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The evaluation of cosmetic and pharmaceutical emulsions aging process using classical techniques and a new method: FTIR

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Abstract

The purpose of this paper is to show how the utilization of Fourier Transform Infrared (FTIR) spectroscopy can be interesting in stability studying of cosmetic or pharmaceutical "oil in water" (O/W) emulsions. In this study temperature storage tests were performed to accelerate the aging process and evaluate the stability of five emulsions. Emulsions were analyzed by FTIR and classical methods (conductivity, viscosity, pH, texture analysis) in order to determine a method that would enable predicting the emulsion's stability. During the aging process, modifications of chemical functions are measured by FTIR (using spectrometric indices), such modifications included: a decrease of unsaturation index, an increase of carbonyl index and a broadening of the carbonyl band. This band was deconvoluted to evaluate the contribution of different species in the broadening phenomenon, which seems to be caused by the appearance of free fatty acids. Conductimetry seems to be the most sensitive technique to assess physical modifications during emulsion's aging. Concerning the most unstable emulsions, a progressive increasing of conductivity was observed several months before the emulsion destabilizes. Consequently, FTIR and conductimetry are two complementary techniques. Conductimetry is a useful technique to predict emulsion destabilization while FTIR allows the measurement of chemical modifications and helps to understand the chemical mechanisms which occur during the oxidation.

Keywords: Emulsion; Aging; Oxidation; FTIR; Deconvolution; Conductivity

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1. Introduction

"Oil in water" (O/W) or "water in oil" (W/O) emulsions, which represent the majority of cosmetic and pharmaceutical creams, evolve with time. They

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are thermodynamically unstable, usually splitting into two distinct phases. This instability could be manifested at different time rates and through a variety of physicochemical destabilizing processes, for example, creaming (or sedimentation), flocculation, coalescence or phase inversion (Florence and Rieg, 1983; Borwankar et al., 1992; Dickinson, 1992; Hiemenz and Rajagopalan, 1997).

From a commercial viewpoint, it is important that new products be marketed as quickly as possible. However, such products should have a storage stability of several months at ambient temperature and under widely varying external influences. Nevertheless, the shelf life assessment of O/W or W/O emulsions remains one of the most time consuming and difficult issues for industrial scientists. The final objective is to save time by predicting whether the emulsion is unstable or not before it breaks and separates into two layers visible by naked eye.

For that reason cream stability studies are based on instability acceleration techniques (centrifugation, heat exposure with storage temperatures ranging from 0 °C to 60 °C). The comparison of accelerated tests achieved by different teams (Sagon, 1983) display diverging experimental procedures concerning storage duration and temperature for tests. Even the AFNOR (T 73-409) standard does not provide much information except that storage should be performed at $23 \pm 2\,^{\circ}\mathrm{C}$ and that samples should be exposed to a range of temperatures between 0 °C and 40 °C for several weeks and compared to samples exposed to ambient temperature.

We studied the aging of five O/W emulsions having as variables the oil type as well as the addition of NaCl. All studied emulsion where stored for a period of time of 12 months at different temperatures which are 0 °C, 25 °C (ambient room temperature), 40 °C and 50 °C. Thus, we were able to study the effect of variables on the stability of emulsions during their storage at different temperatures. A new method was used in this study: Fourier Transform Infrared (FTIR) spectroscopy. FTIR allows a qualitative and semi-quantitative analysis of the chemical composition of emulsions. This method makes it possible to find out the functional and structural groups which account for chemical and physical aging without destroying internal equilibrium of the emulsion. Studies of thermal degradation by FTIR have been performed on oils (Moya Moreno et al., 1999; Guillén and Cabo, 2000) or road bitumen (Lamontagne et al., 2001) but no study deals with the assessment of stability and thermal aging of emulsions by FTIR. In fact, FTIR is used only to follow the degradation of the raw materials (Barreiro-Iglesias et al., 2002; Sliwinski et al., 2003) or to measure the hydration of the cream on the skin (Gloor et al., 1981). Actually, many methods are applied to evaluate destabilization processes, but none is actually recognized (Curt, 1994). However, to complete our study and compare results, emulsions are also analyzed by different classical methods (viscosity, pH, texture analysis, etc.) as well as conductivity which is considered as the most sensitive technique to physical alterations (Delonca and Passet, 1973; Pearce and Kinsella, 1978; Kato et al., 1985; Latreille and Paquin, 1990).

Thus, the first aim of this paper is to determine by FTIR the structural modifications in the emulsion during aging. The second goal is to compare the results obtained by the different analytical techniques at different storage temperatures in order to determine a method to predict emulsion's stability.

2. Materials and methods

2.1. Materials

The following substances were used for the preparation of emulsions:

Oils: sweet almond oil (COOPER, France), apricot cores oil (COOPER, France), olive oil (COOPER, France);
Humectant: glycerine (glycerol, COOPER, France);
Emulsifier: Simulsol 165 (glyceryl stearate, SEPPIC, France), Montanov 68 (cetearyl alcohol and cetearyl glucoside, SEPPIC, France);
Thickener: Carbopol® 940 (carboxyvinylic polymer C940, BF GOODRICH);
Preservative: Sepicide CI (imidazolidinyl urea, SEPPIC, France); methylparaben (methyl-parahydroxybenzoate, COOPER, France), propylparaben (propyl-parahydroxybenzoate, COOPER, France).

Demineralized water was used to prepare the emulsions.

Table 1
Composition of O/W emulsions

	C1	C2	E1	E2	E3
Oil (20.0% v/v)	Sweet almond	Sweet almond	Sweet almond	Olive	Apricot cores
Emulsifier (5.0% w/v)	Simulsol 165	Simulsol 165	Montanov 68	Montanov 68	Montanov 68
Humectant (5.0% v/v)	Glycerine	Glycerine	Glycerine	Glycerine	Glycerine
Gelifiant (0.6% w/v)	Carbopol 940	Carbopol 940 + 0.5% NaCl			
Preservative (0.3% w/v)	Sepicide CI	Sepicide CI	Methylparaben/ propylparaben (50:50)	Methylparaben/ propylparaben (50:50)	Methylparaben/ propylparaben (50:50)
Water Ad. (100.0% v/v)	Demineralized water	Demineralized water	Demineralized water	Demineralized water	Demineralized water

2.2. Emulsions preparation

Five O/W emulsions (C1, C2, E1, E2, E3) with various compositions were prepared according to a direct emulsification process (Roussos, 1983) and the following standardized formula represented in Table 1.

