Influence of Concentration and Temperature on the Flow Behavior of Oil-in-Water Emulsions Stabilized by Sucrose Palmitate

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ABSTRACT: To study the influence that concentration and temperature exert on the viscous behavior of emulsions stabilized by a sucrose ester (SE) of high hydrophilic-lipophilic balance (HLB), flow curves and droplet size distributions were determined. Flow curves of presheared emulsions always exhibited a shear-thinning behavior at intermediate shear rates, a tendency to a limiting viscosity at high shear rates, and a metastable region at low rates. This behavior can be fitted to a Carreau model. Both SE and oil concentrations increase emulsion viscosity as a result of a more structured system with a lower droplet size and polydispersity. An increase in temperature usually leads to a decrease in emulsion viscosity. However, at high oil concentration, coalescence and phase separation take place at low temperature. On the other hand, at high temperature, droplet bursting due to shear forces, leading to an increase in viscosity, may result. Despite the strong structural breakdown caused by steady shear, master flow curves may be obtained by using superposition methods.

JAOCS 74, 1203–1212 (1997).

KEY WORDS: Droplet diameter, emulsifier, emulsion, flow behavior, rheology, sucrose ester.

Highly concentrated oil-in-water (o/w) emulsions are structured materials of great technological interest in view of their many industrial applications (e.g., foodstuffs, cosmetics, pharmaceuticals, agrochemicals, bitumen, etc.).

The role of the emulsifier is to provide long-term stability to the system because it prevents droplet coalescence by adsorbing at the o/w interface and increasing the repulsive interactions among droplets (1). However, the development of extensive flocculation of droplets to form a weak gel-like particulate network is also desirable to enhance stability because the creaming rate is significantly decreased (2).

New emulsifiers must possess suitable functional properties to confer stability against coalescence and creaming, and they must be competitive in terms of costs, availability, and toxicity. Sucrose esters are good candidates as emulsifiers for the food industry because they are nonionic surfactants that may be produced from natural products, such as sucrose and vegetable oil (3). Moreover, a wide range of hydrophilic-lipophilic balance (HLB) values exist for sucrose esters, although, as stated by Akoh and Nwosu (4), a suitable emulsifier should be selected by experimentation because the HLB value indicates behavioral characteristics but does not imply emulsifying efficiency.

Knowledge of the droplet size of the dispersed phase and its polydispersity, as well as the rheological behavior of the emulsion, is important in characterizing emulsion stability and improving the understanding of the emulsification process (5).

The flow properties of concentrated emulsions are governed by the different interaction forces that occur in the system, which in turn depend on the volume fraction of the disperse phase, the concentration and nature of the emulsifier, the chemical composition of the continuous phase, and interfacial properties. Other structural parameters important to emulsion rheology are droplet size and shape, polydispersity, and rheological properties of the continuous phase (6,7). Shear forces may substantially modify the balance between repulsive and attractive forces and therefore the stability and viscoelasticity of the emulsions. Several modifications may then take place, depending on shear magnitude and shear time, namely, a reversible flocculation–deflocculation process, shear-induced coalescence, and disruption of the droplets (8,9).

The ability of the sucrose palmitate studied to form highly stable emulsions was established in a previous paper (10). This work explores the influence that sucrose ester and oil concentrations and temperature during treatment exert on the flow behavior and droplet size of o/w emulsions that are stabilized by a sucrose palmitate of high HLB and stored at low temperature.

EXPERIMENTAL PROCEDURES

Different o/w emulsions were prepared with a Ryoto sucrose palmitate (P-1570, HLB = 15) from Mitsubishi-Kasei Food

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Corporation (Tokyo, Japan). This emulsifier was used as received. Sunflower oil was purchased off the shelf. The o/w emulsions were prepared in an Ultra-Turrax T-50 homogenizer from Ika (Staufen, Germany). 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 ester concentration (SE) ranged from 1 to 5% (w/w) and the oil concentration (O) from 60 to 85% (w/w). Emulsions were stored at 5°C.

Flow curves and transient tests were measured with Haake Rotovisco RV-20 and RV-100 rheometers (Karlsruhe, Germany), equipped with CV-100 and CV20N measuring heads and ME15 ($R_e/R_i = 1.078$), ME16 ($R_e/R_i = 1.037$), and ME31 ($R_e/R_i = 1.037$) sensor systems. All samples had the same recent thermal and rheological history. Before flow curves were obtained, samples were presheared for 10 min at a shear rate of 300 s^{-1}, and then the shear rate was decreased to 0.1 s^{-1} in 15 min. Three replicates of each test were done.

Droplet size measurements were conducted in a Coulter Counter Model Z_B apparatus from Coulter Electronics Limited (Luton Beds, England) with a 100-µm orifice tube, whose measurement range was from 1.6 to 40 µm.

A multifactor analysis of variance (MANOVA) was carried out on the resulting rheological and droplet size experimental values.

RESULTS

Droplet size distribution. Droplet size distribution curves were obtained for each emulsion according to the foregoing experimental procedure. The experimental results deviate from a normal distribution and show a wide range of sizes (1 to 30 µm). Results are shown in Figure 1, in which the volume percentage of droplets is plotted vs. diameter *d* as a function of sucrose palmitate and O, respectively.

The high degree of polydispersity obtained is a consequence of the emulsification conditions. Thus, disruption of droplets is followed by a coalescence process, which is favored by the intense mechanical energy supplied and above all by the high temperature during emulsification (11). This high temperature is required to solubilize the surfactant in the continuous phase. Moreover, the turbulent flow field achieved during emulsification (the Reynolds number for the emulsification process is in the order of 10^4), as well as the increase in viscosity produced during emulsification, contributes to the spread in droplet size. This last effect was observed before (12).

A sigmoidal-type equation was used to fit the undersize cumulative frequency f_c for the experimental size distribution curves (10):

$$f_c = 1/\left[1 + \left(d_{1/2}/d\right)^b\right] \qquad [1]$$

where $d_{1/2}$ is the median for the droplet diameter and b is a parameter that varies inversely with the spread or dispersion of sizes. Furthermore, values of the Sauter mean diameter, which is inversely proportional to the specific surface area of the droplets (13–15), have been obtained as follows:

$$d_{sv} = \sum n_i\, d_i^3 / \sum n_i\, d_i^2 \qquad [2]$$

where n_i is the number of droplets with diameter d_i. According to Otsubo and Prud'homme (16), d_{sv} is the appropriate average diameter dominating the flow behavior for concentrated emulsions.

The key parameters are b, d_{sv}, and, to a lesser extent, $d_{1/2}$. They have been successfully related to some rheological parameters (10) as well as to the influence of some processing variables on the rheological characteristics of emulsions (14,15).

