

# An Investigation into the Supramolecular Structure of Ternary Gel Systems Using Oscillatory Rheometry, Microscopy, and Low Frequency Dielectric Spectroscopy

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**Abstract** □ A series of ternary gel systems based on cetostearyl alcohol (CSA) and cetomacrogol 1000 or sodium lauryl sulfate have been studied using oscillatory rheology, differential interference contrast (DIC) microscopy, cryoscanning electron microscopy (cryo-SEM), and low-frequency dielectric analysis in order to elucidate the nature of the lamellar structures formed in relation to composition. The effects of altering the concentration of CSA (0.25% to 8% w/w) for 1% and 2% w/v cetomacrogol 1000 and 0.5% and 1% w/v sodium lauryl sulfate systems have been investigated, with marked increases in the storage and loss moduli seen on increasing the concentration of CSA for both surfactants. DIC microscopy indicated that at low CSA concentrations, needlelike structures were seen which, on increasing the concentration, were observed to congregate into nuclei. At concentrations of 4% CSA and above, neospherical structures were also observed. Cryo-SEM revealed that the needlelike objects were sheet structures ascribed to lamellar gel phases, while the nuclei were folded "rosettes" formed by those sheets, with the spherical structures being ascribed to cetostearyl alcohol. It was also noted that the lamellae were more tightly folded at 8% w/w CSA, which may be associated with the higher rheological moduli for these systems. Low-frequency dielectric analysis was performed over a frequency range of  $10^4$  Hz to  $10^{-2}$  Hz. A decrease in both the dielectric loss and capacitance was observed as the concentration of cetostearyl alcohol was increased. The dielectric data were described in terms of an equivalent circuit model based on a modified Maxwell–Wagner response. A good correlation was found between the fitted and experimental data and the effect of altering the gel composition on specific features of the equivalent circuit are discussed.

## Introduction

Despite the widespread use of semisolid emulsions for topical application, the physical characterization of these systems remains a persistent difficulty. This problem may be ascribed to the physical complexity of creams as the emulsifying agents, which are present in excess of the quantities required to form interfacial monolayers between the oil and aqueous phases, form a range of structures

within the continuous phase, resulting in the system exhibiting viscoelastic behavior. Several authors (e.g., refs 1–6) have emphasized the importance of interdroplet liquid gel network formation in determining the rheological properties and physical stability of creams. For example, Barry and Saunders<sup>7</sup> have demonstrated that the influence of alkyltrimethylammonium bromide chain length on the rheological properties of liquid paraffin creams may be attributed to differences in smectic structure formation with cetostearyl alcohol, while Eccleston<sup>8</sup> has correlated changes in the rheological properties of cetrinide creams to alterations in the physical structure of the continuous phase formed via the interaction of cetrinide and fatty alcohols in water.

A number of techniques have been used for the evaluation of creams, including rheology (e.g., refs 1–3), microscopy,<sup>9,10</sup> and thermal analysis.<sup>5,11,12</sup> In addition, a limited number of studies using low-frequency dielectric spectroscopy have also been described.<sup>13–16</sup> This method involves the application of an oscillating electric field to a sample and the measurement of the response in terms of the real and imaginary components of the complex capacitance  $C^*$  at frequency  $\omega$ , with

$$C^*(\omega) = C(\omega) - iC''(\omega) = \frac{A\epsilon_0}{d} [\epsilon'(\omega) - i\epsilon''(\omega)] \quad (1)$$

where  $C$  and  $C''$  are the real and imaginary capacitances,  $i$  is the square root of  $-1$ ,  $A$  is the electrode area,  $d$  is the sample thickness,  $\epsilon_0$  is the permittivity of free space and  $\epsilon'$  and  $\epsilon''$  are the real and imaginary permittivities. The term  $C$  is synonymous with the measured (real) capacitance while  $C''$  is also referred to as the dielectric loss  $G/\omega$  where  $G$  is the conductance. The dielectric loss incorporates both a.c. and d.c. conductance processes. More details of the approach are available from a number of texts.<sup>17–19</sup> A facet of the approach is to develop a circuit model which gives an equivalent response to that of the sample, thereby facilitating assignment of circuit elements to specific structures within the system. This approach has been adopted in a recent study<sup>16</sup> in which the response of Aqueous Cream BP was successfully modeled in terms of a modified Maxwell–Wagner response, thereby presenting the possibility of relating specific features of the cream to components of the circuit. With further development, this approach has clear potential as a means of characterizing complex semisolid materials.

It is now well established that the interaction between the surfactant and long chain alcohol (and the chemical

