ON THE PHYSICAL SIGNIFICANCE OF THE ADJUSTING PARAMETERS IN THE EVALUATION OF THE FLOCCULATION RATE OF AN OIL-IN-WATER NANOEMULSION

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SUMMARY

Recently a versatile methodology for the evaluation of the mixed flocculation-coalescence rate (k_{FC}) of oil-in-water (o/w) nanoemulsions was proposed (Rahn-Chique et al.*, 2012c). The value of k_{FC} is obtained fitting a theoretical expression of the turbidity of the emulsion (τ_{teo}) to its observed behavior (τ_{exp}) over a short period of time. The expression of τ_{teo} contains an additional parameter which was originally introduced to account for the fraction of collisions between the drops that lead to their aggregation (x_a). Hence, under some approximations, the value of ($1-x_a$) should represent the fraction of collisions that leads to the coalescence of the drops. Here, two sets of ionic nanoemulsions, and two sets of latex particles are used to study the dependence of x_a with the average radius of the emulsion. The results suggest that despite its original justification, ($1-x_a$) is more likely to represent the contribution of the 'spherical' scattering of light to the total optical cross section of the aggregates formed.*

Recently, a theoretical expression for the turbidity of an emulsion (τ) as a function of time was deduced (Rahn-Chique *et al.,* 2012a, b, c). This general expression assumes that τ results from the scattering of light by: the original drops of the emulsion (primary drops), aggregates of primary drops, larger spherical drops (secondary drops) resulting from the coalescence of primary drops, and mixed aggregates produced by the flocculation of primary and secondary drops.

$$\tau = n_1\sigma_1 + x_a \sum_{k=2}^{k_{max}} n_k \sigma_{k,a} + x_s \sum_{k=2}^{k_{max}} n_k \sigma_{k,s} + x_m \sum_{k=2}^{k_{max}} n_k \sigma_{k,m} \qquad (1)$$

where $\sigma_{k,a}$, $\sigma_{k,s}$ and $\sigma_{k,m}$ represent the optical cross sections of an aggregate of size k, the one of a spherical drop of the same volume, and the cross section of a mixed aggregate: a combination of clusters and drops with a total volume equivalent to k primary drops; x_a is the fraction of collisions that only lead to the flocculation of the drops; x_s is the fraction of collisions that results in their coalescence; and x_m is the fraction of mixed aggregates produced either by the partial coalescence of an aggregate of size k, or by the flocculation of a smaller aggregate and a large drop resulting from coalescence. Eq. 1 does not consider the effect of Ostwald ripening in the population balance of the drops, although its influence on the aggregation rate can be appraised (Cruz-Barrios *et al.,* 2014).

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If the last term of Eq. 1 is disregarded, a simplified expression susceptible of direct experimental evaluation results:

$$\tau = n_1\sigma_1 + x_a \sum_{k=2}^{k_{max}} n_k \sigma_{k,a} + x_s \sum_{k=2}^{k_{max}} n_k \sigma_{k,s} \qquad (2)$$

and n_k is the number density of aggregates of size k existing in the dispersion at time t (von Smoluchowski, 1917):

$$n_k = \frac{n_0 \left(k_{FC} n_0 t\right)^{k-1}}{\left(1 + k_{FC} n_0 t\right)^{k+1}} \qquad (3)$$

In Eq. 3 n_0 represents the total number of aggregates at time t= 0 $\left(n_0 = \sum n_k (t=0)\right)$ and k_{FC} is an average aggregation-coalescence rate. Notice that in the absence of mixed aggregates x_s= (1-x_a). However, if mixed aggregates exist in the dispersion and Eq. 2 is used to fit the experimental variation of the turbidity, then $x_s + x_a \neq 1$. Moreover, the value of the actual coefficients x_a and x_s is altered (see Appendix B in Rahn-Chique *et al.,* 2012a). The values of k_{FC} and x_a result from the fitting of Eq. 2 to the experimental variation of the turbidity as a function of time. For that purpose, the emulsion must be suddenly destabilized through the variation of a suitable formulation variable. In the case of an ionic nanoemulsion this is readily achieved injecting a high concentration of salt into the sample vessel. In the case of a non-ionic nanoemulsion this can be attained by rising the temperature of the system.