Flow behavior. The flow curves shown in this work were obtained, after a period of intensive shear, by continuously decreasing the shear rate. Thus, they must be considered dependent on the kinetics of restructuring of these systems; these resulted from the experimental protocol followed,

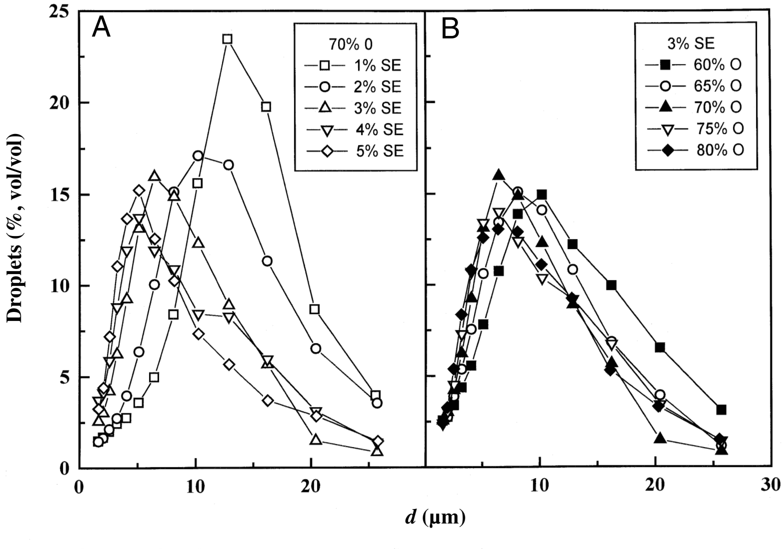

FIG. 1. Droplet size distribution curves: (A) influence of sucrose ester concentration (SE); (B) influence of oil concentration (O). Abbreviation: *d*, droplet diameter.

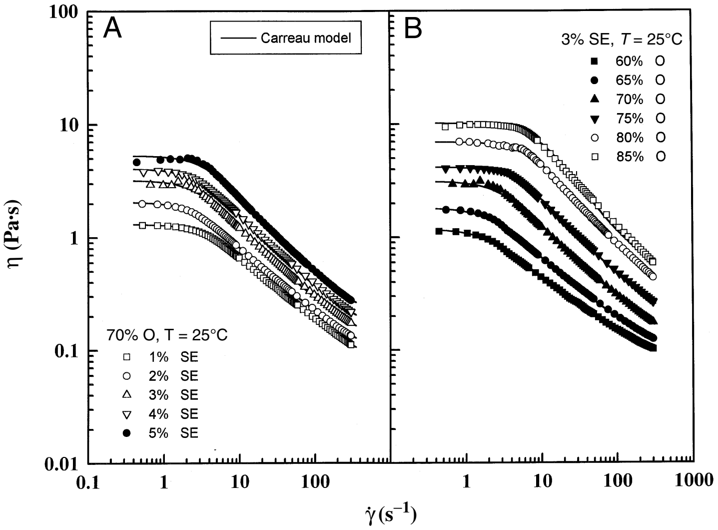

FIG. 2. Flow curves obtained at 25°C: (A) influence of SE; (B) influence of O. Abbreviations: η, viscosity; $\dot{\gamma}$, shear rate; for others see Figure 1.

which was the same for all emulsions studied. The flow behavior under these experimental conditions was qualitatively similar. Flow curves show three clearly different regions (Figs. 2 and 3). The first one, for low shear rates, exhibits a tendency to a constant viscosity, η_0, which may be considered as a metastable equilibrium between the restructuring kinetics and the shear rate decrease. After this, the flow curves present a power-law decrease in viscosity, followed by a tendency to a high-shear limiting viscosity, η_∞. This flow behavior has also been found in other types of emulsions, such as salad dressing (14,15). Otsubo and Prud'homme (17) have also reported a strong dependence of viscosity on shear rate for o/w emulsions in the highly concentrated region. These authors, however, have not found a low-shear constant viscosity, although the results reported by these authors do not refer to presheared samples. The Carreau model fits the foregoing behavior fairly well:

$$(\eta - \eta_\infty)/(\eta - \eta_0) = 1/[1 + \dot{\gamma}/\dot{\gamma}_c)^2]^s \qquad [3]$$

where $\dot{\gamma}_c$ is a critical shear rate for the onset of the shear-thinning region, and s is a parameter related to the slope of this intermediate region.

The rheological results will be discussed on the basis of the influence that the variables considered in the present study exert on the Carreau model parameters.

Statistical analysis. A MANOVA with three replicates of each emulsion was carried out to establish which variable exerts a significant influence on both the rheological and size distribution parameters. A variation of a given factor was considered significant when the probability P for this factor

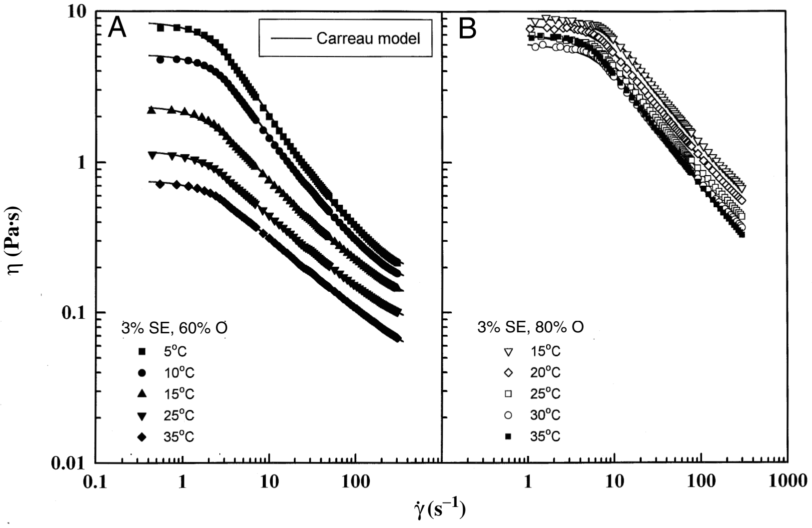

FIG. 3. Influence of temperature on flow behavior of emulsions with 3% sucrose palmitate and A, 60% oil; B, 80% oil. See Figures 1 and 2 for abbreviations.

was less than 0.05. The probability was determined from the F-ratio of the mean squared deviations to the residual mean squared deviations.

The multifactor analysis of variance performed on size distribution parameters showed that, except for $d_{1/2}$ (P[SE] = 0.44; P [O] = 0.701), O and SE have a significant influence on size distribution parameters. The MANOVA carried out on the parameters of the Carreau model showed that all variables studied (SE and O and temperature) exert significant influence. The only exception is the influence of temperature on the critical shear rate $P\ [\dot{\gamma}_c] = 0.14$.

