Flow Behavior of Sucrose Stearate/Water Systems

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The aim of this work was to carry out a rheological study of aqueous systems containing a nonionic surfactant derived from sugar. The compositions studied ranged from the micellar region up to the occurrence of fully developed liquid crystals. This study was carried out at 50°C.

Systems up to 2% (wt) sucrose stearate exhibited a power-law decrease in the steady-state apparent viscosity with shear rate. At higher sucrose stearate concentrations, the flow curves exhibited two well-defined regions depending on shear rate, so that the apparent viscosities fitted the Carreau model A [Carreau, P.J., D. De Kee and M. Daroux, *Can. J. Chem. Eng. 57*:135 (1979)]. The existence of three composition ranges is proposed. An increasingly stronger micellar structure, as surfactant concentration rises, extends up to 10% (wt) sucrose stearate. Between 15% and 35% (wt) sucrose stearate, the results obtained are consistent with the occurrence of a lamellar liquid-crystal dispersion in an isotropic micellar solution. The liquid crystalline content in the dispersion steadily increases with surfactant concentration up to reaching a fully developed lamellar liquid crystal at 40% (wt) sucrose stearate.

KEY WORDS: Flow behavior, food emulsifier, food surfactant, liquid crystal, micelle, phase behavior, rheology, sucrose esters, viscoelasticity, viscosity.

Surfactants derived from a natural source, such as sugar, are being used more and more often. Sucrose esters are valuable as new nonionic surfactants that consist of sucrose as the hydrophilic group and a fatty acid as the lipophilic group. A wide range of hydrophilic-lipophilic balance (HLB) values can be attained with these products. This is important because the HLB influences ultimate applications. Low HLB values can be obtained by using fatty acids with long chainlength and by using highly esterified sucrose, whereas high values can be obtained by using fatty acids with short chainlength and sucrose with low degrees of esterification (1).

Sucrose esters are known to be useful for various applications. The best-known use is as a food additive (2). Some additives have been legally approved by Japan, the European Community, the Food and Agriculture Organization of the United Nations (FAO)/World Health Organization and the U.S. Products with three or fewer fatty acids have emulsifying, foaming, stabilizing and conditioning properties (3). Sucrose esters also are used as detergents. In fact, about 10% of their total production is employed for this purpose. Characteristics of sucrose esters used as detergents are summarized as follows. They are free from any risk of toxicity, excellent in cleansing dirt, agricultural chemicals and bacteria adhering to vegetables; there is little risk of environmental pollution; they leave fewer residues than synthetic detergents on food materials and foodstuffs; and have superior performance in removing milk residue from nursing bottles when compared to synthetic detergents (4). Furthermore, they are potentially valuable in the cosmetic (5) and pharmaceutical industries. They can form closed vesicles, which are useful for drug-carrying microcapsules, biometrical biological membranes and artificial cells (6,7). Sucrose ester detergents have been proposed as a suitable mild medium to suspend purified membrane proteins (9). All of these applications imply an added advantage because sucrose ester production opens up new uses for sucrose, the cheapest and most readily available polyhydric alcohol.

Knowing the phase behavior of these systems is of great importance in their practical applications because different types of micelles and liquid crystals may arise. Thus, some binary phase diagrams with either water or decane as solvents are available in the literature (9). The critical micelle concentrations found for these systems are similar to those of other nonionic surfactants of comparable chainlength (8). It has been reported that no cloud points are observed up to 100°C and that several thermotropic transitions occur. Cubic, hexagonal and lamellar liquid crystals, along with gel phases, also can be observed. The existence and extent of these phases have been found to be dependent on surfactant concentration, temperature and the esterification degree of sucrose (9).

The different association structures occurring in these systems significantly affect their flow properties. In fact, the microstructure-rheology relationship has been established for other water-surfactant systems (10–14). It is important to determine the rheology of these systems to carry out quality control, sensory studies, process engineering (pumping, mixing, etc.) and product development. Rheology can be used to provide information about the microstructure but, in turn, a certain rheological behavior may be achieved by calculated changes in microstructure (14).

Thus, the aim of this work was to study the rheological behavior at steady shear of an aqueous system containing a widely-used sucrose ester at concentrations ranging from the micellar region up to the appearance of liquid crystals. The extent of the linear viscoelastic domain also was studied by means of strain sweep tests.

