670. *Dielectric Properties of Some Aluminium Soaps and of their Solutions in Toluene.*

By S. M. Nelson, A. Gilmour, and R. C. Pink.

In dilute toluene solutions of aluminium disoaps, the dielectric loss is due almost entirely to direct-current conductivity. In more concentrated solutions, which form rigid gels, part of the dielectric loss is caused by the restricted displacement and accumulation of ions along internal boundaries in the gel. In solutions of the aluminium trisoaps, in which aggregation is limited to the dimer, the dielectric loss is due solely to direct-current conductivity. The stability of the ions in a solvent of such low dielectric constant as toluene is explained by the shielding effect of the hydrocarbon chains which prevents close approach of the ionic charges localised in the centre of the aggregates.

In a previous paper [1] it was shown that the dielectric loss in hydrocarbon solutions of a number of bivalent metal soaps was due to direct-current conductivity. The variations in the conductivity of these solutions with changes in concentration and temperature were explained in terms of an association of molecules and ions into aggregates, the equivalent conductivity increasing with increase in aggregate size. In certain calcium oleate solutions, however, which were highly viscous, it was noted that the measured dielectric loss contained a component due to some cause other than ionic conduction.

The present paper describes an investigation of the dielectric properties of some aluminium soap solutions in toluene in which a similar phenomenon has been observed. Unlike the bivalent metal carboxylates, the aluminium disoaps in hydrocarbon solvents form viscoelastic gels even at low concentrations and it was expected that a study of the dielectric properties of the soaps might help to elucidate the nature of this gel structure.

Experimental

Preparation and Purification of Materials.—Aluminium dilaurate was prepared by the method described by Smith, Pomeroy, McGee, and Mysels.[2] The soap was washed free from

---

[1] Nelson and Pink, *J.*, 1954, 4412.

[2] Smith, Pomeroy, McGee, and Mysels, *J. Amer. Chem. Soc.*, 1948, **70**, 1053.

chloride and then extracted with dioxan at 40° until free from uncombined fatty acid. After the soap had been dried, traces of dioxan were removed at low pressure. The trilaurate and trioleate were prepared by Mehrotra's method.[3]

Analytical data (Al) for two samples of each of these three soaps are—Dilaurate: Found: 6·22, 6·19. Calc.: 6·09. Trilaurate: Found: 4·25, 4·27. Calc.: 4·32. Trioleate: Found: 3·12, 3·23. Calc.: 3·10%.

Preparation of the Gels.—In order to exclude moisture, the aluminium dilaurate gels were prepared under a slight positive pressure of dry air at 40—60° with mechanical stirring. Under these conditions the soap swelled rapidly, forming first a viscous suspension of undispersed soap and, finally, a transparent gel. Stirring was continued for 10 min. after the system had become visibly homogeneous. In the peptised systems the peptiser was added with the solvent.

Apparatus.—Dielectric-loss measurements in the frequency range 100 cycles/sec. to 300 kcycles/sec. were made with the capacitance bridge described previously.[1] Measurements in the range 100 kcycles/sec. to 40 megacycles/sec. were made by the method due to Hartshorn and Ward [4] involving variation of reactance in a tuned circuit. The dielectric cells were similar to those employed previously.

Where relaxation effects are absent in the dielectric, and the whole of the dielectric loss is due to direct-current conduction, it can be shown from a consideration of the voltage–current vectors that the dielectric loss factor ε'' is inversely proportional to frequency. The specific conductance σ can then be calculated from eqn. (1),

$$\sigma = 5{\cdot}5 \times 10^{-13}\varepsilon''f \text{ ohm}^{-1} \text{ cm.}^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where f = frequency in cycles/sec.

The conductivity in some of the systems was also measured directly by applying 1·5 v across the sample in the dielectric cell and observing the current by a sensitve galvanometer (6000 mm./μA at 1 metre) calibrated by means of known high resistances. To reduce electrode polarisation effects, a reversing switch was employed to change the direction of the current flow through the cell, but not through the galvanometer, at the rate of one reversal every 2 sec. With systems in which the whole of the loss was due to direct current conductivity, the two methods showed excellent agreement.

