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Dielectric spectroscopy of a glass-forming emulsion

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The dielectric behaviour of an aqueous solution-in-oil emulsion in which the liquid within the particles forms a glassy structure on being taken below its glass transition temperature is reported. Measurements have been made for a single concentration of oil/solution/surfactant which gave a stable emulsion structure over the temperature range 225–340 K, indicating a glass transition at 218 K. The principal features of the low-frequency dielectric response are considered in terms of the model response discussed earlier by the authors and the physical bases of the individual response components are established.

1. Introduction

In an earlier paper [1] it was shown that neither the simple Maxwell–Wagner barrier approach nor the model proposed by Hanai [2, 3] were capable of describing the nature of the dielectric dispersions observed in the measurement of water-in-oil emulsions. Here we present experimental data obtained over wide frequency and temperature ranges on a single water-in-oil emulsion and show that the general model response outlined in [1], together with the use of the cooperative cluster model of relaxation [4], gives an effective description of the detail of the experimentally observed behaviour, and from this description a coherent interpretation of the mechanisms involved can be developed. In order to facilitate interpretation of the emulsion spectral data we have chosen to use a mixture of ammonium and calcium nitrate solutions. Freezing of these solutions results in the formation of a glassy structure with the characteristic α-relaxation temperature behaviour of such structures and a glass transition temperature. T_g, in the region of 220 K. Furthermore the emulsions have the ability to be taken through the glass transition without the emulsion structure breaking down catastrophically [1]. This feature has enabled us to be specific about the role of the aqueous solution within the emulsion particles.

In our earlier overview of the dielectric properties of water-in-oil emulsions [1] we presented a schematic representation of the dispersion characteristics and reproduce this in Fig. 1. As before, we present the dispersion data in terms of the complex capacitance,

$$C(\omega) = C'(\omega) - iC''(\omega) \qquad (1)$$

where the loss component, $C''(\omega)$ may, with generality, be expressed in terms of a frequency-dependent conductance, $G(\omega)$, as

$$C''(\omega) = G(\omega)/\omega \qquad (2)$$

with ω the radian frequency and $i = (-1)^{\frac{1}{2}}$

In Fig. 1 we have indicated four relaxation processes characterized by the relaxation times τ_i ($i = 1$–4). The relaxations τ_1 and τ_2 give rise to loss peaks in the dielectric modulus (inverse capacitance) whereas in the capacitance representation of Fig. 1 they are associated with equal magnitudes of the real and imaginary components [1]. τ_3 and τ_4 are associated with maxima in the (capacitive) loss and are defined to be the inverse of the frequencies of maximum loss. The scales in Fig. 1 have been chosen to be representative for measurements made in the region of room temperature for the entire response. It is obvious that the frequency range required to cover the complete range of the dispersions is large and normally beyond the capability of a single measuring instrument. However, because of the strong temperature dependence of the relaxation times, the low-frequency region can be brought into a measuring window by raising the temperature and, conversely, the high-frequency region is accessible on cooling the sample, as long as the integrity of the emulsion is retained at both high and low temperatures.

Generally the structural stability limits the temperature range over which any emulsion can be examined. For example with the particular system presented here we have not been able to investigate the very low-frequency Maxwell–Wagner loss peak that lies below 1μ Hz in Fig. 1. The large capacitance value of the Maxwell–Wagner blocking layer requires this dispersion to be associated with a single thin (molecular) surface layer at the electrodes of the dielectric cell. Reports of such blocking layers have been given elsewhere [5]. Here we are particularly interested in the"bulk" properties of the water-in-oil emulsion and not, in any detail, in the nature of the electrode layers, although we shall show that they are diffusive and likely to be formed from charge double layers.

2. Experimental procedure

The emulsion has been prepared by emulsifying a mixture of the solutions of 47.5% ammonium nitrate and 47.5% calcium nitrate (in the form of the tetrahydrate), with 3% oil and 2% of a short-chain surfactant. The emulsion was prepared in a planetary mixer with a primary orbital speed of 180 r.p.m. and a secondary orbital speed of 500 r.p.m. Measurement of the samples was carried out using a cell with platinum electrode plates of area 1.63×10^{-4} m^2 and an empty cell capacitance of 0.236 pF. All measurements were made in the frequency range 10^{-4}–10^6 Hz using a Chelsea dielectrics interface with a Solartron frequency response analyser. The samples were stable during measurement over the temperature range 325–224 K. Good reproducibility was achieved both from run to run on a single sample and also from sample to sample.

