethanol two times. Sodium chloride (NaCl; Merck 99.5%), and isopentanol (iP; Scharlau Chemie 99%) were used as received. Millipore's Simplicity water was employed (conductivity <1μS·cm^{-1} at 25ºC).

Dispersion preparation and characterization

An equilibrated system of water + liquid crystal + oil with 10% wt SDS, 8% wt NaCl, 6.5% wt iP and a weight fraction of oil f_o= 0.80 ($f_o + f_w$= 1, ϕ= 0.84) was suddenly diluted with water at constant stirring until the final conditions were attained: 5% wt SDS, 3.3% wt iP, and f_o= 0.38 (φ= 0.44). This procedure allowed the synthesis of mother nano-emulsions (MN) with an average radius of 72.5nm. An appropriate aliquot of MN was then diluted with a suitable aqueous solution containing SDS, NaCl and iP (W/SDS/NaCl/iP) in order to obtain systems with f_o= 0.35, 0.30, 0.25, 0.20, 0.15 and 0.10, and salt concentrations of 2 and 4% wt

NaCl. To avoid the risk of perturbation and/or contamination of a unique sample, each of these emulsions was divided into 15 vials and stored at 25°C. These vials were used later to study the evolution of the emulsion during 6h. The whole procedure was repeated thrice with independently-prepared mother nano-emulsions. In all cases, the concentration of SDS and iP was kept fixed at 5% wt and 3.3% wt, respectively. An additional set of emulsions was prepared leaving a set of MN to evolve in time until their average radius reached R ~500nm (mother macro-emulsion: MM). As before, aliquots of MM were diluted with W/SDS/NaCl/iP solution in order to prepare systems with the same physicochemical conditions of the nano-emulsions, but with a higher particle radius. The average size of the dispersions, and their drop size distribution (DSD) were measured using a LS 230 (Beckman-Coulter). Out of the total of 24 systems, 6 representative emulsions were selected to illustrate in this work the behavior of the drop size (Table I).

Evaluation of k_{FC}

At specific times an aliquot was taken from one bottle of the set of vials corresponding to each system. The aliquot was diluted with an aqueous solution of SDS in order to reach a volume fraction of oil equal to $\phi = 10^{-4}$ ([SDS]= 8 mM). Then, the value of the turbidity was measured using a Turner spectrophotometer (Fisher Scientific) at $\lambda = 800$nm (Rahn-Chique *et al.*, 2012a, c). This procedure was repeated for 6h. When the whole set of measurements was complete, Eq. 9 was fitted to the experimental data of the turbidity (τ=230Abs) as a function of time using Mathematica 8.0.1.0.

The optical cross sections of the aggregates used in Eq. 9 are valid whenever

$$C_{RGD} = \left(4\pi R/\lambda\right)\left(m_r - 1\right) << 1 \quad (28)$$

where λ: wavelength of light in the liquid medium, and m_r the relative refractive index between the particle and the solvent. In the case of a dodecane/water emulsion (m_r= 1.07), the values of C_{RGD} corresponding to radii R= 50, 60, 70, 80, 100 and 500nm are 0.07, 0.09, 0.10, 0.12, 0.15 and 0.75, respectively. These values are reasonably low, guaranteeing errors in the cross sections lower than 10% within the Rayleigh-Gans-Debye approximation (Kerker, 1969).

The values of k_{FC}, $t_{0,teo}$ (theoretical starting time of the aggregation process), and x_a were directly obtained from the fitting of Eq. 9 to the experimental data. The theoretical value of the radius is a parameter of the calculation which can be systematically varied (R_{teo}= $R_{exp} \pm \delta$) to optimize the fitting, and guarantee a value of $t_{0,teo}$ close to the experiment. The errors bars were calculated using the procedure described in (Rahn-Chique *et al.*, 2012a, c). The effect of buoyancy during these measurements is known to be negligible (Cruz-Barrios *et al.*, 2014).

For the evaluation of k_{FC}, aliquots of the concentrated emulsion were taken periodically, and diluted. Hence, the number of particles per unit volume used in the determination of k_{FC} corresponds to a dilute (d) system ($k_{FC,d}$) and not to the actual, concentrated (c) emulsion ($k_{FC,c}$) under study. Simple arithmetic shows that $k_{FC,d}$ has to be multiplied by the dilution factor in order to obtain $k_{FC,c}$.