EXPERIMENTAL PROCEDURES

Sucrose stearate from Ryoto Sugar Ester (Tokyo, Japan) was used as received. This product is 70% (wt) monoester and 30% di- and triester (15). Fatty chain distribution corresponds to 70% stearic and 30% palmitic acid. Aqueous systems of up to 45% (wt) sucrose stearate (SE) were prepared to find a fully developed liquid crystalline structure. Within this composition range, a schematic phase diagram was determined from 5 to 60°C. Phase boundaries are accurate to better than ±2% (by wt) and ±2°C. The liquid crystalline regions were identified by polarization microscopy with a Carl Zeiss Standard 142 microscope (Oberkochen, Germany) equipped with a "M-35" camera, whose stage was connected to a thermostatic circulator.

The rheological measurements were conducted in a Haake Rotovisco RV-20 rheometer (Karlsruhe, Germany).

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A CV-100 measuring head with a Mooney-Ewart (ME-15) sensor system (Re/Ri = 1.078) (Haake Mess-Technik, Karlsruhe, Germany)was used to study the flow behavior of systems containing 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40 and 45% (wt) SE at 50°C. Shear rate was varied between 0.1 s^{-1} and 300 s^{-1}. A CV-20N measuring head with a Mooney-Ewart (ME-45) sensor system (Re/Ri = 1.078) (Haake Mess-Technik) was used to carry out strain sweep tests. The results obtained for systems containing 1, 2, 3, 4, 11, 14 and 15% (wt) SE at 50°C are given. These tests were carried out at a fixed frequency of 1 Hz and with an angle of displacement varying from 0.3° to 10°. All the samples had the same recent past history. Thus, sealed flasks containing the systems prepared *in situ* were allowed to reach the required test temperature by introducing them in the thermostatic circulator, used to keep the samples at 50°C, while carrying out the rheological measurements. All the samples were left for 10 min in the sensor system before running any measurements to allow for some stress relaxation to be reached.

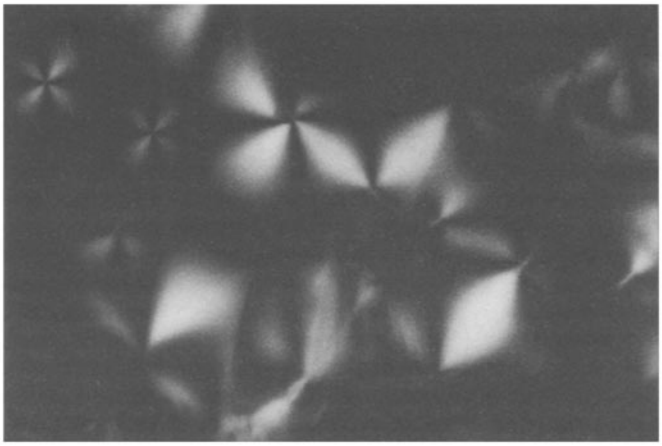

FIG. 2. Liquid-crystalline portions in an isotropic matrix (15% wt SE); 50°C; 200 times.

RESULTS

Phase behavior. The schematic phase diagram determined for the sucrose stearate used in this work is shown in Figure 1. This surfactant turns out to be barely soluble in water below 43°C (0.5% by wt). A phase transition boundary is suggested at 43°C. Below this temperature a two-phase region occurs from 0.5% to 10% (wt), above this a hydrated solid phase is formed.

Above 43°C to following features can be noted: A single isotropic micellar solution is formed at compositions up to 10% (wt); as the SE concentration was increased, polarization microscopy revealed that weakly birefringent textures appeared over the observation field in such a way that acceptable photomicrographs could only be taken at and above 15% (wt). In fact, some liquid crystalline portions "swimming" on an isotropic matrix were detected (Fig. 2). This may be associated with the occurrence of a lamellar liquid crystalline dispersion in micellar phase, because mosaic textures, along with positive and negative focal-conic units, could be observed. These features became more and more pronounced as surfactant concentration increased, due to the fact that a higher birefringence and a greater liquid crystalline content were found in the dispersion (Fig. 3). The boundaries of this region could not be accurately determined by either mere visual observation of phase separation or analysis of textures observed, but they were determined by means of the concentration dependence of the rheological parameters obtained, as shown below. At 40% and 45% (wt) SE, a highly birefringent monophasic mesophase was found, which displayed the typical oily streaks and mosaic (Fig. 4) textures of a lamellar liquid crystal. The realm of existence of this liquid crystal may well be extrapolated to higher SE concentrations.

