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# A comparison of electrical and rheological techniques for the characterisation of creams

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**Abstract**

Two complex semi-solid emulsion systems, one ionic and one non-ionic, have been evaluated using both conventional (conductivity measurements and continuous flow rheology) and oscillatory (dielectric spectroscopy and oscillatory rheology) methods. The results of specific conductivity measurements indicated differences in charge mobility, with the ionic cream showing a considerable higher conductivity (171.0 $\mu$S/cm compared to 9.3 $\mu$S/cm for the non-ionic system). Dielectric spectroscopy allowed a more sophisticated electrical analysis to be obtained, and a discussion is given of how the data relates to the current model for interpreting the low frequency response. Flow and oscillatory results indicated that greater internal structuring, leading to higher elasticity, was achieved for the ionic system. It is demonstrated that both techniques yield different yet complimentary information on the cream structure. The study has indicated that the use of dielectric spectroscopy and oscillatory rheometry, in addition to conventional methods, may lead to a better understanding of the emulsion microstructure.

*Keywords:* Conductivity; Creams; Dielectric; Rheology

## 1. Introduction

Semi-solid emulsion systems (creams) are widely used as a means of both altering the hydration state of the skin and delivering drugs via the topical route. A considerable problem associated with the formulation and manufacture of creams has been the establishment of reliable techniques for their characterisation, largely because of the complexity of their physical structure. Continuous flow and single-point conductivity measurements (e.g. Nürnberg and Muckenschnabel, 1982; Cajkovac and Stivic, 1983; Kallioinen et al., 1994) have been widely used to characterise cream bases, although the interpretation of data may not always be straightforward.

An alternative, but related electrical approach, is dielectric analysis. This technique involves the application of an alternating electric field to a sample over a range of frequencies and the measurement of the sample response. This response will comprise an in-phase and out-of-phase component with respect to the fluctuations in field direction, hence two parameters may be measured

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at any single frequency (Craig, 1995). These two components are the capacitance (C) and dielectric loss ($G/\omega$, where G is the conductance and $\omega$ is the angular frequency). Previous studies (Rowe et al., 1988; Goggin et al., 1994) have indicated that the technique may be highly useful in the characterisation of creams, as not only may all the information given by conductivity measurements be obtained, but in addition information on the microstructure of the cream is given from both the absolute values of capacitance and dielectric loss and also from the shape of the spectra. It should be emphasised that while conductivity measurements are usually single point determinations, the equipment used in fact operates at a set frequency, hence these values are essentially single frequency dielectric loss measurements. The assumption is made that the conductivity is independent of frequency under the conditions of measurement.

In addition to dielectric measurements, oscillatory rheology may also be used to characterise creams. This technique works on a similar principle to dielectric analysis in that an oscillating mechanical (as opposed to electrical) signal is applied to a sample over a range of frequencies. Consequently, the two components obtained yield information on the solid-like (G′, storage modulus) and liquid-like (G″, loss modulus) behaviour of the sample.

To test the concept of using the two dynamic techniques in conjunction for the characterisation of creams, we have chosen two complex semi-solid emulsions (Table 1). Both contain a multi-component emulsifier, consisting of: a lipophilic surfactant (glycerol monostearate), a hydrophilic surfactant (either ionic sodium lauryl sulphate or non-ionic Polysorbate 60) and an auxiliary emulsifier (a homologue admixture of two fatty alcohols, cetyl and stearyl). The two creams exemplify a special group of semi-solid emulsions, namely amphiphilic creams, whose structure comprises a crystalline gel network of complex emulsifiers, with oil and water phases distributed through that network. It is important to develop means of characterising the level of liquid crystal structuring within the cream, as this will in turn have a profound effect on the physical properties of the product. Hence, the objective of the present study was to compare two electrical and two rheological characterisation techniques as methods for evaluating the microstructure of the creams.

## 2. Materials and methods

All the components used in the formulations (Table 1) were of pharmacopoeial quality. The creams were prepared by heating the water and oil phases in separate containers up to 70–75°C, mixing them using a high-speed agitation, and cooling the resulting emulsion down to room temperature using a slow-speed agitation.

