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Optimization of Oil-in-Water Emulsion Stability: Experimental Design, Multiple Light Scattering, and Acoustic Attenuation Spectroscopy

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To find an optimal formulation of oil-in-water (O/W) emulsions ($\phi_o = 0.05$), the effect of emulsifier nature and concentration, agitation speed, emulsifying time, storage temperature and their mutual interactions on the properties and behavior of these dispersions is evaluated by means of an experimental design (Nemrodw software). Long-term emulsion stability is monitored by multiple light scattering (Turbiscan ags) and acoustic attenuation spectroscopy (Ultrasizer). After matching surfactant HLB and oil required HLB, a model giving the Sauter diameter as a function of emulsifier concentration, agitation speed and emulsification time is proposed. The highest stability of $C_{12}E_4$-stabilized O/W emulsions is observed with 1% emulsifier.

Keywords Emulsification, emulsion stability, experimental design, mechanical agitation, nonionic surfactants, rheology

INTRODUCTION

According to Becher, "an emulsion is a heterogeneous system, consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets, whose diameters, in general, exceed 0.1 µm. Such systems possess a minimal stability, which may be accentuated by such additives as surface-active agents (surfactants), finely-divided solids, etc."[1] In this respect, surfactants may be present as monolayer or liquid crystals; polymers are another class of emulsifiers. Simple emulsions belong to two types: oil-in-water (O/W) and water-in-oil (W/O). There are also two kinds of multiple (double) emulsions: W/O/W and O/W/O. The so-called aqueous phase may contain inorganic or organic solutes and the oily phase, often a mixture of species, can be of mineral, vegetable or animal origin. In spite of their thermodynamic instability, natural emulsions are not rare (e.g., milk, rubber-tree latex). Synthetic ones are more often formulated products used in extremely various fields, such as food, cosmetics, pharmacy and medicine, biotechnology, agrochemicals, petroleum, fabric, leather or metal processing, pulp and paper industry, paints and lacquers, detergence, lubrication, road construction, automotive fuels, explosives.[2–5] It also happens that emulsions, desirable or not, are formed temporarily during industrial processes (e.g., polymerization, oil extraction). Fundamentally, emulsions ask questions concerning their preparation or formulation, their flow properties, their stability and their destruction.[6–8] The answers are related to the understanding of the mechanisms governing the formation of such emulsions, therefore to the control of their formulation and processing. While formulating emulsions, composition variables (nature and proportions of ingredients and their order of addition), temperature and process parameters have to be considered: the former, including temperature, will mainly determine the type of emulsion, whereas the latter will partly govern its stability. In fact, sooner or later, an emulsion will break and undergo phase separation. The observed changes involve reversible phenomena (flocculation, creaming, sedimentation), if particles only migrate, and irreversible phenomena (Ostwald ripening,

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coalescence), if particle size is altered. Among the properties enhancing emulsion stability, let us list: a low dispersed-phase volume fraction, a low density difference between phases, a low (but not too low) interfacial tension, a high viscosity of the continuous phase, a high mechanical resistance and elasticity of the interface, a high ζ potential, a high solubility of the emulsifier in the continuous phase (Bancroft's rule), a narrow droplet size distribution. Increasing temperature often accelerates emulsion breaking. Except in special cases where spontaneous emulsification can occur,[9,10] and without neglecting the advantages of a lot of emulsification techniques,[11,12] mechanical agitation under turbulent flow regime remains the most common emulsification method, especially in large-scale operation.[12–16] Emulsification under mechanical agitation is described either by a kinetic model adapted to take into account the parameters of formulations or by a hydrodynamic approach better suited to describe the emulsification process.[17] The formulation, properties and stability of emulsions have been described throughout the literature.[18–21] As for the theoretical analysis and comparison of emulsification processes, they have given rise to a few recent papers.[11,12,17,20,22] The present study aims at a better understanding of the effect of emulsifier and process variables on oil-in-water (O/W) emulsion properties and behavior: droplet size distribution (DSD), viscosity, shelf stability and breakup modes, by evaluating and optimizing emulsifier properties and process parameters in order to prepare the most stable (optimal) mixture. Emulsion stability will be monitored with two recently developed techniques (multiple light scattering and acoustic attenuation spectroscopy), still rarely used and providing immediately applicable practical guidelines for the control of emulsion properties.

MATERIAL AND METHODS

Materials

A mineral, mainly naphthenic, oil, "T22" (Nynas, Sweden), was used throughout as the dispersed phase. The nonionic surfactants, whose characteristics are reported in Table 1, were given by SEPPIC (Castres, France).

Distilled water was used throughout.

Methods and Instruments

A rotor-stator stirrer, Ultra-Turrax type, IKA T47 S7 (Janke and Kunkel, Germany, 10 000 rpm, 170 W, 18 teeth on the rotor, inside and outside diameters: 35 mm and 40 mm, respectively) was used.

Conductivity measurements were performed with a LF538 digital conductometer (Wissenschaftlich-Technische Werkstätten, Germany).

TABLE 1
Formulas and HLB values[a] of emulsifiers

Commercial name	Chemical name (or average formula)	HLB value[a]
Simulsol P2	$C_{12}E_2$[b]	6.6
Montane 20	Sorbitan laurate	8.6
Simulsol T 150CT	Oxo-$C_{10}E_3$	9
Simulsol P4	$C_{12}E_4$	9.7
Simulsol NW342	Oxo-$C_{10}E_3P_4E_2$	11
Simulsol OX 103CT	Oxo-$C_{10}E_6$	12
Simulsol 96	$C_{18}=E_{10}$[c]	12.4
Montanox 20	polyethoxylated sorbitan monolaurate (20 mol E)	16.7

[a] Hydrophile-lipophile balance.[1,19]

[b] In the formulas of the $C_iE_jP_k$ type, i, j and k represent the average length of the carbon chain C (linear if no prefix, or deriving from Oxo alcohols), the number of moles of ethylene oxide, E, and propylene oxide, P, involved in the alkoxylation, respectively. These commercial surfactants still contain some unreacted alcohol.

[c] C_{18} = oleyl alcohol chain.

Emulsion viscosity was measured with a C-VOR 200 Bohlin rotational viscometer (Malvern, UK). 1 hour after the end of the emulsification process, about 40 μL of emulsion were maintained at 25 ± 2°C in a cylindrical cell (cone-plate device). The same spindle (S61) was used throughout.

Photomicrographs of emulsion samples were taken with a binocular optical microscope Olympus BH2-RFCA.

The mean droplet size, expressed as the Sauter (surface average) diameter, d_{32} ($d_{32} = (\sum n_i d_i^3)/(\sum n_i d_i^2)$), and droplet size distribution (DSD) were measured with a Mastersizer 2000 (Malvern, UK) laser diffraction apparatus. The samples were analyzed 1 hour after preparation.