TABLE I
COMPOSITION OF THE EMULSIONS STUDIED. WEIGHT FRACTION OF OIL (f_o), SALT CONCENTRATION, INITIAL RADIUS, AND PARTICLE DENSITY OF THE CONCENTRATED ($n_{0,c}$) AND DILUTE ($n_{0,d}$) SYSTEMS

ID	f_o	% NaCl	$R_{0,exp}$ (nm)	$n_{0,c}$ (m^{-3})	$n_{0,d}$ (m^{-3})
A	0.35	2	74	2.5×10^{20}	5.9×10^{16}
B	0.30	4	156	2.3×10^{19}	6.3×10^{15}
C	0.25	2	165	1.6×10^{19}	5.3×10^{15}
D	0.25	4	204	8.6×10^{18}	2.8×10^{15}
E	0.30	2	505	6.8×10^{17}	1.9×10^{14}
F	0.25	2	560	4.2×10^{17}	1.4×10^{14}

If an aliquot of volume V_c is removed from a concentrated emulsion with an aggregate density n_c, and diluted with aqueous solution until reaching a final volume V_d, the new aggregate density n_d fulfills the relationship

$$n_d\left(t\right)V_d = n_c\left(t\right)V_c \quad (29)$$

and this allows the definition of a dilution factor f_d :

$$n_d\left(t\right) = n_c\left(t\right)\left(\frac{V_c}{V_d}\right) = n_c\left(t\right)\frac{1}{f_d} \quad (30)$$

$$f_d = n_c\left(t\right)/n_d\left(t\right) \quad (31)$$

Using the expression of Smoluchowski for a total number of aggregates at time t:

$$\frac{n_{0,d}}{1+k_{FC,d}n_{0,d}t} = \left(\frac{1}{f_d}\right)\frac{n_{0,c}}{1+k_{FC,c}n_{0,c}t} \quad (32)$$

the following equality is obtained:

$$n_{0,d}\left(1+k_{FC,c}n_{0,c}t\right) = \left(\frac{1}{f_d}\right)n_{0,c}\left(1+k_{FC,d}n_{0,d}t\right) \quad (33)$$

but for any time t, and in particular for t= 0:

$$f_d = n_c\left(0\right)/n_d\left(0\right) = n_{0,c}/n_{0,d} \quad (34)$$

and therefore,

$$k_{FC,c}n_{0,c} = k_{FC,d}n_{0,d} \quad (35)$$

which means that the value of k_{FC} obtained from the turbidity measurements of the dilute systems has to be divided by the dilution factor in order to get the rate of flocculation and coalescence of the actual concentrated emulsions:

$$k_{FC,c} = k_{FC,d}\frac{n_{0,d}}{n_{0,c}} = k_{FC,d}\frac{1}{f_d} \quad (36)$$

Prediction of the average radius

The variation of the average radius of the emulsions as a function of time was estimated under different premises:

1) An order-of-magnitude estimation of the mixed flocculation/coalescence rate was obtained using the experimental radius of the emulsions to compute an approximate number of drops n= ϕ/V_1 (where $4/3\pi R^3$). A rough Smoluchoswki's rate (k_S) was calculated from the fitting of this data to Eq. 12 supposing that the number of aggregates was equal to the number of drops. Following, R_a was computed using Eq. 11, assuming $R_{k,a} \approx R_{k,s} = \sqrt[3]{k}\,R_0$.

2) Only Ostwald ripening occurs. The LSW radius was evaluated using Eq. 8. The value of V_{OR} ($2.6\times10^{-28}m^3\cdot s^{-1}$) was estimated from Eqs. 4 and 6 using $\gamma = 1.1mN\cdot m^{-1}$, $C(\infty) = 5.4\times10^{-9}cm^3\cdot cm^{-3}$, $V_M = 2.3\times10^{-4}m^3\cdot mol^{-1}$, $D_m = 5.4\times10^{-10}\,m^2\cdot s^{-1}$ (Sakai *et al.*, 2002).

3) Only flocculation and coalescence occur. The procedure described under k_{FC} evaluation was used to calculate k_{FC}. The value of R_a was estimated using Eq. 14.

4) Flocculation, coalescence and Ostwald ripening occur. The procedure described under k_{FC} evaluation was used to calculate k_{FC}. Following, Eq. 25 was employed to estimate R_a.