Conductivity measurements were performed with a CDM 2 meter (Radiometer, Denmark), fitted with a CDC 104 electrode, using a frequency of 50 Hz at room temperature (25°C). Dielectric measurements were performed using a low frequency Dielectric Spectrometer (Dielectric Instrumentation Ltd., UK) with parallel platinum electrodes (area approximately 0.5 $cm^2$, separation distance 1 mm) and a voltage of 0.1 $V_{rms}$. Frequency sweeps between $10^{-2}$ and $10^4$ Hz at 25°C were obtained for each emulsion. At least three measurements were performed for each cream using both techniques, with a coefficient of variation of $< 5\%$ found.

All rheological measurements were performed using a Carrimed controlled-stress rheometer (TA

Table 1
The formulation of two amphiphilic creams

| Component | Ionic cream (% w/w) | Non-ionic cream (% w/w) |
|---|---|---|
| Cetostearyl alcohol | 9.0 | 9.0 |
| Glycerol monostearate | 3.0 | 3.0 |
| Sodium lauryl sulphate | 3.0 | — |
| Polysorbate 60 | — | 8.0 |
| Liquid paraffin | 12.0 | 15.0 |
| Isopropyl myristate | 3.0 | 3.0 |
| White soft paraffin | 25.0 | 12.0 |
| Glycerol | 5.0 | 5.0 |
| Purified water | 40.0 | 45.0 |

Table 2
Dielectric parameters (capacitance C, dielectric loss G/ω, low frequency logarithm capacitance slope) and specific conductivity ($k$) for the two creams

| Cream | C at $10^{-1}$ Hz ($10^{-5}$ F) | C at $10^3$ Hz ($10^{-8}$ F) | G/ω at $10^{-1}$ Hz ($10^{-5}$ F) | G/ω at $10^3$ Hz ($10^{-7}$ F) | Log capacitance slope (0 to −1.5 log Hz) | $k$ (μS/cm) |
|---|---|---|---|---|---|---|
| Ionic | 2.360 | 1.420 | 1.028 | 2.228 | 0.1553 | 171.0 |
| Non-ionic | 1.585 | 0.067 | 1.574 | 0.177 | 0.4056 | 9.3 |

Instruments Ltd., UK) at 25°C. Flow experiments involved stress sweeps from 0–100 Pa over 1 min, followed by decreasing the stress to 0 Pa over 1 min. Oscillatory sweeps were performed from 1–10 Hz using a torque of 489 μNm over 15 min. Repeat measurements showed a coefficient of variation of < 10%.

## 3. Results and discussion

Conductivity measurements gave values of 9.3 μS/cm for the non-ionic cream and 171.0 μS/cm for the ionic system (Table 2), hence the ionic cream yielded a far higher specific conductivity ($k$). While these $k$ values may be due to the differences in the degree of structuring and/or the type of emulsion, they may also simply reflect the higher level of free ions within the ionic system, hence it is not possible to unequivocally interpret such a single point determination.

The dielectric responses of the two creams are shown in Fig. 1. The ionic system again yielded a higher response, but in this case information is given over a range of frequencies, providing spectra which may be interpreted in terms of the emulsion microstructure (Rowe et al., 1988; Goggin et al., 1994).

The model currently used is based on the work of Hill and Pickup (1985), which proposes that a number of systems may be considered to comprise two layers, a bulk layer and an electrode layer which is composed of components of the materials under study which have been adsorbed onto the electrodes. The response may be described by

$$C\omega' = \frac{C_1}{1 + \omega^2 . (R^2 . C_1)^2} \quad (1)$$

and

$$C\omega'' = G(\omega)/\omega = \frac{C_2\omega . (R_2 . C_1)}{1 + \omega^2 . (R_2 . C_1)^2} \quad (2)$$

where $C'_\omega$ and $C''_\omega$ are the real and imaginary components of the response at a frequency ω and R is the resistance (1/G) of the slab, while the subscripts 1 and 2 refer to the bulk and electrode layers respectively. These equations predict that at low and high frequencies, two responses will be seen corresponding to the electrode and bulk layers respectively. These separate layers yield information on the structure of the system and may be used as a diagnostic tool. In particular, the presence of an electrical 'blocking' layer on the electrodes is indicated by the slope of the low frequency (below 1 Hz) capacitance, with an effective blocking layer resulting in a flat capacitance slope. Similarly, the absolute values of the capaci-