Preliminary data for the approach to the glass transition from higher temperatures have been reported earlier [1]. The data presented here have been measured on a fresh batch of solutions and complement the earlier information.

3. Results

Fig. 2 presents a temperature-normalized plot of the data measured for the τ_3 (and τ_1) relaxation in the temperature range 273.8–224.8 K. In this figure the dispersion data measured at each temperature have been overlaid to give a single master plot. The temperature-labelled points in the upper part of the figure have been obtained from the equivalent frequency and amplitude shift of the datum point at 1 Hz and 10^{-8}F and indicate the shift required from the datum temperature of 244.7 K in order to construct the master plot. We note that there is no change in the magnitude of the response with temperature but a large change in the relaxation time. This latter information is replotted in Fig. 3a in the form of an Arrhenius plot of the peak loss frequency ($\tau_3{}^{-1}$) and shows the characteristic temperature response of a glassy material exhibiting an α-transition with a glass temperature value, T_g, of approximately 218 K and a high-temperature activation energy of 1.36 eV. From the observation of the glassy response we can associate, unambiguously, the τ_3 relaxation process with the water (and salts) within the emulsion particles.

An alternative plot of the data in the region of the glass transition is given in Fig. 3b where we present the same relaxation rate data as a function of (T–T_g) in a double log plot. The straight-line behaviour has been recognized [6] as characteristic of the formation of a glassy structure and the magnitude of the exponent obtained here, 5.3, is indicative of typical glassy behaviour [7]. In this form of plot, perfect crystallization gives an infinite gradient and hence we are far from such a phase transition here.

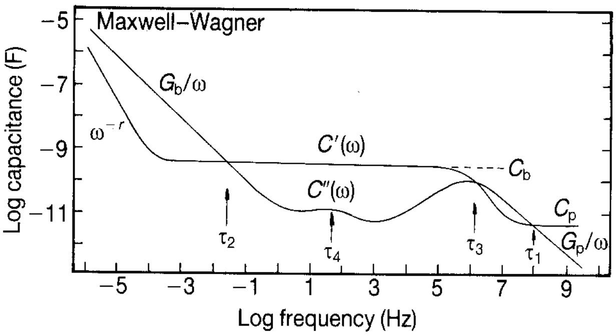

Figure 1 Schematic illustration of the dispersions observed in water-in-oil emulsions. The diagram is scaled for room temperature and the individual relaxation processes are indicated by their relaxation times. Processes τ_1 and τ_2 give rise to loss peaks in the dielectric modulus, whereas τ_3 and τ_4 exhibit loss peaks in the capacitance. At the lowest frequencies the dispersion is due to a Maxwell–Wagner process which truncates the conductance loss G_b/ω.

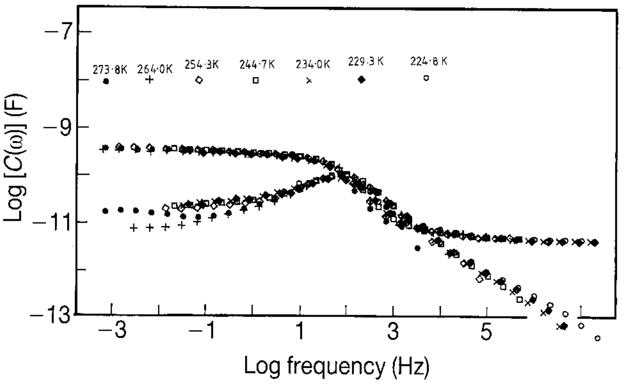

Figure 2 A temperature normalized plot for the τ_3 relaxation process. The plot has been constructed from data measured in the temperature range 224.8–273.8 K. The plot shows that the loss peak shape is a function of the temperature. The plot is scaled for 244.7 K and the points in the upper part of the figure give the inverse shifts in frequency and magnitude which were required in order to construct this plot. The datum point was 1 Hz and 10^{-8} F. (●) 273.8 K; (+) 264.0 K; (◇) 254.3 K; (□) 244.7 K; (×) 234.0 K; (◆) 229.3 K; (○) 224.8 K.