RESULTS

Fig. 1 illustrates the frequency dependence of the dielectric loss for aluminium dilaurate gels in toluene at three concentrations at 25° over a wide frequency range. The data refer to the systems after they had matured for at least 2 days and had acquired constant loss values. It will be seen that the two most concentrated systems show a considerable departure from a conductivity plot (*i.e.*, $\varepsilon'' \propto 1/f$ corresponding to the broken line in Figs. 1 and 2), approaching the 45° slope required by direct-current conductivity below 500 cycles/sec. Direct measurement of conductance confirmed that the loss below this frequency was almost entirely due to direct-current conductivity. Specific conductivities measured by the direct method (i) and calculated from the loss data at the lowest frequency of measurement (ii) are shown in the Table.

Specific conductivity of aluminium dilaurate in toluene.

Concn. (g./100 ml. of soln.)	0·44	2·52	4·86
Specific conductivity (10^{10} ohm^{-1} cm.$^{-1}$), method (i)	1·61	0·805	1·02
,, ,, ,, method (ii)	1·61	0·887	1·17

Effect of Peptising Agents.—Fig. 2 illustrates the effect of lauric acid as peptiser on the dielectric loss of the 2·52% aluminium dilaurate gel at 25°. The effect of lauric acid on the mechanical properties of the gel was to render it less friable and more elastic. From Fig. 2 it is clear that peptising action is also accompanied by an increase in conductivity and by a change in the shape of the log ε''–log f curves, the departure from a conductivity slope of 45° becoming less apparent. Lauric acid in amounts greater than 1 mol. had no further significant effect on the dielectric properties.

Effect of Temperature.—The dielectric losses of the unpeptised and the peptised gels were measured at 40°. In all cases a small increase in the dielectric loss (*ca.* 5—10%) on the values at 25° was observed.

[3] Mehrotra, *Nature*, 1953, **172**, 74.

[4] Hartshorn and Ward, *J. Inst. Elect. Engrs.*, 1936, **79**, 597.

Analysis of the ε''–f *Curves.*—Where the loss factor due to direct-current conductance represents only a part of the total loss, the observed loss factor may be regarded as the sum of two distinct effects :[5]

$$\varepsilon''_{\text{obs.}} = \varepsilon''_{\text{d.c.}} + \varepsilon''_{\text{r}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $\varepsilon''_{\text{d.c.}}$ is given by eqn. (1) above and ε''_{r} is the dielectric loss resulting from relaxation phenomena involving dipoles or ions. ε''_{r} may then be obtained provided the direct-current conductivity is measured separately. In Fig. 3 the dielectric data for a 2·52% aluminium dilaurate gel are analysed in this way. The direct-current conductivity losses calculated from the measured conductivity are shown by the broken curve. On plotting $\varepsilon''_{\text{obs.}} - \varepsilon_{\text{d.c.}}''$ on the same co-ordinates, a maximum is obtained in the region of 10 kcycles/sec. Fig. 4 shows plots of $\varepsilon''_{\text{obs.}} - \varepsilon''_{\text{d.c.}}$ against log f for the three unpeptised gels at 25°. In addition to causing an increased loss, increase in concentration of the gel also leads to a small decrease in the frequency of maximum absorption. The errors in the results of Fig. 4 are large (±10%), because they were obtained from the difference of measured quantities.

FIG. 1. FIG. 2.