Turbiscan (Formulaction, France), allows optical characterization of various types of dispersions, namely monitoring of emulsion stability. The recently developed Turbiscan ags, equipped with an auto-sampler, was used in this study. The fresh emulsion (20 mL) is contained in a flat-bottomed cylindrical glass measurement cell. During *ca.* 45 seconds, each sample is scanned by a near-infrared pulsed light source (LED, $\lambda = 880$ nm). Two synchronous detectors collect transmission and backscattering ($\theta = 135°$) intensity data, relative to the initial reference state every 40 μm. A pattern of intensity versus sample height is obtained, giving a macroscopic fingerprint of the sample at a given time (Figure 1). This kind of apparatus, already used successfully to study emulsion stability,[11,23,24] is able to discriminate destabilization processes consisting of droplet migration (creaming, sedimentation) or droplet growth (flocculation, coalescence, Ostwald ripening) and to detect any of those

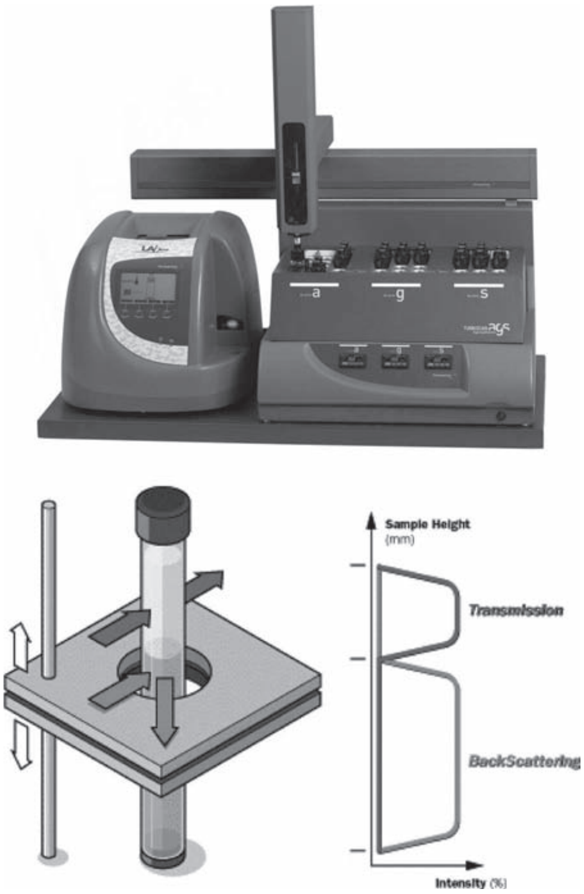

FIG. 1. Turbiscan ags device (Formulaction, France).

phenomena much earlier than the naked eye, especially in the case of opaque and concentrated systems. Moreover, the various destabilization rates can be calculated. The acquisition of intensity data was repeated over 24 hours or even 21 days at 23 ± 2°C, yielding a superimposition of the product fingerprints characterizing emulsion breaking behaviors.

On the other hand, emulsion DSD could be followed in their original, concentrated state, in a continuous mode with another nonintrusive technique: acoustic (ultrasound) attenuation spectroscopy, using the Ultrasizer (Malvern, UK; Figure 2). Acoustic attenuation spectroscopy for particle size measurement of emulsion consists of transmitting ultrasound of different frequencies, typically from 1 MHz up to 150 MHz through a sample with the attenuation being accurately measured. In order to make DSD measurements, it is necessary to measure and calculate the model matrix for particle-dispersion system (Water-$C_{12}E_4$-T22 in our case). The measured attenuation of the sound wave as a function of frequency is called the acoustic attenuation spectrum and constitutes a signature for the particular emulsion. If a sample is kept in the cell of the analyzer for a long time (according to emulsion stability), destabilization kinetics can be plotted.

Emulsion Formulation

Although the aqueous solubility of some surfactants is very low (e.g., Simulsol P2 and P4 with cloud points much lower than room temperature), the emulsifier was

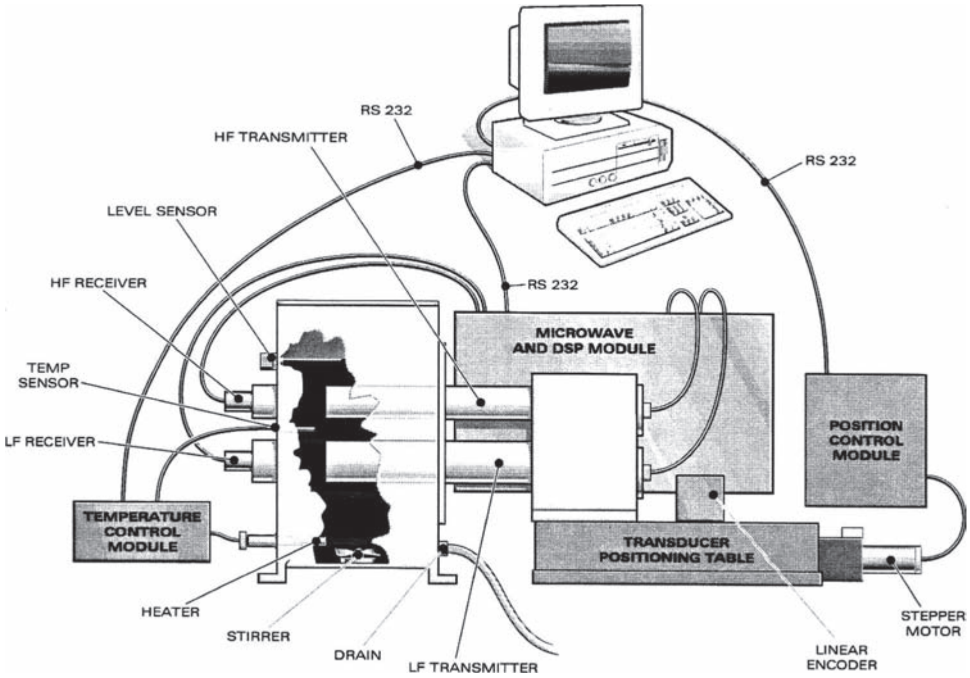

FIG. 2. Ultrasizer schematic device (Malvern, UK).

first dissolved or dispersed in water before dropwise addition of the Nynas T22 oil under stirring (Ultra-Turrax) at a constant temperature of 15 ± 2°C, until a volume fraction of 0.05 of dispersed phase. The reported emulsifier concentration (in wt%) was calculated with respect to the volume of the continuous phase. These emulsions can be considered as simplified models of environmentally-friendly cutting fluids.

RESULTS AND DISCUSSION

Emulsion Type

The conductivity measurements, carried out with addition of 10^{-2} M NaCl, confirm the O/W type of all the formulated emulsions.

Effect of Emulsifier

The emulsifiers used are commercial nonionic surfactants whose biodegradability can be assumed as satisfactory.[25] Made of amphiphilic molecules, they adsorb, mainly as monolayers, at the oil-water interface, thus, decreasing interfacial tension and preventing coalescence by steric stabilization, but may also exist as monomers and aggregates in both bulk phases, between which the various molecular species partition according to their respective solubilities.[26,27] They are often characterized by their hydrophilic-lipophilic character expressed on the HLB scale.[1,4,19,28,29] Because of the lack of data on the required HLB of the Nynas T22 oil, seven emulsions were prepared with different nonionic surfactants (Table 1), all other things being equal (1 wt% emulsifier, emulsification for 60 seconds at 7500 rpm), to find the "best one," that is, the emulsifier giving the smallest droplet average size. Figure 3 shows the variation of the Sauter diameter, d_{32}, versus the HLB value of the emulsifier. With a HLB number of 9.7, $C_{12}E_4$ (Simulsol P4) gives the smallest d_{32}. This can be compared with recent works using this emulsifier with paraffinic or other mineral oils.[30,31] We can thus assume a required HLB value of 9.7 for Nynas T22. Besides, let us mention that there is much incertitude and lack of data concerning the required HLB values of such mineral oils largely used in industrial formulations and that they have to be determined experimentally.[32]