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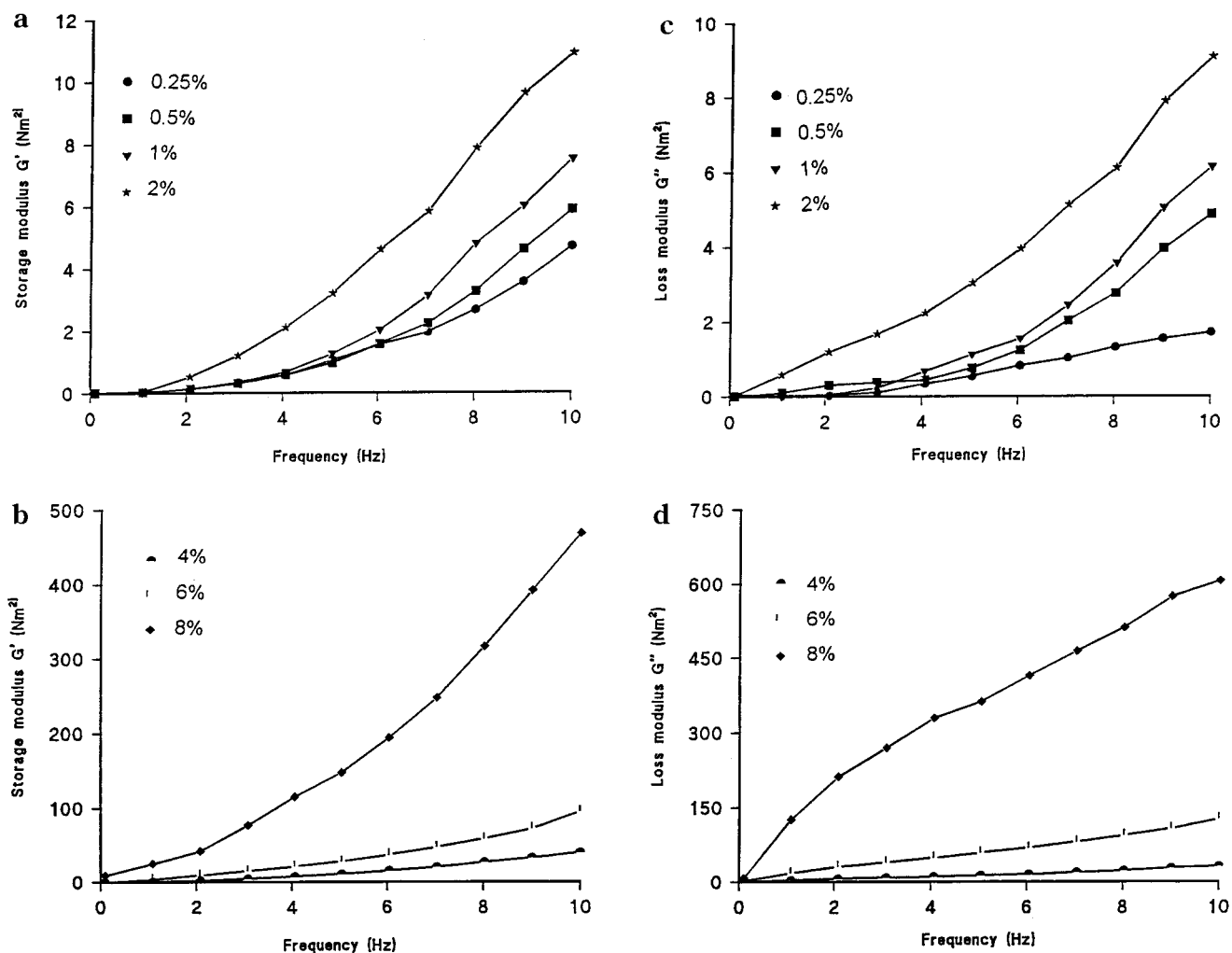


Figure 1—Rheological storage moduli (a, b) and loss moduli (c, d) for ternary systems containing 1% cetomacrogol 1000, water, and cetostearyl alcohol (concentrations as indicated) at 298 K.

compositions of both components) is a key factor in determining the rheological properties of the cream. In addition, it is also accepted that the basic structure of o/w creams consists of hydrated lamellae composed of the alcohol and surfactant, bulk aqueous and oil phases, and, depending on composition, precipitated hydrates of the long chain alcohol. However, considerably less is known regarding the distribution of components on a supramolecular level and how this distribution may be related to product performance. In this investigation, a series of ternary gels (systems containing surfactant, alcohol and water) have been prepared using a range of compositions in order to systematically study the development of structure within the gels. Such systems have been previously used as model creams (e.g., refs 20–22), as these gels may contain all the components of the cream except for the oil phase, thereby simplifying analysis and aiding understanding of the nature of the lamellar phases formed. The rheological behavior of each system has been characterized using oscillatory rheometry and the appearance of the gels noted using differential interference contrast (DIC) microscopy, an optical technique which allows high contrast imaging of unstained samples, and cryo-SEM. In addition, the use of low-frequency dielectric spectroscopy as a means of cream characterization has been further developed via examination of these relatively simple controlled systems. Particular emphasis has been placed on monitoring the cetostearyl alcohol concentration dependence on structure formation in relation to viscoelastic properties. The influ-

ence of this ratio on the rheological behavior has not been extensively studied; hence, there is a clear relevance of such knowledge to cream formulation. In addition, the study of systems containing varying ratios facilitates examination of the formation of macroscopic structures, thereby aiding understanding cream structure.

## Materials and Methods

**Materials**—Cetostearyl alcohol was supplied by Unilever Research, Port Sunlight, Wirral; commercial grades of this material contain 50–70% stearyl alcohol and 20–35% cetyl alcohol, with smaller quantities of other alcohols such as myristyl alcohol present. Cetomacrogol 1000 was also supplied by Unilever Research, Port Sunlight, Wirral and is based on the formula  $\text{CH}_3(\text{CH}_2)_m(\text{OCH}_2\text{CH}_2)_n\text{OH}$ , where  $m$  is 15–17 and  $n$  is 20–24. Sodium lauryl sulfate was obtained from BDH. Deionized water was used throughout the study.

**Composition and Manufacture of Ternary Systems**—Systems were prepared containing 1% w/v and 2% w/v cetomacrogol 1000 and 0.5% and 1% w/v sodium lauryl sulfate with up to 8% cetostearyl alcohol. The water phase was heated in a jacketed and baffled mixing vessel to 70 °C, after which the surfactant was dissolved and the cetostearyl alcohol added and allowed to liquefy. The mixture was then mixed at 10000 rpm using a Heidolph Diax 600 homogenizer disperser mixer for 15 min. The heater was then turned off, and the system was mixed to ambient temperature at 500 rpm. All systems were stored for 14 days prior to testing in order to allow time for the microstructure to develop.

**Rheological and Microscopic Measurements**—Oscillatory rheological determinations were carried out using a Carrimed CSL