Despite the sound theoretical justification of Eq. 2, the physical meaning of x_s and x_a cannot be assured. This is more evident if the number density of the aggregates of size k is factored out in the right hand side of the equation to yield:

$$\begin{aligned} \tau &= n_1\sigma_1 + \sum_{k=2}^{k_{max}} n_k \left[x_a \sigma_{k,a} + x_s \sigma_{k,s} \right] \\ &= n_1\sigma_1 + \sum_{k=2}^{k_{max}} n_k \sigma_{k,eff} \end{aligned} \qquad (4)$$

It is clear from Eq. 4 that the expression in brackets has the form of an effective cross section of an aggregate of size k: $\sigma_{k,eff}$, which depends on two adjustable parameters (x_s and x_a). In this case, the parameters can take any real value. Moreover, there might be cases in which the constraint $x_s + x_a = 1$ is satisfied but $|x_s| + |x_a| > 1$. In this scenario, the connection between the stability of the dispersion with the values of these parameters can be much more complex. However, due to the analytical form of $\sigma_{k,eff}$ in Eq. 4, the parameters can still be interpreted as weight factors, related to the topology of the aggregates formed. They measure the relative tendency of a cluster to either show an extended structure characterized by $\sigma_{k,a}$ or to be essentially globular, typified by the optical cross section of a sphere: $\sigma_{k,s}$. In any event, $\sigma_{k,eff}$ characterizes the cross sections of the actual aggregates existing in the dispersion, whatever their shape or origin might be. Thus, the dependence of $\sigma_{k,eff}$ with: k, the wavelength of the incident light (λ), the average radius of the primary particles (R), etc., should be useful in order to portray the actual shape of the aggregates, and therefore, the actual evolution of the system.

It is important to remark at this point that, regardless of the meaning of x_s, the significance of k_{FC} is unique, and its method of evaluation is robust (Urbina-Villalba *et al.,* 2015). However, x_a and x_s provide a great deal of information that should be extracted from the systematic variation of the formulation variables of the system. In the cases in which Eq. 2 can be adjusted to the experimental data under the premises of the original formulation (Rahn-Chique *et al.,* 2012a, b), at least four scenarios are possible:

1) x_a ~1 and $0<x_s<1$: aggregation of the primary drops only occurs; drops do not coalesce. This case is illustrated in Figure 1 by a dodecane (C_{12}) in water emulsion (R= 217.5nm) stabilized with SDS (Mendoza *et al.,* 2013).

2) x_s ~1 and $0<x_a<1$: coalescence occurs just after aggregation; only larger drops are formed due to the rapid coalescence of aggregated drops.

3) $0<x_s<1$ and $0<x_a<1$: both pure aggregation and coalescence occur; the relative degree of coalescence with respect to flocculation is simply given by the ratio x_s/x_a. This case is illustrated in Figure 2 by a bromo-dodecane (Br-C_{12}) in water emulsion stabilized with Brij 30 (Cruz, 2014). At low temperature only aggregation occurs. As the temperature increases, the degree of coalescence augments ($x_a \to 0$).

4) $x_s + x_a = 1$ but $x_s \in \Re, x_a \in \Re$ mixed aggregates are formed; these are produced by the aggregation of primary drops with larger drops (formed by coalescence), or by the partial coalescence of primary drops within a large aggregate. This case is illustrated in Figure 1 by the behavior of the emulsion of R= 72nm at low salt concentration (Rahn-Chique *et al.,* 2012a), and in Figure 2 by the performance of a dodecane (C_{12}) in water emulsion stabilized with Brij 30 (polyoxyethylene (4) lauryl ether, $C_{12}E_4$) at low temperatures (Cruz, 2014).

The alternative interpretation of the parameters based on the topology of the aggregates formed means that x_s and x_a can take any real value. However, in this case, the parameters do not provide any direct information about the coalescence process. The geometrical characteristics of the aggregates could probably be deduced from a systematic study of $\sigma_{k,eff}$. Only then a connection between the effective optical cross section and the degree of coalescence of the original drops can be established.