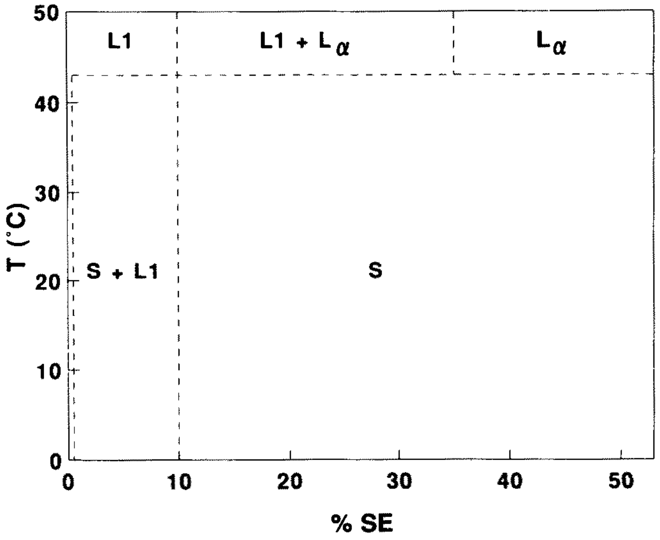

FIG. 1. Schematic phase diagram of the "SE/water" system. S, solid; L1, micellar solution; and L_α, lamellar liquid crystal.

Flow behavior. Apparent viscosities as function of shear rate in a composition range from 1% (wt) to 45% (wt) SE (at 50°C) are shown in Figures 5 and 6. For those systems containing 1% (wt) and 2% (wt) SE, a power-law decrease in viscosity with shear rate can be observed, although a

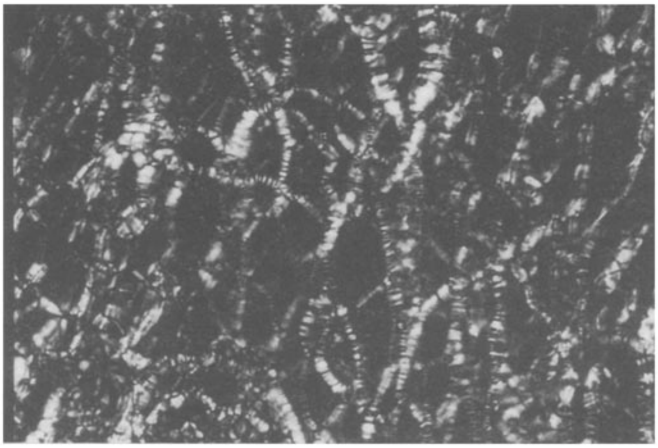

FIG. 3. Oily-streaks texture in a portion of lamellar liquid crystal (35% wt SE); 50°C; 200 times.

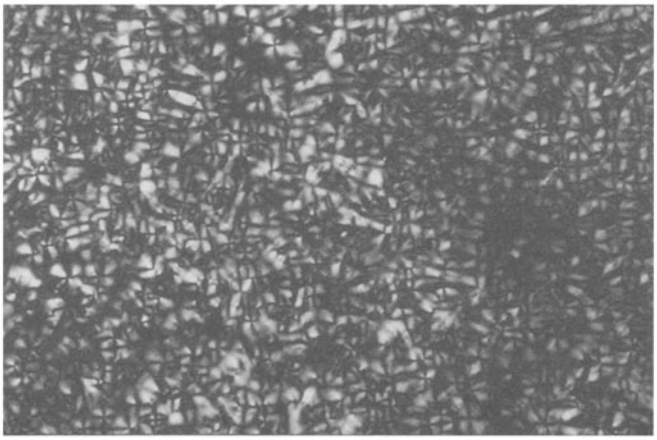

FIG. 4. Mosaic texture of a lamellar liquid crystal (45% wt SE); 50°C; 200 times.

tendency to a constant viscosity region (η_∞) occurs at high shear rate.

At higher SE concentrations, the existence of two regions dependent on shear rate is worth pointing out: i) As shear rate is increased from the lowest value reached, a steady viscosity, or at least the tendency to a limit viscosity, can be observed and this first region extends up to an experimental critical shear rate, which depends on the SE concentration; and ii) above this critical shear rate, the apparent viscosity significantly drops with increasing shear rate. Different rheological models can fit the obtained results. However, the Carreau model A (16) was chosen because it includes a time constant related to the elastic constant of the majority of polymers (17). The Carreau model A equation can be described as follows:

$$\eta/\eta_0 = 1/[1 + (t_1\dot{\gamma})^2]^s$$

where η_0, limit viscosity; t_1, time constant; and S, an adimensional parameter.

In Figures 5 and 6, curves derived from the Carreau model A also are compared to the experimental ones. This model provides a reasonably good representation of experimental data, except for the systems containing either 1% or 2% (wt) SE, which show a decrease in viscosity within the experimental shear rate range. A plateau would probably be found for systems containing up to 2% SE (wt) if reliable data were available below the lowest shear rate reached.