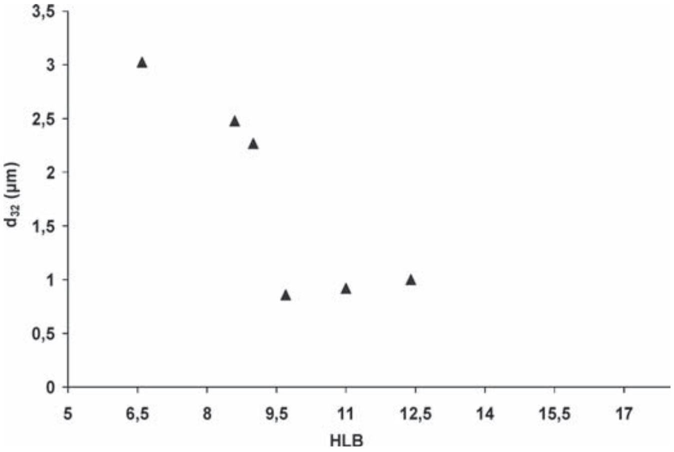

FIG. 3. Variation of the Sauter diameter, d_{32}, versus emulsifier HLB (1 wt% surfactant, 60 seconds, 7500 rpm).

Aquatic toxicity of $C_{12}E_4$ is not negligible,[25,33] the reported EC50/LC50 values (effective concentration, 50%/lethal concentration, 50%) ranging between 0.05 and 0.96 mg/L for algae and fish, respectively,[33] but this species is highly biodegradable, especially in aerobic conditions.[25] The most serious concern could be the toxicity of its intermediate metabolites; however, from the average concentrations determined in 29 sites in Europe, Canada, and the United States, low levels of risk were concluded for alcohol ethoxylates in the aquatic environments of those regions.[33]

Determination of Emulsification Process Parameters

The nature of the emulsifier ($C_{12}E_4$) being fixed, the number of independent variables in an experimental design may be reduced to three: $C_{12}E_4$ concentration (X_1), emulsification time (X_2) and agitation speed (X_3). The effect of the storage temperature will also be studied, separately. Thus, the effects of the three above mentioned variables, X_i (each one taking two values or levels), on the response, Y (d_{32}), will be determined by means of a 2^3 factorial design, involving 8 trials.[34] The double advantage of such a design is to evaluate the individual effect of each parameter, the other ones being kept constant, and the significant interactions between the parameters on the emulsification process. Let us notice that such a practical methodology, aiming at reducing the number of experiments in complex systems, has been only scarcely turned to account for the study of emulsion stability.[35,36]

Let us assume that the variations of Y (d_{32}) obey an eight parameter, second order equation of the following type:

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 + b_{133} X_1 X_2 X_3 \quad [1]$$

Tables 2 and 3 summarize the variables (parameter) notations, their actual and reduced values and the effect matrix presenting the corresponding experimental responses, Y and their average value. By means of the Nemrodw design software,[37] the effect of each variable, between its limit values, on d_{32} was evaluated (Figure 4). In a first approximation, it then appears that only emulsifier concentration, X_1, agitation speed, X_3 and their interaction show significant effects on the Sauter diameter.

TABLE 2
Experimental design parameters: symbols and values

Parameter	Lower level (−1)	Upper level (+1)
X_1: Weight concentration of $C_{12}E_4$ (%)	0.25	4
X_2: Emulsification time (seconds)	10	120
X_3: Agitation speed (rpm)	3000	10000

TABLE 3
Effect matrix and corresponding responses

Trial (m)	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	Y exp d_{32} (μm)
1	−1	−1	−1	+1	+1	+1	−1	4.96
2	+1	−1	−1	−1	−1	+1	+1	18.94
3	−1	+1	−1	−1	+1	−1	+1	3.70
4	+1	+1	−1	+1	−1	−1	−1	20.19
5	−1	−1	+1	+1	−1	−1	+1	2.96
6	+1	−1	+1	−1	+1	−1	−1	6.32
7	−1	+1	+1	−1	−1	+1	−1	1.70
8	+1	+1	+1	+1	+1	+1	+1	5.14
average								7.99

The average response with respect to the variation of a single parameter, X_i, or a product of parameters ($X_i X_j$ or $X_1X_2X_3$), is given by:

$$\overline{Y} = \frac{1}{8}\sum_{m=1,8}(X_iX_jX_k)\,Y_m \qquad (i \neq j \neq k = 1, 2, 3) \tag{2}$$

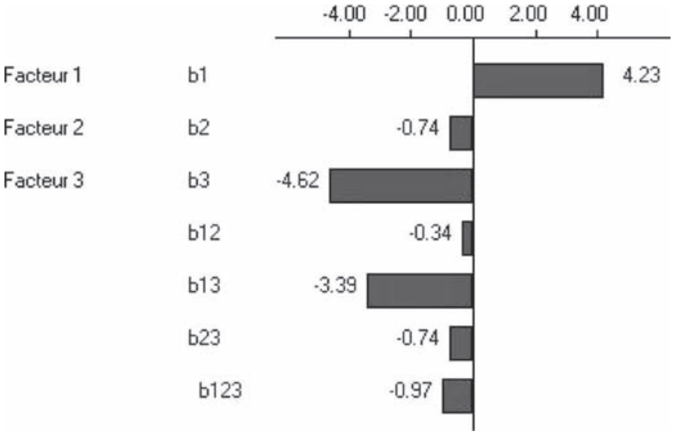

FIG. 4. Effects estimates (Nemrodw software).

TABLE 4
Global effects calculated for Y response

	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$
Y	4.659	−0.307	−3.959	0.323	−2.959	−0.305	−0.307

The corresponding values appear in Table 4.

Figure 5 illustrates the slight effect of the emulsification time, X_2 when X_1 or X_3 takes its high or low value (Figures 5a or 5c, respectively). Obviously, the latter ones show greater influences. Thus, with X_1 at its high (4%) or low level (0.25%), emulsification time, X_2, has no or little effect on d_{32} (Figure 5a); this null or small effect of time is also observed for low and high X_3 values with emulsification time, X_2 (Figure 5c). This confirms several published results.[35,36,38] On the contrary, the high influence of X_1 and X_3 and their significant interaction are evidenced on Figure 5b. On the whole, increasing agitation speed and, to a lesser extent, emulsification time, and lowering $C_{12}E_4$ concentration yield finer emulsions.

Therefore, the simplest, adequate model expressing the significant effects of the two main parameters only keeps four terms, with the coefficients b_0, b_1, b_3, and b_{13} in Equation. (1).

A statistical analysis of the variance allowed us to establish the most adequate model expressing significant effects. This model was calculated by determining the coefficients of the equation:

$$\begin{aligned} Y^* = d_{32}(\mu m) &= b_0 + b_1X_1 + b_3X_3 + b_{13}X_1X_3 \\ &= 8.18 + 4.89\ X_1 - 3.95\ X_3 - 3.04\ X_1X_3 \end{aligned} \tag{3}$$

The Y^* values are reported in Table 5.

The three-dimensional function $d_{32} = f(X_1, X_3)$ is presented in Figure 6. It is a curved surface presenting no minimum, so that, within the domain studied, d_{32} is the smallest for X_1 at its minimum ($X_1 = -1$, or 0.25 wt% $C_{12}E_4$) and X_3 at its maximum ($X_3 = +1$, or 10 000 rpm). Figure 7 shows an excellent correlation between model and response (d_{32}).