Figure 1 shows the variation of x_a as a function of the salt concentration previously reported for a dodecane-in-water emulsion stabilized with SDS (Rahn-Chique *et al.,* 2012a). It is clear that this parameter changes as a function of the ionic strength of the aqueous solution. According to the DLVO theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948) the increase of the

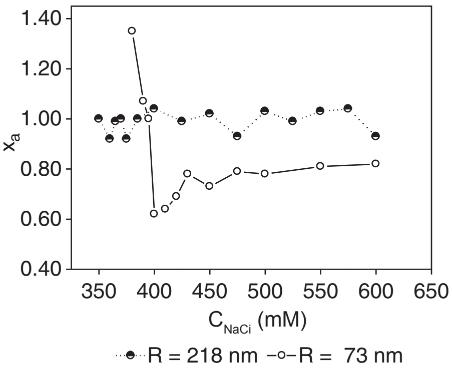

Figure 1. Change of x_a *vs* C_{NaCl} for dodecane-in-water nanoemulsions with average radius of (○) 73 nm, and (●) 218 nm.

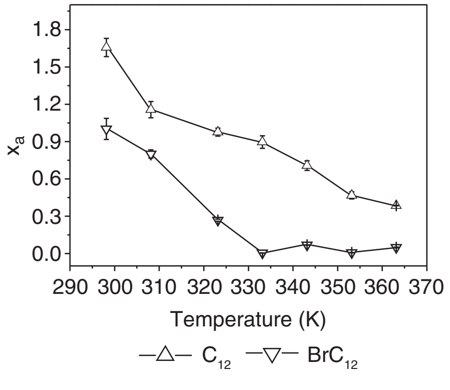

Figure 2. Variation of x_a *vs* absolute temperature (T) for oil-in-water emulsions composed of (△) dodecane (C_{12}) and (▽) bromo-dodecane (Br-C_{12}) stabilized with Brij30.

ionic strength of the external phase is expected to screen the surface charges of the drops inducing their flocculation. Since flocculation is a previous necessary step in the route to coalescence, it was formerly expected that the value of x_a should decrease with the increase of the ionic strength. However, according to the possible evolution of the system specified above (ítems 1-4), it was found that mixed aggregates might be formed below 380mM NaCl (x_a>1, x_s<0), pure aggregation exclusively occurs around 390mM NaCl (x_a ~1), and the mixed process of pure aggregation and coalescence occurs above 400mM NaCl. These results correspond to a nanoemulsion with an average radius of 73nm (Figure 1). However, when the same experiments are repeated using a nanoemulsion with an average radius of 217.5nm, it is found that $0.91<x_a<1.05$ ($x_s \approx 0$); that is: only flocculation occurs (Figure 1). It is clear, therefore, that either the process of coalescence depends on the radius of the drops, or the parameters x_a and x_s do not necessary represent the degree of aggregation and coalescence.

In order to advance in the comprehension of the physical meaning of x_s and x_a we explore here the radius dependence of x_a for two sets of oil-in-water nanoemulsions. For the experimental conditions selected (ionic strength I =500mM NaCl, surfactant concentration C_s =8mM), the dodecane-in-water emulsions previously referred (73 and 217.5nm; Figure 1), show values x_a equal to 0.79 and 1.2, respectively. However, in this work, the oil phase of the emulsion is composed of a mixture of dodecane, tetrachloroethylene and squalene, purposely prepared in order to minimize the effects of buoyancy and Ostwald ripening in the emulsions. Additionally, Eq. 4 was adjusted to two sets of suspensions of latex particles with R =150 and 188nm. These particles are solid and cannot coalesce. Therefore, any value of x_s different from zero obtained by the fitting of Eq. 4 to the experimental data will necessarily indicate that this parameter cannot be exclusively understood as the fraction of collisions leading to the coalescence of the drops in an unstable emulsion.

Experimental Details

Materials

N-dodecane (C_{12}, Merck 98%) was eluted twice through an alumina column prior to use. NaCl (Merck 99.5%), Isopentanol (IP, Scharlau Chemie 99%), tetrachloroethylene (TCE, JT Baker 100%), and squalene (SQ, Aldrich 99%) were used as received. Millipore´s Simplicity water was used in all cases (conductivity <1μS·cm^{-1} at 25ºC).