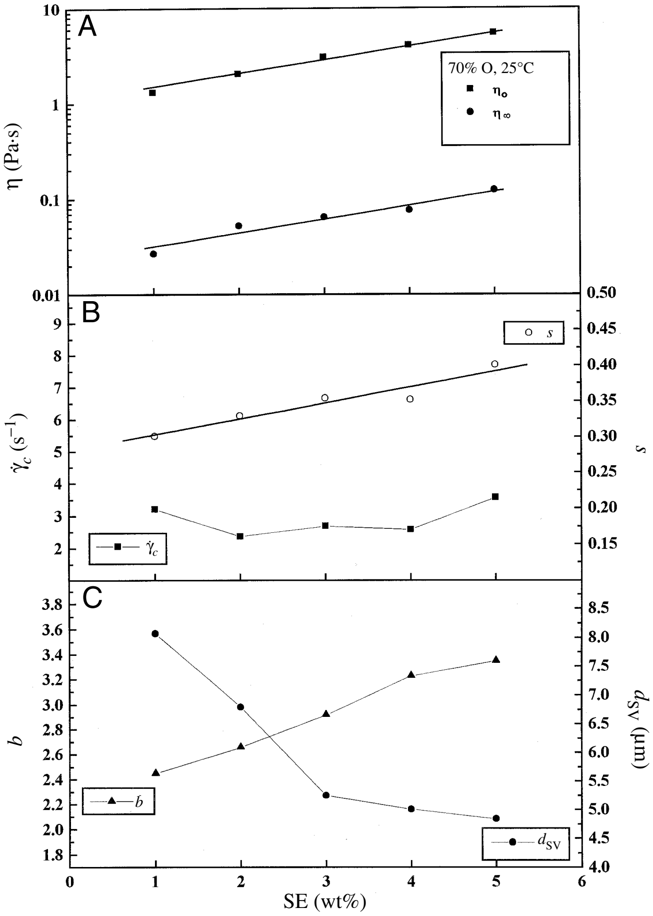

FIG. 4. Influence of SE: A), B) Carreau model parameters; C) size distribution parameters. (A) Carreau model parameters η_0 (constant viscosity) and η_∞ (limiting viscosity); (B) Carreau model parameters $\dot{\gamma}_c$ (critical shear rate) and s (slope); (C) size distribution paramters b (a parameter that varies inversely with size dispersion) and d_{SV} (average diameter).

DISCUSSION

Influence of sucrose ester concentrations. According to the results shown by Abran *et al.* (18), sucrose monopalmitate produces collapse of the air/water interface at about 30 Å^2/molecule. Extrapolation of this result to the o/w emulsions studied indicates that the surfactant is always in excess (from 5 to 15 times the amount necessary to saturate the interface as a monolayer). Hence, the previously reported good results of stability against coalescence shown by these emulsions can be explained (10). The only significant destabilization mechanism found in absence of shear was creaming at low O or very low SE.

As shown in Figure 2, an increase in SE produces a significant rise in viscosity ($P < 0.0001$). Thus, low- and high-shear rate-limiting viscosities undergo an exponential increase with SE (Fig. 4).

These results agree with those obtained from the droplet size distribution curves. Figure 4 shows that an increase in SE leads to emulsions with lower Sauter mean diameters and narrower size distributions (parameter b increases). Both factors can produce a rise in viscosity (6). An increase in viscosity may also be related to a higher level of droplet flocculation as emulsifier concentration is raised, although in this study, the preshear applied on the samples must have produced an almost complete breakdown of the gel-like particulate network.

Furthermore, the statistical analysis shows a significant influence of SE on parameter s ($P < 0.0001$). Thus, Figure 4 shows a linear increase of s with SE, which suggests either that the emulsion becomes more sensitive to the variation of shear rate or that the emulsion restructuring rate is higher.

Influence of oil concentration. Figure 2 shows that an increase in O leads to an important increase in viscosity (i.e., η_0 increases one order of magnitude when O is raised from 60 to 85%). Thus, η_0 and η_∞ undergo an exponential increase (Fig. 5). These results may be related to the values of droplet size and polydispersity (Fig. 1). Consequently, an increase in O decreases both polydispersity, [because parameter b increases ($P < 0.0001$)] and the Sauter mean diameter ($P = 0.003$), which means that the specific surface area of the droplets is raised (Fig. 5). However, the dependence of viscosity on droplet size seems to be qualitatively affected by O. Thus, the decrease in d_{sv} is much greater at low O, at which only a slight increase in viscosity takes place. At high concentration, however, a small decrease in d_{sv} produces a much higher increase in viscosity. Otsubo and Prud'homme (16) also found a change in the dependence between viscosity and interfacial specific area above a critical value ($\phi = 0.63$).

On the other hand, the statistical analysis demonstrated a significant influence of O on s ($P < 0.0001$) and $\dot{\gamma}_c$ ($P < 0.001$). Thus, a linear increase in the slope and an exponential increase in the critical shear rate were found as O is raised (Fig. 5).

In summary, the influence of O on the flow properties for these emulsions is qualitatively similar to the influence of the emulsifier content. Nevertheless, an increase in O has a greater influence on $\dot{\gamma}_c$ than a rise in sucrose ester concentration, which is related to the onset of the metastable region (η_0). All changes observed may be understood by taking into account that O increases the emulsion packing of droplets, even above the value that corresponds to a suspension of monodispersed spherical particles. Under such conditions, a thin liquid film of continuous phase is formed among adjacent drops (16,19). At the highest O, the network structures of the previously mentioned films are considered to control the rheological properties.

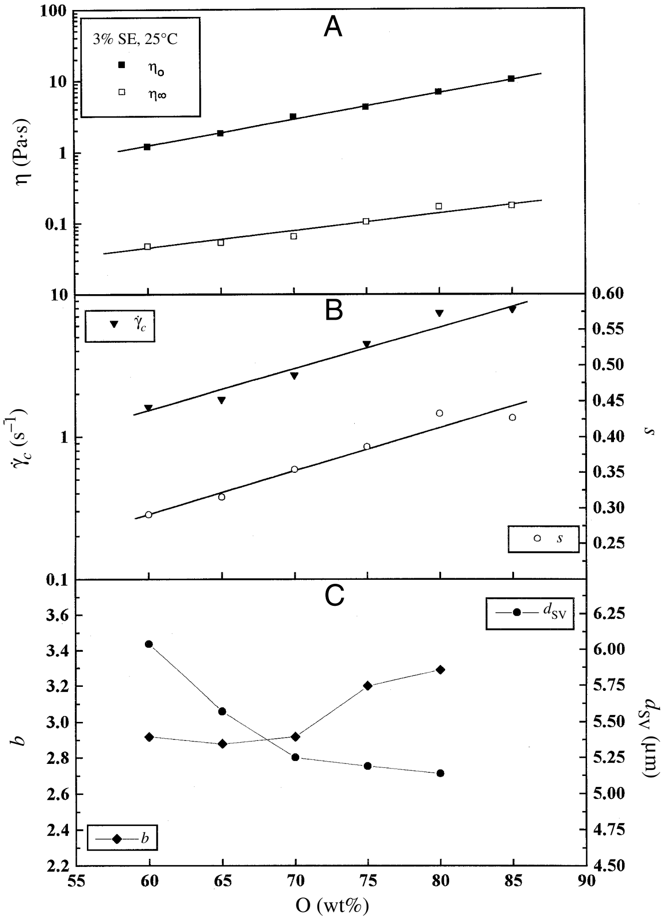

FIG. 5. Influence of oil concentration: (A,B) Carreau model parameters; (C) size distribution parameters. For abbreviations see Figures 1, 2, and 4.