The choice of the emulsions' composition was in a way that enabled us to accomplish two different studies. Firstly we prepared emulsions C1 and C2 where the polymer differ only by NaCl addition in the case of C2 in order to decrease the hydrogen bond of the carbomer network and fluidize the emulsion (Möes, 1972; Martini and Seiller, 1999; BF Goodrich Co., 2002). Hence for this study our objective is to determine the influence of the electrolyte NaCl on the emulsion's stability. The second study concerns the influence of oil type on the emulsion's stability where for emulsions E1, E2 and E3, only the oil type differs, but the proportion of substances are the same for all emulsions (Table 1).

The oil phase (oil, emulsifier) and aqueous phase (water) are heated at 75 °C. For emulsions E1 and E2, the Carbopol® is dispersed gradually into the aqueous phase and neutralized by a 10% sodium hydroxide solution to obtain a pH of around 7.

Both phases (the oil phase was added to the aqueous phase) were mixed together at 75 °C with a Polytron® (homogenizer rotor-stator) at 20,000 rpm for 3 min. Then they are stirred at 300 rpm for 20 min. Preservatives and glycerine are added at 30 °C. Then the emulsion is stirred for 5 min at room temperature in order to homogenize it.

2.3. Stability test

To test the stability of these emulsions and accelerate the aging process, we have stored four batches of each emulsion at:

- low temperature 0 °C,
- ambient temperature 25 °C,
- and high temperature 40 °C and 50 °C for 12 months.

These temperatures are chosen from numerous references, usual tests of cosmetic or pharmaceutical manufacturers (Wilkinson and Moore, 1982; Sagon, 1983; Reng, 1999; Anchisi et al., 2001), AFNOR (T 73-409) and ICH standards (ICH, 1994).

Storage at various temperatures is a well known test method: the primary requirement of this accelerated test is that the temperature stress applied should speed up, but not alter the mechanism of deterioration operating under normal storage conditions (Parkinson and Sherman, 1972). This method is easy to carry out because the breaking of emulsions is accelerated by thermal stress.

All analyses were carried out 24 h after their fabrication, then every other month. Thus, we can assess the evolution of the aging process by these different techniques and then compare them.

2.4. Measurements

2.4.1. FTIR measurements

2.4.1.1. FTIR equipment and technique. Spectra were recorded on a Fourier Transform Infrared Nicolet

Protégé 460 spectrometer coupled with a Nicolet Nic-Plan IR microscope equipped with a motorized support. The data were acquired with the Nicolet software Omnic using Happ-Genzel as an apodization function, 1.8988 cm s^{-1} mirror velocity and a Mertz-type phase correction. Sixty-four scans of symmetrical interferograms were averaged and the spectrum was calculated from 4000 to 650 cm^{-1} at 4 cm^{-1} spectral resolution.

A thin film of emulsion is deposited on one half of the ZnSe window (13 mm diameter, 1 mm thickness) and placed under the microscope. When the sample is deposited, the evaporation in air occurs automatically without drying it. This avoids spectra saturation due to water contained in the emulsion.

Spectra were related to the background collected on the clean other half of the window and spectra are recorded on the deposit. The motorized support enabled the recording of several spectra from the same deposit for different areas.

2.4.1.2. Spectrometric indices calculation and validity.

Since the deposit thickness varies every time an experiment is performed, the intensity of different spectra for the same sample changes. Thus, the spectra should be normalized in order to be compared.

The evolution at each emulsion was followed by spectrometric indices. Ratios between band area values, instead of band absolute absorbance values, were used in order to take into account experimental variations and also the band broadening corresponding to the presence of new vibrations.

The band area ratios allow the calculation of several functional and structural indices (Guillén and Cabo, 2000; Lamontagne et al., 2001; Permanyer et al., 2002). The band areas are measured from valley to valley (Pieri et al., 1996). Only bands that are most sensitive to oxidation (Dubois et al., 1996; Lazzari and Chiantore, 1999) have been taken into account and indices most likely to be altered are described:

Unsaturation index (related to the absorption band $\nu_{\mathrm{C=CH}}$ at 3006 cm^{-1}):

$$\frac{A_{3006}}{A_{3006} + A_{2921} + A_{2851}}$$

Carbonyl index (related to the absorption band $\nu_{\mathrm{C=O}}$ at 1746 cm^{-1}):

$$\frac{A_{1746}}{\Sigma A_i}$$

where ΣA_i represents the sum of the area between 1800 and 650 cm^{-1}.

To define the repeatability of measurements, 10 spectra were recorded for each sample (two deposits and five spectra of each deposit). An estimation of the index's variability has been established and relative errors and standard deviations of all indices have been specified.

The statistical tests are given by:

- Standard deviation, $\mathrm{Sr} = \sqrt{(\sum_i (X_i - \mathrm{mean})^2/(n-1))}$ (n is the number of tests),
- Standard error, $\mathrm{Se} = \mathrm{Sr/mean} \times 100$,
- Repeatability $= \sqrt{2} \times t \times \mathrm{Sr}$ (t is the Student's value test).

The results reported in the tables and figures are an average of these 10 spectra with a standard error that does not exceed 5%.

2.4.2. Conductivity measurements

The conductivity of each emulsion was measured using a conductivity meter (Hanna, model HI 93 3000) at 25 °C. All conductivity measurements were realized at three different levels of the emulsion: at the surface, in the middle and at the bottom of the sample. Modifications of conductivity value allow the detection of creaming, sedimentation or phase inversion (Seiller and Martini, 1999).

According to many authors (Delonca and Passet, 1973; Pearce and Kinsella, 1978; Kato et al., 1985; Latreille and Paquin, 1990), conductimetry is often used to determine the nature of an emulsion and to control its stability during time. Actually, this method is sensitive to small changes in the emulsion's structure.