Figure 7 shows that experimental limit viscosities are not significantly different from those derived from the Carreau model A equation. The limit viscosity remains constant up to 10% (wt) SE. Above such a concentration, a nearly linear increase in the limit viscosity up to 35% SE (wt) is observed. Critical shear rate values, derived from the model by taking the reciprocal of t_1, are plotted against SE concentration in Figure 8. The critical shear rate was defined as that above which the apparent viscosity significantly decreased with shear rate. As can be deduced from the graph, the critical shear rate rises sharply with surfactant concentration up to 10% (wt) SE. Then, the rate of increase slows so that a smooth peak is reached around 30–35% (wt) SE. Parameter S values also are plotted in Figure 8. No significant differences are observed with increasing surfactant concentration below

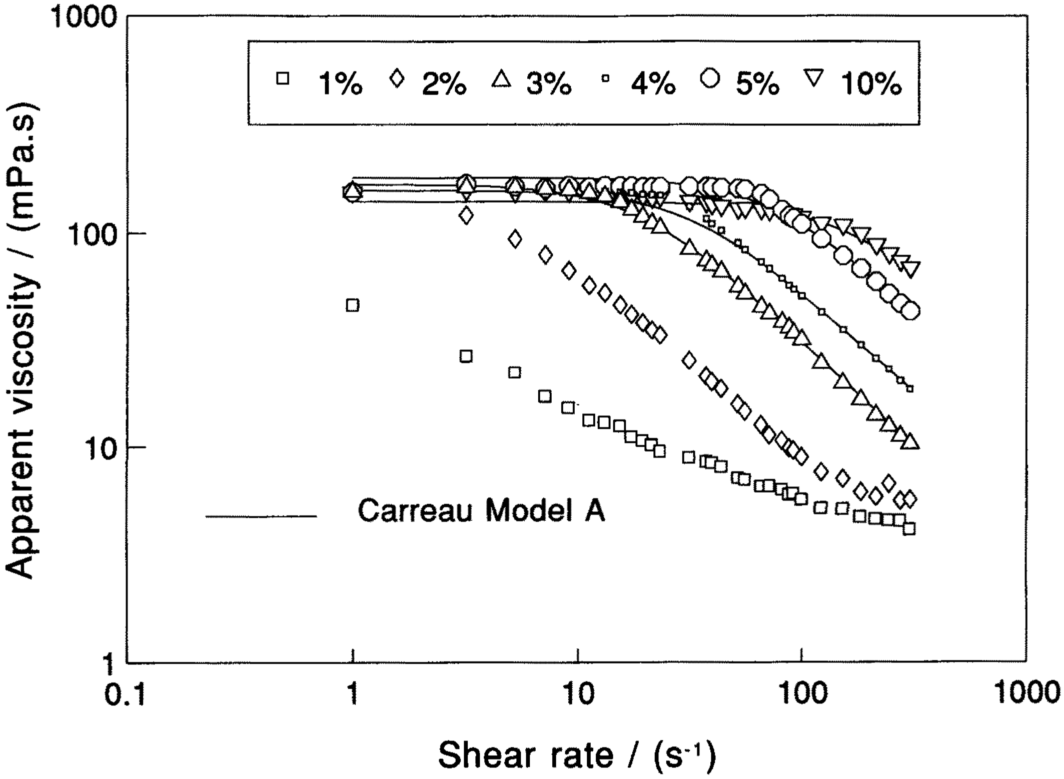

FIG. 5. Steady-state viscosity values *vs.* shear rate for systems containing up to 10% SE (wt).