TABLE 5
Correlation between response and model

Y exp.	Y corrected	Y^*	Deviation
4.96	4.25	4.24	0
18.94	20.02	20.01	0.01
3.70	3.7	4.20	0.5
20.19	20.2	20.06	0.14
2.96	2.43	2.38	0.05
6.32	6.03	6.08	0.08
1.70	1.7	2.38	0.68
5.14	5.14	6.08	0.9

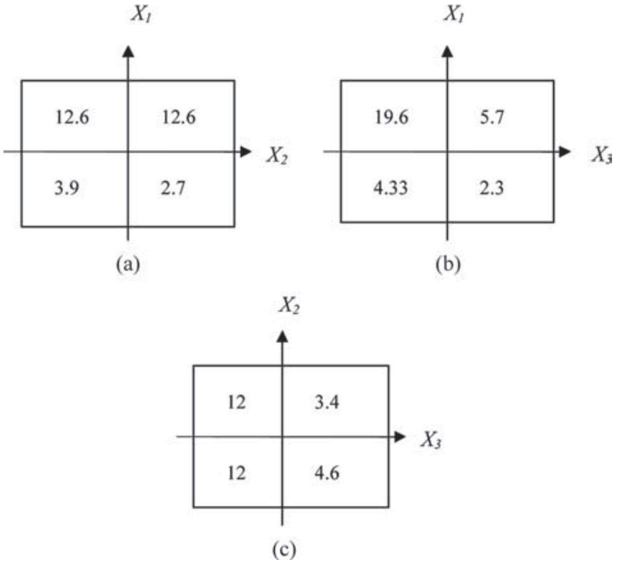

FIG. 5. Interaction effects graphs (a) between X_1 and X_2; (b) between X_1 and X_3, (c) between X_2 and X_3..

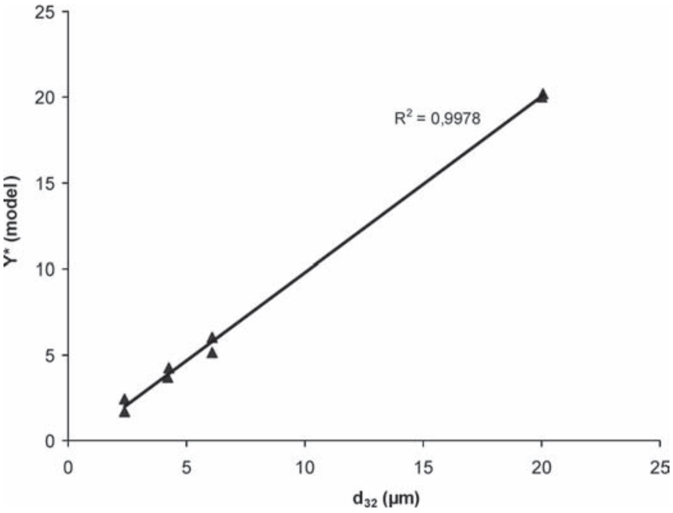

FIG. 7. Correlation between d_{32} and model.

Emulsification Parameter Optimization

Beside formulation properly said, one of the main challenges in the preparation of stable emulsions is the determination of the optimal process parameters during emulsification. In principle, the evaluation of the kinetic stability of an emulsion requires a long period of time. Accelerated aging tests can be applied to overcome this problem. Many studies use centrifugation,[7] ultrasound,[39] or other techniques,[8] but, till now, none of them is reliable or precise enough to describe and explain the mechanisms that govern destabilization phenomena.[40–43] A lot of relationships, namely cited in,[16,17,22] have been established between d_{32} and various parameters for emulsification in turbulent regime under mechanical agitation. All those studies and the present one conclude that emulsion stability is linked to mean droplet diameter and to the variation of rheological properties.[31,35] In fact, when d_{32} is small, viscosity variation is slow and the emulsion is more stable.

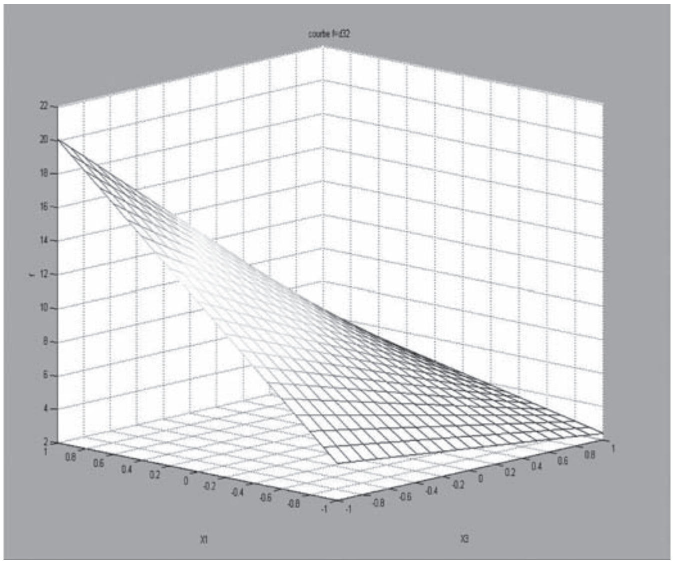

FIG. 6. Three-simensional curved surface response.

The experimental design allowed us to set the best ranges for the parameters that affect emulsion stability:

- a low emulsifier concentration,
- an intermediate emulsification time,
- a high agitation speed.

As regards emulsifier concentration, 0.25% $C_{12}E_4$ yielded an emulsion with bimodal distribution and very poor stability. On the other hand, some authors[17,19,21] recommend an average agitation speed because the energy needed for emulsification is lower compared with that lost in the aqueous phase under the form of heat. Namely, for a speed of 10 000 rpm during 60 seconds, we recorded an increase of the emulsion temperature (40°C). Let us now check the optimum values of $C_{12}E_4$ concentration and agitation speed and, finally, find the best emulsification time. A classical, very efficient process was used for the determination of this optimum: the value of one parameter was fixed and the other two varied within the limits set above. Figures 8–10 illustrate our results. After Figure 8 (d_{32} versus $C_{12}E_4$ concentration under 7500 rpm and during 60 seconds), emulsion is more stable for lower emulsifier concentrations and the smallest drop size is obtained for a concentration of 1%. Figure 9 shows d_{32} versus emulsification time and we can see that emulsification is accomplished in two steps: during the first one, a period of time shorter than 60 seconds, we have recorded a fast

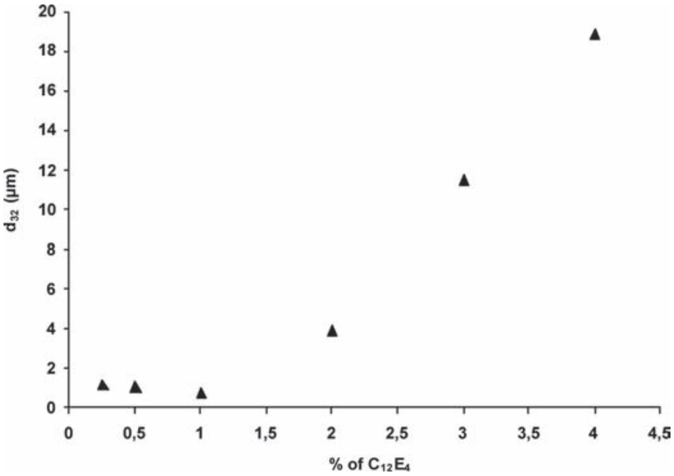

FIG. 8. Variation of the Sauter diameter, d_{32}, versus $C_{12}E_4$ concentration (7500 rpm, 60 seconds).

