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Linear viscoelastic properties of sucrose ester-stabilized oil-in-water emulsions

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Synopsis

This paper deals with the influence of composition [sucrose ester SE and oil O concentrations] and temperature on the linear viscoelasticity properties of highly concentrated oil-in-water emulsions, using a hydrophilic sucrose palmitate as emulsifier. Different oil-in-water emulsions were prepared using a sucrose palmitate ($SE = 1-5$ wt %) with a hydrophilic–lipophilic balance of 15, sunflower oil ($O = 60-80$ wt %) and water. Oscillatory measurements were carried out in the linear viscoelasticity region. The relaxation time spectra of the emulsions were calculated using regularization techniques and were fitted to an empirical model proposed by Madiedo (1996). The results obtained are explained on the basis of the relationship among linear viscoelasticity properties, droplet size distribution, and characteristics of the continuous phase. Thus, an increase in sucrose palmitate concentration produces higher values of the linear viscoelasticity functions and a broader plateau region in the relaxation time spectrum, which suggests a certain enhancement of the elastic network. © *1998 The Society of Rheology.* [S0148-6055(98)01206-1]

I. INTRODUCTION

Oil-in-water (o/w) emulsions are manufactured by dispersing the oil phase into the aqueous continuous phase in the form of small droplets (most commercial emulsions have droplet sizes in the range of 0.1–10 μm) [Walstra (1983)]. In order to obtain stable emulsions with suitable droplet size distributions (DSD), the emulsification process requires a considerable amount of mechanical energy (in the order of 1–100 MJ/m^3 depending on emulsification machine) [Walstra (1993)]. It is worth pointing out that the emulsification process is a highly complex unit operation which depends on many variables (temperature, residence time, agitation speed, etc.) [Gallegos and Franco (1998)]. It is involved in many different industries to produce a wide variety of emulsions (foodstuffs, cosmetics, pharmaceuticals, petrochemicals, agrochemicals, etc.) [Walker (1984); Yuki *et al.* (1990); Desai, 1990], which may be formulated to cover a wide range of disperse phase volume fractions ϕ from dilute to highly concentrated emulsions, with ϕ approaching a value of 1.

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Stability is a primary requirement for the commercial application of emulsions. However, emulsions are thermodynamically unstable because of their large interfacial area and droplets tend to aggregate spontaneously. An emulsion is considered stable when the number, size distribution, and arrangement of droplets do not undergo any discernible change over the storage time scale.

An emulsifier is typically added to improve both the emulsification process and the emulsification stability. The emulsifier molecules adsorb at the oil–water interface and reduce the interfacial tension, thereby favoring emulsification and forming a protective barrier around the oil droplets [Dickinson (1994)]. This increases interdroplet interactions and provides enhanced stability against coalescence. The role of these interactions is fundamental in highly concentrated emulsions, in which very close packing of droplets is found and the continuous phase consists of a thin film separating adjacent droplets. This produces highly viscoelastic responses [Otsubo and Prud'homme (1994)] and may lead to the development of an extensive flocculation of droplets to form a weak gel-like particulate network depending on the nature and concentration of the emulsifier [Dickinson (1989)]. The extensive flocculation process provides enhanced stability to the emulsion since the creaming rate is significantly decreased [Franco *et al.* (1995a,b, 1997)].

The viscoelastic properties of the emulsions depend on the state of flocculation. Unflocculated or weakly flocculated emulsions show a crossover point between G' and G'', which is related to a characteristic relaxation time for the onset of the terminal or flow region. This relaxation time increases sharply with ϕ because of the stronger interactions among droplets [Tadros (1993)]. However, emulsions using a mixture of sucrose ester (SE) and egg yolk proteins as emulsifiers usually show extensive flocculation, depending on the energy input and temperature during the emulsification process, which has been previously related to the development of a plateau region in the relaxation time spectrum [Franco *et al.* (1995b, 1997)]. Other highly concentrated emulsions stabilized only by proteins also show gel-like responses (G' is much higher than G'', both are almost parallel) with a wide plateau region [Guerrero and Ball (1994); Gallegos *et al.* (1992)].

In a previous paper, the ability of a highly hydrophilic (hydrophilic–lipophilic balance, HLB = 15) sucrose palmitate, used as the only emulsifier, to form highly stable emulsions was established [Partal *et al.* (1994)]. The flow behavior and droplet size of o/w emulsions stabilized by this sucrose palmitate has also been studied [Partal *et al.* (1997)]. An evolution towards smaller sizes and narrower distributions was observed as sucrose palmitate and oil concentrations were raised, which led to an increase in the emulsion viscosity.

The objective of the present paper is to study the influence of composition (sucrose palmitate and oil concentrations) and temperature on the linear viscoelasticity properties of highly concentrated o/w emulsions using a hydrophilic sucrose palmitate as an emulsifier. The relationship among the linear viscoelasticity functions, droplet size distribution, and stability is also analyzed.