Examination of the data within Fig. 2 shows that the individual dispersions at temperatures within the α-region are not identical; there is a broadening of the loss peak as the glass transition temperature is approached from above. Each data set, up to 340 K, has been fitted to the Dissado–Hill hypergeometric dispersion function [4] for which the limiting behaviours at high and low frequencies, with respect to the frequency of maximum loss, ω_p, are

$$C(\omega/\omega_p) \propto (i\omega/\omega_p)^{n-1} \qquad \omega \gg \omega_p \qquad (3a)$$

and

$$C(\omega = 0) - C(\omega/\omega_p) \propto (i\omega/\omega_p)^m \qquad \omega \ll \omega_p \qquad (3b)$$

respectively, with $0 \leqslant m,\ n \leqslant 1$. The values of the dispersion exponents m and $1 - n$, as functions of temperature, are given in Fig. 4 from which it can be seen that, on cooling, the broadening is asymmetric with m reaching its minimum value at 250 K, whereas

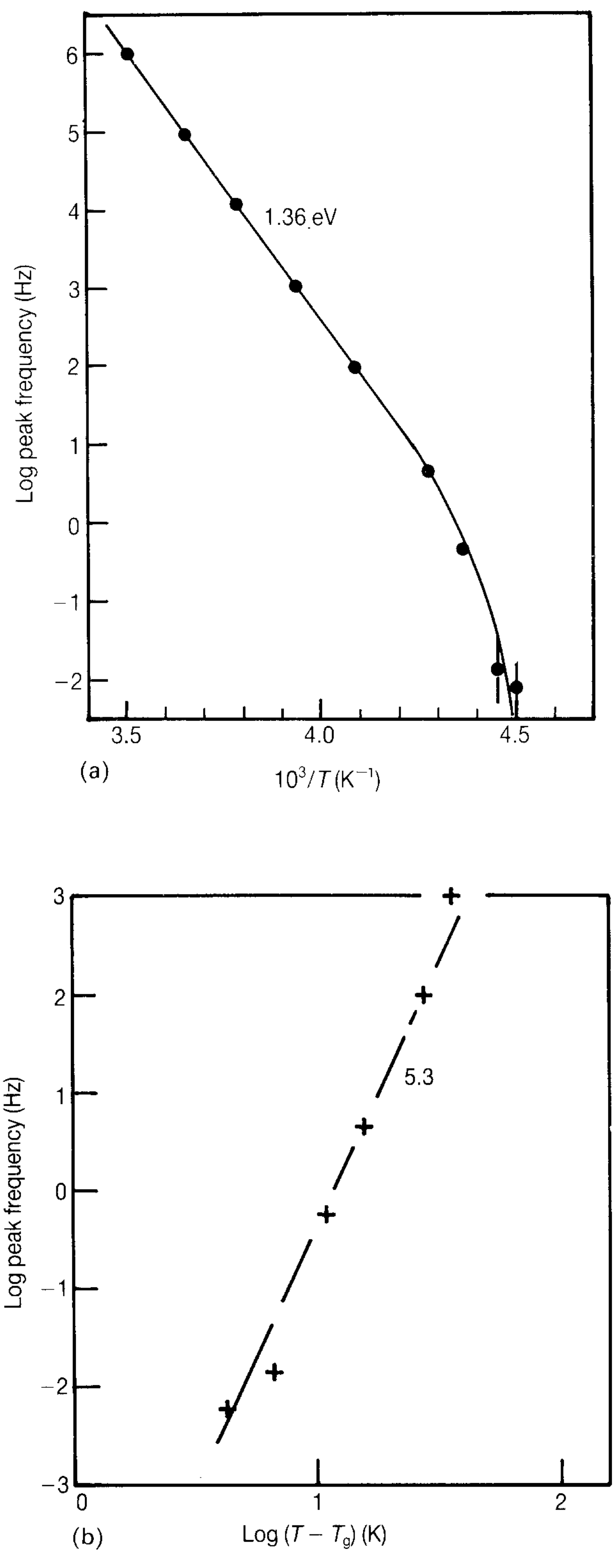

Figure 3 (a) An Arrhenius plot of the inverse of the relaxation times, the peak loss frequency, for the τ_3 relaxation. The plot is characteristic of an α-relaxation with a high-temperature asymptotic activation energy of 1.36 eV and a glass transition temperature of about 218 K. (b) Log/log plot of the peak loss frequency as a function of the temperature difference $T - T_g$. The line has a gradient of 5.3 and at the larger temperature difference the onset of the 1.36 eV activated process can be seen.