2.4.3. Classical characterizations

pH measurements were carried out with a pH meter (Hanna, model 8521). This parameter was used to detect the formation of acid species during storage.

The texture analysis was performed with a Texture analyzer (type: TA-XT2i, Haake) in compression-traction mode. The following parameters are calculated (Fig. 1) (Friedman et al., 1963; Szczesniak, 1963; Piccerelle et al., 2002):

- parameters related to hardness, $F_{\max}$ (positive peak) and S+ (area under the positive curve);

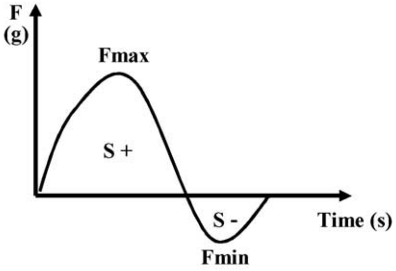

Fig. 1. Curve type of analysis texture.

- parameters related to adhesiveness, F_{min} (negative peak) and S− (area under the negative curve).

Viscosity measurements were carried out with a viscosimeter VT500 (Haake®) with imposed shear rate. This technique determines the apparent viscosity (η_a) of the emulsion at shear rate value of 200 s^{-1} (Eouani, 2001). At this shear rate, we try to reproduce the spreading of the cream on the skin.

All these measurements are made at room temperature (samples were taken out of the incubator or refrigerator 2 h before analysis). The results, given in the tables and used to compute variations, are an average of three measurements.

3. Results

3.1. Macroscopic observations

Emulsions C1 and C2 are stable during the 12 months of storage for all temperatures studied.

Concerning emulsions E1, E2 and E3, a destabilization is observed during the aging only for samples stored at 50 °C and 40 °C for only E2 and E3:

- destabilization of the emulsion E1 after 10 months at 50 °C;
- destabilization of the emulsion E2 after 4 months at 50 °C and after 8 months at 40 °C;
- creaming of the emulsion E3 after 2 months at 50 °C and after 6 months at 40 °C.

3.2. FTIR analysis

The infrared band assignments, determined by reference to previous works (Colthup et al., 1964; Lazzari and Chiantore, 1999; Guillén and Cabo, 2000), are given in Fig. 2 for emulsion E1 for example: they are the same for all studied emulsions and correspond principally with the functions of oil which the emulsion is made of.

Spectral changes take place during aging:

- decreasing of the unsaturation band $\nu_{\mathrm{C{=}CH}}$ at 3006 cm^{-1};
- increasing and progressive broadening of the carbonyl absorption band $\nu_{\mathrm{C{=}O}}$ at 1746 cm^{-1} (visible in Fig. 3);
- almost complete disappearance of bands between 1130 and 800 cm^{-1} which are attributed to glycerine (visible in Fig. 3).

Structural modifications, as visible in Fig. 3 for emulsion E3 at 50 °C, are detected by FTIR spectroscopy only for samples stored at 40 °C and 50 °C. Indeed, no evolution was measured for emulsions stored at 0 °C and 25 °C during the whole experiment as revealed in Fig. 4 for emulsion E3 (presumed unstable). This one describes the evolution of the carbonyl index (related to $\nu_{\mathrm{C{=}O}}$ band) versus time for different storage temperatures. So all emulsions were stable at 0 °C and 25 °C during 12 months. The same structural modifications were observed for emulsion E1 and E2 at 50 °C, but these modifications appeared earlier in emulsion E3 as it destabilizes first.

Modifications of unsaturation and carbonyl indices during the storage at 50 °C are summarized in Table 2. For all emulsions, a decrease of the unsaturation index (that corresponds to a decrease in the unsaturated chains) is measured except for emulsion E3 (no significant variation have been observed). Concerning emulsion E2, even though the data in Table 2 do not show a variation between T_0 and $T_{12\mathrm{months}}$, we can observe in Fig. 5 a decrease of this index through a period of 6 months. Then the unsaturation index increases and afterwards it stabilizes.

Concerning the carbonyl index, the increase is more important for the most unstable emulsions, that is to say E2 and E3. For emulsions C1 and C2 the carbonyl index variations are very faint (almost negligible for C1), thus those two emulsions are almost stable according to this index.

Moreover for the emulsions which are destabilized (E1, E2 and E3), a progressive decrease of bands

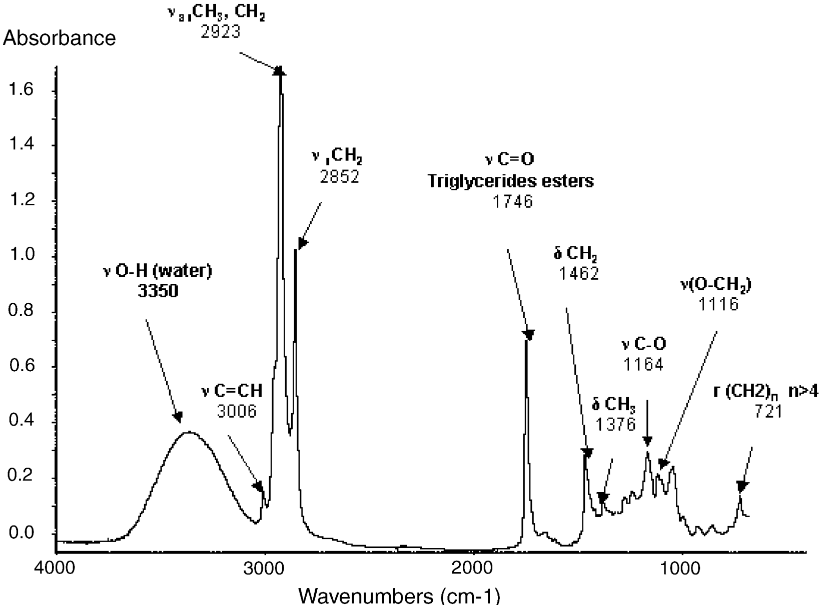

Fig. 2. FTIR spectrum of emulsion type between 4000 and 650 cm^{-1} (resolution of 4 cm^{-1}, 64 scans).

between 1130 and 800 cm^{-1} is observed at the moment of their destabilization. They decrease until complete disappearance (Fig. 3). These bands are attributed to glycerine after a comparison with all excipients (oil, Montanov, glycerine, etc.).