II. EXPERIMENT

Different oil-in-water emulsions were prepared using a Ryoto sucrose palmitate (P-1570, HLB = 15) from the Mitsubishi–Kasei Food Corporation (Tokyo, Japan). This emulsifier was used as received. Sunflower oil was purchased in a local store. Oil-in-water emulsions were prepared using an Ultra-Turrax T-50 homogeneizer. Sunflower oil was added to a solution of the emulsifier in distilled water at 55 °C, and mixed at a speed of 5000 rpm for 3.5 min. The sucrose palmitate concentration (SE) ranged from 1% to

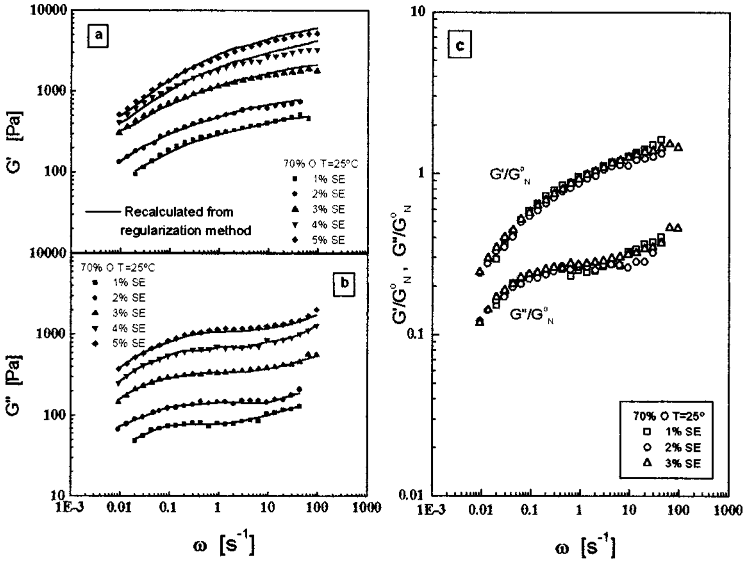

FIG. 1. Influence of sucrose palmitate [(a),(b)] on the storage and loss moduli; and normalized linear viscoelasticity functions for sucrose palmitate-stabilized emulsions (c) ($T = 25\,°\mathrm{C}$).

5% (wt) and the oil content (O) from 60% to 80% (wt) ($\phi = 0.59-0.77$). Emulsions were stored at 5 °C.

Oscillatory shear measurements were performed in a Haake RS100 RheoStress rheometer, using a cone-and-plate sensor system C35/4 (4°, 35 mm). The stress range for linear viscoelasticity was determined through a dynamic stress sweep at a fixed frequency (6.28 rad/s). All samples had the same recent past thermal and rheological history. Rheological tests were carried out in the range of 5–35 °C.

The relaxation time spectrum for each emulsion at each temperature was calculated by using a commercial software program (RHEOSPEC), which is based on regularization techniques.

III. RESULTS AND DISCUSSION

A. Influence of sucrose palmitate concentration

The evolution of the storage and loss moduli with frequency as a function of the sucrose palmitate concentration is shown in Figs. 1(a) and 1(b). Both moduli show a continuous increase with emulsifier concentration. The storage modulus G' is always higher than the loss modulus G'' within the experimental frequency range. Hence, the emulsions present a predominantly elastic response, although a crossover point tends to appear in the low-frequency regime. Moreover, there is a tendency for G' to exhibit a plateau region [Fig. 1(a)]. This zone, at intermediate frequencies, is known as the plateau region and may be related to the formation of an elastic structural network due to interactions among the emulsifier molecules located at the oil–water interface of adjacent droplets [Dickinson (1989); Franco *et al.* (1995b)]. This behavior is typical of highly concentrated emulsions such as commercial or model mayonnaises [Gallegos *et al.* (1992); Guerrero and Ball (1994)] and salad dressings [Muñoz and Sherman (1992); Franco *et al.* (1995b)]. The plateau region has been extensively described in polymer rheology in terms of an entanglement network among polymer chains in which the motion of molecules is constrained by the neighboring molecules [Ferry (1980); Wu (1989)]. When the emulsion is stabilized by proteins [Gallegos *et al.* (1992); Guerrero and Ball (1994)], the three-dimensional network is favored by entanglements among protein segments adsorbed at the oil–water interface. The same behavior was reported when a sucrose stearate was used in combination with egg yolk [Franco *et al.* (1995b)].

Taking into account that the emulsions studied are stabilized exclusively by a low molecular weight surfactant (sucrose palmitate) and have high values of disperse phase volume fraction (oil droplets), the plateau region was attributed to an extensive flocculation process that favors emulsion stability by forming a gel-like particulate network [Dickinson (1989)] due to interdroplet interactions. Similar effects were reported by Ebert *et al.* (1988) for highly concentrated emulsions stabilized by a cetyltrimethylamonium-bromide surfactant.

In the plateau region, the loss tangent passes through a minimum, which has been used to calculate an approximate value of the plateau modulus, G_N^0 [Wu (1989); Arendt *et al.* (1994); Franco *et al.* (1995b)]. The plateau modulus is a viscoelastic parameter, defined as an extrapolation of the entanglement contribution to G' or G'' at high frequency [Baumgaertel *et al.* (1992)]. This parameter may be approximated from the minimum in $\tan\delta$ as follows [Wu (1989)]:

$$G_N^0 = [G']_{\tan\delta \to \text{minimum}}. \tag{1}$$

As a result, the plateau modulus G_N^0 undergoes an exponential increase when sucrose palmitate concentration is raised [Fig. 2(a)], as corresponds to a more structured system.