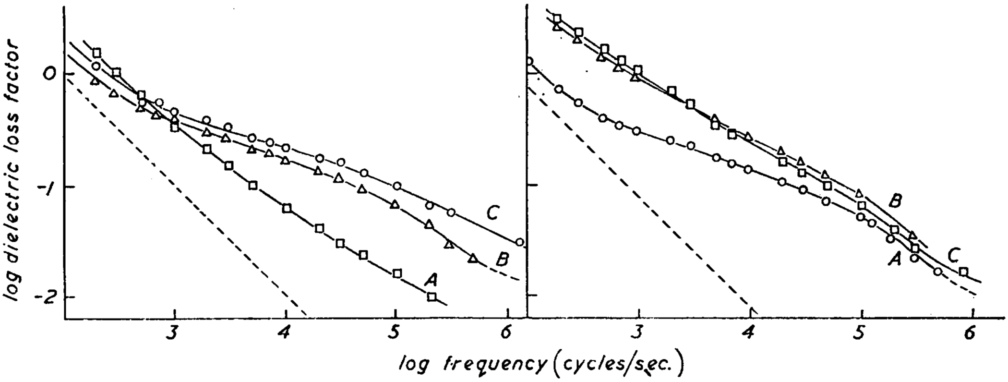


FIG. 1. *Effect of frequency on dielectric loss of aluminium dilaurate gels* (A, 0·44; B, 2·52; C, 4·86%).
FIG. 2. *Effect of peptiser on dielectric loss of an aluminium dilaurate gel* (2·52%) *in toluene* (A, *unpeptised gel;* B, 0·398 *mol. of lauric acid;* C, 1·06 *mol. of lauric acid*).

Dielectric Constant.—In all the aluminium disoap systems the measured capacitance was observed to decrease with increasing frequency (Fig. 5). The increase in capacitance at low frequencies observed in the 0·44% system, which was almost wholly conducting, may be explained largely by electrode polarisation.

The Aluminium Trisoaps.—Solutions of aluminium trilaurate and trioleate in toluene were found to have high dielectric losses, which in every case varied inversely with frequency, indicating that the losses were due to direct-current conductivity. The specific conductivity calculated from the loss data for solutions of aluminium trilaurate in toluene are shown in the Table, while the effect of temperature on the conductivity is shown in Fig. 6.

Aluminium trilaurate, %	0·853	0·990	1·630	2·204	2·65
Specific conductivity, 10^{10} ohm^{-1} cm.$^{-1}$ ...	1·64	3·07	14·50	34·05	74·90

The conductivities observed in these solutions cannot be accounted for simply by the presence of free fatty acid or water, since even concentrated solutions of fatty acids in toluene show a negligible increase in dielectric loss over that of the pure solvent, while in the case of the trisoaps addition of a trace of water leads to a marked fall in conductivity as a result of hydrolysis to the aluminium disoap.

Dielectric Properties of the Solid Soaps.—The dielectric loss of the solid disoaps was found to be very low, provided care was taken to extract free fatty acid and to prevent absorption of moisture by the soap sample. Solid aluminium trilaurate, in contrast, showed large losses at low frequencies with a marked dependence of the dielectric loss on frequency, as illustrated in Fig. 7, which includes the loss data for the disoap. It will be seen that the loss for the disoap passes through a shallow maximum at a frequency of about 1 megacycle/sec.

[5] Carter, Magat, Schneider, and Smyth, *Trans. Faraday Soc.*, 1946, **42**, *A*, 213.

FIG. 3. *Analysis of dielectric loss of an aluminium dilaurate gel in toluene* ($\sigma_{D.C.} = 0{\cdot}805 \times 10^{-10}$ ohm^{-1} cm.$^{-1}$) (A, $\varepsilon''_{obs.}$; B, $\varepsilon''_{d.c.}$; C, $\varepsilon''_{obs.} - \varepsilon''_{d.c.}$).

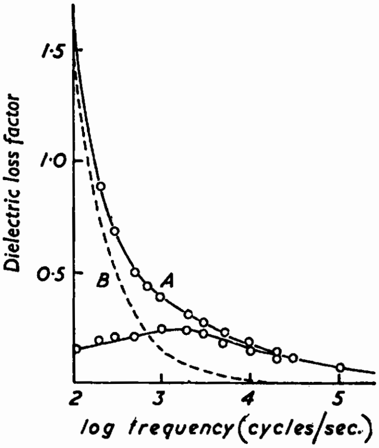


FIG. 4. *Dielectric absorption of aluminium dilaurate–toluene gels* (A, 0·44; B, 2·52; C, 4·86%).