Results and Discussion

Depending on the chemical nature (ionic or non-ionic) of the surfactant and the method of preparation of the emulsion (low *vs* high energy), the polydispersity (measured in terms of the coefficient of variation) of a nanoemulsion (%CV= SD×100/R_{exp}, where SD is the standard deviation of the drop size distribution, and R_{exp} is the experimental average radius) can be high. When the present MN and MM systems are diluted with a saline solution, the polidispersity reaches values between 37 and 77% in only a few minutes. If this polydispersity is translated into the standard deviation of the radius, very large error bars result (Figure 1). These errors are conveniently obliterated in the scientific literature either by evaluating the reproducibility (precision) of the measurements, or by referring to the polydispersity index only. Large error bars complicate the comparison with the theory. In the absence of a better criterion, we contrast our theoretical approximations with the average value of the measurements despite the magnitude of the error bars.

The theoretical approximations used in this paper assume that the destabilization processes occur simultaneously but independently of each other. Moreover, only the processes of flocculation, coalescence and Ostwald ripening are included. The emulsions were gently shaken before each measurement to include the larger drops possibly located within the cream.

As previously discussed, the destabilization processes affect each other. For example, coalescence influences Ostwald ripening by constantly changing the average radius of the emulsion. Hence, the experimental drop size is expected to show a more pronounced time dependence than the one predicted by the theoretical approximations. Conversely, if one of the processes does not occur in a given sample, the experimental curve should lie below the theoretical approximation which takes it into account. Moreover, only Ostwald ripening is able to decrease the average size (whenever the complete dissolution of the smaller particles does not occur). Otherwise the average radius always increases.

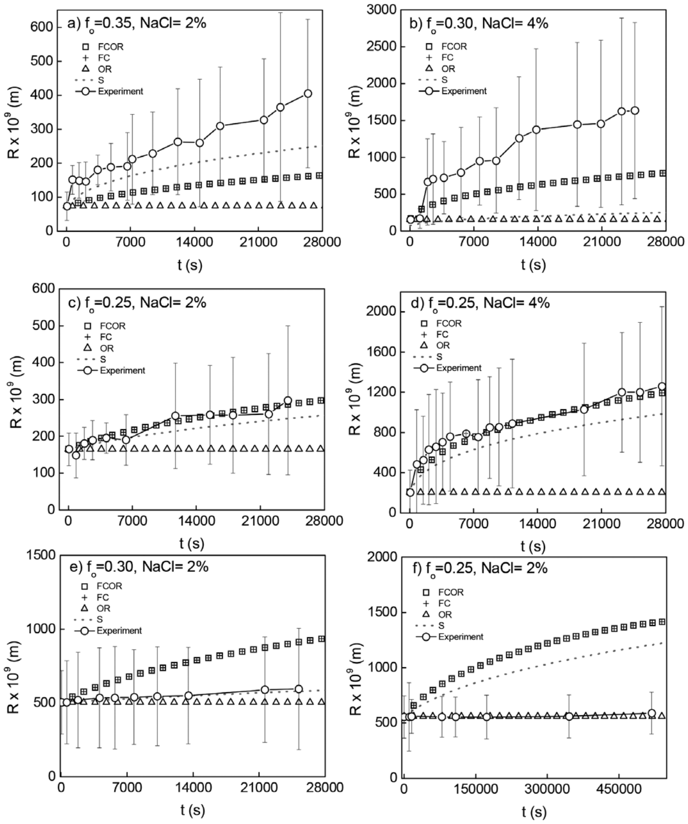

Figure 1. Comparison between the experimental data and the predictions of average radius as a function of time for systems A to F (Table I). The values of the mixed flocculation/coalescence rates are given in Table II. S, OR, FC, and FCOR, stand for the predictions of the theory for Smoluchowski (Eq. 12), Ostwald ripening according to LSW (Eq. 8), flocculation and coalescence (Eq. 14, with $R_{k,a} \approx R_{k,s} = \sqrt[3]{k}\, R_0$), and all processes combined (Eq. 25).

The variation of the drop size is a sound measurement of the overall stability of the systems. In all cases studied the drop size increased as a function of time. A few systems were selected to illustrate this dependence. Three typical situations were found:

1) The average radius of the emulsion was substantially higher than the predictions of Eq. 25 using Eq. 14 to approximate R_{FC}. This is illustrated by systems A and B of Tables I and II (curve FCOR in Figures 1a, b).

2) Only flocculation and coalescence (FC) occur without a sensible contribution of ripening (systems C and D, Figures 1c, d). In this case, the forecast of Ostwald ripening (OR) according to LSW is too low, and the prediction of Eq. 25, FCOR coincides with the one of FC. Both FCOR and FC lie very close to the experimental data.