Influence of temperature. Figure 3 shows flow curves of two selected emulsions as a function of temperature. Within the range of concentrations studied, an increase in temperature always produced a decrease in emulsion viscosity. A particular situation was shown by the emulsion with the highest O (80% oil and 3% SE). It was not possible to obtain flow curves at temperatures below 15°C. Droplet coalescence was induced under the experimental shear conditions, and finally phase separation occurred. Otsubo and Prud'homme (17) recently reported shear-induced coalescence at very high O. Furthermore, this system also shows anomalous thermal behavior at high temperature.

The statistical analysis, carried out on the Carreau parameters, showed a definite influence of temperature on η_0 ($P < 0.0001$) and η_∞ ($P < 0.0001$), as well as a lesser effect on parameter s ($P = 0.034$). However, temperature does not exert any significant influence on parameter $\dot{\gamma}_c$ ($P = 0.14$).

Thus, a typical exponential decrease was found for parameters η_0 and η_∞ with absolute temperature, which can be described by an Arrhenius-type equation (Figs. 6 and 7):

$$\eta_0 = A \exp (E_a/RT) \qquad [4]$$

TABLE 1
Activation Energies as a Function of Emulsion Concentration[a]

SE (%)	O (%)	E_a (η_0) (kJ/mol)	E_a (η_∞) (kJ/mol)
1	70	15.7	36.3
3	70	32.9	37.4
5	70	32.7	35.4
3	60	59.2	42.3
3	80	—	35.0

[a]Abbreviations: SE: sucrose ester concentration; O: oil concentration.

$$\eta_\infty = A \exp (E_a/RT) \qquad [5]$$

where A is a preexponential constant, which represents the viscosity (η_0 or η_∞) of the emulsion at infinite temperature, and E_a is an activation energy. The values of these parameters are presented in Table 1 as a function of O and SE. The temperature dependence of η_0 and η_∞ for emulsions containing 3% and 5% SE is similar, as may be deduced both from Figure 6 and from the values shown in Table 1.

The influence of temperature on parameter s depends on the emulsion studied (Figs. 6 and 7). Generally, the sensitivity of the emulsion to shear (parameter s) does not seem to be influenced by temperature. There is a slight tendency for s to in-

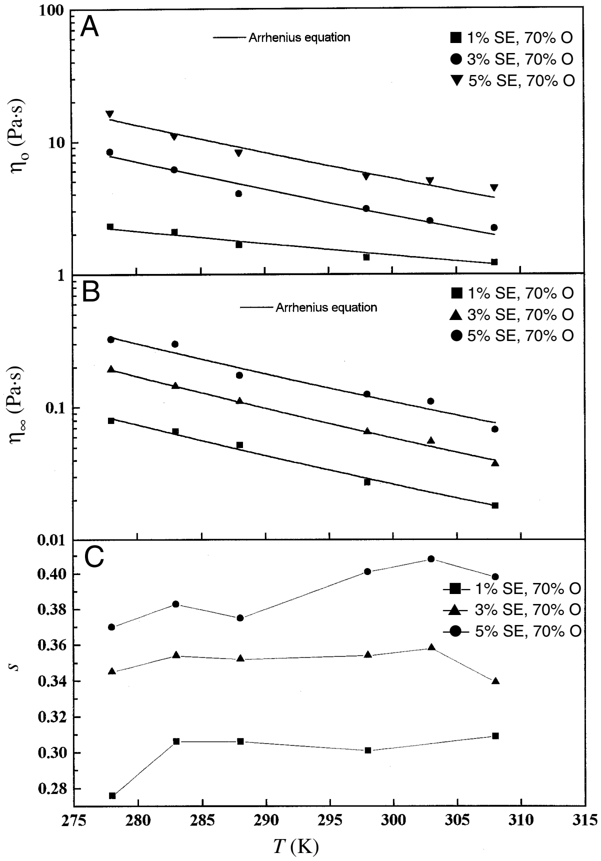

FIG. 6. Influence of temperature on Carreau model parameters for emulsions with different sucrose palmitate concentrations. For abbreviations see Figures 1 and 4.

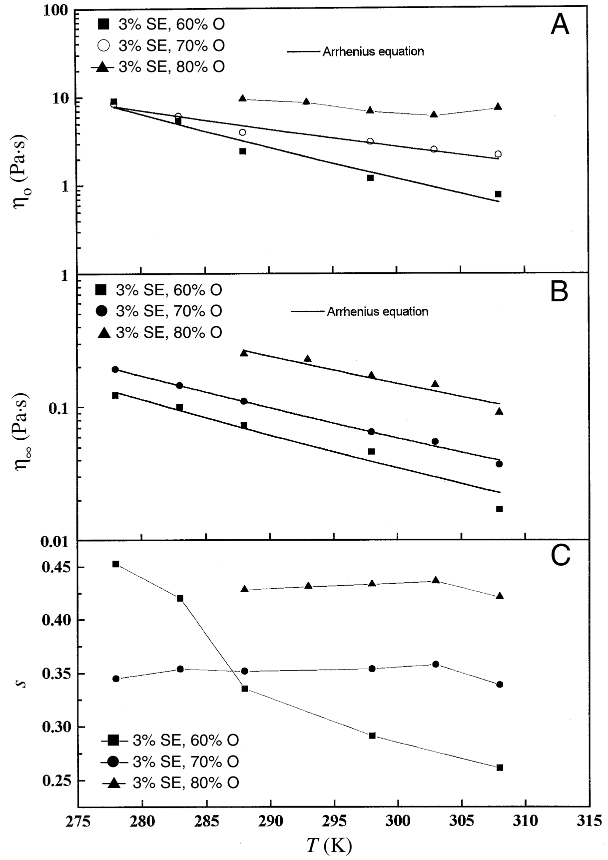

FIG. 7. Influence of temperature on Carreau model parameters for emulsions with different O. For abbreviations see Figures 1 and 4.