Lattices 1 and 2 were obtained from Ikerlat Polymers S.L., and correspond to polystyrene sulfate lattices AJ30 (R= 150.5nm) and AJ40 (R= 188nm). Each latex was cleaned during 15 days with Millipore's water using a Serum Replacement device (Advantec MFS), until the conductivity of the discarded water was equal to 1.1μS·cm^{-1}. Their surface charge measured in 10.5mM NaCl solution was -1.73 ± 0.03μCoul· cm^{-2} (latex 2), and -1.68 ± 0.09μCoul· cm^{-2} (latex 1).

Dispersion preparation and characterization

All nanoemulsions were prepared by the method of phase transition by composition (Solè *et al.,* 2006; Maestro *et al.,* 2008; Wang *et al.,* 2008). The oil phase was a mixture of C_{12}, TCE and SQ in the proportion 56:23:21% wt. The initial weight fraction of oil was φ_w= 0.5. The original mixture contained: C_{SDS}= 10% wt, C_{NaCl}= 12% wt, C_{IP} 6.5% wt. Emulsions were prepared by a sudden dilution and stirring of the mixture following the protocol specified in Mendoza *et al.,* (2013). In order to obtain mother emulsions of different radii, the rate of addition of water to the concentrated system was varied. Water was either added using a Dosimat (Metrohm) or a syringe. For emulsions A - H approximate fluxes of 150, 120, 100, 80, 18, 15, 5, and 0.5ml·min^{-1} were used. The resulting emulsions are labeled in order of increasing average radii from A to H (constant ϕ), and from I to L (variable ϕ). Numbers 1, 2, 3 distinguish measurements with different number of particles (Table I). All mother emulsions contained: C_{SDS}= 1.5% wt, C_{IP} 1% wt, and φ= 0.068. They were diluted with a suitable aqueous solution of SDS in order to adjust the final concentration of the surfactant to 8mM, and the volume fraction of oil between $4.3\text{x}10^{-5} < \varphi < 4.4\text{x}10^{-4}$.

In the case of the lattices, the suspensions were sonicated and their particle size distribution assessed previous to the measurements, in order to avoid the presence of clusters in the original sample. The appropriate concentration of salt was added in the final dilution of the suspension.

The average size of the dispersions, their drop size distribution (DSD) and the zeta potential (ζ) of the particles were measured using a LS230 and a Delsa 440SX from Beckman-Coulter (Table II).

Evaluation of k_{FC}

The change in the absorbance (Abs) as a function of time was

TABLE I
VOLUME FRACTION OF OIL φ, AND NUMBER OF PARTICLES PER UNIT VOLUME N_0 OF ALL NANOEMULSIONS STUDIED IN THIS WORK

ID	Theoretical radius (nm)	φ	x_a	n_0 (esp) (part/ml)
A	59.0	$4.4 \text{ x } 10^{-4}$	0.80	$8.1 \text{ x } 10^{11}$
B	61.0	$4.4 \text{ x } 10^{-4}$	0.86	$6.7 \text{ x } 10^{11}$
C	72.0	$4.4 \text{ x } 10^{-4}$	0.76	$3.9 \text{ x } 10^{11}$
D	104.0	$4.4 \text{ x } 10^{-4}$	0.71	$8.6 \text{ x } 10^{10}$
E	179.0	$4.4 \text{ x } 10^{-4}$	0.97	$1.7 \text{ x } 10^{10}$
F	177.0	$4.4 \text{ x } 10^{-4}$	0.90	$1.3 \text{ x } 10^{10}$
G	241.0	$4.4 \text{ x } 10^{-4}$	0.99	$5.3 \text{ x } 10^{9}$
H	276.0	$4.4 \text{ x } 10^{-4}$	1.14	$3.4 \text{ x } 10^{9}$
I-1	68.5	$4.3 \text{ x } 10^{-5}$	0.65	$2.0 \text{ x } 10^{10}$
I-2	72.0	$8.6 \text{ x } 10^{-5}$	0.59	$4 \text{ x } 10^{10}$
I-3	76.0	$1.3 \text{ x } 10^{-4}$	0.61	$6 \text{ x } 10^{10}$
J-1	143.0	$4.1 \text{ x } 10^{-4}$	0.76	$2 \text{ x } 10^{10}$
J-2	147.8	$8.2 \text{ x } 10^{-4}$	0.75	$4 \text{ x } 10^{10}$
J-3	153.0	$1.2 \text{ x } 10^{-3}$	0.80	$6 \text{ x } 10^{10}$
K-1	162.5	$5.6 \text{ x } 10^{-4}$	0.73	$2 \text{ x } 10^{10}$
K-2	180.0	$1.1 \text{ x } 10^{-3}$	0.89	$4 \text{ x } 10^{10}$
K-3	177.2	$1.7 \text{ x } 10^{-3}$	0.90	$6 \text{ x } 10^{10}$
L-1	180.5	$6.8 \text{ x } 10^{-4}$	0.83	$2 \text{ x } 10^{10}$
L-2	191.0	$1.4 \text{ x } 10^{-3}$	0.96	$4 \text{ x } 10^{10}$
L-3	217.5	$2.0 \text{ x } 10^{-4}$	0.99	$6 \text{ x } 10^{10}$
Latex 1	150.5	$3.6 \text{ x } 10^{-4}$	Fig. 4	$2 \text{ x } 10^{10}$
Latex 2	188.0	$7.0 \text{ x } 10^{-4}$	Fig. 4	$2 \text{ x } 10^{10}$