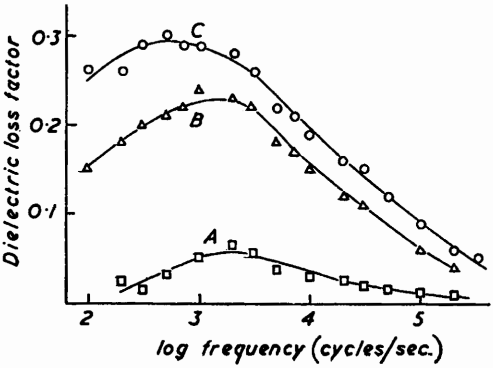


FIG. 5. *Effect of frequency on the apparent dielectric constant of aluminium dilaurate–toluene gels* (A, 0·44; B, 2·52; C, 4·86%).

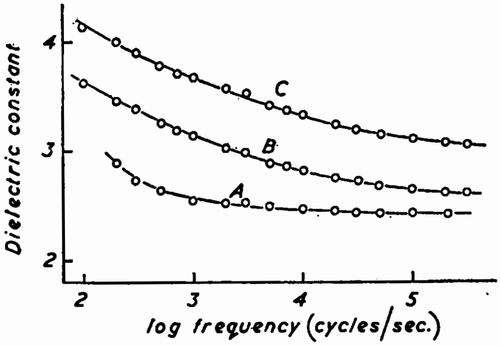
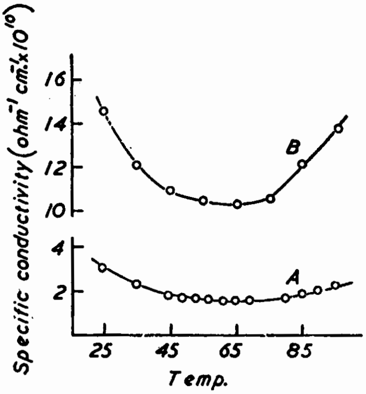


FIG. 6. *Effect of temperature on conductivity* (A, 0·99; B, 1·63%).



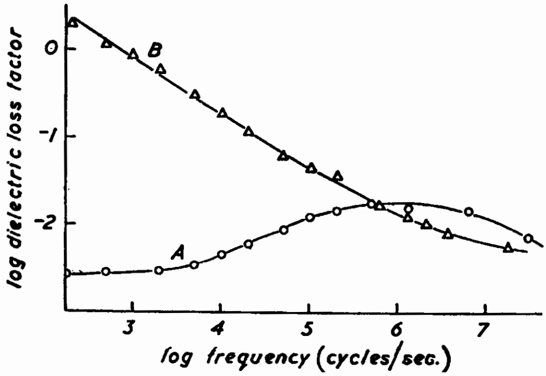


FIG. 7. *Effect of frequency on dielectric loss of aluminium dilaurate* (A) *and aluminium trilaurate* (B).

DISCUSSION

Like the solutions of bivalent metal soaps, the aluminium soap gels show appreciable direct-current conductivity. An important difference, however, is that in the former the dielectric loss can be entirely accounted for by direct-current conduction, while in the gels, a component of the loss is due to some other cause. This component increases in magnitude, and the frequency at which it shows a maximum is lowered, with increase in concentration of the soap (Fig. 4).

Various theories of dielectric absorption have been proposed to account for power loss in alternating fields.[7] Most of the proposed mechanisms, however, lead to the same kind of formal expression [eqn. (3)] for the variation of loss factor with frequency

$$\varepsilon'' = A\omega\tau/(1 + \omega^2\tau^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where A is a constant, ω is the angular frequency, and τ is the time constant or relaxation time for the process in question. It is clear from this equation that ε'' passes through a maximum when $\omega\tau = 1$. Although electrical measurements alone cannot always distinguish between the different mechanisms it is usually possible, on the basis of other properties of the system, to ascribe the absorption, in major part, to one or other cause.