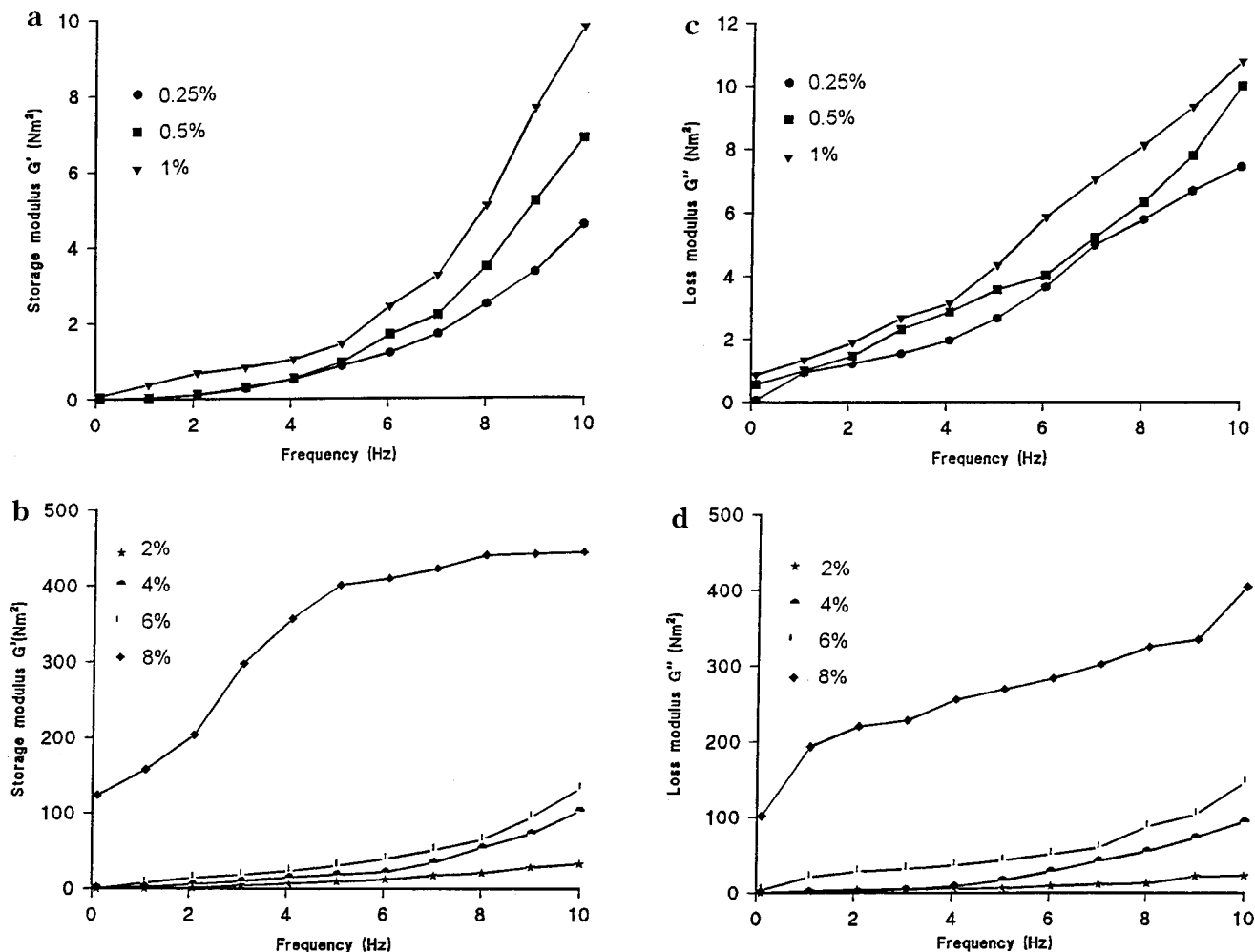


Figure 2—Rheological storage moduli (a, b) and loss moduli (c, d) for ternary systems containing 0.5% sodium lauryl sulfate, water, and cetostearyl alcohol (concentrations as indicated) at 298 K.

500 controlled stress rheometer (TA Instruments Ltd., Surrey, UK), used in cone and plate mode. An oscillating stress of 0.1–10 Hz was applied to each sample at 298 K. The torque used was 200  $\mu$ N which was established by torque sweep to be within the linear viscoelastic range. Samples were run at least three times to ensure reproducibility, with the values having a coefficient of variation within 5%. The plate and cone were cleaned thoroughly between runs.

Differential interference contrast microscopy was carried out using an Olympus BX50 microscope. A Nikon fully automatic single lens reflex camera was employed for the photographic work. The scanning electron microscopy studies were carried out using a Cambridge Scientific S360 instrument fitted with an Oxford Instruments cold stage. Undiluted samples were placed on the sample holder which was immersed in liquid nitrogen ( $-196^{\circ}\text{C}$ ). The material was then loaded into the microscope fracture chamber, also at  $-196^{\circ}\text{C}$ , and fractured. The sample was subsequently transferred to the vacuum chamber ( $-196^{\circ}\text{C}$ ), the vacuum applied, and the surface water sublimed. After removal from the vacuum chamber, the sample was electroplated with gold under an argon atmosphere.

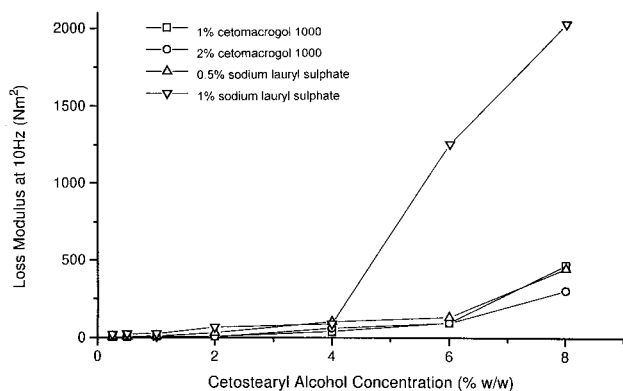
**Dielectric Analysis**—Dielectric studies were conducted using a low-frequency dielectric spectrometer (Dielectric Instrumentation Ltd., Worcs.) which measures between the limits of  $10^6$  to  $10^{-4}$  Hz. Measurements were conducted in a stainless steel cell comprising two circular parallel plates (area 12.6  $\text{cm}^2$ , electrode separation distance 1 mm), as described in a previous study.<sup>16</sup> Three measurements are taken at each frequency, with averaged results being within a coefficient of variation of 2%. Samples were measured over a frequency range of  $10^5$ – $10^{-2}$  Hz at  $25^{\circ}\text{C}$  using a field of 0.1 V rms. Empty cell runs were performed between runs to ensure cell cleanliness; repeat runs of each sample showed the spectra to be superimposable. Equivalent circuit analysis was

performed based on the model proposed by Hill and Pickup<sup>23</sup> using the Winfit 2.0 computer program supplied by Novocontrol GmbH, as described in previous studies.<sup>16,24</sup>

## Results

**Rheological Studies**—The frequency-dependent rheological responses of the nonionic systems containing 1% cetomacrogol 1000 are shown in Figures 1a–d in terms of the storage and loss moduli. A marked increase in both storage and loss were noted on increasing the concentration of cetostearyl alcohol, with a similar trend being noted for the 2% w/v cetomacrogol 1000 systems. Likewise, Figure 2a–d shows the responses of the ionic systems containing 0.5% sodium lauryl sulfate, with an increase in storage and loss again being noted as the concentration of CSA increases. However, it was noted that in this case a more marked increase in both components was seen between 6% and 8% w/v CSA. A similar trend was seen for the 1% w/v SLS systems, although the increase in moduli at higher CSA concentrations was considerably more marked. The relationship between the loss modulus at 10 Hz and cetostearyl alcohol composition is summarized in Figure 3 for the four surfactant systems. The same general trend of a nonlinear increase in loss moduli was observed in all cases, although clearly the 1% ionic gels gave the highest responses, particularly at higher CSA contents.