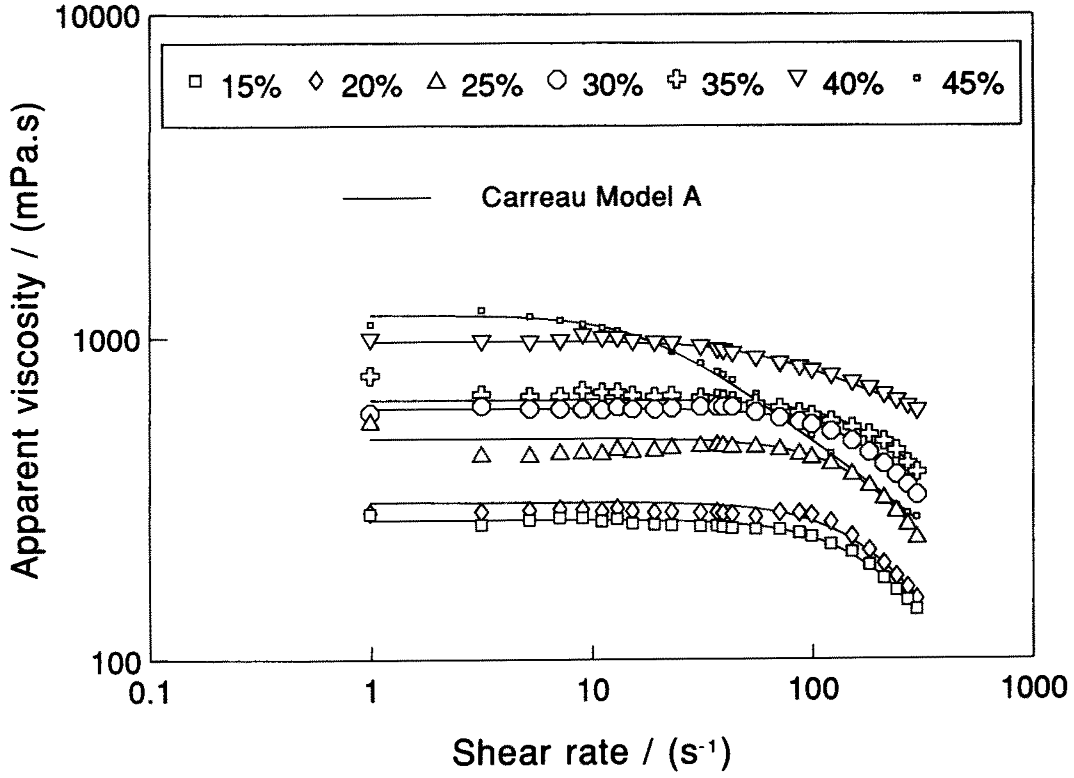

FIG. 6. Steady-state viscosity values *vs.* shear rate for systems containing 15–45% SE (wt).

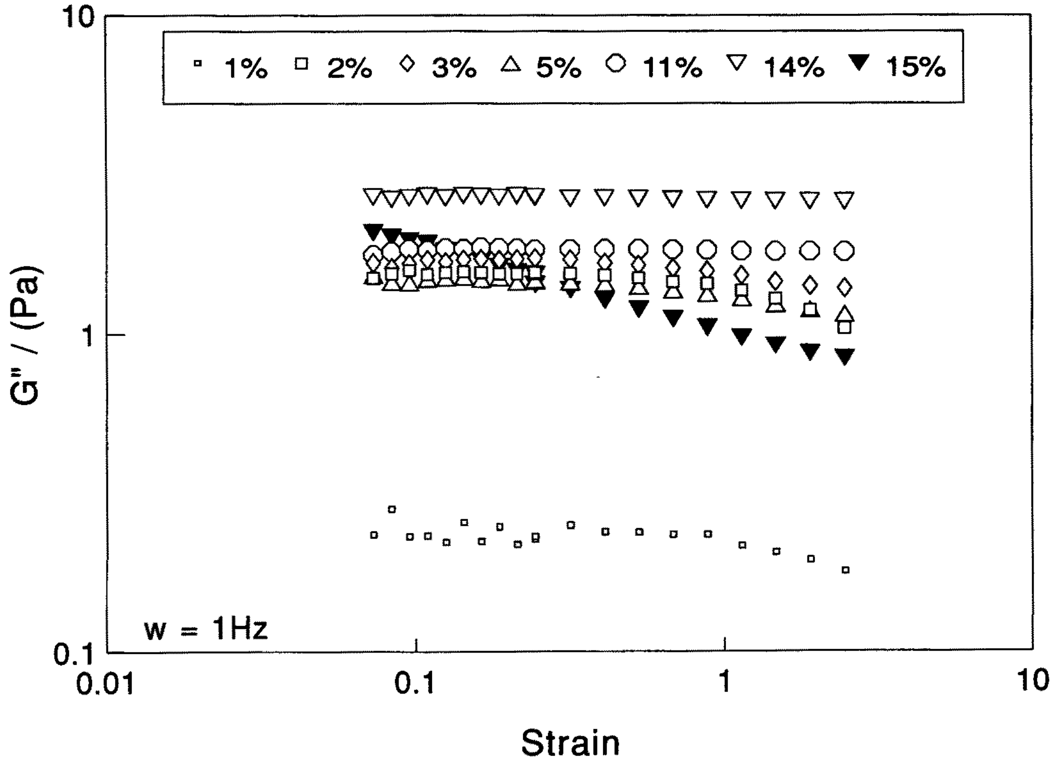

FIG. 7. Experimental and calculated limit viscosity values *vs.* SE concentration.

35% (wt) SE. However, around that and higher concentrations, a decrease in S is noticed.