$1 - n$ continues to decrease as the glass transition temperature is approached. Similar behaviour has been observed in other glassy systems [7]. It can be noted that for the lowest temperature for which the data used in constructing Fig. 2 have been measured and at the highest frequencies, there is evidence for a further dispersion in the loss component. This dispersion is small in magnitude and exhibits a temperature dependence which is less than that of the α-process in the same temperature region.

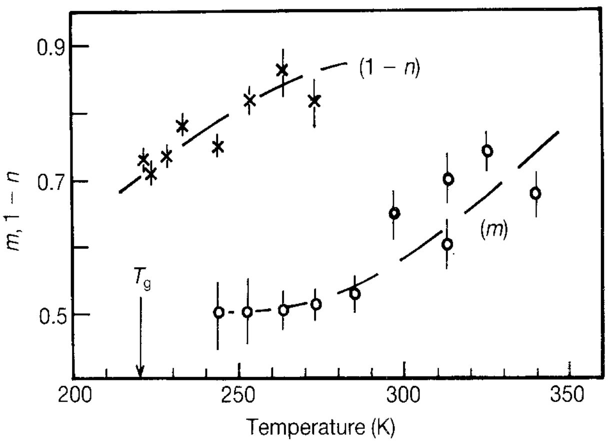

Figure 4 Dissado–Hill dispersion parameters m and $1 - n$, as defined in Equation 3, for the τ_3 relaxation process. Note the different nature of the approaches to the glass transition temperature at 218 K.

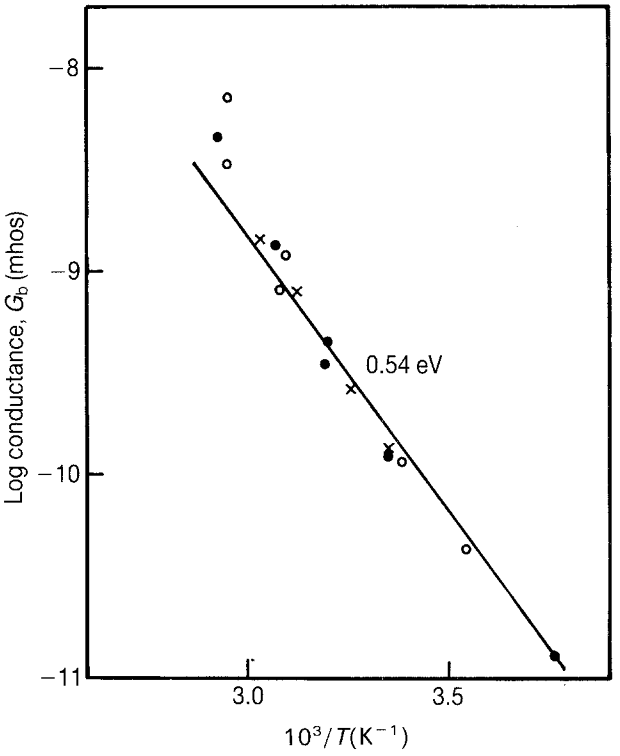

Figure 5 Arrhenius plot of the low-frequency conductance, G_b. At the highest temperatures the emulsion is becoming unstable. The different symbols indicate different samples.

The temperature dependence of the low-frequency relaxation process (τ_2) is dominated by that of the conductance, G_b, as the magnitude of the capacitance, C_b, is essentially temperature independent. Fig. 5 shows that the conductance is activated with an energy of 0.54 eV at temperatures below 330 K. At temperatures greater than this the emulsions tend to be unstable and the onset of the instability is seen in the figure as an additional increase in the conductance. The instability can also be detected from the normalized dispersion characteristic of Fig. 6 as a