TABLE II
LIGHT-SCATTERING DETERMINATION OF THE AVERAGE RADIUS OF THE EMULSIONS*

Emulsion	Average radius (nm)	C_{RGD} (λ= 800nm)	Zeta potential (mV)	Standard deviation
A	51.0	0.10	-46.4	4.3
B	54.0	0.10	-46.4	4.3
C	66.0	0.12	-46.4	4.3
D	107.0	0.20	-47.0	2.8
E	184.0	0.35	-62.6	0.7
F	201.0	0.38	-66.3	2.5
G	270.0	0.51	-76.9	1.3
H	316.0	0.60	-83.1	3.4
I	80.0	0.08	-72.0	5.2
J	170.0	0.17	-82.0	4.1
K	188.0	0.29	-88.4	2.0
L	201.0	0.32	-93.8	6.1
Latex 1	150.5	0.57	-72.0	3.3
Latex 2	188.0	0.71	-76.0	3.8

* Coefficient of application of the Raleigh-Gans-Debye theory: C_{RGD}, and Zeta potential of the drops.

measured using a Turner spectrophotometer (Fisher Scientific) at λ= 800nm. For each emulsion a fixed electrolyte concentration of 500mM NaCl was employed, following the procedure described in Rahn-Chique (2012a, c). First, an approximate value of the initial absorbance (Abs_0) was evaluated by diluting 2.4ml of emulsion with 0.6ml of pure water. The initial time of aggregation ($t_{0,exp}$) was assumed to be the time necessary to attain an absorbance of Abs_0 during the actual measurement. In all experiments, 2.4ml of emulsion were diluted with 0.6ml of brine to reach a specific salt concentration. The concentration of SDS was kept fixed at 8mM, and the absorbance was recorded for 60s (emulsions A - D, I - L, lattices), and for 300s (emulsions E - H).

The analytical form of the optical cross sections used in the evaluation of Eq. 4, are given in Rahn-Chique *et al.,* 2012a, c). These are valid whenever:

$$C_{RGD} = \left(4\pi R/\lambda\right)\left(m-1\right) \ll 1 \qquad (5)$$

where λ: wavelength of light in the liquid medium, and m: relative refractive index between the particle and the solvent. Table II shows that the values of C_{RGD} calculated for the present dispersions are reasonably low.

Eq. 4 was fitted to the experimental data of the turbidity (τ = 230Abs) using a symbolic algebra package (Mathematica 8.0.1.0). The values of k_{FC}, $t_{0,teo}$ and x_a (x_s= 1-x_a) were directly obtained from this fitting. The average radius of the emulsion was systematically varied (R_{teo}= R_{exp} ±δ) in order to maximize the quality of the fitting and guarantee a value of $t_{0,teo}$ close to the experiment. The errors were calculated using the procedure described in (Rahn-Chique *et al.,* 2012a, c).