**Microscopy Studies**—Representative DIC photomicrographs for the 1% cetomacrogol 1000 systems are shown



**Figure 3**—The effect of cetostearyl alcohol concentration on the rheological loss moduli (10 Hz) of ternary systems containing cetomacrogol 1000 or sodium lauryl sulfate.

in Figure 4a–d. At low concentrations of CSA (0.25% w/w, Figure 4a), needlelike structures are seen, while as the concentration increases to 1% (Figure 4b), nuclei are seen in the center of clusters of the needle structures. This effect is further enhanced at 4% w/w CSA (Figure 4c), with a number of small (<5  $\mu\text{m}$ ) spherical structures seen. At 8% w/w CSA, a preponderance of these spherical structures is seen (Figure 4d). Similar trends were seen for the 2% cetomacrogol systems, with a representative photomicrograph being shown in Figure 4e. The appearance of the ionic creams was similar, with a representative photomicrograph being given in Figure 4f. However, it is interesting to note that for equivalent CSA concentrations (8% w/w), the ionic creams showed a lower density of the spherical structures than was seen for the cetomacrogol 1000 systems; the significance of this will be discussed in a subsequent section.

Figure 5a,b shows representative cryo-SEM images of the 2% w/w and 8% w/w CSA for the 2% cetomacrogol 1000 systems. Figure 5a shows rosette-type structures which correspond in size and appearance to the nuclei seen in Figure 4b; the SEM images indicate that these nuclei are in fact concentric layers rather than continuous structures. The highest concentration CSA systems (Figure 5b) showed a highly folded structure in which neospherulitic objects were distributed. The size range of these spheres (approximately 5–10  $\mu\text{m}$ ) corresponds reasonably well to that the spherical objects seen at the equivalent concentration using DIC microscopy (Figure 4).

**Dielectric Analysis**—The dielectric responses of the ternary systems containing 1% and 2% cetomacrogol 1000 and a concentration range of 0.25 to 8% cetostearyl alcohol are shown in Figure 6a,b. The real and imaginary relative permittivities are expressed in terms of the capacitance  $C(\omega)$  and dielectric loss  $G(\omega)/\omega$ , where  $G(\omega)$  is the conductance, which are related to the former parameters via

$$\epsilon'(\omega) = \frac{C(\omega)d}{A\epsilon_0} \quad (2)$$

and

$$\epsilon''(\omega) = \frac{G(\omega)}{\omega} \frac{d}{A\epsilon_0} \quad (3)$$

where  $d$  and  $A$  are the interelectrode distance and electrode area, respectively. An increase in the cetostearyl alcohol concentration led to a fall in both the capacitance and loss components of the sample over the majority of the frequency range under study, with a marked decrease seen between 0.5% and 2%. Similar trends were seen for systems

containing 2% cetomacrogol 1000. Furthermore, the responses of systems comprising 0.5% and 1% sodium lauryl sulfate and varying quantities of cetostearyl alcohol showed similar concentration dependence, as shown in Figure 7a,b. The capacitance of some of these systems became noisy at frequencies between  $10^3$  and  $10^4$  Hz due to the instrument approaching the limits of measuring capability; hence, these data have not been included. Clearly, however, the real and imaginary permittivities show a general trend of a decrease with CSA concentration. Such observations are of interest but somewhat limited in applicability in the absence of more sophisticated structural analysis; hence, the responses have been studied in terms of an equivalent circuit model.

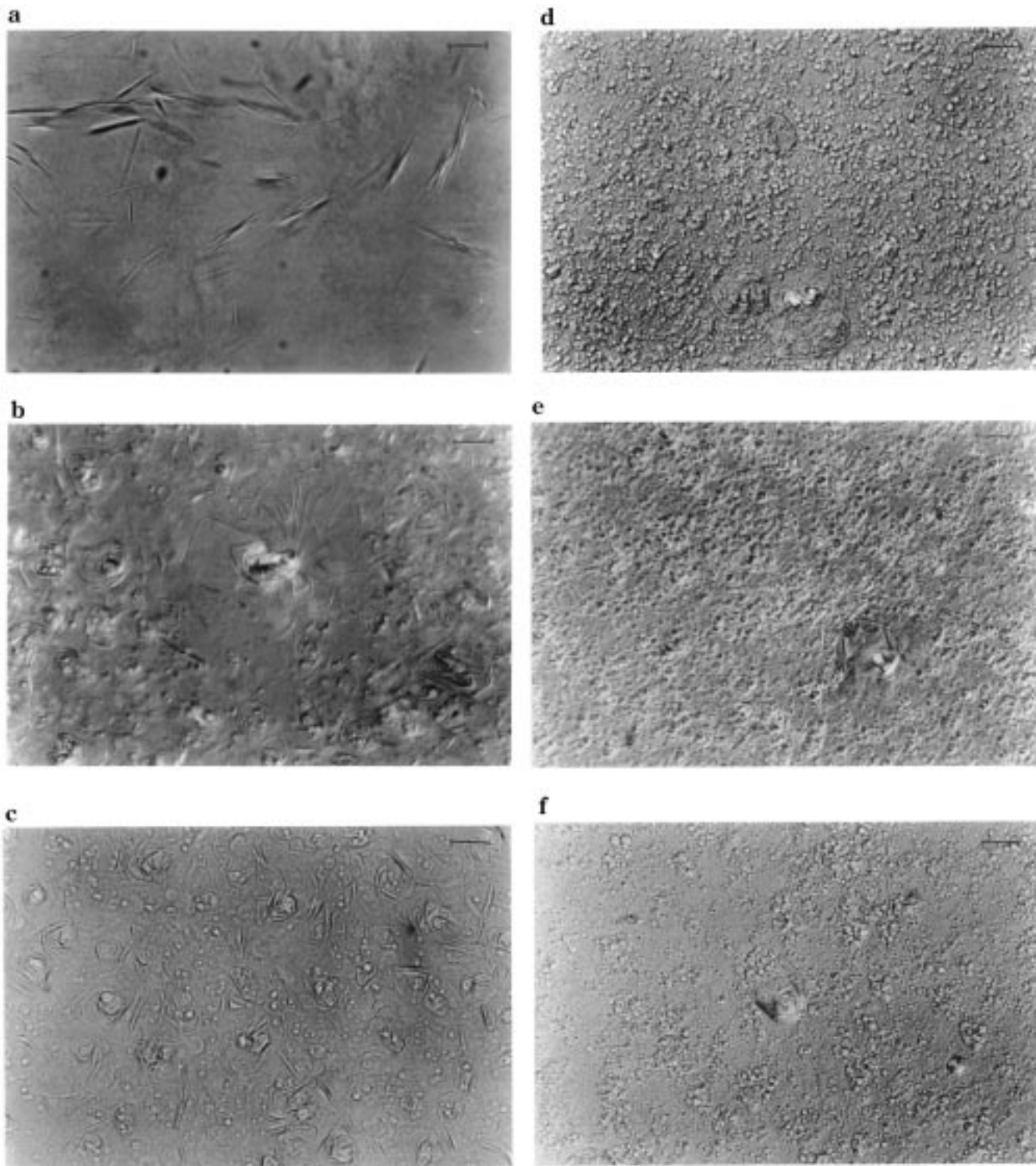
**Circuit Analysis of the Response**—The circuit model which was developed for this study is based on earlier studies on related systems<sup>16–18</sup> and our own studies on complex semisolid systems.<sup>19,24,25</sup> The diagram which was found to yield the optimum fit is shown in Figure 8. The circuit corresponds to a modified Maxwell–Wagner response,<sup>23</sup> comprising a dispersive (frequency dependent) capacitor  $C_s$  in series with a parallel RC circuit, these two main features corresponding to a barrier (electrode surface) and a bulk response, respectively. The barrier response corresponds to a thin layer adsorbed onto the electrode surfaces and may be described by