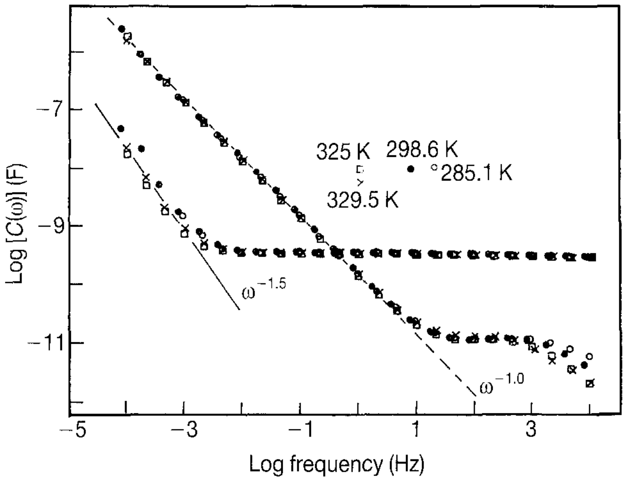

Figure 6 The dispersion characteristics, in normalized form, of the τ_2 relaxation process. Over the complete temperature range investigated the loss is dominated by a constant conductance of about 10^{-9} mhos whilst the dispersion in the capacitance has a power-law form with exponent -1.5. As shown in the Appendix, this requires a Maxwell–Wagner blocking capacitance with dispersion proportional to $(i\omega)^{-0.5}$ which is the characteristic of a diffusive barrier layer at the electrodes. The plot is scaled at 325 K.

change in the pattern of the trace of the datum point with temperature at the highest temperature for which this process could be measured (329.4 K).

Fig. 6 shows that the capacitance, at the lowest frequencies, decays with frequency as $\omega^{-1.5}$. As there is no dispersion in the conductance, i.e $C''(\omega) \propto 1/\omega$, the exponent 1.5 requires that the capacitance dispersion is due to a Maxwell–Wagner blocking layer which we are not able to observe directly in the available frequency range but is of the form [8]

$$C(\omega) \propto \omega^{-0.5} \tag{4}$$

as outlined in the Appendix. The inverse square root dependence on frequency is characteristic of the presence of a surface barrier layer through which charge exchange at the electrodes takes place by diffusion [9], and has been observed in other water based emulsion and gel systems [9, 10].

The final feature for which we present data is the dispersion characterized by the relaxation time τ_4. In Fig. 1 this is shown as a single loss peak, of small magnitude and was observed as such in the data presented earlier [1]. The detailed information contained in Fig. 7 shows that, for the material investigated here, there is evidence for two separate loss processes with different relaxation times but similar magnitudes. In Fig. 8 we give the temperature dependencies of the maximum loss frequencies for these two processes as functions of the reciprocal temperature and observe that they are activated with energies of about 0.17 and 0.5 eV for the lower and higher frequency processes, respectively. It should be noted that these values can only be approximated, because the separation of the data into the individual responses cannot be carried out to a good accuracy for the broad loss peaks which have been observed.

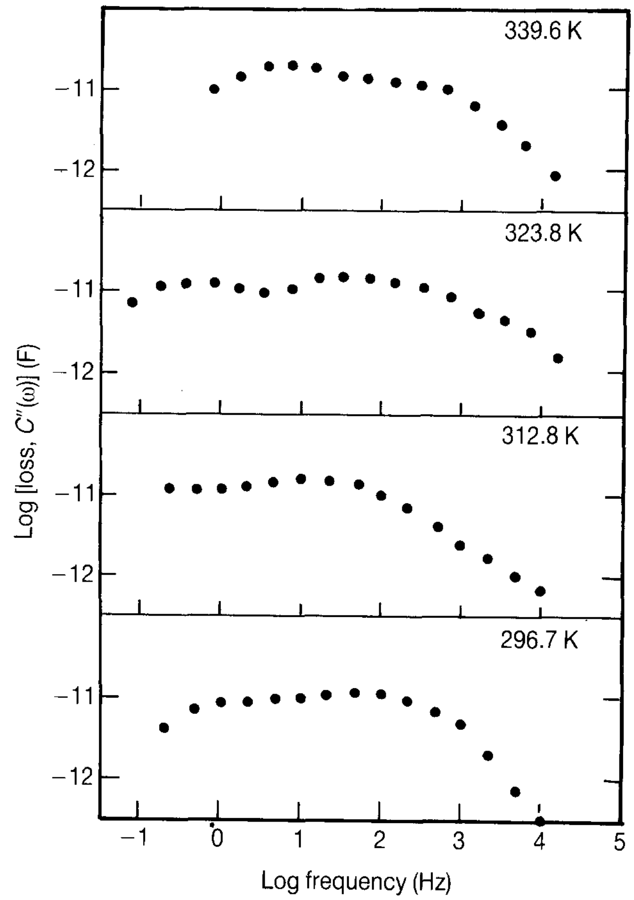

Figure 7 A selection of observed dispersions for the τ_4 relaxation. It is clear that two dispersions are present and as the temperature is reduced these overlap more strongly. The individual loss peaks are broad.