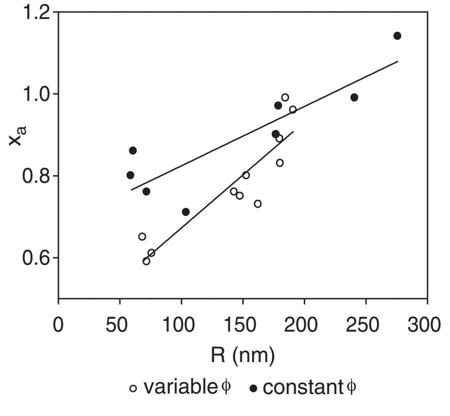

Figure 3. Change of x_a *vs* radius for the nanoemulsions prepared in this work (see Tables I and II).

Results and Discussion

The mayor problem for the assessment of coalescence in a nanoemulsion is that the drops cannot be seen under the microscope. If the emulsion is left to evolve for a certain period of time, until their drops can be appreciated, it is then uncertain if bigger drops are the result of coalescence or Ostwald ripening. Besides, since emulsions are polydisperse dispersions, this contribution is assumed by the third term of Eq. 2, which is the only one that accounts for spherical drops bigger in size that the primary (original) drops.

Figure 3 shows that for both Set I (variable φ) and Set II (constant φ) evaluations, the value of x_a increases with the radius of the drops. For 217.5nm, x_a ~1, while for 73nm it varies between 0.59 and 0.76, as previously reported (Rahn-Chique *et al.,* 2012a; Mendoza, 2013). Under the premises of the original theory this suggests that smaller drops are more likely to coalesce under the present experimental conditions. This might be connected with the fact that the coalescence time between two drops shows a maximum value ~2µm and, hence, it increases first and then decreases depending on the size of the drop and the properties of the interface (Toro-Mendoza *et al.,* 2010). However, no sound functional dependence was found, and it was also observed that the fraction x_a also increases with the absolute value of the zeta potential $|\zeta|$, φ, the quotient φ/R proportional to the total interfacial area A_T=$(3\varphi/R)V_T$ (where V_T is the total volume of the emulsion), and φR^2 (Table III). In all cases the regression coefficients are very poor, so a true meaningful functional dependence cannot be established. Interestingly, the data of Set II shows that the value of ζ increases smoothly and monotonically from a minimum value of -46.4mV (up to a maximum value of -83.1mV) as the interfacial area of the emulsion decreases. This was expected on the grounds of previous theoretical simulations carried out by our group: as the interfacial area decreases, more surfactant is available to saturate the oil/water interfaces, which leads to an increase in the surface charge of the drops. However, a completely different variation was observed for the systems of Set I (in which ζ increases with φ/R).

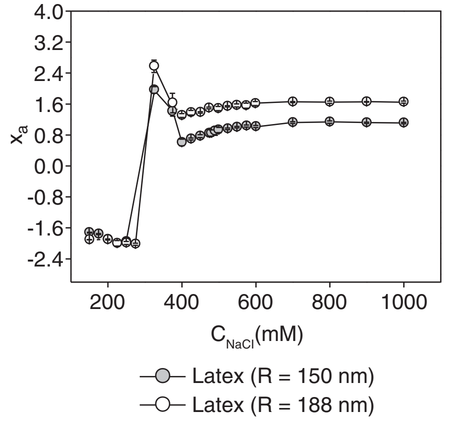

Figure 4. Variation of x_a *vs* C_{NaCl} for two polystyrene lattice with R= 150 and 188nm.

Figure 4 shows the dependence of x_a on the ionic strength of the solutions for two latex dispersions of different radii. The value of x_a is negative and fairly constant at very low salt concentrations (<250mM), then increases abruptly until reaching a maximum (~325mM), decreases until 375mM (secondary minimum), and finally increases steadily, reaching an asymptotic value at 1000mM equal to 1.11 for R= 151nm and 1.65 for 188nm, respectively. An approximate homogeneity coefficient, in the same spirit of the one proposed by Broide and Cohen (1990), can be evaluated using these values:

$$\left(R_2/R_1\right)^{\lambda_h} = x_{a,2}/x_{a,1} \qquad (6)$$

A value of λ_h of ~7/4 (1.75) was obtained. A similar procedure using the values of k_{FC} instead of the ones of x_a gives: λ_h= 2.63. So, it is clear, that even in the case of solid particles there exists a dependence of x_a and k_{FC} on the particle size.