Strain sweep tests. Oscillatory shear experiments, at a frequency of 1 Hz, were conducted by varying the strain amplitude to search for the linear viscoelastic domain, that is to say, the strain range where the structure of the sample is not destroyed by shear. This may be identified as the range in which neither the storage modulus (G′) nor the loss modulus (G″) are influenced by strain. G′ gives an idea of the elastic components in the sample, while G″ is associated with the energy dissipated due to viscous effects (18).

As can be observed in Figure 9, G′ is not influenced by strain, within the experimental range covered, below 15% (wt) SE. G′ values for compositions ranging from 2% to 15% (wt) SE lie between 0.8 and 3 Pa. The system containing 1% (wt) SE exhibited a significantly lower G′, which tested the instrument's lower limit of sensitivity. Therefore, this result is not presented in Figure 9, even though an average value of about 0.02 Pa might be proposed. In any case, it is worth emphasizing that when SE concentration is increased from 1% to 2% (wt), the storage modulus goes up about two decades.

The strain dependence of G″ is shown in Figure 10, which shows a pattern similar to that of Figure 9. However, some differences can be noted—only at 11% and 14% (wt) SE does G″ remain independent of strain within the whole experimental range covered. Nevertheless, a significant linear viscoelastic range could be attained for compositions ranging between 1% and 14% (wt) SE. At 15% (wt) SE, G″ drops throughout the strain range covered, and the same behavior is found at higher SE concentrations. This, along with the G′ fall, precluded the determination of the linear region for these systems. Finally, in this case, an increase in SE concentration from 1% to 2% (wt) only gives rise to a rise in G″ of about one decade.

DISCUSSION

A global analysis of the rheological parameters obtained at steady shear, as well as of the microphotographs showing the liquid crystalline textures, made it possible to draw some conclusions about the influence of SE concentration on the association structure and rheology of these systems. The rheological behavior at 50°C was found to be consistent with the phase behavior determined. Therefore, three composition ranges can be established by analyzing the obtained results.

The first one extends up to about 10% (wt) SE and is characterized by a sharp increase in critical shear rate. In other words, the shear rate range over which viscosity remains constant is wider as surfactant concentration increases. This may be attributed to the existence of an increasingly stronger micellar structure, due to the fact that the size and number of micelles must increase with surfactant concentration (19). As a result, intermicellar interactions play an increasingly important role. Because we are dealing with a nonionic surfactant, such intermicellar forces must be connected to steric repulsions between head groups on adjacent micelles and long-range forces associated with solvation of the head groups (20).

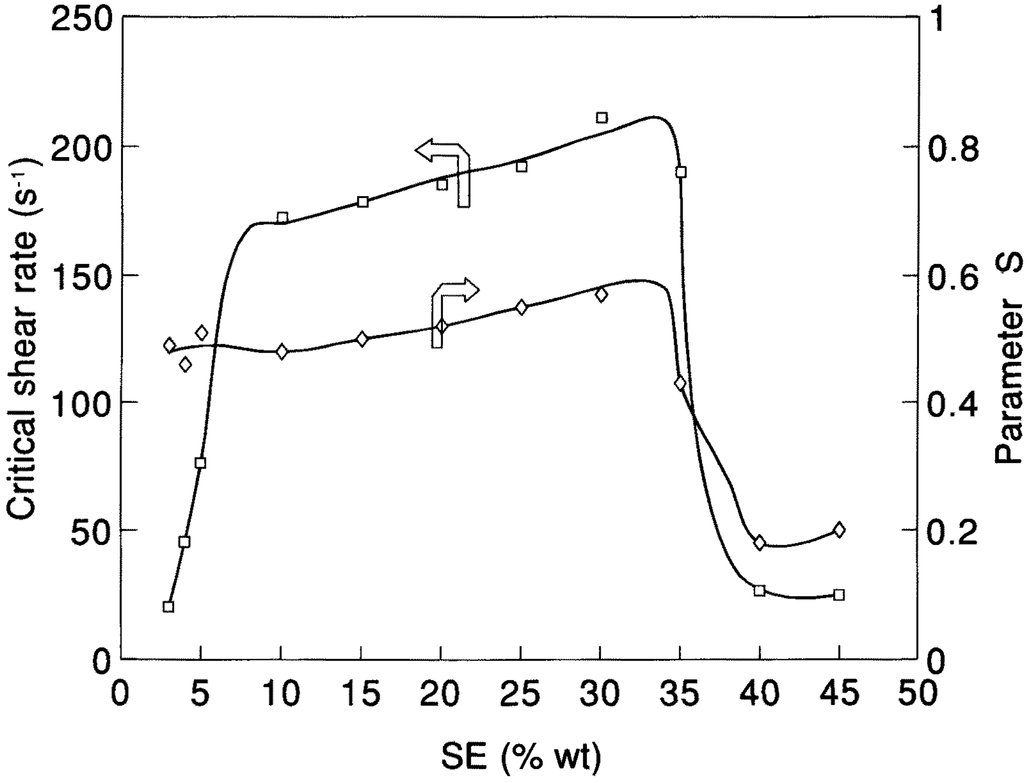

FIG. 8. Critical shear rate and parameter S values *vs.* SE concentration.