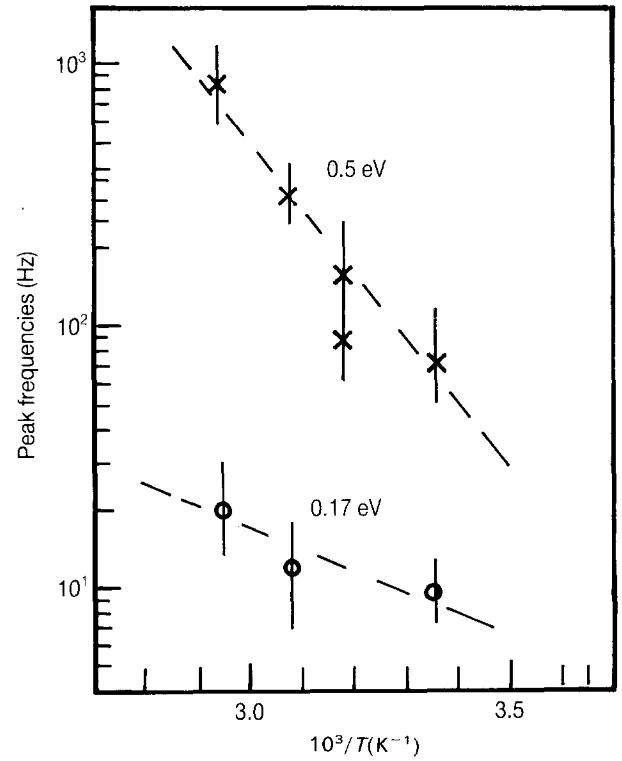

Figure 8 Arrhenius plots of the two τ_4 relaxation processes. Because of the breadth of each relaxation and the overlap it is difficult to obtain accurate values for the activation energies.

4. Discussion

A summary of the observed responses is given in Table I. As expected, the high-temperature behaviour of the glass transition loss peak, the α/β process [11], has a high activation energy. This is generally associated with the strongly viscous nature of the cooperative forces that impede the rotation of the initial clusters of the structured liquid which form at temperatures well above the glass transition temperature, T_g. The approach to the transition temperature is seen in the change in the relaxation rate, the frequency of maximum loss, away from the activated value below 240 K in Fig. 3. There can be no doubt that this behaviour is due to the glassy structure formed by the nitrate solutions and hence we assign the τ_3 loss peak process to relaxation within the particles of aqueous solution. We note that the Dissado–Hill spectral shape parameters, Fig. 4, tend to indicate Debye-like properties ($m \rightarrow 1$; $n \rightarrow 0$) for temperatures much higher than the glass transition temperature but that $m \rightarrow 0.5$ and $n \rightarrow 0.3$ at the transition. The latter values indicate particles that possess only a moderate long-range order, which is established some 50 K above T_g, together with a poor short-range order which is, however, changing rapidly in the region of T_g, as would be expected as the local glassy structure becomes rigid. For temperatures in excess of $T_g + 50$ K the individual particles act as independent polar entities and approach the classic Debye model.

The relaxation process, τ_1, is defined by the intersection of the high-frequency (MHz) capacitance and the loss component of the τ_3 relaxation. The former is essentially the product of the capacitance of the cell and the macroscopic relative permittivity of the emulsion and is constant at about 7×10^{-12}F. As the empty cell capacitance is 0.236 pF the relative permittivity, ε_∞, is 28. Hence C_b is neither the response of "free" water nor a simple volume concentration of the permittivities of the solutions and the oil. As C_∞ is not temperature dependent, the temperature dependence of τ_1 reflects that of G_p, the high-frequency conductance, i.e. of the glass transition process modified by the effect of the change in the high-frequency component of the dispersion.

The data in Table I show that we have observed two processes with activation energies of about 0.5 eV: the bulk conductance, for which we have excellent data, which exhibits an activation energy of 0.54 eV and the poorly defined loss peak which forms the higher frequency component of τ_4. The conductance arises from the motion of charges through the oil/surfactant films which separate the aqueous particles. It is known [12] that the same charges may become trapped within the film and although not able to contribute to the net motion of charge (and thereby contribute to the conductance) they can contribute to local polarization either by rotation or by limited path motion. Both the latter processes give rise to loss peak behaviour, as observed here. It has not been a simple matter to deconvolute the data in Fig. 7 in order to obtain the individual response shapes, but from the lowest temperature data, that at 296.7 K, it is likely that n is small and hence we can deduce that the local order around the pertinent charge is high $(1 - n \rightarrow 1)$. This is in agreement with the order inherent in a thin film of oil/surfactant when it forms a coherent and close-packed barrier layer between two water particles and also with the relatively high magnitude of the activation energy which characterizes the process.