Due to the limit of detection of the instrument, the slowness of the aggregation process and the effect of creaming, it is not possible to measure the temporal evolution of the absorbance of emulsions for salinities below 300mM. However, previous measurements corresponding to a set of hexadecane/water nanoemulsions (R= 184nm) stabilized with 0.5mM SDS at different salt concentrations (García-Valera *et al.* 2014) showed a maximum point at 325mM (x_a= 1.54), a pronounced minimum at 340mM (x_a= 0.15) followed by a progressive increase until 525mM (secondary maximum, x_a= 1.17), and a smooth decrease until 1M (x_a= 0.87). This behavior is similar to the one observed in the case of latex particles except for the final decrease (C_{NaCl} >700mM), and the initial negative values at low ionic strength. With respect to the latter phenomenon it must be remarked that the fittings of Figure 4 correspond to a time lapse of 60s, and the half life time of the emulsions at low ionic strength can be hours or even days. When this happens, the variation of the turbidity as a

TABLE III
APPROXIMATE (ROUGH) REGRESSIONS
OF X_a *vs* DIFFERENT VARIABLES (P)

ID	Variable (P)	Equation$x_a = x_a$(P)	Regresion coefficient
Set I	R	$x_a = 0.0026\ R + 0.4138$	0.8266
Set I	ζ	$x_a = 0.0127\ \zeta + 0.2654$	0.6736
Set I	φ	$x_a = 188.5\ \varphi + 0.6292$	0.8555
Set I	φ/R	$x_a = 4.0 \times 10^{-5}\ \varphi/R + 0.6157$	0.7847
Set I	φ/R²	$x_a = 0.0055\ \varphi/R^2 + 0.6510$	0.8991
Set II	R	$x_a = 0.0014\ R + 0.6794$	0.7658
Set II	ζ	$x_a = 0.0086\ \zeta + 0.3811$	0.8374
Set II	φ/R	Non linear	–
Set II	φ/R²	$x_a = 0.0105\ \varphi/R^2 + 0.7631$	0.8252

function of time is extremely slow. In some dodecane-in-water emulsions we had observed that the Eq. 2 is able to fit very low salt concentrations with negative coefficients, but this situation is reversed if the time of measurement is extended for a considerably longer period of time.

It is clear that the behavior described above for the latex dispersions is not consistent with our former interpretation of the parameters x_a and x_s (= 1-x_a) since it will imply the occurrence of coalescence between solid particles at least between 400 and 600mM of NaCl. However, the experimental behavior is also inconsistent with the simple geometrical interpretation of the parameters x_a and x_s based on the form of the effective optical cross section (Eq. 4). In this regard, it is well established that at low salt concentrations solid particles tend to form compact aggregates (reaction limited cluster aggregation, RCLA regime) with a fractal coefficient (d_f) near 2.1, while at higher ionic strength they tend to form open structures with a fractal coefficient of 1.7 (diffusion limited cluster aggregation, DLCA; Lin *et al.* 1989). Hence, if x_s= 1-x_a measures the 'globularity' of the aggregates, it is expected that the value of x_a increases with the ionic strength while x_s decreases. Instead, a rather complex pattern of evolution is found. Notwithstanding, the simulations suggest that the fractal coefficient of emulsions may evolve with time, showing coefficients that increase from 2.1 to 2.8 (Urbina-Villalba *et al.,* 2006, 2009). Moreover, the aggregates formed can be a mixture of open and globular structures. In this regard, the fractal coefficient of an Apollonian sphere (a cluster of polydispersed spheres embedded within a bigger sphere) is 2.47 (Borkovec *et al.,* 1994). This value is similar to the one recently found by Lozsán (2012) of d_f= 2.4 for a set of oil-in-water nanoemulsions composed of a mixture of hexadecane and dodecane, under similar experimental conditions than the ones studied in this report (Cs= 8mM, φ= 5.0 x 10^{-4}, C_{NaCl}= 600mM). This sort of aggregates would justify mixed contributions between the optical cross section of an open (extended) structure, and the one of a sphere.