3.3. *Conductivity*

Although the conductimetry is considered as a simple technique, it can be used to detect certain physical modifications in the emulsions.

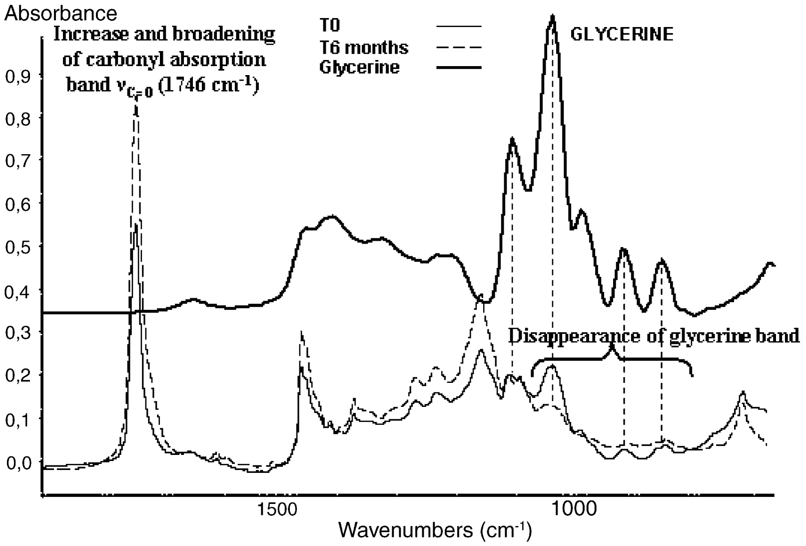

Fig. 3. FTIR spectra of emulsion E3 before and after a thermal stress during 6 months at 50 °C.

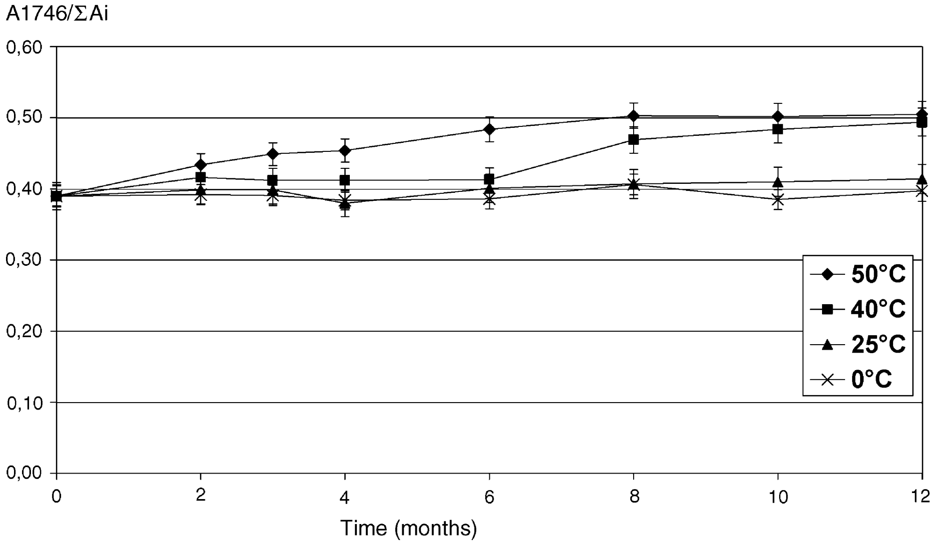

Fig. 4. Evolution of carbonyl index (related to $\nu_{C=O}$) of emulsion E3 vs. time for different storage temperatures.

Table 2
Variation indices (%) during a storage of 12 months at 50 °C

	Indices related to bands		Stability (visual observations)
	$\nu_{C=CH}$ (3006 cm^{-1})	$\nu_{C=O}$ (1746 cm^{-1})	
C1	−42.3	+7.2	Stable
C2	−31.0	+4.2	Stable
E1	−27.8	+14.9	Unstable
E2	+1.4	+32.2	Unstable
E3	+1.0	+29.5	Unstable

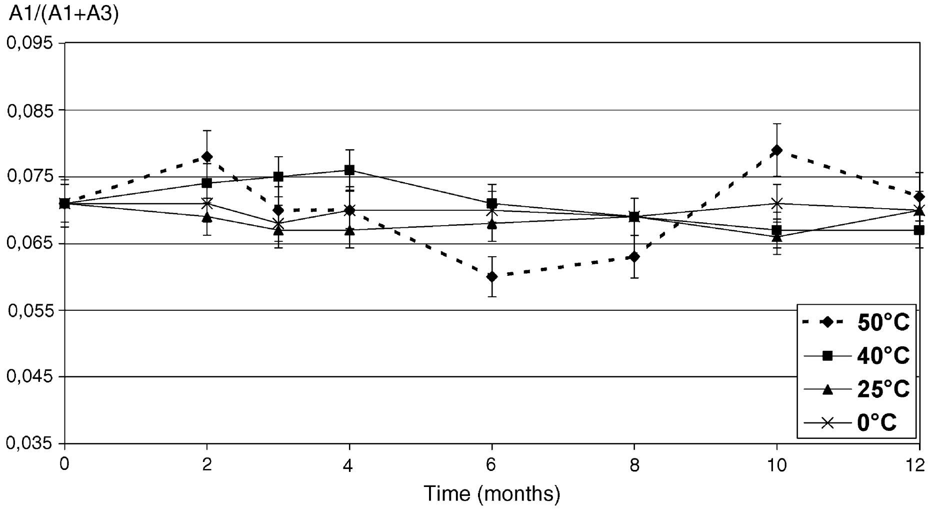

Fig. 5. Evolution of unsaturated index (related to $\nu_{C=C}$) of emulsion E2 vs. time for different storage temperatures.