Dielectric-loss mechanisms other than that of direct-current conduction may be grouped into three main types, namely: (1) orientation of dipoles (Debye theory); (2) restricted displacement and accumulation of ions along internal boundaries in inhomogeneous dielectrics (Maxwell–Wagner theory); (3) accumulation of ions and space charge formation in the vicinity of the electrodes.

Any interpretation of the results in terms of space charge effects at the electrodes is unsatisfactory, since it would be expected that solutions of bivalent metal oleates and aluminium trisoaps would also show dielectric absorption. On the contrary, these solutions showed no anomalies of this kind.

The relaxation times which describe molecular-orientation processes, even when associated with high internal viscosity, are normally much too small for dielectric-loss maxima of the Debye type to occur at audio-frequencies. Only when very large dipoles, such as certain protein molecules [8] or the co-operative rotation of dipoles as in long-chain alcohols [9] are encountered, are the relaxation times sufficiently large to produce an audio-frequency response. Although very large aggregates are known to exist in aluminium soap gels,[10] rotation of such aggregates as a whole is unlikely, since they possess no net dipole moment.

In view of the large part played by direct-current conduction, a possible account of the audio-frequency dielectric loss may be found in terms of restricted movement of ions. It is significant that the dielectric absorption is observed only for systems of high viscosity where a non-uniform conductance path might be expected. Following this argument, a mechanism based on Maxwell–Wagner theory is proposed here to account, qualitatively, for the dielectric absorption in aluminium soap gels.

Evidence exists that aluminium soap gels in hydrocarbon solvents comprise a more or less random arrangement of long chains of soap molecules.[11] The aggregation of soap molecules to the extent necessary to produce gelation would lower the electrical conductivity in two ways. First, the mobility of the charge-carriers, which themselves are probably bulky, would be greatly reduced because of the high viscosity and, secondly, a proportion of the charged micelles would be effectively immobilised by actual incorporation into the chains. This is reflected in the dielectric-loss results for aluminium dilaurate

---

[6] Debye, *Verh. deutsch. physik. Ges.*, 1913, **15**, 777; Maxwell, " Electricity and Magnetism," Oxford Univ. Press, 1928; Wagner, *Archiv Electrotecnik*, 1914, **2**, 371; Murphy and Lowry, *J. Phys. Chem.*, 1930, **34**, 598; Whitehead and Marvin, *Trans. Amer. Inst. Elect. Engrs.*, 1929, **48**, 313; see, Manning and Bell, *Rev. Mod. Phys.*, 1940, **12**, 215, for other references.

[7] Oncley, *Chem. Rev.*, 1942, **30**, 433.

[8] Meakins and Welsh, *Austral. J. Sci. Res.*, 1951, *A*, **4**, 359.

[9] Gray and Alexander, *J. Phys. Colloid Chem.*, 1949, **53**, 23; McBain and Working, *ibid.*, 1947, **51**, 974.

[10] Gray and Alexander, ref. 9; McGee, *J. Amer. Chem. Soc.*, 1949, **71**, 278; McBain and Working, ref. 9.

[11] Cf. Murphy and Lowry, ref. 6.

in toluene (Fig. 1) where the more dilute systems are more conducting than the concentrated rigid gels.

In addition to increasing the resistance to motion of charged particles, gelation would also render the conductance path non-uniform. This is to be expected in a gel structure where the ions are large and would result in an accumulation of charge-carriers at points in the structure where there are steric barriers to their movement. The restricted displacement and accumulation of ions in this way is equivalent to a condenser charging current, and their return to an equilibrium distribution, to a discharge current. Thus, the conductance path, instead of being represented by a pure resistance is now represented by a resistance in series with a capacity.[12] The ionic accumulations, which may properly be regarded as equivalent to a dielectric polarisation, would make a contribution to the measured capacity of the sample. The charge q at time t after the application of a direct potential V to a capacity C_1 in series with resistance R_1 is given by eqn. (4). The time