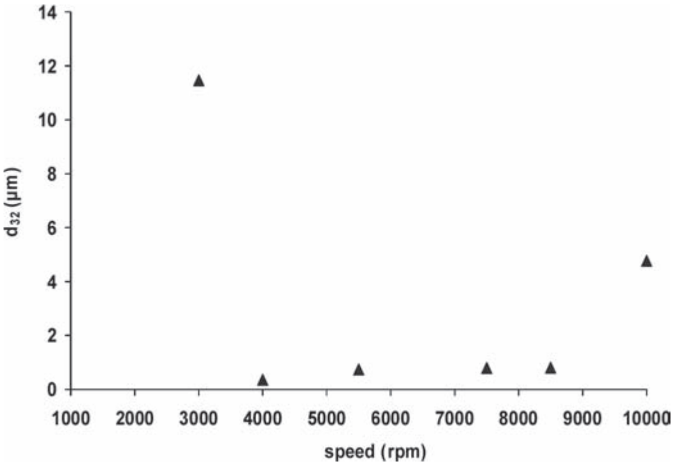

FIG. 10. Variation of the Sauter diameter, d_{32}, versus agitation speed (60 seconds, 1 wt% surfactant).

d_{32} decrease favored by the interfacial tension decrease caused by emulsifier adsorption, and agitation shear. The second step consists of a plateau where, after a slight increase, d_{32} remains fairly constant for any emulsification time, showing that a stationary state is reached, due to a balance between rupture and coalescence of the droplets, corresponding to the smallest possible, therefore optimal, d_{32} value. This validates the experimental design and clearly shows that, above 40 seconds, time have little effect on emulsification process and that a relatively short time is sufficient.[2,12,19] As shown in Figure 10, plotting d_{32} versus agitation speed, we notice that low values of the Sauter diameter are obtained within the range 4000–9000 rpm, but, in fact, a 7500 rpm speed affords a very stable, monodisperse emulsion, contrary to those obtained at 4000 and 5500 rpm giving unstable emulsions characterized by bimodal DSD. Moreover, at 7500 rpm there is almost no foam formation, which happens at higher agitation speed. A sample of our emulsion, prepared at 10 000 rpm, after 60 seconds, clearly shows an agglomeration of the small droplets, denoting an eventual destabilization (Figure 11). Therefore, for our system, the optimum conditions appear to be: 1% $C_{12}E_4$ concentration, 7500 rpm and 60 seconds.

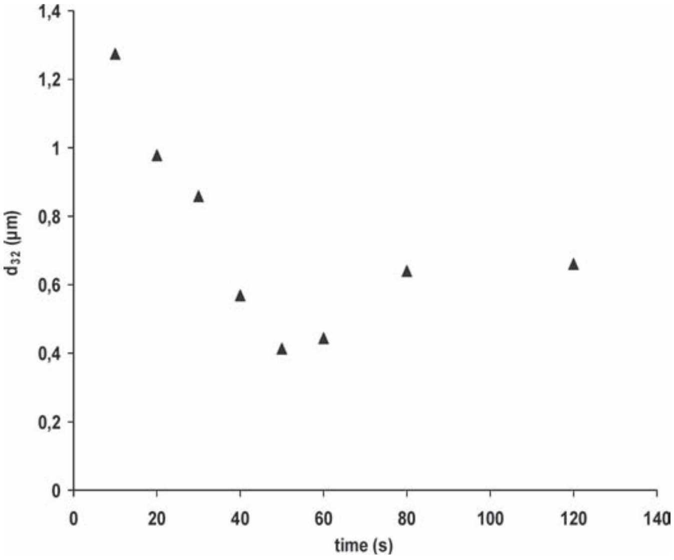

FIG. 9. Variation of the Sauter diameter, d_{32}, versus emulsifying time (7500 rpm, 1 wt% surfactant).

Viscosity

Stokes' law states that the rate of phase separation (V) between liquids 1 and 2 (of respective densities ρ_1 and ρ_2) depends on gravity (g) particle radius (r), and the viscosity (η) of the continuous medium (aqueous phase).

$$V = 2r^2(\rho_1 - \rho_2)\ g/9\,\eta \qquad [4]$$

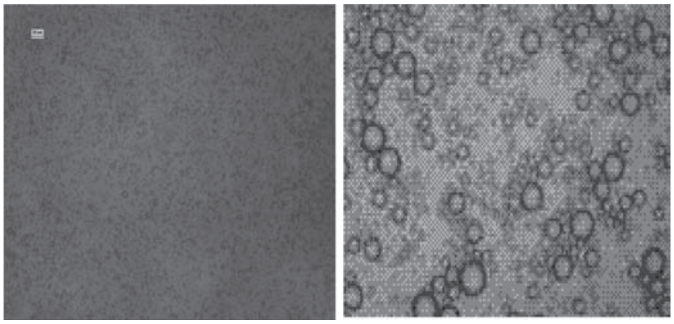

FIG. 11. Microscopic view of emulsions (a) under optimal conditions $d_{32} = 0.18\ \mu m$, (b) 1 wt% $C_{12}E_4$, 10 000 rpm, 60 seconds) × 100.

The relative viscosity η_ρ of very dilute emulsions ($\phi \leq 0.02$) only depends on the volume fraction of the dispersed phase, φ, according to Einstein's relation:

$$\eta_\rho = \eta/\eta_0 = 1 + (5/2)\,\phi \qquad [5]$$

where η_ρ and η_0 are the shear viscosities of the emulsion and the continuous phase, respectively. This relation is obeyed provided that there is no interaction (repulsive Coulombic or attractive Van der Waals forces) between rigid, spherical droplets. If this is not the case, especially for more concentrated emulsions, an empirical, polynomial form may be used:

$$\eta = 1 + \alpha\phi + \beta\,\phi^2 + \chi\,\phi^3 + \cdots \qquad [6]$$

with β theoretically equal to 14.1, according to.[1]

To study the effect of these key parameters on the flow properties of the formulated emulsions, their viscosities were determined as a function of shear rate for two different emulsifying times (10 seconds and 60 seconds). From Figures 12 and 13, both emulsions at 1% appear to be Newtonian. However, if viscosity values are plotted versus shear rate, we notice that, after 10 seconds, the emulsion is indeed Newtonian (Figure 14), whereas, after 60 seconds, it becomes slightly shear-thinning in the studied shear rate range (Figure 15). The viscosities of these emulsions are slightly higher than that of water at 25°C (1 mPa.s).

Stability Measurements

Emulsion stability, that is, ability to keep particle size unchanged with time and during storage,[7,44,45] is a great scientific challenge, of prime practical importance for many

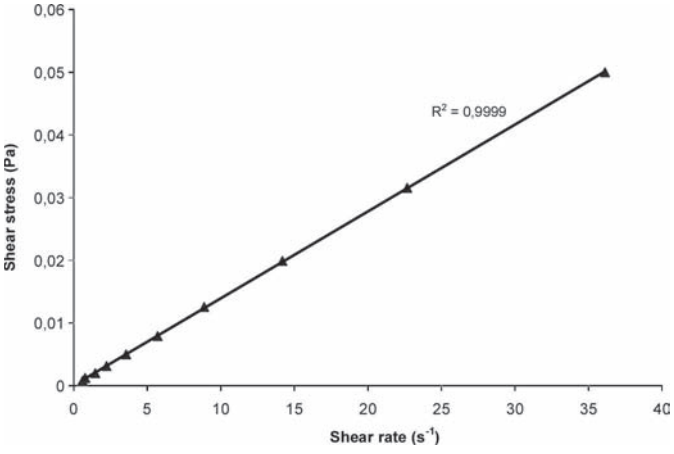

FIG. 12. Variation of shear stress versus shear rate (1 wt% surfactant, 10 seconds).