crease with temperature up to 30°C. This increase is more important when the SE or the disperse phase concentrations are high. Under these conditions, at which the network structures of the continuous-phase film are fully developed, thermal agitation enhances structural breakdown. A completely different effect was observed for the less-concentrated emulsion (60% O), where temperature produced a significant decrease in parameter *s* (Fig. 7). This emulsion is below the maximum packing volume fraction for monodisperse spheres. The low content in disperse phase and the unfavorable values of the structural parameters *b* and d_{sv} shown by this emulsion lead to a decrease in viscosity and stability, as may be deduced from the stability diagram shown in a previous paper (10). This explains why the emulsion presents the lowest values of *s* and η_0 at high temperature. Nevertheless, this emulsion was also most affected by shear (*s*) and had the highest value of η_0 at the lowest temperature (Fig. 7). This emulsion probably restructures to a higher extent under such conditions.

Shear produces phase separation of the emulsion with 80% oil and 3% sucrose ester at low temperatures. This emulsion also presents a deviation from Arrhenius behavior at 35°C. At this temperature, an increase in η_0, even higher than that corresponding to 25°C, has been observed (Fig. 7). When this emulsion is sheared at constant shear rate (i.e., 300 s^{-1} at 25°C), a minimum in viscosity may be observed (Fig. 8). After this minimum, which is also known as stress undershoot, the emulsion viscosity increases with time. A possible explanation for this increase follows: When a certain value of shear rate is exceeded, so that the shear stress relative to the interfacial stress (the capillary number, Ca = $\eta\dot{\gamma}\, d_{SV}/2\sigma$, σ being the interfacial tension) overcomes a critical value, the drops become unstable and eventually burst (20,21). Because the critical capillary number depends on several factors, such as the type of flow, the internal-to-external viscosity ratio, the development of interfacial tension gradients, and the shear history (22,23), only a rough estimation should be considered

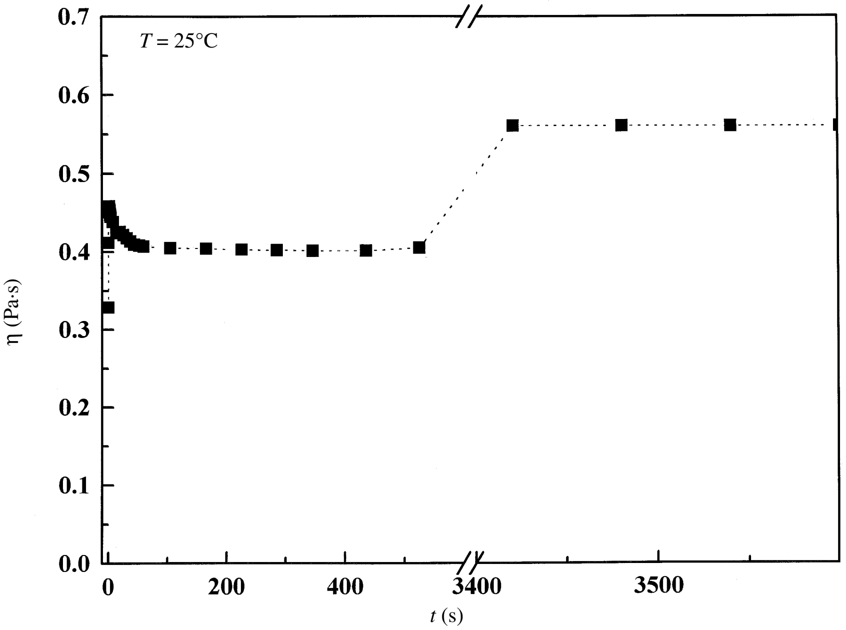

FIG. 8. Transient flow curve obtained at constant shear rate (300 s^{-1}) for the emulsions containing 3% SE and 80% O. For abbreviations see Figures 1 and 2.

for a highly concentrated emulsion. By assuming a value of 5 $mN\cdot m^{-1}$ for the interfacial tension, which is close to the values reported for sucrose stearate or sucrose palmitate aqueous solutions against different oil phases (5,24,25), the critical diameter above which droplets become unstable is about 15–40 μm, under the experimental conditions. Bursting of the largest droplets might be responsible for the above-mentioned increase in viscosity and therefore for the deviation from Arrhenius behavior. Further studies are being carried out on the evolution of droplet size under shear flow for highly concentrated emulsions.

As a result, this atypical thermal behavior may be explained by taking into account the following considerations: The flow curves are obtained after an intense prior shear; shear induces deformation and even breaks up the oil droplets (1,8); as a consequence, the flow curves obtained for this type of food emulsion are the result of strong structural breakdown, which can be attributed to either irreversible (coalescence, droplet bursting) or reversible processes (deflocculation) (26–28); and finally, a high concentration of the dispersed phase leads to a close packing of droplets, which may be distorted from their spherical shape (6) and may favor both the break-up of droplets, because interfacial tension gradients appear, and shear-induced coalescence. Therefore, at high temperature and O (35°C and 80% O), a redistribution of droplet size may be induced by shear, leading to an increase in viscosity. On the contrary, at high O and low temperature (80% O and 5°C), shear-induced coalescence prevails, and phase separation takes place. This effect happens less at lower O, where droplets are less distorted, as may be deduced from the highest value of η_0 at 5°C for the emulsion with 60% oil.

Master flow curves. The superposition methods are based on theoretical approximations that imply the formulation of molecular models. The best known are based on the theories of Rouse (29) and Bueche (30,31), which were developed for diluted monodisperse molecular solutions of polymers. The theoretical predictions of Bueche allow the use of a shift factor to obtain a master flow curve by using a dimensionless viscosity.

Temperature or a concentration shift factor, calculated empirically, has been used extensively to apply the superposition methods to more complex systems, such as concentrated polymer solutions (32,33), liquid crystals (34), surfactant solutions (35), or emulsions (14).

Time–temperature superposition. According to the Bueche theory, a plot of the dimensionless viscosity vs. $a_T\cdot\dot{\gamma}$, where a_T is a shift factor, should be universal for all temperatures. The curve shape would represent the shear rate dependence of the viscosity at a constant temperature and would be extended through a wider shear rate range than the one studied experimentally. Moreover, the dependence of the shift factor on temperature would provide information about the influence of temperature on viscous behavior.