Conclusion

The fact that the temporal variation of the turbidity of a suspension of solid particles can be fitted with Eqs. 2 and 4 employing a parameter $x_s \neq 0$ (x_s= 1-x_a) is a strong indication that this parameter does not necessarily account for the fraction of collisions leading to the coalescence of the drops in an emulsion. However, the alternative hypothesis regarding the direct connection of this coefficient with the globularity of the aggregates is also inconsistent with the typical behavior of the fractal coefficient exhibited by dispersions of solid particles. Hence, further research is necessary. For this purpose, the value of the effective optical cross section as a function of size and ionic strength, and the percentage contribution of x_a and x_s to the effective cross section can be very valuable.

Whatever the case may be, our results show a clear dependence of x_a on the radius of the drops, which explains the discrepancy between the values of this parameter previously found for two similar dodecane-in-water with average radii of R= 73nm (Rahn-Chique *et al.,* 2012) and 217.5nm (Mendoza, 2013).

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ACERCA DEL SIGNIFICADO FÍSICO DE LOS PARÁMETROS DE AJUSTE EN LA EVALUACIÓN DE LA TASA DE FLOCULACIÓN DE UNA NANOEMULSIÓN DE ACEITE EN AGUA

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RESUMEN

Recientemente se propuso (Rahn-Chique et al.*, 2012) una metodología versátil para la evaluación de una tasa mixta de floculación-coalescencia (k_{FC}) en nanoemulsiones aceite/agua (o/w). El valor de k_{FC} se obtiene mediante el ajuste de una expresión teórica de la turbidez de la emulsión (τ_{teo}) al valor observado (τ_{exp}) durante un período corto de tiempo. Sin embargo, la expresión de τ_{teo} también contiene un parámetro adicional originalmente propuesto para tomar en cuenta la fracción de colisiones entre las gotas de la emulsión que llevan a su agregación (x_a). Es por ello, que bajo ciertas aproximaciones, el valor de (1-x_a) representa la fracción de colisiones que lleva a la coalescencia de las gotas. Aquí, dos conjuntos de nanoemulsiones iónicas y dos conjuntos de partículas de látex son empleados para estudiar la variación de los valores de x_a con el radio promedio de las partículas de la emulsión. Los resultados sugieren que pese a su justificación original, (1-x_a) probablemente representa la contribución de la luz 'esféricamente' dispersada a la sección transversal óptica total de los agregados formados.*

SOBRE O SIGNIFICADO FÍSICO DOS PARÂMETROS DE AJUSTE E A AVALIAÇÃO DA TAXA DE FLOCULAÇÃO DE UMA NANOEMULSÃO DE ÓLEO NA ÁGUA

Yorlis Mendoza, Kareem Rahn-Chique, Neyda García-Valera, Eliandreína Cruz-Barrios, Clara Rojas e German Urbina-Villalba

RESUMO

Recentemente foi proposta (Rahn-Chique et al.*, 2012) uma metodologia versátil para a avaliação de uma taxa mista de floculação e coalescência (k_{FC}) e nanoemulsões óleo/agua (o/w). O valor de k_{FC} se obtém mediante o ajuste de uma expressão teórica da turbidez da emulsão (τ_{teo}) ao valor observado (τ_{exp}) durante um período curto de tempo. No entanto, a expressão de τ_{teo} também contém um parâmetro adicional originalmente proposto para tomar em conta a fração de colisões entre as gotas da emulsão que levam a sua agregação (x_a). É por isto que, em determinadas aproximações, o valor de (1-x_a) representa a fração de colisões que leva à coalescência das gotas. Aqui, dois conjuntos de nanoemulsões iônicas e dois conjuntos de partículas de látex são empregados para estudar a variação dos valores de x_a com o raio médio das partículas da emulsão. Os resultados sugerem que apesar da sua justificação original, (1-x_a) provavelmente representa a contribuição da luz 'esfericamente' dispersada à seção transversal óptica total dos agregados formados.*