$$C_s = C_{s=0} (i\omega/\omega_s)^{-s} \quad (4)$$

where  $s$  is the power law index which indicates the frequency dependence of  $C_s$  and  $C_{s=0}$  is the capacitance when  $s = 0$  and  $\omega_s$  is a characteristic frequency. It is essential to incorporate the response of such electrode barrier layers when modeling dielectric data of liquid and semisolid systems, particularly in the low-frequency region, as such features may result in high real and imaginary  $C$  values in the sub-Hz range. The nondispersive parallel RC circuit  $R_1C_1$  represents the bulk resistance (inverse conductivity) and capacitance of the sample, while the series element  $R_2C_2$  comprises a nondispersive resistance in series with a dispersive capacitor given by

$$C_2 = C_{r=0} (i\omega/\omega_n)^{-n} \quad (5)$$

which is identical in form to eq 4, the index  $n$  indicating the power law behavior of the capacitance element. The fitted data are shown as continuous lines in Figures 6 and 7 and the circuit element values for the various systems given in Table 1. While minor changes in capacitance and resistance values may not be regarded as significant due to the inevitable approximations involved in the modeling, changes of 1 order of magnitude or more represent differences which are greater than those expected from the errors arising from the modeling process. The values of  $C_1$  did not show a marked sensitivity to changes in formulation; this value can be considered to be equivalent to the dielectric constant of the sample which, given the high content of water in all the creams, may not be expected to vary greatly with comparatively small changes in the concentration of the minor components. It was noted, however, that the 2% cetomacrogol systems appeared to have higher  $C_1$  values, the reasons for this being unclear at present. The values of  $R_1$  increased on raising the CSA composition, reflecting the greater tortuosity of charge movement through these systems. It is also noted that the  $R_1$  values for the ionic creams were lower than the nonionic by approximately 1 order of magnitude. The values of  $R_2$  and  $C_{r=0}$  have been associated with the behavior of thin layers within samples,<sup>19,24</sup> as indicated by the high values of capacitance compared to  $C_1$ . Indeed it has been argued



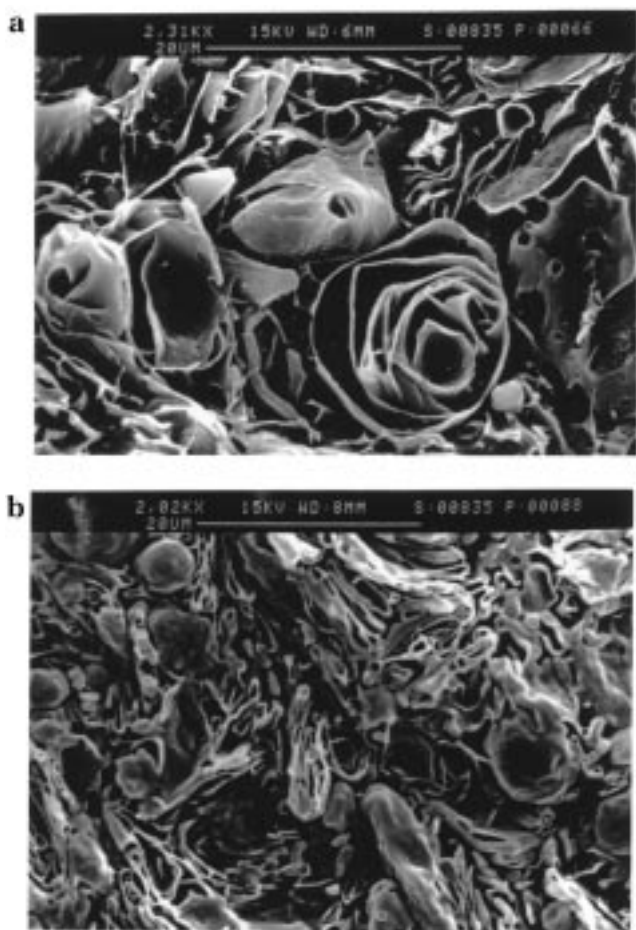
**Figure 4**—DIC images of ternary systems containing water and (a) 1% cetomacrogol 1000, 0.25% w/w CSA; (b) 1% cetomacrogol 1000, 1% CSA; (c) 1% cetomacrogol 1000, 4% CSA; (d) 1% cetomacrogol 1000, 8% CSA; (e) 2% cetomacrogol 1000, 8% CSA; (f) 0.5% sodium lauryl sulfate, 8% CSA. Bar = 25  $\mu$ m.

that examination of these values may yield insights into the lamellar structure of creams.<sup>19</sup>