However, the shift factor cannot be calculated directly from the Bueche theory for such complex systems as the concentrated emulsions of this study. The superposition has been carried out by plotting a dimensionless viscosity $\eta(\dot{\gamma},T)/\eta_0(T)$ (plus an arbitrary constant A used for clarity in distinguishing the curves) vs. the shifted shear rate ($a_T\cdot\dot{\gamma}$) by using a shift factor that was calculated empirically (35,36). Figure 9 shows that a master flow curve was obtained for each emulsion. This fact suggests that these emulsions are ther-

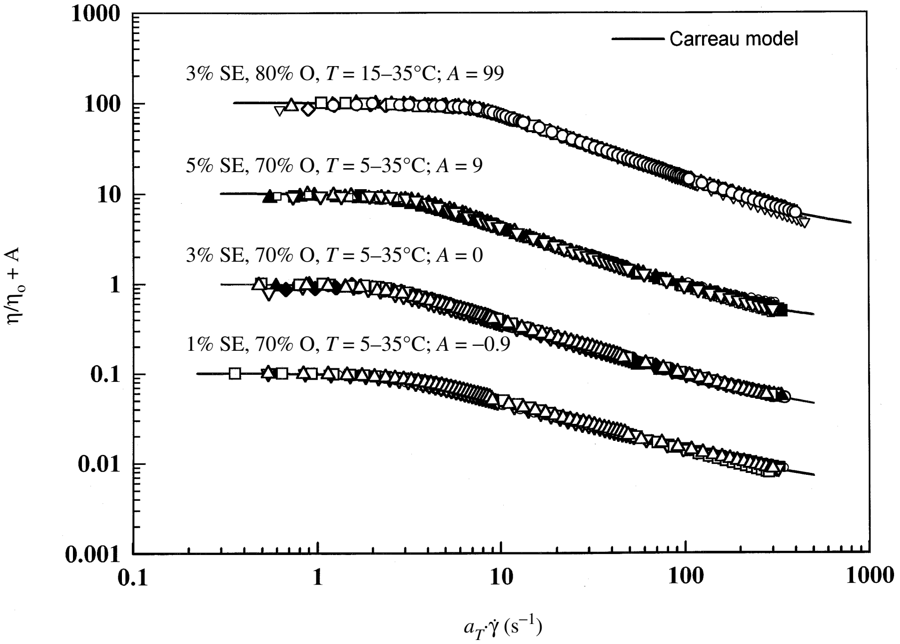

FIG. 9. Temperature-reduced master curves for different oil-in-water sucrose palmitate emulsions.

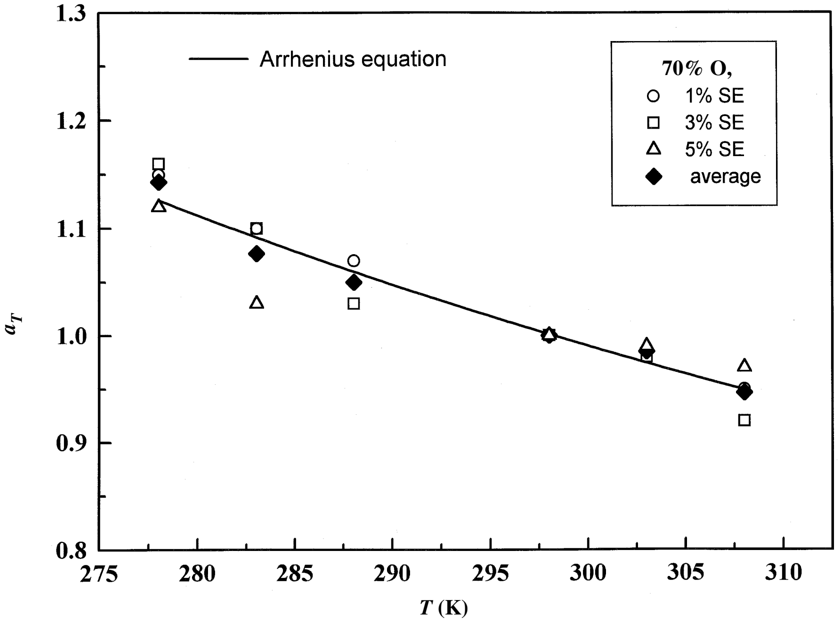

FIG. 10. Influence of temperature on the shift factor for the emulsions at different SE. Abbreviation: a_T, shift factor. For other abbreviation, see Figure 1.

morheologically simple when they have been submitted to high preshear and the immediate flow response is studied. The only exception was the emulsion with 60% O and 3% SE, whose flow curves undergo a change in the slope of the power law region at low temperature (Fig. 3).

Each master flow curve may be described by a modified Carreau model, expressed as follows:

$$(\eta/\eta_{0,T_0} - \eta_{\infty,T_0}/\eta_{0T_0})/(1 - \eta_{\infty,T0}/\eta_{0,T_0}) = \left\{1/\left[1 + (a_T \cdot \dot{\gamma}/\dot{\gamma}_{c,T_0})^2\right]\right\}^{S}{}_{T_0} \quad [6]$$

where η_{0,T_0}, η_{∞,T_0}, $\dot{\gamma}_{c,T_0}$, and s_{T_0} are the values of Carreau model parameters at the temperature of reference, 25°C.

Variation of the shift factor with temperature for emulsions containing 70% oil at different SE is shown in Figure 10. The differences between the values of a_T, at each temperature, are small and randomly distributed. Thus, there is no definitive relationship with SE concentration. Therefore, an average a_T may be used to superimpose the flow curves of all emulsions, independently of the SE (except for 60% O). Figure 11 shows the values of the shift factor of the flow curves from emul-

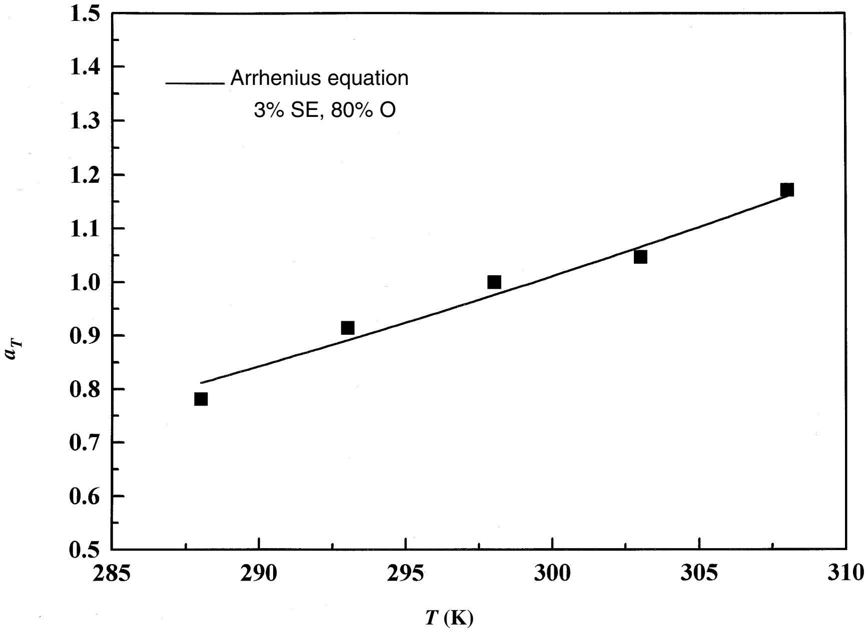

FIG. 11. Influence of temperature on the shift factor for the emulsion 3% sucrose ester and 80% oil. See Figure 10 for abbreviation.