The evolution of G' and G'', and also of the other viscoelastic functions with frequency (i.e., loss tangent), is rather similar up to 3% sucrose palmitate. This similarity allows one to superpose all the viscoelastic functions (between 1% and 3% sucrose palmitate) by using the plateau modulus as a normalization factor [Fig. 1(c)]. However, the normalization procedure fails at the highest concentrations of the emulsifier (4% and 5%), because an increase in loss tangent was observed from 3% to 5%.

As has been previously reported [Partal *et al.* (1997)], an increase in SE concentration produces a decrease in droplet size and polydispersity, which leads to an increase in the specific interfacial area a [Fig. 2(b)]. Assuming spherical droplets, ‘‘a’’ is related to the Sauter mean diameter as follows:

$$a = 6/d_{sv}, \quad d_{sv} = \frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2}, \tag{2}$$

where n_i is the number of droplets having diameter d_i.

However, there is a critical concentration (3% SE) above which the slope of this increase is lower. To understand this change, the properties of the continuous phase used for the preparation of the emulsions should also be taken into consideration. Thus, the emulsions containing 70% oil and 1%–3% SE were prepared from a continuous phase containing 3%–10% SE, which were isotropic micellar solutions (L_1) at the temperature of emulsification (50 °C), as may be seen in the phase diagram shown in a previous paper [Calahorro *et al.* (1992)]. At concentrations higher than 10% (as corresponds to emulsions containing 4% and 5% SE) the initial continuous phase was always a dilute dispersion of lamellar liquid-crystalline (L_α) portions in an isotropic micellar matrix, at the emulsification temperature (50 °C). Therefore, the above-mentioned critical concentration corresponds to the transition from L_1 micellar solution to the $L_1 + L_\alpha$ dispersion. As a result, a remarkable increase in the low-shear limiting viscosity η_{oc} is observed for the surfactant–water system [Fig. 2(c)]. This increase seems to impair the emulsification process, leading to a lower increase in the interfacial area [Fig. 2(b)].

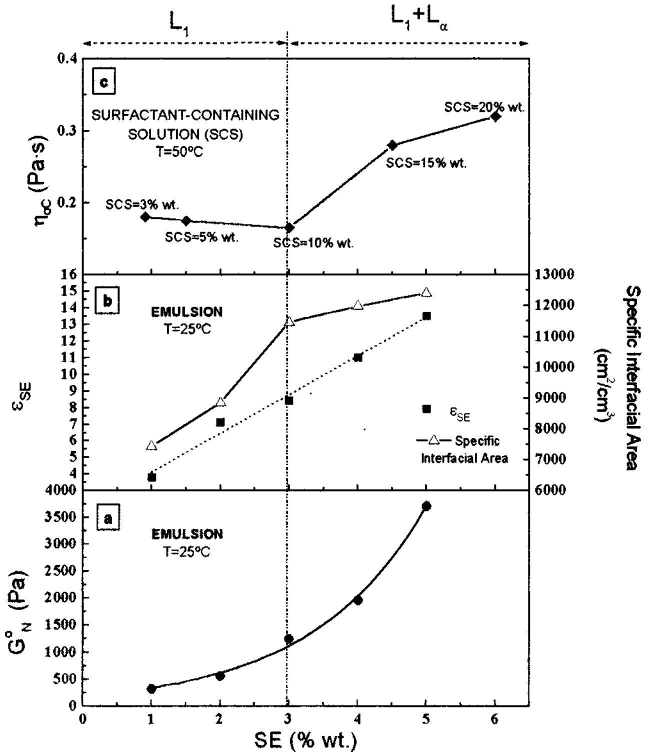

FIG. 2. (a) Influence of sucrose palmitate concentration on the plateau modulus; (b) excess of surfactant over the amount necessary to saturate the interface as a monolayer and specific interfacial area as a function of sucrose palmitate concentration; (c) viscosity of the initial surfactant-containing solution (SCS) at which oil is added (please note that the concentration of this solution is SCS $=$ SE$\times$3.3) at 50 °C.

On the other hand, the excess of surfactant over the amount necessary to saturate the interface as a monolayer (ϵ_{SE}) continuously increases with SE concentration [Fig. 2(b)]. The excess of surfactant has been calculated as follows:

$$\epsilon_{\mathrm{SE}} = \frac{(C\rho/a\phi)}{C_{\mathrm{sat}}} - 1, \tag{3}$$

where C is the sucrose palmitate concentration, ρ is the emulsion density, ''a'' is the specific interfacial area, ϕ is the disperse phase volume fraction (oil droplets), and C_{sat} is the concentration necessary to saturate the interface as a monolayer. Taking into account the surface pressure-area isotherm obtained by Abran *et al.* (1988) for the sucrose palmitate, the C_{sat} value was estimated as 0.365×10^{-6} g/cm^2 [Partal *et al.* (1997)].