3) Only ripening takes place (systems E and F, Figures 1e, f). The curves corresponding to FC and FCOR largely surpass the experimental data. Instead, the LSW prediction reproduces very well the experimental measurements. In fact, only in the systems in which the initial average radius is large (showing the slowest variation of the average radius with time) the prevalence of Ostwald ripening is observed.

Within the period of time considered, the standard contribution of Ostwald ripening to the drop size is very small. Hence, the FCOR rates are very similar to the ones of FC. If only OR occurs, any other theoretical approximation to the average radius should lie above the experimental curve. If FC mostly contributes, it is difficult to appraise the effect of Ostwald, since the rates of FC and FCOR are similar. Accordingly, there are systems in which only Ostwald ripening might prevail (Figures 1e, f), and others in which FC predominates (Figures 1c, d).

However, Figures 1a and b show an unexpected behavior: the experimental curve lies above the theoretical approximation for FCOR. This might be the result of a synergistic effect resulting from the mutual influence of the different destabilization phenomena. It might also be the result of the lack of accuracy of the theoretical equations used. In particular, it could be the consequence of our inability to estimate the average radius of an aggregate properly, since in these evaluations it was assumed that $R_{k,a} \approx R_{k,s} = \sqrt[3]{k}\, R_0$.

Figure 2 illustrates the effect of the initial time of measurement, the k-dependence of the cross section on the average radius of the aggregates (Eq. 16), and the magnitude of Q ($Q = Q_s = Q_a$) in Eq. 15, on the predictions of Eq. 25 for systems A and B. It is clear that in these cases, the aggregates formed appear to be more extended than globular ($R_{k,a} = k^m R_0$, $m \approx 0.75$). As a consequence, the optical scattering coefficient that fits the experimental data lies approximately between one tenth (Q= 0.0025) and one third (Q= 0.11) of the values predicted by Mie theory (0.022 and 0.30, respectively) for spherical

TABLE II
PARAMETERS OBTAINED FROM THE FITTING OF Ec. 9 TO THE EXPERIMENTAL DATA. THE ERRORS LISTED RESULT FROM THE AVERAGE OF THE ERRORS OF THREE INDEPENDENT MEASUREMENTS (RAHN-CHIQUE, 2012a)

ID	$R_{0,teo}$ (nm)	x_a	$k_{FC,d}$ ($m^3 \cdot s^{-1}$)	$k_{FC,c}$ ($m^3 \cdot s^{-1}$)	t_0 (s)
A	90	0.51 ±0.18	(9.1 ±1.6)×10^{-21}	(2.3 ±0.4)×10^{-24}	54.9
B	141	0.15 ±0.16	(1.3 ±0.2)×10^{-18}	(2.8 ±0.4)×10^{-22}	18.6
C	173	0.97 ±0.04	(4 ±6)×10^{-20}	(1.5 ±2.1)×10^{-23}	39.9
D	181	0.33 ±0.04	(2.0 ±0.2)×10^{-18}	(7.0 ±0.7)×10^{-22}	14.5
E	520	1.5 ±0.2	(2 ±12)×10^{-20}	(4 ±30)×10^{-24}	26.6
F	424	1.6 ±0.2	(1.6 ±1.1)×10^{-20}	(1.1 ±0.7)×10^{-23}	8.1