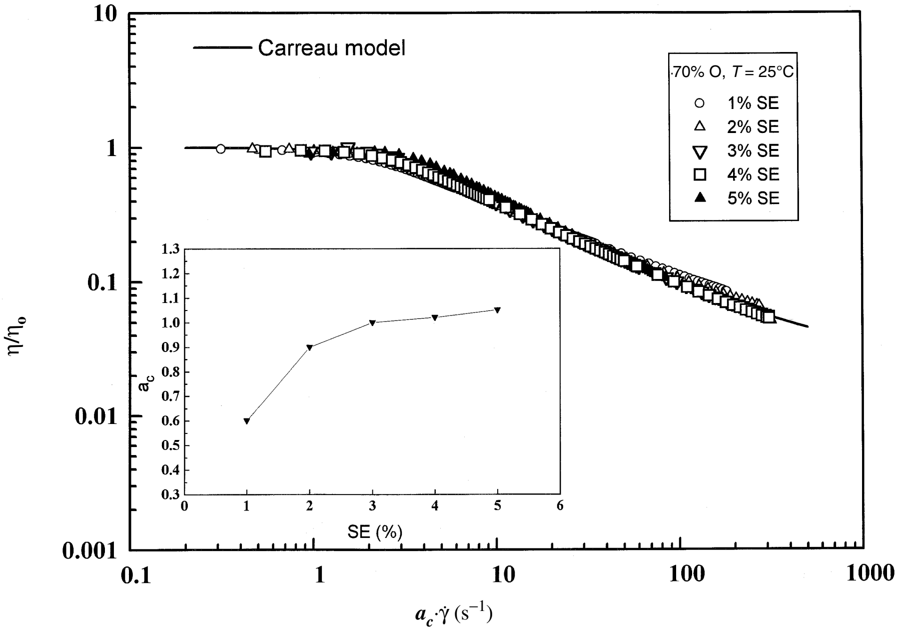

FIG. 12. SE-reduced master flow curve for the emulsion with 70% oil. For abbreviations, see Figures 1, 2, and 10.

sions with 80% oil and 3% sucrose ester.

The dependence of the shift factor upon temperature may be described by an Arrhenius-type equation, as has been reported by previous authors (32,37):

$$a_T = A \exp (E/RT) \qquad [7]$$

where E has a value of −13.2 kJ/mol for the emulsion with 80% O and 4.1 kJ/mol for the average a_T. Because the flow curves are normalized by using η_0 and the slope of the power law region was not significantly modified by the thermal agitation, the changes produced in the shift factor are due to the modification of the critical shear rate by temperature. Statistical analysis did not show any significant influence as a consequence of the error inherent in the fitting procedure. In fact, a_T changes in inverse proportion to $\dot{\gamma}_c$ as reported before (35).

These results show that the influence of shear rate on the structural recovery/breakdown process does not depend on temperature, as may be deduced from the applicability of the time–temperature superposition. Furthermore, the SE does not modify the influence of temperature on critical shear rate for the onset of the metastable region because a_T does not depend on the concentration of the emulsifier.

Time–concentration superposition. Superposition of the flow curves, at 25°C, from emulsions with 70% oil and different SE was carried out by the previously described procedure. A dimensionless viscosity, $\eta(\dot{\gamma},\text{SE})/\eta_0(\text{SE})$, was plotted vs. $a_c \cdot \dot{\gamma}$, where a_c is the shift factor calculated empirically and which only depends on SE (Fig. 12). The master curve obtained may be described by a modified Carreau model:

$$\left(\eta/\eta_{0,\text{SE}_0} - \eta_{\infty,\text{SE}_0}/\eta_{0,\text{SE}_0}\right)/\left(1 - \eta_{\infty,\text{SE}_0}/\eta_{0,\text{SE}_0}\right) = \left\{1/\left[1 + \left(a_c \cdot \dot{\gamma}/\dot{\gamma}_{c,\text{SE}_0}\right)^2\right]\right\}^{S_{\text{SE}_0}} \qquad [8]$$

where η_{0,SE_0}, $\eta_{\infty,\text{SE}_0}$, $\dot{\gamma}_{c,\text{SE}_0}$, and s_{SE_0} are the values of the Carreau model parameters, corresponding to the reference concentrations, 3% SE and 70% O.

The values of a_c, obtained as a function of SE, are shown in Figure 12. An initial increase followed by a tendency to stabilization at a plateau value was obtained for the shift factor a_c.

Because a master flow curve was obtained, SE does not substantially modify the influence of shear rate on the emulsion during the structural recovery process, although the critical shear rate is clearly modified. However, this influence decreases when SE is raised, as may be deduced from the tendency of factor a_c to reach a constant value above 3% SE (Fig. 12).

ACKNOWLEDGMENTS

This work is part of a research project sponsored by CICYT, Spain (research project ALI90-0503). The authors gratefully acknowledge their financial support.

REFERENCES

1. Walstra, P., Formation of Emulsions, in *Encyclopedia of Emulsion Technology*, edited by P. Becher, Marcel Dekker, New York, 1983, Vol. 1, pp. 57–127.
2. Dickinson, E., Food Colloids—An Overview, *Colloids Surf. 42*:191–204 (1989).
3. Gallegos, C., and M. Berjano, Esteres de sacarosa: Obtención, Propiedades y Aplicaciones en la Industria Alimentaria, *Alimentación Equipos y Tecnología 3*:153–159 (1991).
4. Akoh, C.C., and C.V. Nwosu, Emulsification Properties of Polyesters and Sucrose Ester Blends II: Alkyl Glycoside Polyester, *J. Am. Oil Chem. Soc. 69*:14–19 (1992).
5. Carrillo, A.R., and J.L. Kokini, Effect of Egg Yolk and Egg +

Salt on Rheological and Particle Size Distribution of Model Oil-in-Water Salad Dressing Emulsions, *J. Food Sci. 5*:1352–1366 (1988).