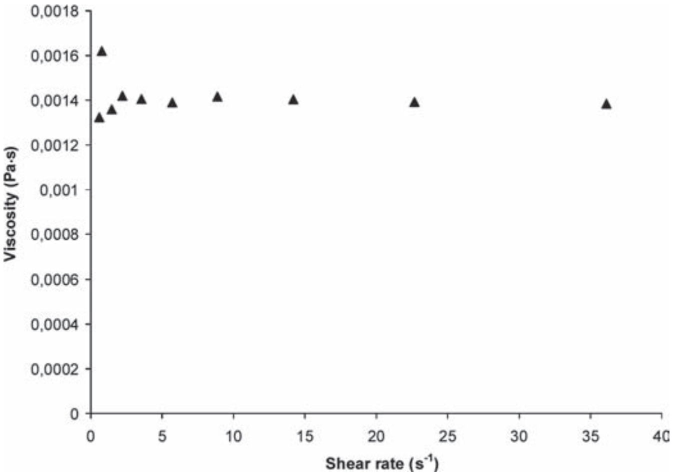

FIG. 13. Variation of viscosity versus shear rate (1 wt% surfactant, 10 seconds).

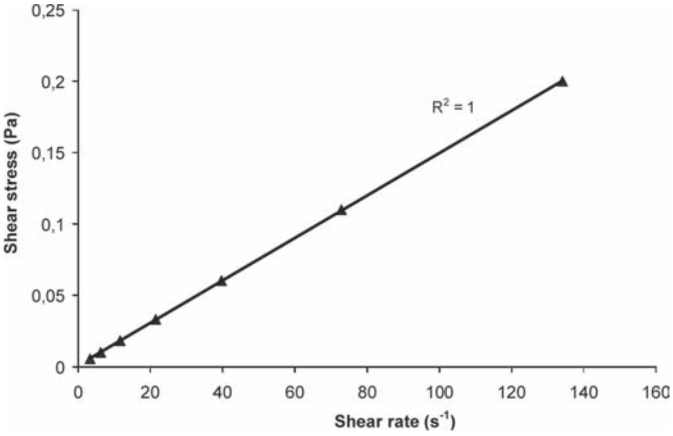

FIG. 14. Variation of shear stress versus shear rate (1 wt% surfactant, 60 seconds).

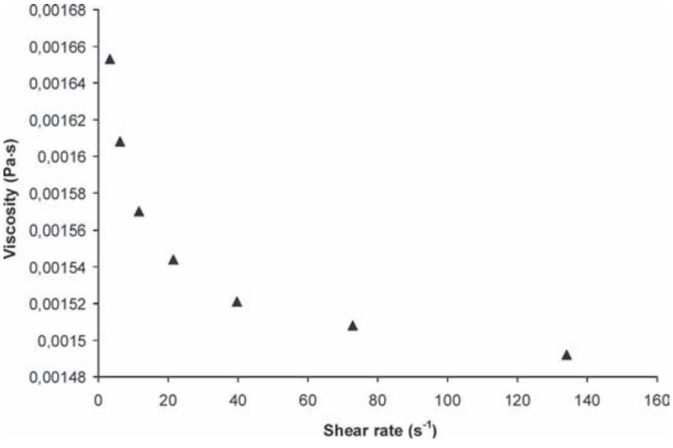

FIG. 15. Variation of viscosity versus shear rate (1 wt% surfactant, 60 seconds).

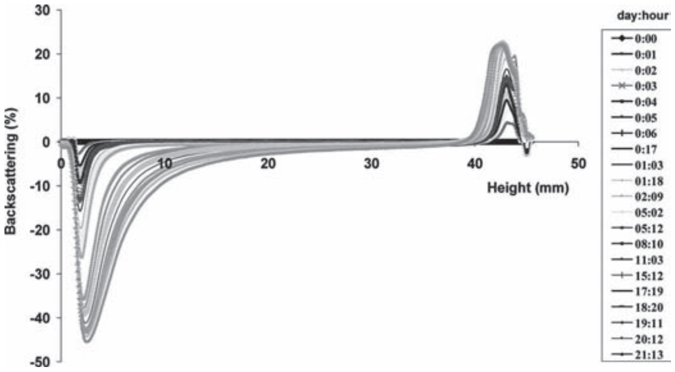

FIG. 16. Backscattering data of T22/$C_{12}E_4$ emulsion (0.5 wt% surfactant, t = 25°C).

industrial formulations. As mentioned above, one of the most efficient techniques allowing to follow emulsion stability directly, that is, without dilution, is the measurement of the intensity of transmitted or back-scattered light by means of the Turbiscan ags. The results of our measurements on emulsions containing 0.5, 1, 2, and 4 wt% emulsifier at 25°C with the Turbiscan ags, are reported in Figures 16–19.

All the emulsions were prepared in the same conditions. For the 1% $C_{12}E_4$ emulsion at 25°C, only transmission data (T) are illustrated (Figure 17). The rather high level of transmitted intensity may suggest that the mixture is a nano- or miniemulsion. For the mixtures containing 0.5%, 2%, and 4% $C_{12}E_4$ at 25°C transmission and backscattering (BS) data are available. As regards BS intensity, the most typical cases are represented in Figures 16, 18, and 19: they exhibit creaming at the top of the sample tube (increase in percentage of backscattered intensity, meaning droplet concentration increase) and clarification at the bottom of the sample with a decrease in BS percentage (water separation). This result is very interesting and validates that obtained by Tadros et al.[30] who performed their experiments with the same surfactant and isohexadecane, a rather similar dispersed phase. Indeed, the solubility of the two systems is high and the interfacial tensions for both oils with the same surfactant concentration are almost identical. In their comprehensive work, Tadros et al.[30] stress that, for an O/W ratio 20/80, 4 wt% is the optimum concentration, whereas in our case, for a T22/water ratio of 5/95, 1 wt% $C_{12}E_4$ is the optimum, so that the surfactant-to-oil ratios are equal in both works.

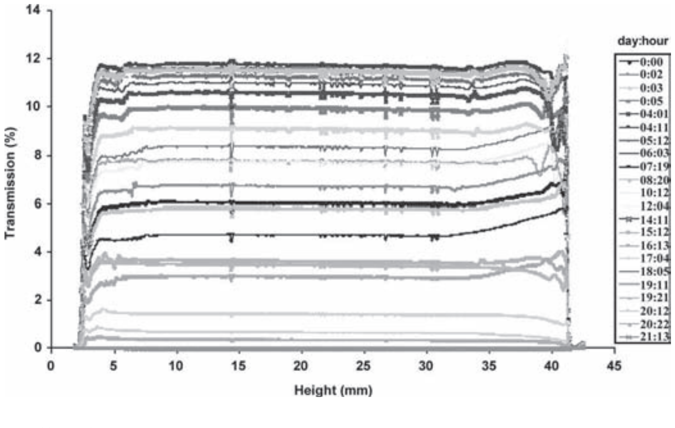

FIG. 17. Transmission data of T22/$C_{12}E_4$ emulsion (1 wt% surfactant, t = 25°C).