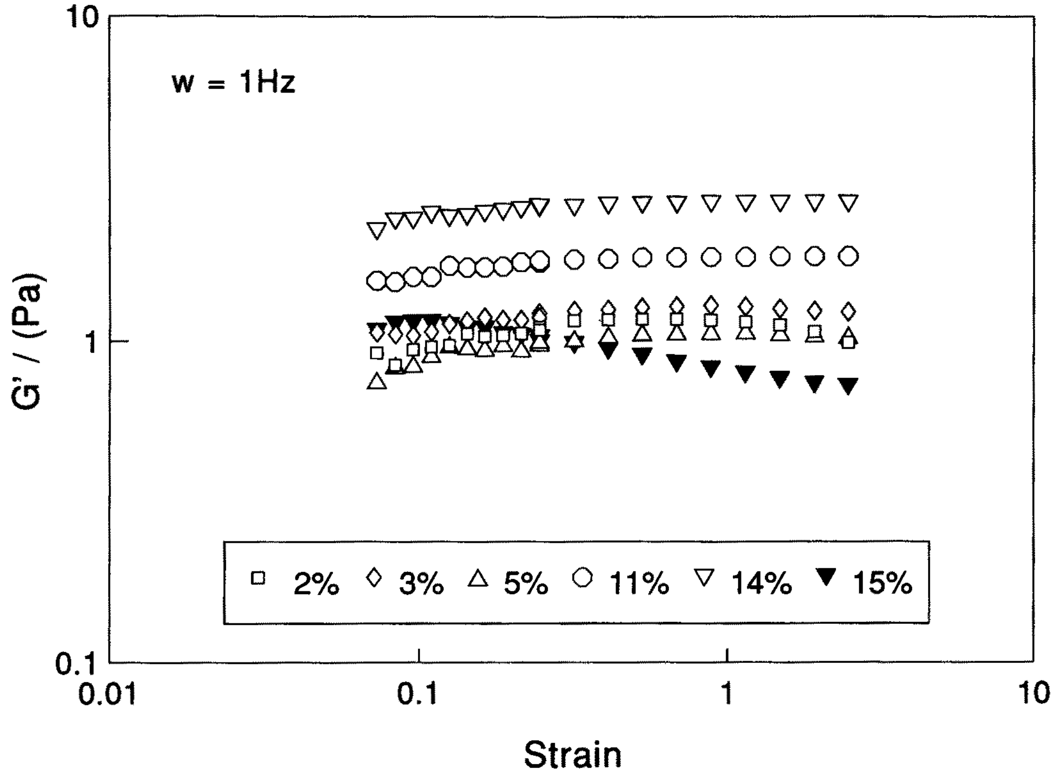

FIG. 9. Storage modulus *vs.* strain for various SE concentrations.