At first, the evolution of medium conductivity versus time and for various storage temperatures have been compared (Fig. 6). During 12-month storage, the results (Fig. 6) show an increase of the medium conductivity for all emulsions mainly for high temperatures (40 °C and 50 °C). The higher the storage temperature is, the more the conductivity increases. However, at 0 °C the conductivity of all emulsions is stable. Thus,

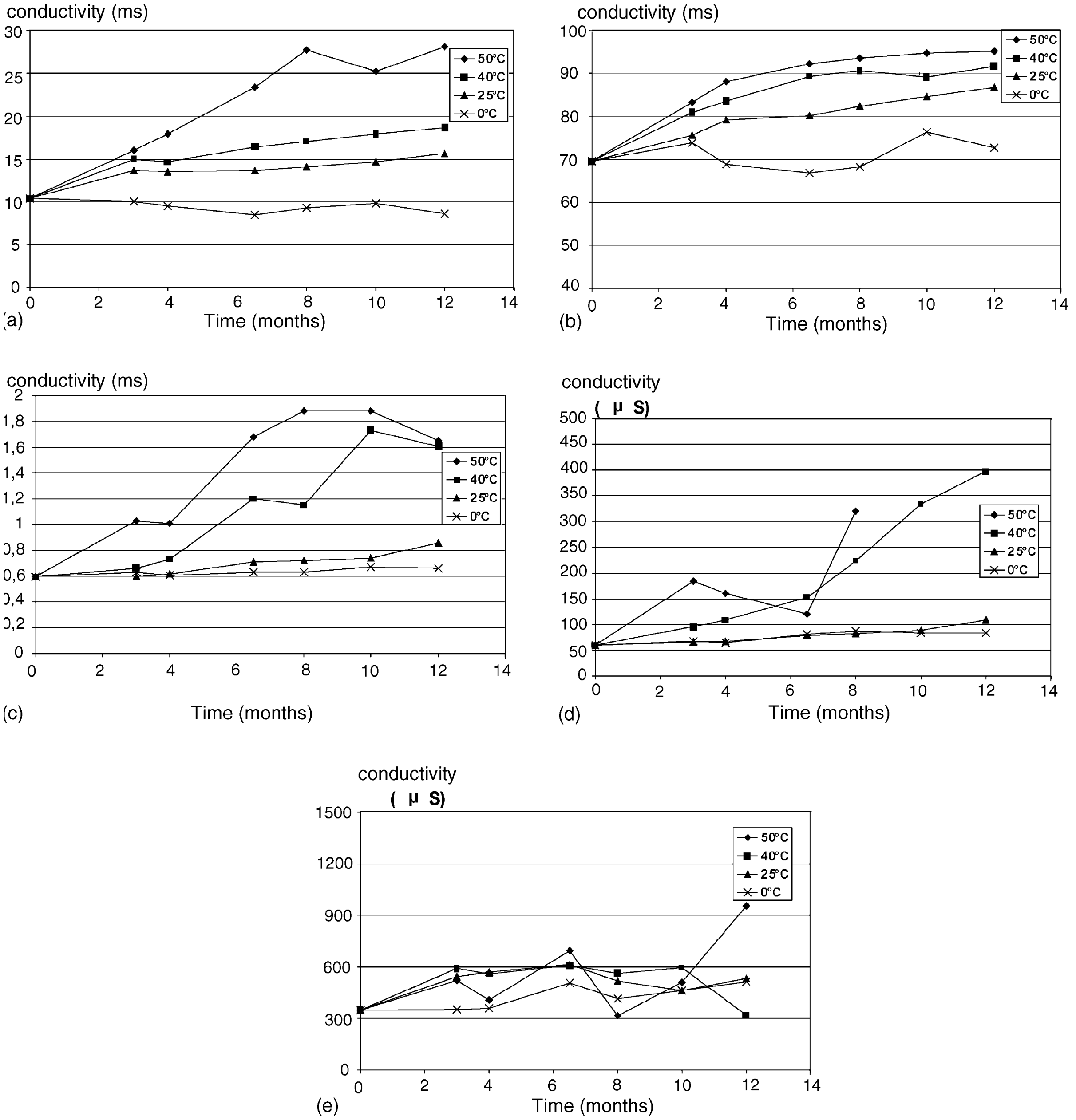

Fig. 6. Medium conductivity evolution of each emulsion vs. time for different storage temperatures. (a) Emulsion C1; (b) emulsion C2; (c) emulsion E1; (d) emulsion E2; (e) emulsion E3.

Table 3
Comparison of accelerated aging at 40 °C and 50 °C with an aging of 12 months at 25 °C based on conductivity values

	25 °C (reference)	40 °C	50 °C
C1	12 months	5 months	3 months
C2	12 months	5 months	3.5 months
E1	12 months	4.5 months	Less than 2 months
E2	12 months	4 months	1 month
E3	12 months	2 months	No correspondence (destabilization)

emulsions are stable at 0 °C. Fig. 6 shows the increased rate, which differs with the emulsion type and its stability. In fact, if we have chosen as reference the aging of 12 months duration at 25 °C, it would be possible to compare this reference with times obtained by an aging at 40 °C and 50 °C.

According to the results in Table 3, it seems that each type of emulsion has its own kinetics of destabilization. Hence, it is not possible to establish a general relationship between the aging temperatures used.

Secondly, the three conductivity measurements (surface, middle and bottom) for the same storage temperature (50 °C) have been compared. Fig. 7 shows the conductivity evolution of all emulsions stored at 50 °C during aging. For the three measurements, an increase of the conductivity is detected when the emulsion ages. So after few months, for the emulsions E2 and E3 which destabilize rapidly (Fig. 7d and e), a decrease of the conductivity in surface is observed. This decrease in surface is followed few months later by an increase of the conductivity in the bottom of the emulsion.

In addition the conductivity measurements of emulsions C1 and C2 (Fig. 7a and b), show a higher stability of C2 than that of C1. In fact, the conductivity of C1 increases with time while that of C2 varies insignificantly. Similarly, the results of emulsions E1, E2, E3 (Fig. 7c–e) confirm the greatest stability of E1 in comparison with E2 and E3.

3.4. Classical methods

The results are obtained by different techniques: emulsions with the weakest modifications are the most stable at a macroscopic scale.