TABLE I Characterization of the relaxation processes

Process	Activation energy (eV)	Comment
τ_t	As for τ_3	Dominated by solution conductance
τ_2	0.54	Dominated by G_b
τ_3	1.36	α-relaxation $T_g = 218$ K Broadening as T_g approached
τ_4	(a) 0.17 (b) 0.5	Broad peak Broad peak

The lower of the two τ_4 relaxation processes is much broader, although even less well defined. Here we note that this process does not contribute to the conductance of the sample even although it has a much smaller activation energy. We associate the low activation energy to the region of distortion formed at the interstices between three or more particles. It has already been proposed [1] that these regions contain the excess oil and we associate the 0.17 eV activation energy to the viscous drag of the oil on a polarizable particle such as an impurity held within this disordered region.

Finally, we turn to the lowest frequency process observed. From the exponents in Fig. 6 we have a conductance truncated by a barrier layer which is itself dispersive in the manner expected of a diffusive layer, $C(\omega) \propto (i\omega)^{-0.5}$. We note that the intersection of the conductance and the loss will occur in the region of 10^{-2} F, some seven orders of magnitude greater than the "bulk" capacitance. Even considering that the barrier layer has a permittivity of water, 80, gives unrealistically small values for its thickness and hence we consider that the barriers, one at each electrode, are formed of charge double layers, which is in accord with the diffusive description from the frequency dependence. We note that the high barrier capacitance has a low effective impedance at "high" frequencies and it is for this reason that the barrier is not dominant in the frequency range above about 1 Hz.

5. Conclusions

The complex dispersion observed over a wide range of frequencies in the millihertz to megahertz region has been shown to be characterizable in terms of the simplest model of an emulsion, namely a dispersion of water particles contained within thin oil layers which are stabilized by a surfactant. It is remarkable that by using aqueous solutions in place of pure water the emulsion can be cooled into the solid glassy-particle phase without destroying the coherence of the structure. At the lowest frequencies and highest temperatures investigated, there was evidence of a giant dispersion which has the characteristics of a Maxwell–Wagner barrier response where the barrier is diffusive in nature but even frequencies of 10^{-5} Hz were not sufficiently low to resolve the barrier response. The barrier capacitance is estimated as about 10^{-2} F and with a bulk emulsion conductance of 10^{-9} mhos at 330 °K the relaxation time is 10^7 s equivalent to 1.6×10^{-8} Hz.

One specific aspect of the data reported here is the observation of two τ_4 loss processes in place of the single process observed earlier [1]. From examination of their activation energies, one has been associated with local charge movement and rotation within the oil phase and the other with impurities within the same phase. Consideration of the packing of aqueous droplets [1] indicates that these impurities probably lie in the interstitial regions at the junction of three or more particles.

Appendix

In the systems examined here we have a conductance of magnitude G_b blocked by a capacitive barrier. If the capacitance is a constant of magnitude C_b this results in a capacitance dispersion for $\omega \gg \tau^{-1} = (G_b/C_s)$ with the real component of the capacitance inversely proportional to the square of the frequency. All the data for the lowest frequency dispersion exhibits a frequency exponent that is greater than -2. We assume that this arises from a power-law behaviour in the capacitive barrier and write this capacitance as

$$C(\omega) = C_s(i\omega)^{s-1} \quad \text{with} \quad 0 < s < 1 \qquad \text{(A1)}$$

For the series connection of blocking layer and conductance the total impedance is given by

$$Z = \frac{1}{C_s(i\omega)^s} + \frac{1}{G_b} \qquad \text{(A2)}$$

from which we obtain the real component of the complex capacitance for frequencies greater than the Maxwell–Wagner relaxation time as

$$C'(\omega) \propto \omega^{-s-1} \qquad \text{(A3)}$$

Hence, even if the barrier itself is not observed, it is possible to deduce the exponent of the barrier dispersion from measurements at frequencies greater than the inverse of the barrier relaxation time. In the limit of a non-dispersive barrier, s becomes unity and Equation A3 recovers the Debye-like behaviour of the classic Maxwell–Wagner response.

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