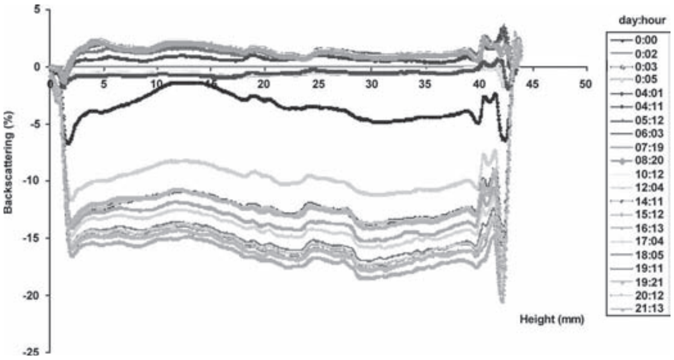

FIG. 18. Backscattering data of T22/$C_{12}E_4$ emulsion (2 wt% surfactant, t = 25°C).

As regards the variation of emulsion conductivity versus temperature, Figure 20 shows that, within the 25–30°C range (the HLB temperature region of $C_{12}E_4$), a sharp conductivity decrease occurs, very likely due to phase inversion. The same curve shape is observed when conductivity measurements are performed while raising or lowering temperature.

The creaming or clarification rate at the top of the samples was followed from the backscattering differential profiles obtained for a long time (21 days) at three storage temperatures: 25°, 40°, and 50°C (Figures 21–23). Emulsion stability is reflected by the thickness of the clarified layer. Creaming is observed for the 0.5 wt% emulsion whereas clarification is noticed for the more concentrated

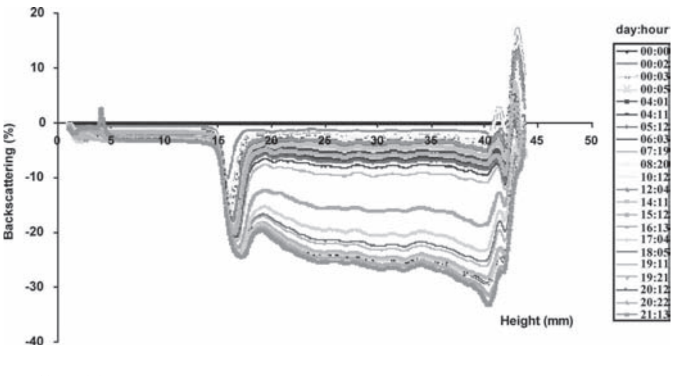

FIG. 19. Backscattering data of T22/$C_{12}E_4$ emulsion (4 wt% surfactant, t = 25°C).

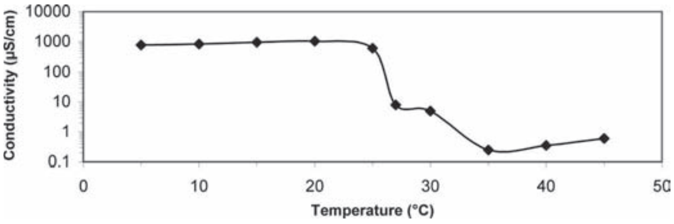

FIG. 20. Conductivity variation of the 1 wt% emulsion versus temperature.

ones. The backscattering data, also reported for the 1% emulsion at 40°C and 50°C, only show small variations (Figures 22 and 23). Figure 24 shows the kinetics of the phase separation, earlier and faster at 50°C than at 40°C. It makes sense that the stability of the 1% O/W emulsion is better at 25°C (no phase separation) than that of the W/O one at 40°C or 50°C. The orders of decreasing stability versus surfactant concentration and temperature are 1% > 0.5% > 2% > 4% and 25°C > 40°C > 50°C, respectively.

It is generally thought and also observed that greater emulsion stability comes with lower d_{32} values and higher emulsifier concentrations, however with a limit.[22,30,46] Obviously, a minimum amount of surfactant is needed to cover the smallest possible droplets, protecting them against coalescence and Ostwald ripening.[47] But, as already noticed by Nikolov et al.[48] there may be "an optimum in emulsion stability as a function of surfactant concentration. This optimum is attributed to the competing role of repulsive structural versus attractive depletion forces. At low micellar concentrations, the depletion interactions between droplets result in a lower stability, while at higher micellar concentrations, the structural forces induce a repulsive energy barrier which enhances emulsion stability. A further increase in

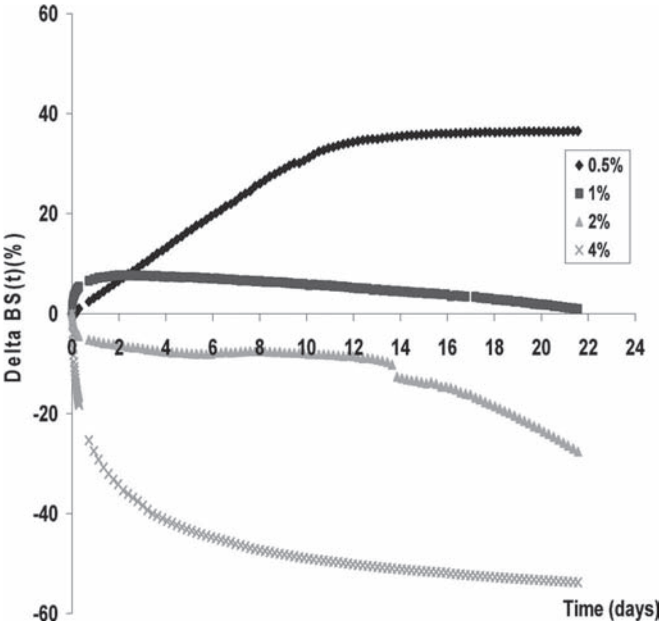

FIG. 22. Backscattering differential profiles [DeltaBS (t) %] versus time of samples (0.5%, 1%, 2%, 4%) at storage temperature of 40°C for 21 days.

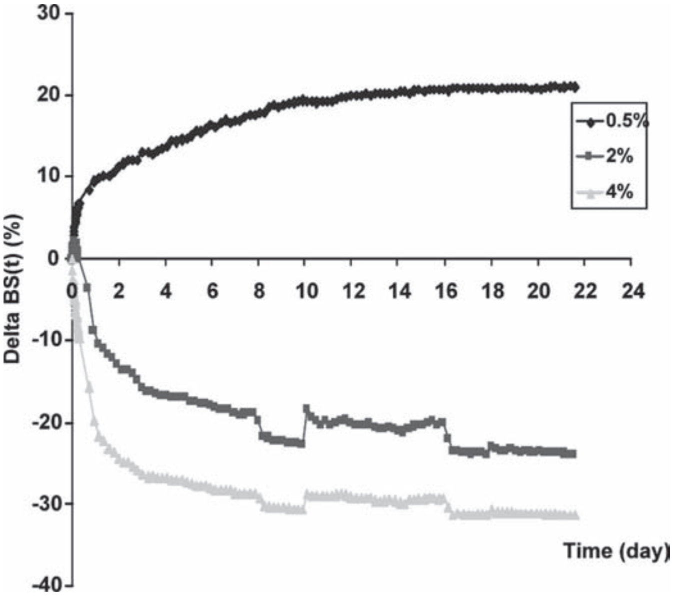

FIG. 21. Backscattering differential profiles [DeltaBS (t) %] versus time of samples (0.5%, 2%, 4%) at storage temperature of 25°C for 21 days.