### Discussion

The study has demonstrated clear compositional dependence of the supramolecular structure and behavior of ternary gel systems. Such changes must be considered in the context of the existing knowledge base associated with

cream formation and structure. During the preparation of creams (or ternary systems), heat is applied which results in the melting of the fatty alcohol which, on dispersion, interacts with the aqueous surfactant to form smectic liquid crystals.<sup>26</sup> Barry and Shotton<sup>27</sup> have suggested that these liquid crystalline phases are elongated into lamellar (“threadlike”) structures via turbulence effects. These lamellae form hydrated networks on cooling to the gel phase, this network being largely responsible for the viscoelastic properties of the cream. Interestingly, on the

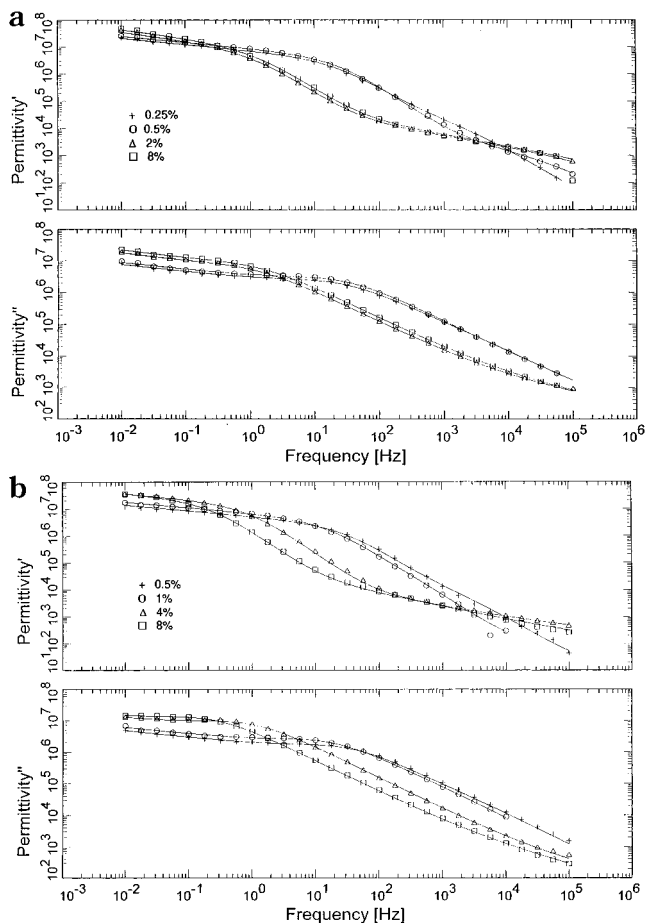


**Figure 5**—Cryo-SEM images of ternary systems containing 2% cetomacrogol 1000, water and (a) 2% w/w CSA (b) 8% CSA.

basis of optical microscopic observations, these authors also suggested the formation of spherulites composed of the liquid crystal/gel phases. The remaining cetostearyl alcohol solidifies either as one of a number of polymorphs or as a hydrate due to the ability of this material to undergo limited swelling in water.

The majority of studies which have examined the rheological properties of creams and ternary systems have used the standard ratios of 9:1 (ionic) and 4:1 (nonionic) alcohol to surfactant; hence, the influence of the ratio used has not been extensively studied. Indeed, Barry and Saunders<sup>28</sup> have reported that the ratio may not be a critical factor in determining the rheological properties of creams. The data presented here do not directly contradict this statement in that the earlier study used a fixed concentration of emulsifier, while the present investigation involved increasing absolute concentrations. Nevertheless, the clear observed dependence of the storage and loss moduli on composition is of interest in terms of controlling the rheological properties of creams and complements earlier studies which have examined the effects of varying the total emulsifier concentration.<sup>26</sup>

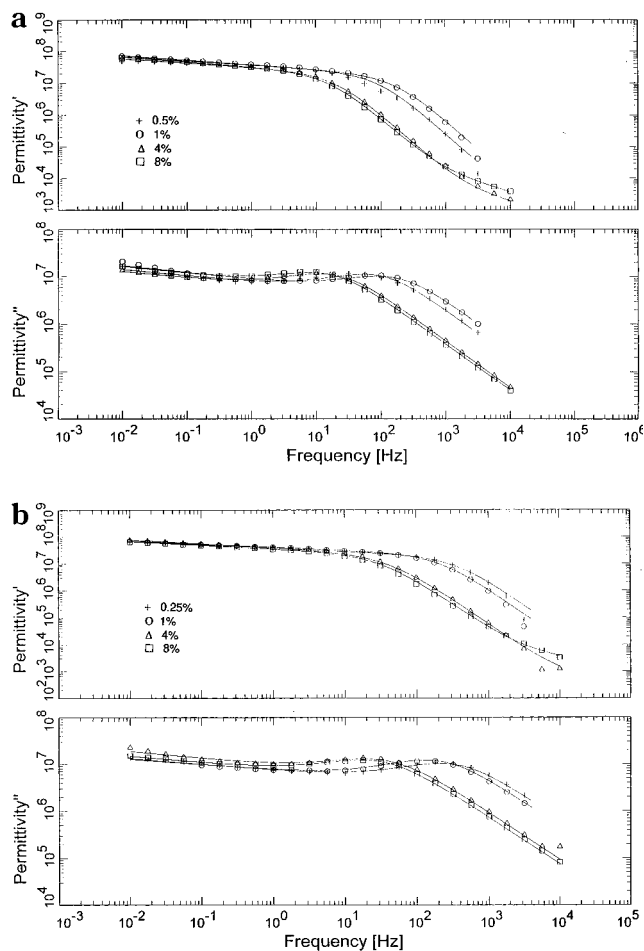
The comparison between ternary systems containing nonionic and ionic surfactants is of interest in that the behavior of the two sets of systems is comparable at low CSA contents. However, at 1% SLS a marked increase in storage and loss moduli is observed at high CSA contents. Earlier studies have suggested that the rate of interaction between ionic surfactants and CSA is far greater than for nonionics, leading to formation of a kinetically stable system over a shorter time period when using the former.<sup>26,28</sup> As the samples under examination here were tested at



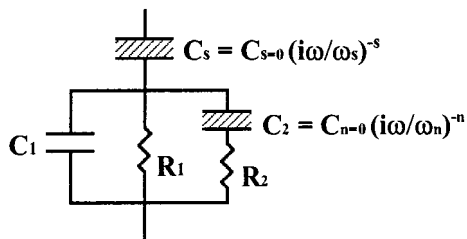
**Figure 6**—Real and imaginary permittivities of ternary systems containing (a) 1% cetomacrogol 1000 and (b) 2% cetomacrogol 1000, water and cetostearyl alcohol (concentration as indicated) at 298K. Solid lines indicate fitting according to circuit diagram shown in Figure 9.

comparable time periods after manufacture, one would expect higher moduli for the ionic systems. In fact, such effects were only observed for the higher CSA content systems, implying that the nature of the surfactant only becomes critical when the structure formed between 4% and 6% CSA is present.