Once the emulsification process is over, the continuous phase of these highly concentrated emulsions consists of a very thin film separating adjacent droplets. The consistency of this film, favored by the increase in ϵ_{SE}, as well as the increase in the specific surface area, explain the large values of the viscoelastic functions and the exponential rise in the plateau modulus shown in Fig. 2(a).

Figure 3 shows the relaxation time spectrum of selected emulsions obtained by means of the Tikhonov regularization procedure using the RHEOSPEC software. As may be observed in Fig. 1, the recalculation of the viscoelastic functions from the relaxation time spectrum obtained by the regularization technique (RHEOSPEC software) is very accurate.

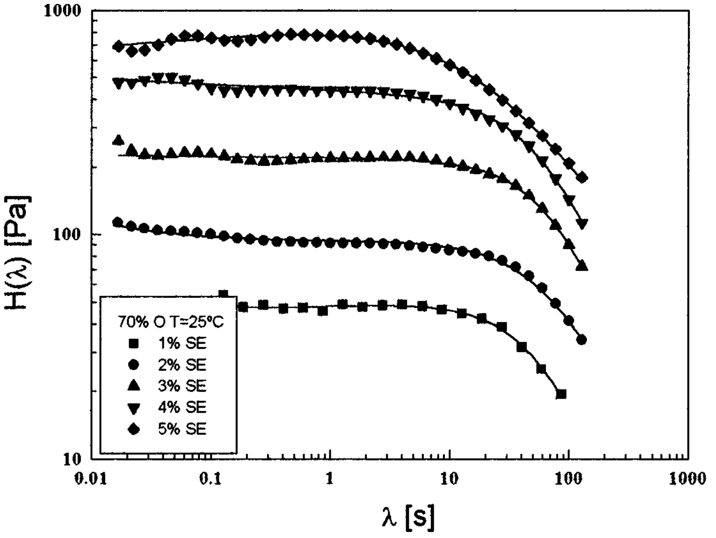

FIG. 3. Influence of sucrose palmitate concentration on the relaxation time spectra for sucrose palmitate-stabilized emulsions ($T = 25\,°\mathrm{C}$).

To express qualitatively the relaxation data, De Rosa and Winter (1994) proposed an empirical model, derived from the Baumgaertel–Schausberger–Winter (BSW) spectrum [Baumgaertel *et al.* (1992)], and the Chambon–Winter (CW) spectrum [Chambon and Winter (1985)]. Although this model was proposed to describe the relaxation process of polymer melts, it has been also used for emulsions as salad dressings [Franco *et al.* (1995b)]. This model requires two functions to describe the transition, plateau, and terminal regions of the relaxation time spectrum. A simple empirical equation, which comprises the three regions of the spectrum, has recently been proposed by Madiedo (1996) and Madiedo and Gallegos (1997):

$$H(\lambda) = \frac{\alpha\lambda^m + \beta\lambda^n}{1+(\lambda/\lambda_t)^p}, \tag{4}$$

where m, n and $(n-p)$ are the slopes of the transition, plateau, and pseudoterminal zones, respectively; and λ_t is a characteristic relaxation time related to the boundary of the plateau region. Since the crossover frequency was not reached for the emulsions studied, λ_t will be considered a fitting parameter in this paper. As may be noted, these parameters are relatively similar to the parameters of the BSW–CW model [Madiedo and Gallegos (1997)]. Parameters α and β have the following expressions:

$$\alpha = \frac{mH_0}{(m-n)\lambda_0^m}, \tag{5}$$

$$\beta = \frac{nH_0}{\lambda_0^n(n-m)}, \tag{6}$$

where λ_0 is a characteristic relaxation time related to the onset of the plateau region and H_0 is the value of the spectrum corresponding to this relaxation time. If the slope of the plateau region is positive, $n > 0$, Eq. (4) predicts a maximum value for $H(\lambda)$ for a relaxation time $\lambda_{\max} = \lambda_t[n/(n-p)]^{1/p}$, which was related by De Rosa and Winter (1994)

TABLE I. Influence of concentration on both the pseudoterminal relaxation time (λ_t) and slope of the plateau region (*n*), for sucrose palmitate-stabilized emulsions.

% SE	% O	*n*	λ_t (s)
1%	70%	0.017	59
2%	70%	−0.006	80
3%	70%	−0.013	84
4%	70%	−0.025	66
5%	70%	0.045	18
3%	60%	0.003	28
3%	65%	−0.035	93
3%	75%	0.004	62
3%	80%	−0.002	144

with the relaxation time at which $H(\lambda)$ equals G_N^0 times *n*. However, this maximum does not always appear. Consequently, the relaxation time spectrum calculated from the regularization method for each emulsion was analyzed according to the Madiedo and Gallegos (1997) model [Eq. (4)].

The relaxation time spectra calculated from the Tikhonov regularization method, for each sucrose palmitate concentration, are shown in Fig. 3. As may be seen, the above-mentioned model satisfactorily describes the relaxation time spectra obtained for these emulsions. The shape of the spectrum is always similar. A plateau region is always clearly observed. Likewise, a region characterized by a trend to reach the terminal zone or flow region may be noted. The increase in emulsifier concentration produces an increase in the relaxation time spectrum higher than one order of magnitude, which is approximately the same increase undergone by G_N^0 and indicates that an enhancement of the elastic network is produced.