6. Rahalkar, R.R., Viscoelastic Properties of Oil–Water Emulsions, in *Viscoelastic Properties of Foods,* edited by M.A. Rao and J.F. Steffe, Elsevier Applied Science, London, 1992, pp. 317–354.
7. Tadros, T.F., Fundamental Principles of Emulsion Rheology and Their Applications, in *First World Congress on Emulsion*, EDS Editour, 4, Paris, 1993, pp. 237–266.
8. Darby, R., Emulsion Rheology, in *Emulsions and Emulsion Technology,* edited by K.J. Lissant, Marcel Dekker, New York, 1984, pp. 45–110.
9. Dickinson, E., Interactions in Protein-Stabilized Emulsions, in *Progress and Trends in Rheology IV*, edited by C. Gallegos, Steinkopff, Darmstadt, Germany, 1994, pp. 227–230.
10. Partal, P., A. Guerrero, M. Berjano, J. Muñoz, and C. Gallegos, Flow Behaviour and Stability of O/W Emulsions Stabilized by a Sucrose Palmitate, *J. Texture Stud. 7*:331–348 (1994).
11. Gallegos, C., M.C. Sanchez, A. Guerrero, and J.M. Franco, Effect of Process Parameters on the Rheological Properties of O/W Emulsions, in *Rheology and Fluid Mechanics of Nonlinear Materials,* edited by D.A. Siginer and S.G. Advani, ASME, AMD, Vol. 217, 1996, pp. 177–183.
12. Walstra, P., Influence of Rheological Properties of Both Phases on Droplet Size of O/W Emulsions Obtained by Homogenization and Similar Processes, *Dechema Monogr. 77*:87–94 (1974).
13. Sprow, F.B., Distribution of Drop Sizes Produced in Turbulent Liquid–Liquid Dispersions, *Chem. Eng. Sci. 22*:435–442 (1967).
14. Franco, J.M., M. Berjano, A. Guerrero, J. Muñoz, and C. Gallegos, Flow Behaviour and Stability of Light Mayonnaise Containing a Mixture of Egg Yolk and Sucrose Stearate as Emulsifiers, *Food Hydrocolloids 9*:111–121 (1995).
15. Franco, J.M., M. Berjano, A. Guerrero, J. Muñoz, and C. Gallegos, Rheology and Processing of Salad Dressing Emulsions, *Rheol. Acta 34*:513–524 (1995).
16. Otsubo, Y., and R.K. Prud'homme, Rheology of Oil-in-Water Emulsions, *Ibid. 33*:29–37 (1994).
17. Otsubo, Y., and R.K. Prud'homme, Effect of Drop Size Distribution on the Flow Behavior of Oil-in-Water Emulsions, *Ibid. 33*:303–306 (1994).
18. Abran, D., F. Boucher, T. Hamanaka, K. Hiraki, Y. Kito, K. Koyama, R.M. Leblanc, H. Machida, G. Munger, M. Seidou, and M. Tessier, On Some Physicochemical Properties of Sucrose Esters and the Stability They Confer to Membrane Proteins, *J. Colloid Interface Sci. 12*:230–236 (1988).
19. Princen, H.M., Highly Concentrated Emulsions. I. Cylindrical Systems, *Ibid. 71*:55–66 (1979).
20. Grace, H.P., Dispersion Phenomena in High Viscosity Inmiscible Fluid Systems and Application of Static Mixers as Dispersion Devices in Such Systems, *Chem. Eng. Commun. 14*:225–277 (1982).
21. Jansen, J.M.H., and H.E.H. Meijer, Droplet Breakup Mechanisms: Stepwise Equilibrium Versus Transient Dispersion, *J. Rheol. 37*:597–608 (1993).
22. Torza, S., R.G. Cox, and S.G. Mason, Particle Motions in Sheared Suspensions, *J. Colloid Interface Sci. 38*:395–411 (1972).
23. Walstra, P., Principles of Emulsion Formation, *Chem. Eng. Sci. 48*:333–349 (1993).
24. Osipow, L., F.D. Snell, D. Marra, and W.C. York, Surface Activity of Monoesters…Fatty Acid Esters of Sucrose, *Ind. Eng. Chem. 48*:1462–1464 (1956).
25. Fisher, G.S., H.J. Zeringue, Jr., and R.O. Feuge, Surface Activity of Sucrose Palmitates, *J. Am. Oil Chem. Soc. 54*:59–61 (1975).
26. Gallegos, C., M. Berjano, F.P. García, J. Muñoz, and V. Flores, Aplicación de un Modelo Cinético al Estudio del Flujo Transitorio en Mayonesas, *Grasas Aceites 39*:254–263 (1988).
27. Figoni, P.I., and C.F. Shoemaker, Characterization of Time-Dependent Flow Properties of Mayonnaise Under Steady Shear, *J. Texture Stud. 14*:431–442 (1983).
28. Alfaro, M.C., J. Muñoz, A. Guerrero, M. Berjano, and C. Gallegos, Comportamiento Reologico de Emulsiones Aceite en Agua que Contienen un Estearato de Sacarosa con un Alto Grado de Esterificacion, *EFCE Publication Series No. 101*:255–259 (1993).
29. Rouse, P.E., A Theory of the Linear Viscoelastic Properties of Dilute Solutions of Coiling Polymers, *J. Chem. Phys. 21*:1272–1280 (1953).
30. Bueche, F., The Viscoelastic Properties of Plastics, *Ibid. 22*:603–609 (1954).
31. Bueche, F., Influence of Rate of Shear on the Apparent Viscosity of A-Dilute Polymer Solutions, and B-Bulk Polymers, *Ibid. 22*:1570–1576 (1954).
32. Ferry, J.D., *Viscoelastic Properties of Polymers*, John Wiley & Sons, New York, 1980, pp. 266–290.
33. Wang, C.S., and J.R. Fried, Viscoelastic Properties of Concentrated Cellulose Acetate Solutions, *J. Rheol. 36*:929–945 (1992).
34. Mewis, J., and P. Moldenaers, Effect of Temperature on the Rheology of Polymeric Liquid Crystals, *Chem. Eng. Comm. 53*:37–47 (1987).
35. Madiedo, J.M., M. Berjano, A. Guerrero, J. Muñoz, and C. Gallegos, Influence of Surfactant Concentration and Temperature on the Flow Behaviour of Sucrose Oleate Aqueous Systems, *Colloids Surf. 82*:59–69 (1994).
36. Brodkey, R.S., and H.C. Hershey, *Transport Phenomena. A Unified Approach,* McGraw-Hill, New York, 1988, pp. 768–769.
37. Armstrong, R.C., and H.H. Winter, Heat Transfer for Non-Newtonian Fluids, in *Heat Exchanger Design Handbook*, edited by E.V. Schlünder, Hemisphere, London, 1983, Vol. 2, p. 2.5.12-1-12.

[Received February 20, 1997; accepted May 19, 1997]