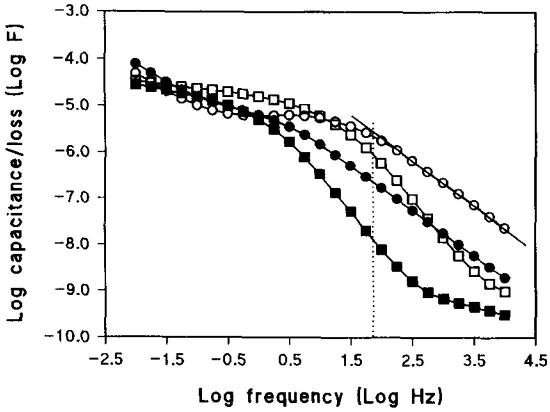


Fig. 1. Dielectric spectra of ionic and non-ionic creams. □ Capacitance of ionic cream, ■ capacitance of non-ionic cream, ○ dielectric loss of ionic cream, ● dielectric loss of non-ionic cream. Dotted line corresponds to 50 Hz, solid line shows the linear conductivity region.

tance indicate the thickness and permittivity of this layer, according to

$$C = A\epsilon/d \qquad (3)$$

where A is the area of the electrodes, $\epsilon$ is the permittivity of the layer and d is the layer thickness. At high frequencies, the response will be dominated by the bulk conductivity G, hence when plotted logarithmically against frequency, $G/\omega$ will have a linear slope of $-1$ in this region, indicating that G is frequency independent (as is assumed when using conductivity meters).

Examination of Table 2 shows that the conductivity and dielectric measurements are in agreement in that higher values for the high frequency dielectric loss and conductivity $\kappa$ were found for the ionic systems. As both of these parameters reflect charge movement through the system, such corroboration is to be expected. However, examination of Fig. 1 indicates that at 50 Hz (the frequency used for the conductivity measurements) the dielectric loss is in the 'crossover' region between the responses of the two layers, hence the conductivity is not independent of frequency and is a reflection of both the bulk and electrode layers. This does not necessarily mean that the conductivity values are unreliable, as the cell systems used for the dielectric and conductivity measurements are different (which will alter the response), but these results do indicate that care must be taken in assuming that the conductivity is frequency independent. A similar phenomenon has been observed for surfactant solutions (Craig and McDonald, 1995) where it was demonstrated that the linear conductivity region may not, in some cases, be seen below the kHz region.

Table 2 also gives values for the slope of the low frequency capacitance. The value for the ionic cream is lower than for the non-ionic, indicating a more rigid 'blocking' layer on the electrodes. Rowe et al. (1988) have suggested that the response in this region may be a reflection of the degree of structuring within gel and emulsion systems, hence the results presented here indicate that the ionic system is more structured. If so, this in turn indicates that the higher conductivity values are simply a reflection of the ionic nature of the emulsion, since previous studies (Goggin et al., 1994) have demonstrated that for the same formulation, greater structuring leads to a lower conductivity.

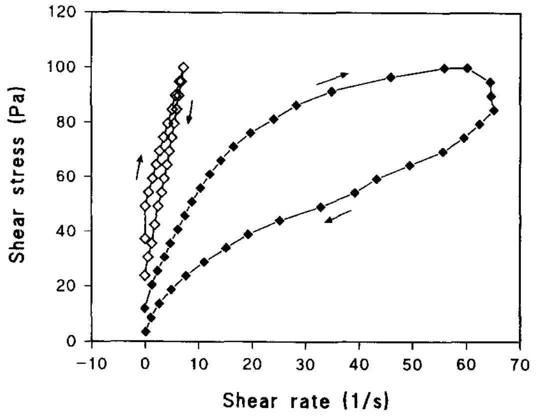


Fig. 2. Flow curves for ionic and non-ionic creams. ◇ Ionic cream, ◆ non-ionic cream.