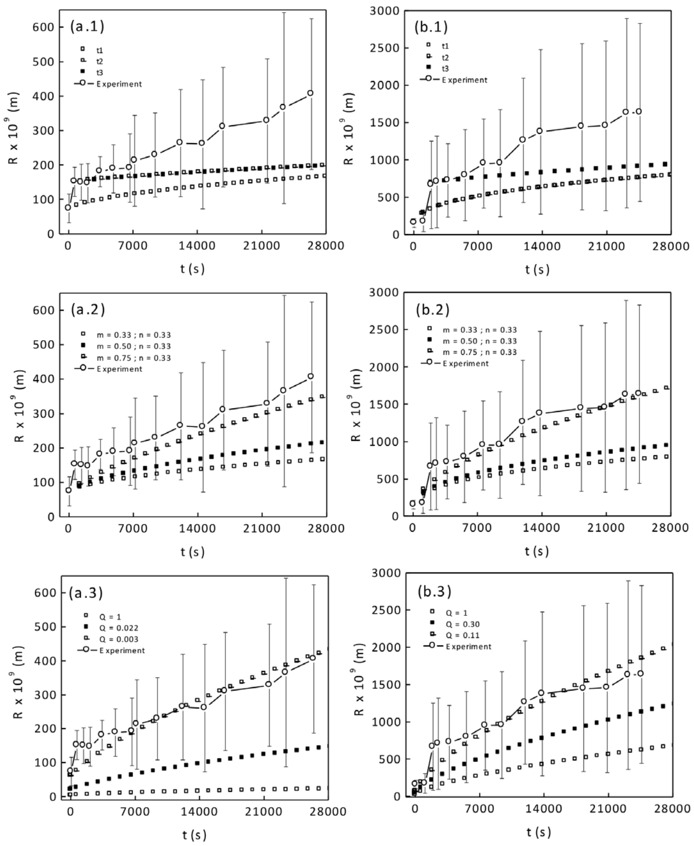

Figure 2. Predictions of Eq. 25 for systems A and B of Figure 1 using different approximations for R_{FC}: a.1) and b.1) changing the initial time of measurement, a.2) and b.2) using different values of m for Eq. 16, and a.3) and b.3) adjusting the value of Q ($Q= Q_s= Q_a$) in Eq. 15.

drops with the same initial average radius. Thus, the discrepancy between the predictions of Eq. 25 and the experiment in the most unstable (concentrated) systems could possibly be adjudicated to the inexact representation of the average radius of the floccules.

It is remarkable that the use of Eq. 27 produces theoretical curves that lie just above the experimental points in those systems in which the FCOR prediction fails to do so (Figures 1a and b). However, the FC contribution is counted twice in this approximation, once through the estimation of the critical radius (Eq. 26) and once –explicitly– in Eq. 27. The coincidence between the predictions of Eq. 27 and the experiment indicates that either the critical radius envisaged by Eq. 8 is too low, or R_{FC} should be twice as high as currently estimated. If this is correct, the discrepancies observed in Figure 1 will rather correspond to a synergistic effect due to the simultaneous occurrence of the processes of destabilization.

Conclusion

A novel methodology able to predict the variation of the average radius of an emulsion as a function of time during a period of –at least– 6h is proposed. The procedure allows discriminating the relative importance of the processes of flocculation/coalescence with respect to Ostwald ripening on the temporal change of the average radius of the emulsions. A satisfactory agreement between theory and experiment is found in most cases, but the reliability of the method depends on the soundness of the theoretical expression used to represent the variation of the average radius of the clusters with the number of individual drops.

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Appendix A

If it is assumed that

$$\frac{dR}{dt} = \left(\frac{dR_{OR}}{dt}\right) + \left(\frac{dR_{FC}}{dt}\right) \tag{A.1}$$

and

$$V_{OR} = dR^3 \Big/ dt = 3R^2 \frac{dR}{dt} = 4\alpha D_m C(\infty) \Big/ 9 \tag{A.2}$$

the second term on the right hand side of Eq. A.1 can be integrated, but the first term leads to an unsolvable integral due to our lack of knowledge on the variation of the radius with t:

$$\int \frac{dR}{dt} = V_{OR} \int \frac{dt}{R^2(t)} \tag{A.3}$$

If on the other hand, it is supposed that

$$\frac{dR^3}{dt} = \left(\frac{dR^3_{OR}}{dt}\right) + \left(\frac{dR^3_{FC}}{dt}\right) \tag{A.4}$$

integration yields:

$$R^3(t) - R^3(t_0) = V_{OR}\left[t - t_0\right] + R^3_{FC}(t) - R^3_{FC}(t_0) \tag{A.5}$$

and simplifying,

$$R^3(t) = V_{OR}\left[t - t_0\right] + R^3_{FC}(t) \tag{A.6}$$

This approximation leads to the correct limit for t= t_0. Moreover, the same *ansatz* leads to

$$3R^2 \frac{dR}{dt} = 3R^2_{OR}\left(\frac{dR_{OR}}{dt}\right) + 3R^2_{FC}\left(\frac{dR_{FC}}{dt}\right) \tag{A.7}$$

or what is equivalent:

$$\frac{dR}{dt} = \frac{R^2_{OR}}{R^2}\left(\frac{dR_{OR}}{dt}\right) + \frac{R^2_{FC}}{R^2}\left(\frac{dR_{FC}}{dt}\right) \tag{A.8}$$

Thus, the total first derivative of the radius is a linear combination of the contributions of ripening and flocculation-coalescence weighted on their relative importance.