However, Table I shows a maximum value in λ_t followed by a decrease, which corresponds to a displacement of the plateau region towards a shorter relaxation time or higher frequency. This displacement has also been found for salad dressing emulsions stabilized by proteins and sucrose ester [Franco *et al.* (1997)]. The slope of the plateau region does not change with SE concentration showing values close to zero. The only exception was the emulsion containing 5% SE, which shows a positive value of *n*, indicative of a higher degree of structure. A significant increase in the stability of these emulsions was also found as SE became higher [Partal *et al.* (1994)].

B. Influence of oil concentration

The evolution of the storage and loss moduli with frequency is similar for all the oil concentrations studied, G' always being higher than G'' [Figs. 4(a) and 4(b)]. Thus, the loss tangent is roughly independent of the oil concentration. As a result, the plateau modulus [which is shown in Fig. 5(a)] was successfully used to normalize both storage and loss moduli as a function of frequency ($a'_\phi \omega$), leading to a master curve for each of them [Fig. 4(c)]. However, some scatter may be observed in G'' at high frequencies [Fig. 4(c)]. An empirical horizontal shift factor, ($a'_\phi = 0.4$) was necessary for the smallest oil concentration because of a frequency displacement of the plateau region as was previously found for salad dressing emulsions [Franco *et al.* (1997)].

Figure 5(a) shows the values of parameter G_N^0 as a function of the disperse phase volume fraction. An increase in this parameter, with a trend to reach an almost constant

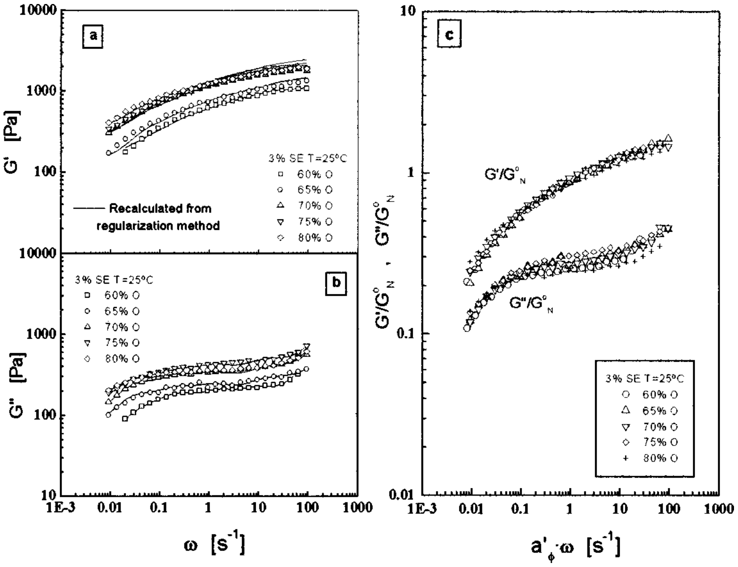

FIG. 4. Influence of oil concentration [(a),(b)] on the storage and loss moduli; and normalized linear viscoelasticity functions for sucrose palmitate-stabilized emulsions (c) ($T = 25\ °C$).

value above 70% ($\phi = 0.68$), was observed. Similarly, the viscoelastic moduli increase with oil concentration but only up to a certain value which depends on frequency. Thus, at low frequencies, the emulsion containing 80% oil has the highest values of G' and G'' [Figs. 4(a) and 4(b)], while at intermediate and high frequencies there are no differences in G' from 70% to 80% and the highest values of G'' correspond to 70% oil. This

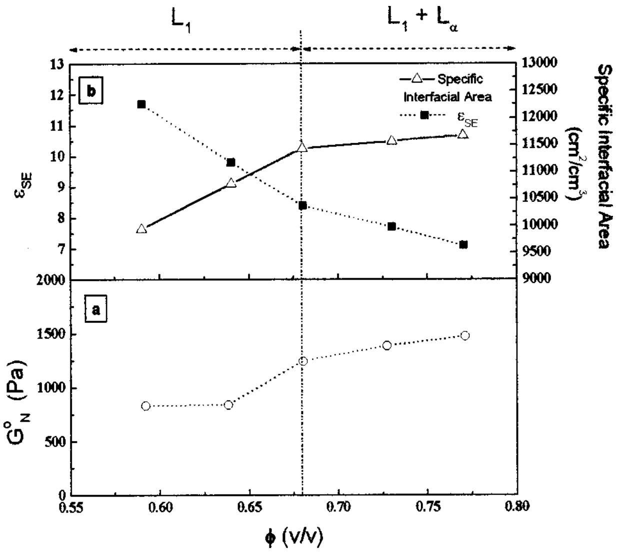

FIG. 5. (a) Influence of disperse phase volume fraction (oil) on the plateau modulus; (b) excess of surfactant over the amount necessary to saturate the interface as a monolayer and specific interfacial area as a function of disperse phase volume fraction.