$$q = C_1V[1 - \exp(-t/C_1R_1)] \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

constant for the charging process is equal to C_1R_1. In alternating fields the equivalent parallel capacity of this net work C_p varies with frequency according to eqn. (5) thus

$$C_p = C_1/[1 + (C_1R_1\omega)^2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

accounting for the decrease in apparent dielectric constant with increasing frequency observed for the aluminium soap gels (Fig. 5). The frequency at which the dielectric absorption shows a maximum is determined by the value of C_1R_1 in eqn. (3), and the actual variation of loss factor with frequency is given by substitution of this value in eqn. (2). These equations refer to the simplest hypothetical case, however, and since it would be expected that the ionic accumulations would be described by a distribution of relaxation times instead of only one, a large number of different values of capacity and resistance, C_1R_1, C_2R_2, ... C_nR_n, must be assumed.

Effect of Peptisers.—The effect of lauric acid in concentrations up to 1 mol. is to increase the direct-current conductivity and to decrease the component of the loss due to absorption as judged by the slope of the log ε''–log f curves (Fig. 2). These trends may be interpreted in terms of a less ordered and more homogeneous structure in which the conduction path is less resistive and more uniform. Such a change in structure would be brought about by a decrease in the average chain-length of the soap aggregates. This picture is consistent with the peptisation mechanism proposed by Gray and Alexander [10] in which the peptiser molecules are preferentially co-ordinated to the aluminium atoms, thus saturating the forces which would otherwise hold the soap molecules together.

The Aluminium Trisoaps.—Unlike the disoaps, aluminium trilaurate dissolves in hydrocarbons to give mobile solutions in which ebullioscopic measurements have shown that the trilaurate is molecularly dispersed. Even in concentrated solutions, aggregation does not proceed beyond the dimer. The explanation of this limited aggregation, which is in strong contrast to the behaviour of the aluminium disoaps, lies primarily in the absence of the hydroxyl group and possibly also in the steric hindrance to further aggregation which is provided by the six hydrocarbon chains of the dimer.

In the absence of any restriction on the movement of ions similar to that provided by the gel structure in the case of the disoaps, it would be expected that the dielectric loss in the trisoap solutions might be caused solely by direct-current conductivity. This is in accord with experiment, the behaviour of the aluminium trisoaps in toluene being similar to that of the bivalent metal oleates. In ionisation processes in the aluminium trisoap solutions, the following equilibria are probably involved:

$$\mathrm{Al(OOC{\cdot}R)_3} \rightleftharpoons \mathrm{Al^+(OOC{\cdot}R)_2 + {}^-OOC{\cdot}R} \quad . \quad . \quad . \quad . \quad . \quad (i)$$

$$\mathrm{Al(OOC{\cdot}R)_3 + {}^-OOC{\cdot}R} \rightleftharpoons \mathrm{Al^-(OOC{\cdot}R)_4} \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

$$\mathrm{Al(OOC{\cdot}R)_3 + Al^+(OOC{\cdot}R)_2} \rightleftharpoons \mathrm{Al_2{}^+(OOC{\cdot}R)_5} \quad . \quad . \quad . \quad (iii)$$

---

[12] Jobling, Nelson, and Gilmour, unpublished work.

Aggregation, by the addition of neutral molecules, may proceed beyond stages (ii) and (iii) but the ebullioscopic results and the steric argument make this improbable. As in the case of the bivalent metal oleates in toluene [1] the stability of these ions in a solvent of such low dielectric constant as toluene is explained by the shielding effect of the hydrocarbon chains which prevents close approach of the ionic charges localised in the centre of the aggregates.

The dielectric loss data for aluminium trilaurate (Fig. 7) suggest that these ionisation processes are important even in the solid and might largely determine the dielectric properties of the trisoap above its melting point. No dielectric measurements, however, have so far been made on the liquid soaps.

THE QUEEN'S UNIVERSITY OF BELFAST.

[*Received, March* 28*th*, 1956.]