The rheological studies allow characterization of the macroscopic behavior of the sample but in themselves yield little information on the specific structural origin of the observed effects. In this respect the microscopic studies (both using optical and electron beam techniques) are of considerable use. DIC microscopy is particularly well suited to the study of such systems as it allows high contrast images to be obtained in complex samples containing materials of similar refractive index. At low CSA concentrations, the DIC microscopy indicated threadlike structures which almost certainly correspond to those described by Barry and Shotton.<sup>27</sup> On raising the concentration of CSA, spherical structures are observed which may again correspond to the observations of Barry and Shotton.<sup>27</sup> However, the cryo-SEM studies indicated that these “nuclei” are in fact folded lamellae rather than continuous structures; hence, their formation may be related to the quantity and degree of curvature of the lamellae. Similarly, as the CSA content was raised to 4%, further spherical structures were seen which, again in the light of cryo-SEM studies, appears to correspond to solid-phase CSA; similar observations using cryo-SEM with regard to the presence of excess CSA have been reported by Rowe and Bray.<sup>10</sup> It is also interesting to note the considerably more extensive



**Figure 7**—Real and imaginary permittivities of ternary systems containing (a) 0.5% sodium lauryl sulfate and (b) 1% sodium lauryl sulfate, water and cetostearyl alcohol (concentration as indicated) at 298K. Solid lines indicate fitting according to circuit diagram shown in Figure 8.



**Figure 8**—Equivalent circuit diagram for the dielectric responses shown in Figures 6 and 7. For explanation of notation see text.

folded lamellar network observed for the 8% systems shown in Figure 5b. Overall, the data presented here indicate that the observed rheological effects may be due to a combination of factors, including the nature of the lamellar material in terms of bilayer composition and water entrapment, the quantity of such material, and the supramolecular organization of the lamellae (e.g., presence as nuclei as opposed to folded lamellae, nature of the folding). The study suggests that this supramolecular structure may be an important consideration in terms of the understanding of the rheology of creams and ternary systems which has yet to be fully explored.

It is noteworthy that the DIC photomicrographs of the ionic ternary systems indicated a smaller quantity of solid-phase CSA compared to the equivalent nonionic systems, suggesting greater integration of the CSA into the lamellar phase (similar observations in a different context have been made by Eccleston<sup>2</sup>). This may in turn result in more

extensive structuring and hence higher viscoelastic moduli. The microscopic observations also serve to explain the concentration dependence of the difference between ionic and nonionic systems, as at low CSA concentrations the quantity of both ionic and nonionic surfactant may be sufficient to allow efficient incorporation of the CSA into the bilayers. As the concentration of CSA is raised, however, the differing penetration properties of the two surfactants becomes a critical factor in determining lamellar formation.

The dielectric data indicated that the bulk resistances of the gels increase with increasing CSA concentration, which may be attributed to more extensive lamellar structuring, as discussed previously.<sup>16</sup> Given the now reasonably well-established link between the bulk resistance and lamellar formation,<sup>16,24,25</sup> it is of interest to compare the dielectric and rheological data, as while the overall trends between the two are comparable, there are also a number of differences. For example, there is no marked change in resistance for 1% SLS systems at high concentrations of CSA, as there was in the rheological responses. The resistance will be a function of the nature of the charge carriers present and the tortuosity of the conduction path within the system. Increasing the content of insoluble CSA is unlikely to result in significant increases in the number and nature of charge carriers present (further evidenced by the increase in resistance with added CSA); hence, the observed effects are almost certainly due to changes in tortuosity of the system. If, however, no parallel trends with the rheology of systems with high CSA content are seen for the ionic systems, then the logical conclusion to be drawn is that the tortuosity (i.e., quantity and folding of the lamellae) is not the determining factor. Instead, the rigidity of the lamellae may be greater for the ionic systems at high CSA contents. As previously stated, the relative importance of the lamellar nature, quantity, and folding in determining the rheological moduli have not yet been fully deconvoluted; hence, it is not yet possible to ascertain these roles with certainty. The data presented here, however, suggest that dielectric analysis may have a role to play in making such determinations. In addition, the circuit model used in the present study appears to allow an excellent fit to a wide range of experimental data. The use of the technique to quantify the bulk resistance has been clearly demonstrated. However, values such as  $C_{n=0}$ , which have been previously associated with lamellar structure,<sup>19</sup> and which here show a decrease with increasing CSA content, may also provide useful information with regard to the structure of these systems. On a crude level, one can, with reference to eq 1, suggest that the observed decrease may be due to greater thickness of the lamellae, although clearly further studies are required before such direct correlations can be made. Nevertheless, the development of this modeling approach will depend first on being able to provide satisfactory fits with a range of experimental data and second with the fitting parameters to be at least intuitively compatible with the observed behavior of the system. In both these respects, the study described here has proved satisfactory.

## Conclusions

The study has provided insights into both the supramolecular structures formed in ternary systems and the use of low-frequency dielectric analysis as an analytical tool, with particular emphasis on circuit modeling. With respect to the former, increasing the CSA content leads to an increase in rheological moduli which may be associated with the formation of a range of supramolecular structures, including previously unreported folded "rosette" systems,