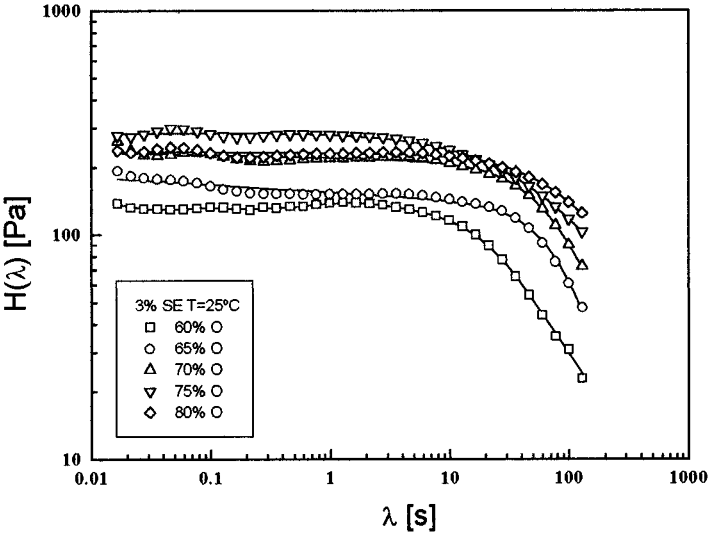

FIG. 6. Influence of oil concentration on the relaxation time spectra for sucrose palmitate-stabilized emulsions ($T = 25\,°\mathrm{C}$).

behavior found at intermediate and high frequencies might be explained in terms of a slight extension of the plateau region, which corresponds to a moderate enhancement of the elastic network.

In order to explain the moderate influence of ϕ on the viscoelasticity functions, the results obtained from the DSD should also be taken into account. Although an increase in specific surface area (smaller droplet size) was observed with increasing oil concentration, the differences were much less pronounced at the highest values of oil content [Fig. 5(b)]. A qualitatively similar evolution was found as SE concentration was raised (note that the initial surfactant–water system used for the emulsification also undergoes a transition from L_1 to $L_1 + L_\alpha$ at 70% oil). However, in this case a continuous decrease in ϵ_{SE} takes place [Fig. 5(b)] leading to a decrease in the consistency of the continuous-phase layer. Both effects contribute to counteracting the trend of the linear viscoelasticity functions to increase with the disperse phase volume fraction.

The relaxation time spectra of these systems are shown in Fig. 6. The plateau region shows a tendency to expand at the maximum oil concentration studied (80% oil), as may be deduced from the values of λ_t (Table I). Moreover, a slight increase in the slope of the plateau region is also produced above 65% oil. Once again, the effect that oil concentration exerts on the relaxation time spectrum is much lower, under the experimental conditions, than the effect produced by SE concentration.

As may be inferred from the stability diagram reported for these emulsions in a previous paper [Partal *et al.* (1994)], an improvement of stability against creaming is detected when oil concentration increases at constant sucrose palmitate concentration. Therefore, the evolution of the DSD and the viscoelastic functions as well as the development of the elastic network, characteristic of the plateau region, yield an improved stability against creaming, as has been reported elsewhere for salad dressing emulsions [Franco *et al.* (1995b)].

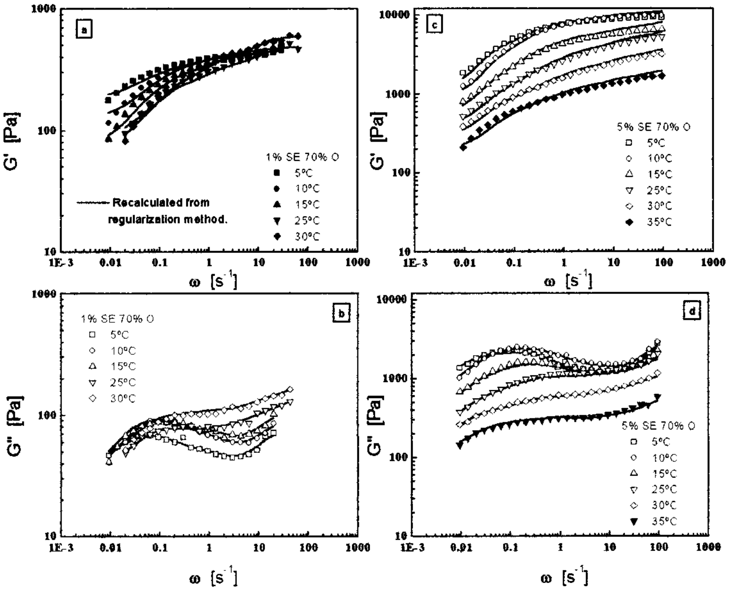

FIG. 7. Influence of temperature on the linear viscoelasticity functions for selected emulsions. (a),(b): 1% SE, 70% oil; (c),(d): 5%, 70% oil.

C. Influence of temperature

Figure 7 shows the evolution of G' and G'' with frequency as a function of temperature for two different emulsions. As may be seen, temperature greatly affects the frequency dependence of both viscoelasticity functions. This thermorheological complexity shown by the emulsions studied makes a time–temperature superposition impossible. The plateau modulus cannot be used as a normalization factor to obtain a unique master curve when temperature is modified.