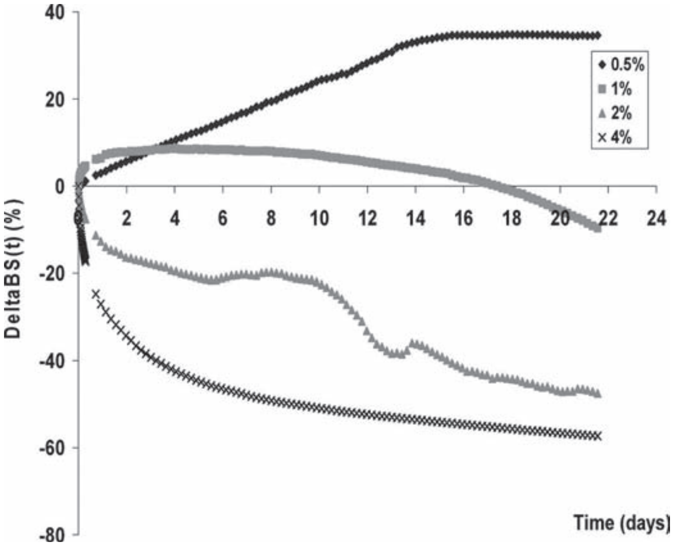

FIG. 23. Backscattering differential profiles [DeltaBS (t) %] versus time of samples (0.5%, 1%, 2%, 4%) at storage temperature of 50°C for 21 days.

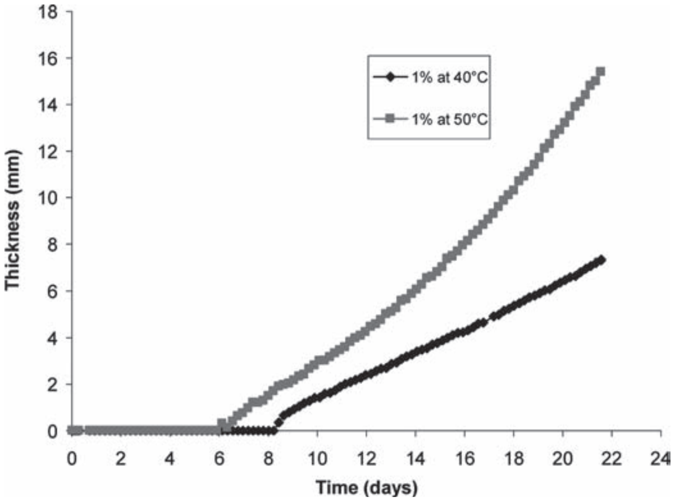

FIG. 24. Thickness versus time for emulsion with 1 wt% $C_{12}E_4$ at 40° and 50°C.

surfactant concentration leads to an increase in polydispersity in micellar size which reduces emulsion stability.'' The higher stability of the 1% emulsion is probably due to such a compromise.

In order to confirm the high stability of the 1% emulsion, the acoustic attenuation spectra were drawn as a function of time (Ultrasizer) (Figure 25). Apart a small change between 24 hours and 72 hours, which should reveal a modified DSD, the spectrum is remarkably constant until 1 month. The evolution of the emulsion DSD versus time in these optimal conditions was also followed. Figure 26 confirms the very small mean droplet size (less than 0.2 µm) and shows a very stable, narrow DSD. After 72 hours, larger droplets seem to appear, yielding a trimodal distribution with secondary maxima at 0.6 µm and *ca.* 1.6 µm, which, apparently, agrees with the attenuation spectra, but, according to those, this could simply be due to the possibly erroneous points around 100 MHz in Figure 26. Anyway, since the ordinate axis is graduated in volume%, the number of ''large droplets'' should be very small.

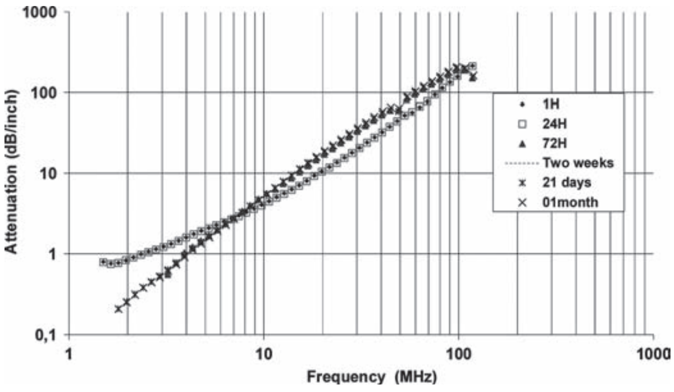

FIG. 25. Acoustic attenuation spectrum versus time storage of T22/$C_{12}E_4$ emulsion (optimal conditions).

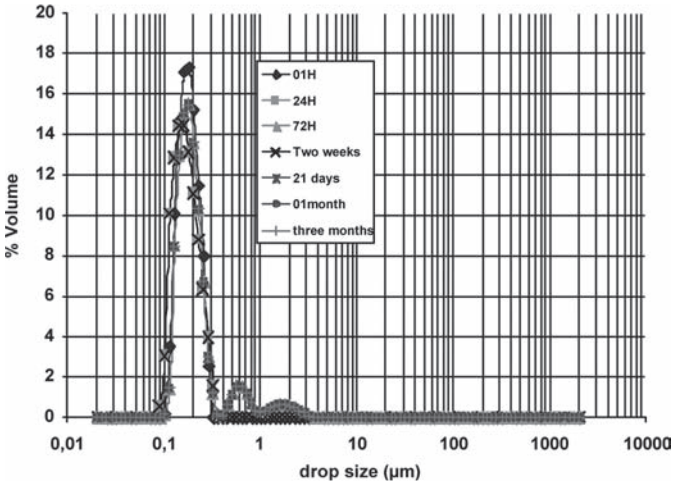

FIG. 26. Volume percentage of droplet size distribution of T22/$C_{12}E_4$ emulsion versus drop size at optimal conditions (1 wt% surfactant, 60 s, 7500 rpm) (kinetic stability perfomed with Ultrasizer measurements).

CONCLUSIONS

Although the tools for characterizing emulsions are now well developed and the mechanisms of emulsification reasonably understood, it is still difficult to predict the exact result of an emulsification process, since this is a combination of a lot of parameters, including formulation and process variables. The goal of this work was to optimize very simple model formulations of ''cutting fluids'' (O/W emulsions stabilized by surfactant). As regards the equipment, mechanical agitation apparatuses, especially rotor-stator devices will certainly continue to be widely used. Optimal conditions were first approached by choosing the emulsifier yielding the finest emulsion, provided it was readily biodegradable: a commercial $C_{12}E_4$ was selected. Then the judicious application of an experimental design to predict optimal formulation of such systems provided guidelines for surfactant concentration, agitation speed and duration. The study of the influence of each parameter and that of the interaction between the parameters allow understanding their effect and mechanisms governing these formulations. These conditions allowed us to perform very stable emulsions having very small droplet size with d_{32} of about 0.18 µm and a rather narrow DSD with a single surfactant. Specific, no intrusive techniques, needing no dilution of 5% emulsions (multiple light scattering with Turbiscan ags and acoustic attenuation spectroscopy with Ultrasizer) helped us to follow destabilization phenomena. The higher stability of emulsions containing 1 wt% $C_{12}E_4$ can be attributed to the competing role of repulsive structural versus attractive depletion forces.

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