Table 1—Fitted Parameters Corresponding to the Dielectric Responses of Ternary Systems Containing Cetostearyl Alcohol (CSA), Water, and Either Sodium Lauryl Sulfate (SLS) or Cetomacrogol 1000 (Cmac), Using the Circuit Diagram Shown in Figure 8

sample	$C_1$ (F)	$R_1$ ( $\Omega$ )	$R_2$ ( $\Omega$ )	$C_{r=0}$ (F)	$n$	$C_{s=0}$ (F)	$s$
0.25% A	$1.04 \times 10^{-10}$	$1.41 \times 10^2$	$2.21 \times 10^2$	$1.61 \times 10^{-5}$	0.429	$1.29 \times 10^{-4}$	0.226
0.5% A	$1.00 \times 10^{-10}$	$1.13 \times 10^2$	$1.64 \times 10^2$	$2.84 \times 10^{-6}$	0.425	$1.56 \times 10^{-4}$	0.222
1% A	$2.31 \times 10^{-10}$	$3.53 \times 10^2$	$4.06 \times 10^1$	$1.37 \times 10^{-4}$	0.630	$2.02 \times 10^{-4}$	0.239
2% A	$1.00 \times 10^{-10}$	$1.22 \times 10^3$	$4.81 \times 10^1$	$2.21 \times 10^{-6}$	0.391	$1.95 \times 10^{-4}$	0.292
4% A	$1.15 \times 10^{-10}$	$7.82 \times 10^2$	$1.92 \times 10^1$	$2.25 \times 10^{-6}$	0.415	$1.75 \times 10^{-4}$	0.351
6% A	$1.00 \times 10^{-10}$	$1.65 \times 10^3$	$4.00 \times 10^1$	$1.10 \times 10^{-6}$	0.368	$1.51 \times 10^{-4}$	0.385
8% A	$1.00 \times 10^{-10}$	$9.20 \times 10^2$	$1.76 \times 10^1$	$3.20 \times 10^{-6}$	0.419	$2.42 \times 10^{-4}$	0.292
0.25% B	$6.05 \times 10^{-9}$	$9.01 \times 10^1$	$1.83 \times 10^2$	$1.25 \times 10^{-5}$	0.478	$2.12 \times 10^{-4}$	0.189
0.5% B	$1.98 \times 10^{-10}$	$1.62 \times 10^2$	$3.79 \times 10^2$	$1.13 \times 10^{-5}$	0.442	$9.01 \times 10^{-5}$	0.213
1% B	$1.10 \times 10^{-9}$	$2.07 \times 10^2$	$9.80 \times 10^2$	$1.05 \times 10^{-5}$	0.385	$1.18 \times 10^{-4}$	0.209
2% B	$1.16 \times 10^{-9}$	$4.59 \times 10^2$	$1.36 \times 10^1$	$3.89 \times 10^{-6}$	0.474	$2.85 \times 10^{-4}$	0.179
4% B	$2.27 \times 10^{-9}$	$9.43 \times 10^2$	$3.27 \times 10^1$	$1.42 \times 10^{-6}$	0.430	$2.43 \times 10^{-4}$	0.203
6% B	$9.02 \times 10^{-10}$	$1.42 \times 10^3$	$3.35 \times 10^1$	$1.91 \times 10^{-6}$	0.461	$2.51 \times 10^{-4}$	0.213
8% B	$1.10 \times 10^{-9}$	$2.74 \times 10^3$	$3.27 \times 10^1$	$2.55 \times 10^{-6}$	0.486	$2.49 \times 10^{-4}$	0.207
0.25% C	$1.00 \times 10^{-10}$	$5.47 \times 10^0$	$2.06 \times 10^2$	$1.24 \times 10^{-5}$	0.490	$2.90 \times 10^{-4}$	0.109
0.5% C	$1.00 \times 10^{-10}$	$7.09 \times 10^0$	$3.71 \times 10^2$	$1.00 \times 10^{-5}$	0.420	$5.35 \times 10^{-4}$	0.130
1% C	$1.00 \times 10^{-10}$	$4.35 \times 10^0$	$4.83 \times 10^2$	$4.56 \times 10^{-5}$	0.420	$5.66 \times 10^{-4}$	0.144
2% C	$1.00 \times 10^{-10}$	$2.05 \times 10^1$	$6.97 \times 10^2$	$5.15 \times 10^{-6}$	0.442	$5.29 \times 10^{-4}$	0.156
4% C	$1.00 \times 10^{-10}$	$3.19 \times 10^1$	$5.48 \times 10^1$	$3.30 \times 10^{-6}$	0.433	$4.58 \times 10^{-4}$	0.136
6% C	$1.00 \times 10^{-10}$	$4.99 \times 10^1$	$5.64 \times 10^1$	$6.01 \times 10^{-6}$	0.422	$4.60 \times 10^{-4}$	0.173
8% C	$1.00 \times 10^{-10}$	$3.81 \times 10^1$	$6.10 \times 10^1$	$6.83 \times 10^{-6}$	0.417	$4.90 \times 10^{-4}$	0.153
0.25% D	$1.00 \times 10^{-10}$	$2.13 \times 10^0$	$4.69 \times 10^2$	$1.09 \times 10^{-5}$	0.417	$5.45 \times 10^{-4}$	0.122
0.5% D	$1.00 \times 10^{-10}$	$1.28 \times 10^0$	$1.16 \times 10^2$	$2.86 \times 10^{-5}$	0.414	$5.62 \times 10^{-4}$	0.115
1% D	$1.00 \times 10^{-10}$	$2.98 \times 10^0$	$3.91 \times 10^1$	$5.37 \times 10^{-6}$	0.424	$5.77 \times 10^{-4}$	0.114
4% D	$1.00 \times 10^{-10}$	$1.53 \times 10^1$	$1.54 \times 10^1$	$1.29 \times 10^{-6}$	0.441	$5.89 \times 10^{-4}$	0.149
6% D	$1.00 \times 10^{-10}$	$1.45 \times 10^1$	$1.43 \times 10^1$	$1.03 \times 10^{-6}$	0.444	$5.32 \times 10^{-4}$	0.122
8% D	$1.00 \times 10^{-10}$	$1.95 \times 10^1$	$2.41 \times 10^1$	$4.80 \times 10^{-6}$	0.413	$5.20 \times 10^{-4}$	0.138

<sup>a</sup> A = 1% cetomacrogol 1000; B = 2% cetomacrogol 1000; C = 0.5% sodium lauryl sulfate; D = 1% sodium lauryl sulfate. % Values in table refer to % CSA.

although the relative roles of the nature, quantity, and arrangement of the lamellae in determining the rheological properties is still not fully understood. The dielectric data showed a clear decrease in imaginary permittivity with CSA content which, via circuit modeling, could be related to an increase in bulk resistance which was associated with the tortuosity of charge movement through the system. Further dielectric parameters were derived which, with further development and correlation using supportive technique, may yield further insights into the structure of these complex systems. Despite the considerable number of cream and gel products on the market, there are still numerous difficulties associated with these systems, including the predictability of viscoelastic properties, issues associated with physical stability, and a poor understanding of the effects of added drugs on both consistency and release. It is hoped that by understanding the macro- and microscopic structure in greater detail using techniques such as those described here these problems may be overcome on a rational basis.

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