Moreover, the influence of temperature on G' and G'' depends on the frequency regime and concentration. At low frequencies, a decrease in temperature leads to an increase in both moduli. This effect becomes more pronounced as oil and sucrose palmitate concentrations increase, that is to say when the emulsion becomes highly structured. At intermediate frequency, a decrease in temperature, below 25 °C, always produces a minimum in G'' and a decrease in the slope of G' versus frequency. However, the influence of temperature on G' and G'' values may decrease, and even reverse in the case of G'', at low SE concentration (i.e., 1% SE, 70% oil). As a result, the plateau region progressively vanished as temperature increases. At low temperature, the elastic network is fully developed, which gives rise to a pronounced plateau region in G' (i.e., 5 °C) and an apparent minimum in G'' (5–15 °C). An increase in temperature weakens the elastic network, and therefore, reduces the plateau region. The consistency of the continuous-phase film is favored by the decrease in temperature. As previously reported, the SE containing aqueous systems tends to form gel-like structures at low temperature [Gallegos *et al.* (1996)].

The values of the plateau modulus obtained for these emulsions are plotted versus the absolute temperature in Fig. 8. The influence of temperature on G_N^0 may be described by an Arrhenius-type equation:

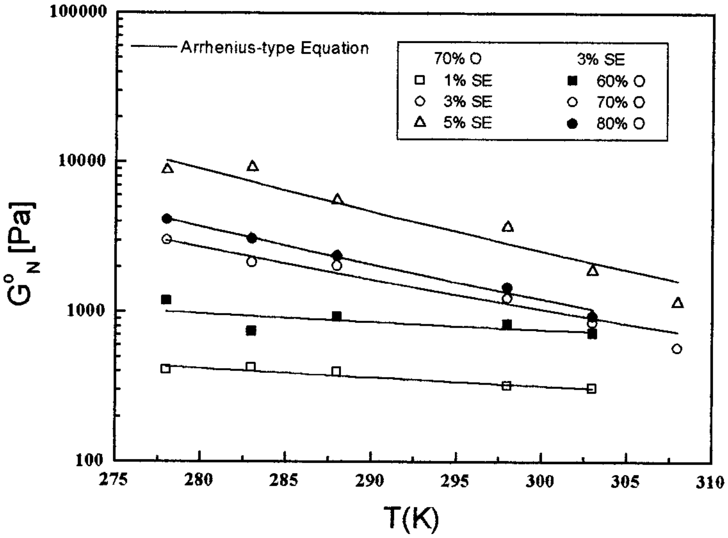

FIG. 8. Influence of temperature on the plateau modulus for selected emulsions.

$$G_N^0 = A \exp\left(\frac{E_a}{RT}\right), \tag{7}$$

where E_a is an activation energy. Figure 8 shows that the influence of temperature on G_N^0 is small for the less-structured emulsions (Table II), which exhibited the larger droplet sizes and wider DSD, as well as the lower values for the viscoelastic functions. On the other hand, those emulsions with the most favorable structural parameters (i.e., small droplet sizes and narrow DSD) also are highly temperature dependent. In general, temperature tends to reduce the difference in the viscoelastic response of the different emulsions.

Figure 9 shows the relaxation time spectra obtained for emulsions containing 3% SE and 70% oil at different temperatures. A very well-pronounced plateau region may be observed at low temperature, which indicates the occurrence of extensive flocculation, and consequently, a fully developed elastic network. An increase in temperature produces a dramatic decrease in the slope of the plateau region which tends to disappear. The same behavior may be observed in Fig. 10(a), in which parameters *n* are plotted versus temperature for different oil and sucrose palmitate concentration. An important reduction in the value of the slope of the plateau region leading to negative values of *n* takes place, regardless of the concentration used. The influence of sucrose palmitate concentration on

TABLE II. Activation energies for emulsions of different concentration.

% SE	% O	$E_a(G_N^0)$ (kJ/mol)
1%	70%	8.67
3%	70%	33.3
5%	70%	43.8
3%	60%	8.48
3%	80%	38.8

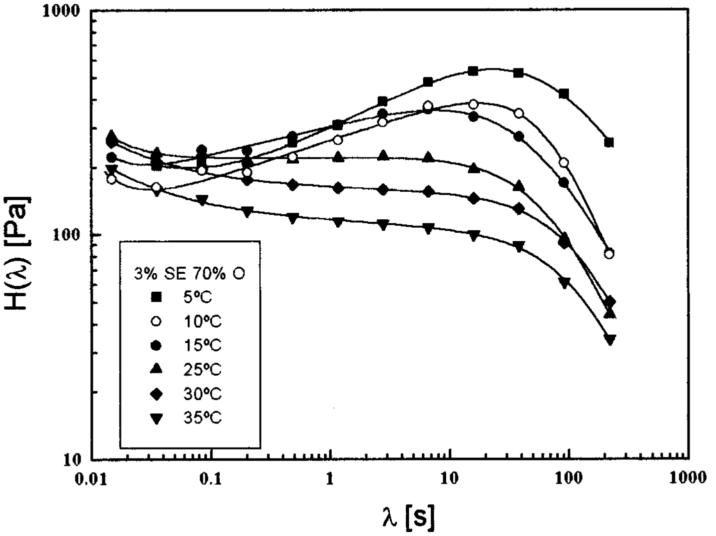

FIG. 9. Influence of temperature on the relaxation time spectrum, for a selected emulsion (3% SE, 70% oil).