Table 4 summarizes results obtained by all techniques and compares evolutions of emulsions during an aging of 6 months at 40 °C (except for FTIR because at 40 °C as the modifications observed before 6 months is insignificant). In fact, viscosity and texture measures can not be effectuated except on emulsions that are homogenous, that is to say not destabilized. At 50 °C, it is impossible to compare evolutions because some emulsions are already destabilized (E2 destabilizes at 4 months and E3 destabilizes at 2 months). Similarly at 40 °C, E2 and E3 destabilize after 6 months and thus we were not able to undergo texture and viscosity measurements after this time duration. That is why comparisons could not be established except over a duration of 6 months. For all emulsions stored at 40 °C a decrease of pH, viscosity and texture parameters (hardness and adhesiveness) are measured during the aging process.

4. Discussion

4.1. FTIR analysis

Modifications of unsaturation and carbonyl indices may be explained by the oxidation of triglycerides (98% of the oil composition). This oxidation induces the formation of hydroperoxides (Wolff, 1967; Karleskind, 1992). The decomposition of these unstable hydroperoxides can be achieved through three main processes:

- Volatile species formation such as aldehydes, alcohol acids and aldehyde acids with shorter chain lengths than the hydroperoxide (spontaneous decomposition by scission).
- Non-volatile species formation with degradation leading to the same chain length as the initial hydroperoxide (non-scission decomposition). They can involve either oxygenated species formation (aldehydic acid, cetonic acid, etc.), or non-oxygenated species formation (the same structure of the initial fatty acid with a double bond additional).
- Polymerization species formation with high molecular weight ($T > 80\,^\circ$C).

At the temperature at which the experiment was carried out, the hydroperoxides can not evolve in polymers but the first two processes are likely to happen.

This may explain that no decrease of unsaturated chains is measured for the emulsion E3: the formation

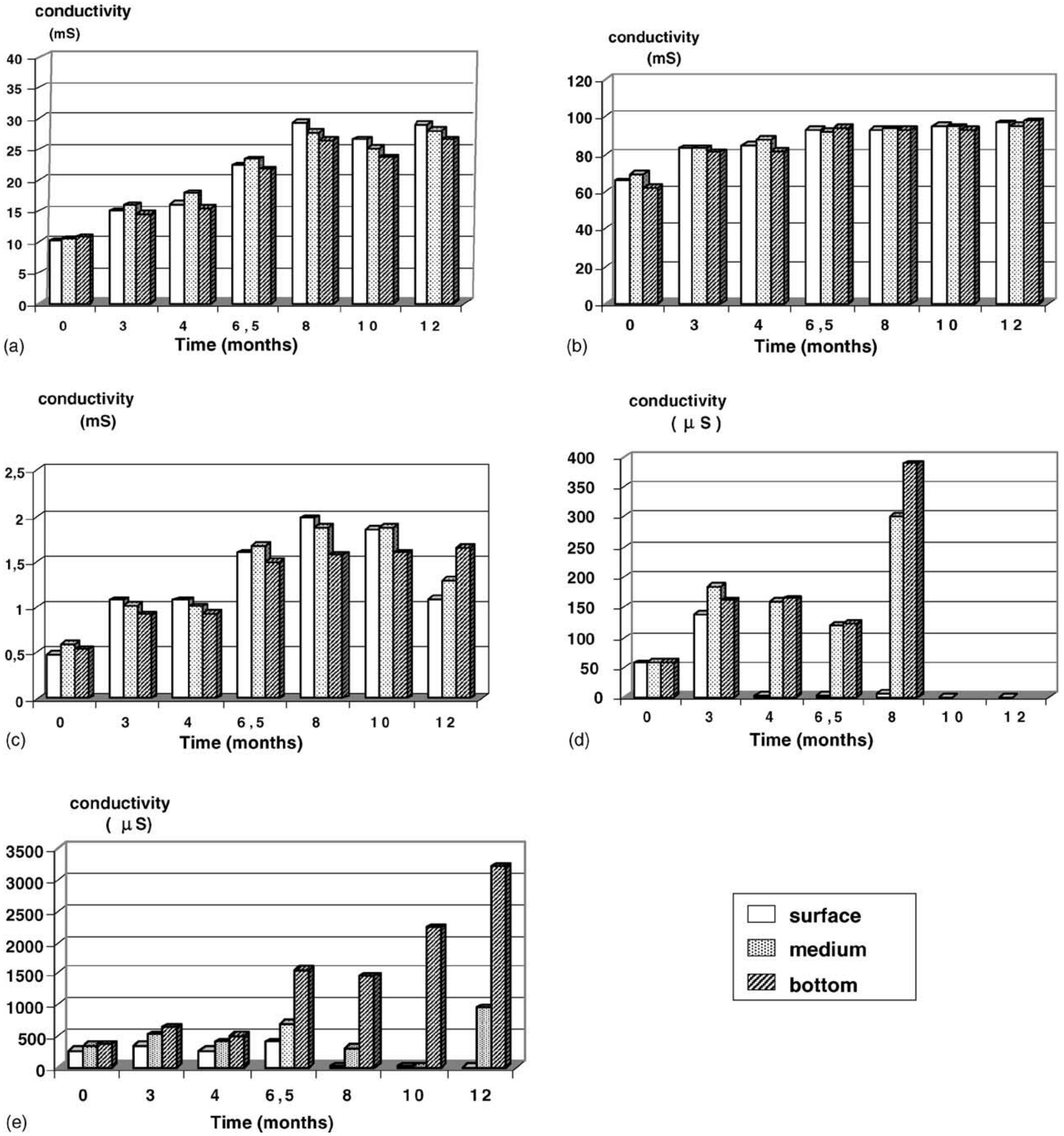

Fig. 7. Evolution of the emulsions' conductivity stored at 50 °C vs. time at three different levels: surface, medium, bottom. (a) Emulsion C1; (b) emulsion C2; (c) emulsion E1; (d) emulsion E2; (e) emulsion E3.