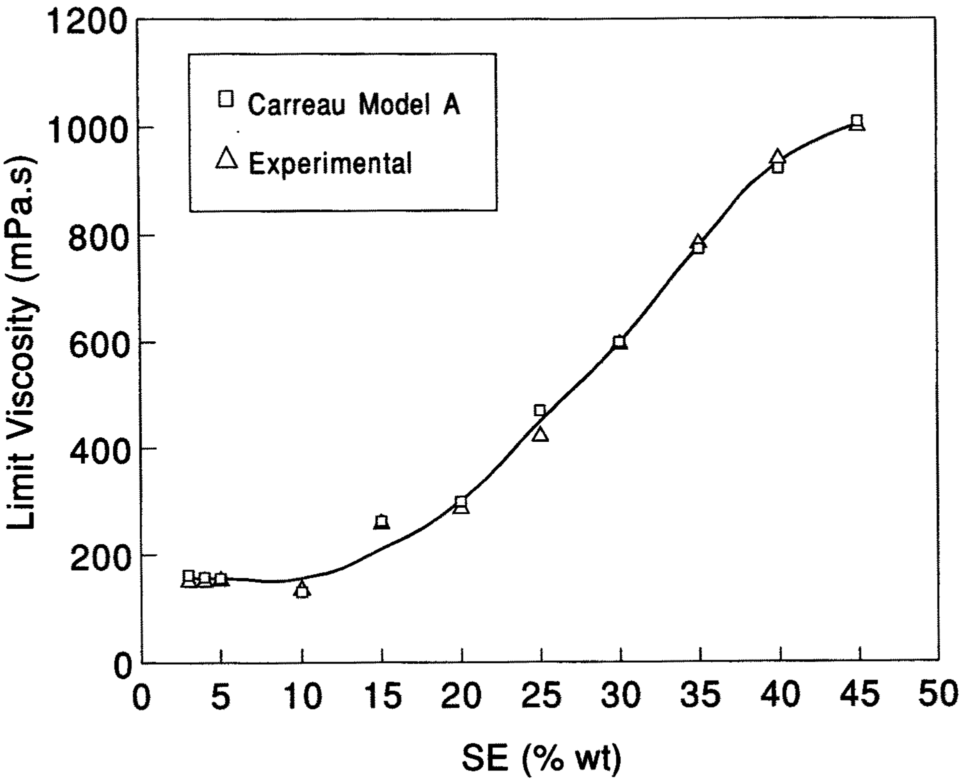

FIG. 10. Loss modulus *vs.* strain for various SE concentrations.

A significantly weaker micellar structure may be expected for the system containing 1% (wt) SE, as can be deduced from the fact that a limit viscosity could not be reached at the lower shear rate available, and from the lower viscosity and dynamic viscoelastic values obtained. Furthermore, it must be pointed out that at 1% (wt) SE, the lowest concentration studied, a measurable viscoelasticity is exhibited. This is important for applications such as emulsifiers and stabilizers for emulsions and foams. The onset of viscoelasticity may be attributed to the overlapping of micelles, which results in hindrance of free movement under flow (21). A further point to consider is that the micellar shape must be similar within this composition range, as may be deduced from the fact that both the limit viscosity and parameter S values do not significantly vary between 3-10% SE. Apart from that, the lack of birefringence, according to the optical study carried out, demonstrates that well-developed lamellar liquid crystals were not yet present.

The increasing importance of intermicellar interactions, as surfactant concentration rises, leads to the formation of liquid crystalline structures. Thus, a second range, corresponding to the occurrence of a lamellar liquid crystalline dispersion in a micellar phase, may be described between 10% and 35% (wt) SE. The appearance of this association structure at an apparently "low" surfactant concentration for this mesophase, may be explained on the basis of the existence of 30% di- and triester in the sucroester used (9). Upon analyzing the surfactant concentration dependence of the parameters that describe the flow behavior of these systems, this composition range can be characterized by the following facts: the limit viscosity keeps growing steadily, the critical shear rate hardly rises, and parameter S only decreases at 35% (wt) SE or higher. Further information was obtained from oscillatory tests. The fact that at 15% (wt) SE and higher, the linear viscoelastic range is significantly reduced may be attributed to a predominant presence of liquid crystalline portions in the dispersion. In fact, liquid crystals are known to be extremely sensitive to either thermal or mechanical influences (22-24). It is noteworthy that whereas the linear viscoelastic domain at 15% (wt) and higher drops substantially, the critical shear rate keeps growing up to 35% (wt) SE. This gives an idea of the structural changes that these samples undergo when flowing. As SE concentration increases, the liquid crystalline content of the dispersion must also increase up to the formation of a monophasic liquid crystal.

The appearance of lamellar liquid crystals is associated with the occurrence of disorder-order transitions from bilayer micelles without a change in micellar shape (19). The systems containing 40% and 45% (wt) SE belong to the third composition range, which may be characterized by the formation of a fully developed lamellar liquid crystal, as demonstrated by polarization microscopy.

The rheological response of these systems is characterized by a significant decrease in parameter S values, as well as critical shear rate values (Fig. 8), and by a further increase in the limit viscosity (Fig. 7). These results show that the lamellar liquid crystal undergoes a higher structural destruction with shear rate, as may be deduced from the fact that their viscosity values at high shear rate are even lower than those of less concentrated systems (Fig. 6).

A three-parameter rheological model was used to define the flow behavior of sucrose stearate/water systems at 50°C. This temperature is slightly higher than the melting point of the crystalline phase. These parameters, along with those derived from strain sweep tests and polarization microscopy observations, allowed us to explain how far the structure of these systems is influenced by surfactant concentration.

Future work will be devoted to carrying out a study on the influence of temperature, as well as to developing a more comprehensive study of the linear and nonlinear viscoelastic behavior of systems containing sucrose stearate.

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