Further information on the structure of the two semisolid emulsion systems was obtained using rheological studies. Linear rheological tests (stress sweeps) revealed significantly different flow curves for the two creams (Fig. 2). The ionic system showed a much higher yield value than the non-ionic one (Table 3), indicating a larger resistance to an external force before the system starts flowing, and thus a greater degree of structuring (Barry, 1974). The overall resistance to flow, expressed by viscosity, was also higher for the ionic system, accompanied by a 20-fold smaller hysteresis loop, which is commonly used as a measure of the level of thixotropy and/or structural breakdown within the system (Table 3, Fig. 2).

Oscillatory studies provide information on both elastic and viscous components of complex viscoelastic rheological behaviour of semi-solids (Ferry, 1970). The overall level of viscoelasticity is given by the tan $\delta$ value, which is the ratio between the loss and storage moduli ($G''/G'$). The values of phase angle $\delta$ (ranging from 0° for an ideal elastic solid to 90° for an ideal viscous liquid) are given over the whole frequency range in the Fig. 3, with representative tan $\delta$ values given in Table 3. The values indicate that the non-ionic creams show greater viscous, as op-

Table 3
Flow parameters (viscosity $\eta$, hysteresis area H and yield value $\tau_Y$) and oscillatory parameters at 1.8 Hz (storage modulus G′, loss modulus G″ and tangent of the phase angle $\delta$) for the two creams

| Cream | $\eta$ at 100 Pa (Pa s) | H (Pa/s) | $\tau_Y$ (Pa) | G′ (Pa) | G″ (Pa) | Tan $\delta$ |
|---|---|---|---|---|---|---|
| Ionic | 13.85 | 93.0 | 41.24 | 2961 | 845 | 0.2842 |
| Non-ionic | 1.71 | 2114.0 | 12.71 | 4929 | 2547 | 0.5154 |

posed to elastic behaviour compared to the ionic systems, which in turn suggest that the ionic creams have greater internal structuring (Eccleston, 1984).

## 4. Conclusions

This study has focused on the assessment of the methods available for the characterisation of semi-solid emulsions. While conductivity and viscosity measurements are undoubtedly of use, considerably more sophisticated information may be obtained using oscillatory dielectric and rheological techniques. In particular, the use of dielectric analysis allows an insight into the degree of structuring within the cream and also indicates the frequency range over which d.c. conductivity dominates the charge transport process, which may not necessarily coincide with the frequency at which commonly used conductivity equipment takes measurements. Similarly, while flow measurements allow useful insights into rheological properties of creams, oscillatory measurements allow direct quantitative assessment of the viscoelastic properties of these systems. Overall, both the dielectric and rheological studies indicate that, in this particular case, the ionic cream shows a greater level of structuring.

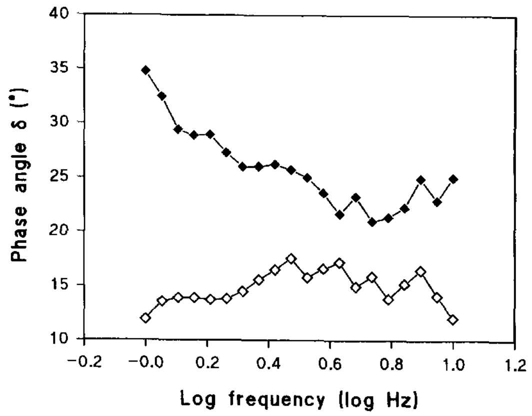


Fig. 3. Variation of phase angle with frequency for two creams. ◇ Ionic cream, ◆ non-ionic cream.

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