Table 4
Variations of the parameters measuring the stability of the emulsions after a 6-month storage at 40 °C (expressed as a relative ratio of the initial characteristics of the sample)

	Conductivity	pH	Texture		Viscosity	Stability (observations)
			Hardness	Adhesiveness		
C1	+57.4	−8.4	−25.7	−29.0	−23.3	Stable
C2	+28.3	−15.3	+6.1	−19.5	+0.1	Stable
E1	+100.0	−40.4	−44.8	−51.0	−14.8	Stable
E2	+154.4	−25.3	−1.1	−6.4	−23.4	Destabilization at $T_{4\text{months}}$ 50 °C and $T_{8\text{months}}$ 40 °C
E3	Destabilization	−48.0	−11.5	−26.3	−57.1	Creaming at $T_{2\text{months}}$ 50 °C and $T_{6\text{months}}$ 40 °C

of short chain by degradation (decrease of unsaturated chains) compensates the non-oxygenated species formation (species with an additional double bond). That is why in Table 2, no variations are observed for E3. This could be explained by the fact that emulsion E3 destabilizes too rapidly (after only 2 months at 50 °C) to be able to observe the unsaturation index decrease. We probably observe the compensation of this index by the formation of non-oxygenated species with an additional double bond. While for emulsion E2, that destabilizes later on, we were able to observe the unsaturation index decrease until a period of 6 months at 50 °C, after which the index is stabilized as seen in Fig. 5.

Modifications of the carbonyl index (related to $\nu_{C=O}$ band) after 12 months of aging at 50 °C are summarized in Table 2 for the five emulsions. They correspond either to an increase of the ester carbonyl functional group or an appearance of other oxidation products. Regarding this index, it appears that emulsion E2 and E3 are the most sensitive to aging. By comparison to other emulsions, E2 and E3 differ from E1 only by the oil used. Probably apricot cores oil and olive oil are more able to produce oxidation products than sweet almond oil. This phenomenon could be explained by the free fatty acid composition of these oils. In fact, those two oils (apricot cores and olive oil) are composed of linolenic acid (fatty acid with three double bonds) whilst sweet almond oil does not contain this fatty acid, but other fatty acids with one or two double bonds (oleic and linoleic) (Table 5). The oxidation mechanism and the formation of oxidation products are enhanced by the presence of double bonds (Frankel, 1984; Karleskind, 1992). Hence we can partially explain the difference in stability between emulsions E1, E2 and E3 by the fatty acid composition of their oils.

Emulsion C1 and C2 that are macroscopically stable, their stability can be differentiated by means of the two indices given in Table 2. This table shows that emulsion C2 is more stable than C1 as the variations of the two indices are less important in the case of C2. This study also enables to show variation of the unsaturation index for emulsions that seem to be stable by the naked eye.

To explain the broadening of the carbonyl band, a Fourier Self-Deconvolution (FSD) was applied to reveal overlapping spectral features that can not be resolved by collecting data at a higher resolution setting (Doumenq et al., 1991). The FSD process is controlled by setting the bandwidth and enhancement parameters to optimize the result. Bandwidth is an estimate of the widths of the overlapped bands and enhancement is a measure of the degree to which features are revealed. The deconvolution is applied in this study with a bandwidth at 7.7915 and an enhancement factor at 1.6.

The deconvolution spectra of emulsions E2 and E3 (Fig. 8), after 6-month storage at 50 °C, display the appearance of additional bands at about the ester C=O stretching. According to O’Connor (1956), the increase of three bands observed at 1736, 1728, and 1718 cm^{-1} indicates the formation of saturated aldehydes (1736, 1728 cm^{-1}) and saturated ketones (1718 cm^{-1}). These species probably result from the spontaneous decomposition of hydroperoxides by scission.

Fig. 8 displays also two bands of weak intensity at 1709 and 1701 cm^{-1} after a period of 6 months. To confirm this appearance, the duration of the experiment is carried up to 10 months. Safar et al. (1994) show that these bands correspond to the appearance of free fatty acids. In fact, the esterification of fatty acids causes a shift of the absorption band of the C=O group from 1708 to 1744 cm^{-1}.

Table 5
Fatty acid composition of studied oils (COOPER, France)

Oil	Fatty acids (% w/w)						
	Arachidic	Palmitic	Palmitoleic	Stearic	Oleic	Linoleic	Linolenic
Sweet almond	–	6.9	0.5	2.1	63.9	25.4	–
Olive	0.4	10.5	0.7	3.0	77.8	5.5	0.7
Apricot cores	0.1	5.4	–	1.1	63.2	27.6	0.1

It seems that these two bands correspond with the oleic acid (Safar et al., 1994) appearance which occurs when it separates from triglycerides.

In the deconvoluted spectrum of emulsion E2 (Fig. 8), the same phenomena are observed due to the appearance of the same functions. However, a band at 1724 cm^{-1} appears also during oxidation. According to literature (Riaublanc et al., 2000), this absorption band is attributable to carbonyl groups on saturated chains, which leads us to deduce that the double bonds of triglycerides disappear gradually with the aging of the emulsion (decrease of unsaturation band at 3006 cm^{-1}).

4.2. Conductivity

Generally, when the emulsion is stable, no modifications of the conductivity are observed. This can be observed in Fig. 6 for the emulsion C2 stored at 50 °C or all emulsions stored at 0 °C for example. However, Fig. 7 has clearly showed that the conductivity of stable emulsions at 50 °C (C1 and E1 in Fig. 7a and c for example) increases although destabilization is not observable at a macroscopic scale.

The results of this conductivity study enables to determine general modifications that could be observed even before the destabilization of the emulsion:

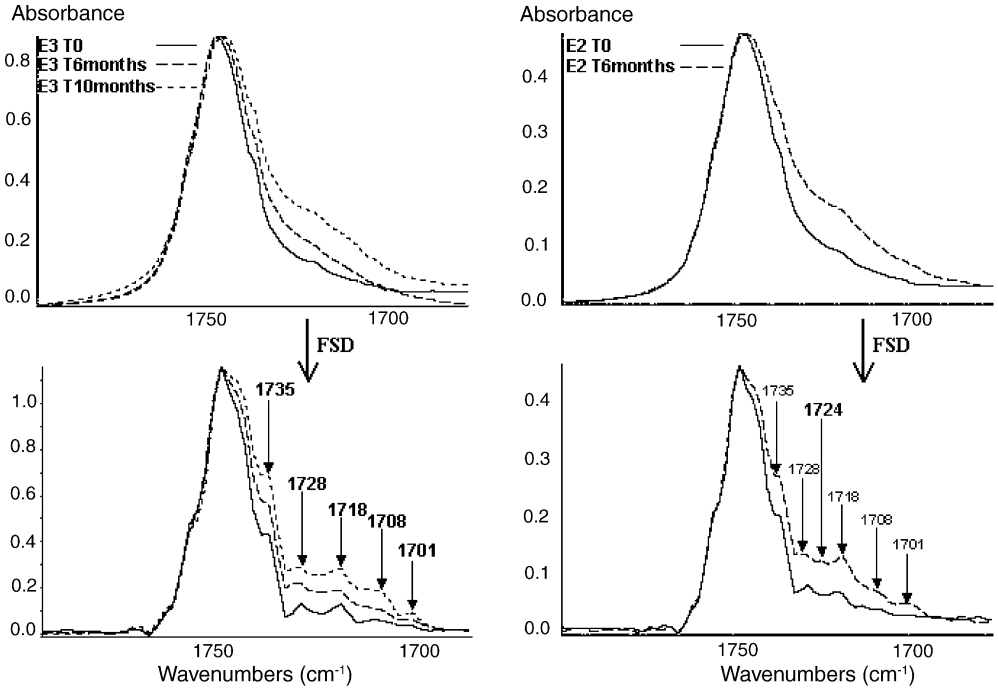

Fig. 8. Original and deconvoluted spectra of E3 and E2 emulsions stored at 50 °C during 6 and 10 months (FSD: Fourier Self-Deconvolution).

a regular increase of the three measurements occurs when the emulsion ages. This increase is followed for the more unstable emulsions (E2 and E3) by:

- a decrease of conductivity in surface (appearance of oil droplets non-conductive);
- an increase of conductivity in the bottom of the emulsion due to the appearance of an aqueous phase at the emulsion's bottom (destabilization).

In fact, the emulsions having the highest conductivities turned out to be the most unstable, where they destabilized a few months after the increase in their conductivity. Thus, an increase of the conductivity could be considered as a sign of the destabilization of the emulsion that takes place sooner or later. The speed of destabilization depends on the emulsion type. Hence, it is not possible to establish a relationship between the kinetics of aging at different temperatures.

4.3. *Classical methods*

Results of classical methods complete information obtained by FTIR and conductivity: a decrease of pH, viscosity and texture parameters (hardness and adhesiveness) are also measured during the aging process.

Only the measurement of apparent viscosity gives a correct predictive assessment on the emulsions' stability. A decrease of viscosity seem to be a sign of destabilization.

To compare with conductivity, viscosity measurements are less sensitive to physical modifications of the emulsion. Conductivity detects variations rapidly in time and at lower temperatures (variations are measured even for batches stored at 25 °C).

Concerning the pH decrease, it can be a consequence of (Hazane et al., 1983):

- either an oxidation of fatty phase with formation of oxidized chains (hydroperoxides);
- or a triglycerides hydrolysis which is manifested by the formation of free fatty acids.

The formation of these free fatty acids confirms the results obtained by FTIR (broadening of the carbonyl absorption band).

Thus, the comparison of the variations measured by the different techniques allows the determination of which emulsions are the most stable. According to the results of Table 4, a stability order is proposed, emulsions are classified from the more stable (C2) to the more unstable (E3) as follows:

$C2 > C1 > E1 > E2 > E3$

For this stability order, the results of texture analysis are not taken into consideration. This method does not appear as a predictive one since the variations obtained by it do not correspond to the stability of the emulsions, where all the other methods confirm this stability order.

As already mentioned in the literature (Möes, 1972; Martini and Seiller, 1999; BF Goodrich Co., 2002), the addition of the electrolyte NaCl modifies the polymer (carbomer) network by decreasing the hydrogen bonds and increasing the fluidity of the emulsion. So the addition of the electrolyte NaCl to the emulsion C2 in the formulation seems to have an effect on the emulsion's stability. For the emulsion E1, E2 and E3 which differ only by their oil composition, we can confirm that the oil nature has an influence on the stability of emulsions of this type. Apricot cores oil and olive oil give emulsions that are more unstable than that obtained by sweet almond oil. This is most certainly due to a more important quantity of triple bonds (linolenic acid) in the composition of these two oils for emulsions E2 and E3.

5. Conclusion

Given these results, FTIR is the only technique which characterizes chemical functions of emulsions as well as their evolutions (increase, decrease or disappearing) during a thermal aging. The unsaturation and carbonyl indices are the most representative of the emulsion's oxidation in this study and can be used for any other emulsions.

For emulsions that are the most physically unstable, a decrease in the unsaturation index (related to the $\nu_{\mathrm{C=CH}}$ band at 3006 cm^{-1}) and an increase in the carbonyl index (related to $\nu_{\mathrm{C=O}}$ band at 1746 cm^{-1}) are measured. Through deconvolution, the increase and the broadening of the carbonyl band $\nu_{\mathrm{C=O}}$ (at 1746 cm^{-1}) are attributed to the formation of aldehydes and ketones. The deconvolution allows also displays the formation of free fatty acids in the emulsion which are characterized with bands at 1709 and 1701 cm^{-1}. Thus, an hydrolysis of the emulsion probably induces a release of free fatty acids.

The main interest of this method is to allow the understanding of the chemical mechanisms which occur during the oxidation. Nevertheless, it does not really allow the prediction of the aging process since at 40 °C few alterations are measured unlike other techniques.

Conductimetry seems to be the most sensitive technique to assess the physical alterations during emulsion's aging and to predict emulsion's stability.

For O/W emulsion, conductivity, which is correlated to the state of dispersion of the emulsion, increases progressively several months before the phases split.

Moreover, conductimetry is a fast and easy-to-use technique which does not require a large amount of product and which does not destroy samples.

However, it seems difficult to evaluate the speed of destabilization from conductivity variations. There is no linear relationship between the conductivity increase and the appearance of the destabilization phenomenon. Therefore, it is only possible to compare the stability of different emulsions.

So it appears that these two techniques are complementary methods: FTIR for the assessment of chemical modifications (characterization of functions which appear or disappear) and conductivity measurements for the assessment of physical modifications of the emulsion (dispersion state) and for a prediction of emulsions' stability.

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