the value of *n* seems to be higher at low temperature. However, oil concentration does not generate important differences at the temperatures studied. As may be seen in Fig. 9, $\lambda_{\max}$ decreases with temperature. Moreover, a value of $n \leqslant 0$ makes the maximum value for the spectrum disappear, and therefore, $\lambda_{\max}$ vanishes. The same effect may be deduced from Fig. 10(b), where $H_{\max}$ and nG_N^0 are plotted as a function of temperature. At low temperature, when $n > 0$, the values of $H_{\max}$ and nG_N^0 are rather coincident. These result resemble the predictions of Baumgaertel *et al.* (1990, 1992) for a polymer melt

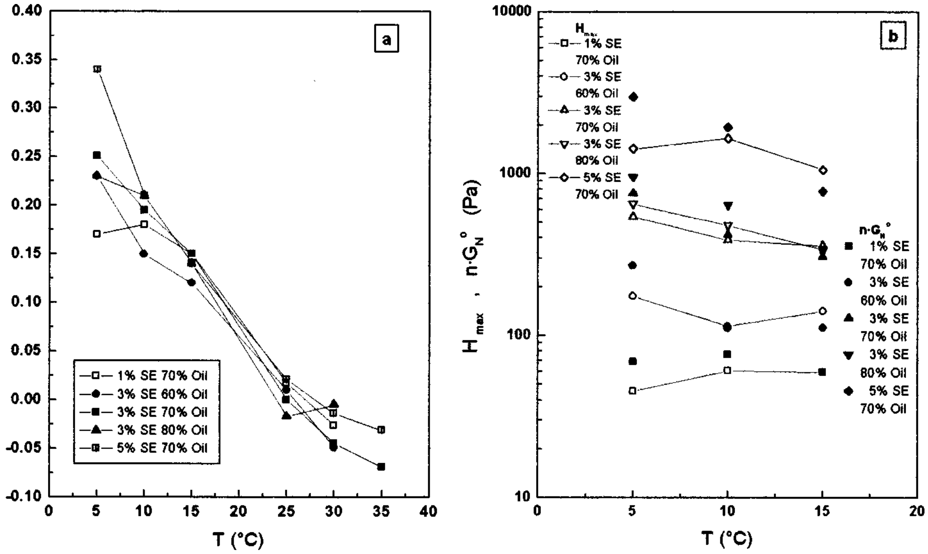

FIG. 10. (a) Slope of the plateau region as a function of temperature for sucrose palmitate-stabilized emulsions. (b) Comparative values of $H_{\max}$ and nG_N^0 as a function of temperature, for sucrose palmitate-stabilized emulsions.

with long linear flexible chains, which shows a well-characterized entanglement formation [Graessley (1974); Doi and Edwards (1988)]. An important consequence of this coincidence is the validation of the analogy between the formation of an entanglement network among polymer molecules and the development of an elastic network produced by interdroplet interactions, favored by the reduction in thermal agitation. As a consequence of the above-mentioned considerations, the increase in thermal agitation produces a remarkable weakening of the network structures.

IV. CONCLUDING REMARKS

The linear viscoelastic properties shown by the emulsions studied are the result of a complex dependence on a number of variables whose performance may be relevant during the emulsification process or once the final emulsion is formed.

The emulsification process depends on the surfactant concentration of the initial continuous phase at which the oil is added, since this generally increases the amount of interfacial area that may be stabilized. However, for the surfactant–water system studied, an increase in the SE concentration also produces a transition from an isotropic micellar solution L_1 to a dispersion of lamellar liquid-crystalline portions in the micellar matrix, $L_1 + L_\alpha$, giving rise to a remarkable increase in the initial continuous-phase viscosity (η_{oc}). This transition interferes with the emulsification process, leading to a specific interfacial area that is smaller than expected. This effect is produced either by increasing the amount of SE or by decreasing the water content (i.e., obtained as the oil concentration of the emulsion is raised).

The linear viscoelastic properties of the final emulsion depend on the DSD obtained, as well as on the consistency of the thin film of the continuous phase located among the droplets. First of all, an evolution towards a higher specific interfacial area, obtained with smaller droplets and wider DSD, produces an increase in the interactions among the emulsifier molecules that surround the adjacent oil droplets. Second, the consistency of the continuous-phase layer is improved by an increase in the excess of surfactant. When both effects increase simultaneously (i.e., by increasing SE content), the result is a remarkable increase in the viscoelastic functions and the plateau modulus as well as a slight spread of the plateau region in the relaxation time spectrum, which suggest a certain enhancement of the elastic network. When both effects are opposite, because of a decrease in the continuous-phase consistency, (i.e., by increasing oil concentration) the results obtained were similar but much less pronounced.

Furthermore, the plateau region in the relaxation time spectrum is clearly expanded when temperature decreases for all the emulsions studied, because of the enhanced formation of an elastic network, due to extensive flocculation of oil droplets. As a result, the stability is substantially enhanced when the emulsion is stored at low temperature.

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