Solutions of Metal Soaps in Organic Solvents.   Part IV.*   Direct-current
Conductivity in Solutions of Some Metal Oleates in Toluene.

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The dielectric loss in toluene solutions of zinc, copper, lead, magnesium, and calcium oleates has been shown to be due to direct-current conductivity. The conductivities and other properties of the metal soaps indicate a gradation in valency type from zinc oleate, which is almost non-polar, to magnesium and calcium which appear to be almost wholly ionic in character.

In concentrated solution the equivalent conductivities increase with increasing concentration and with decrease in temperature. These effects are explained in terms of an association of molecules and ions into aggregates, the equivalent conductivity increasing with increase in aggregate size. Evidence in support of this view is obtained by conductivity measurements in chloroform and by observation of the slow approach to an equilibrium conductivity value in toluene, following a change in concentration or temperature.

DIELECTRIC loss may occur as a result of relaxation phenomena involving either dipoles or ions, or particularly at low frequencies as a result of direct-current conductivity in the dielectric. Where relaxation effects are absent 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 the equation

$$\sigma = 5\cdot5 \times 10^{-13}\varepsilon''f \text{ ohm}^{-1} \text{ cm.}^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where f = frequency in cycles per second. In an investigation of their dielectric properties it became clear that the large losses shown by solutions of some metal carboxylates in non-polar solvents were due to direct-current conductivity, although in very concentrated solutions in some cases there was evidence of superimposed relaxation effects.

The unexpectedly high conductivities observed were thought to merit more detailed investigation and the present paper describes the results of such measurements with solutions of some metal oleates in toluene. The oleates were chosen because of their relatively high solubility in organic solvents at room temperature. Piper, Fleiger, Smith, and Kerstein (*Ind. Eng. Chem.*, 1939, **31**, 307) have shown that lead and copper soaps in liquid paraffin give rise to dielectric losses at low frequencies and have pointed out the importance of the colloidal state of the soap in determining the magnitude of the loss. These effects may be important when transformer oils, for example, remain for long periods in contact with certain metals.

Although many of the properties of metal carboxylates, *e.g.*, their solubility in non-polar solvents and their low melting points (Koenig, *J. Amer. Chem. Soc.*, 1914, **36**, 951), suggest that they are essentially covalent compounds there are indications that the metal–carboxylate bond in some cases exhibits considerable ionic character. Bhatnagar, Kapur, and Hussain (*Proc. Indian Acad. Sci.*, 1939, **9**, A, 143), on the basis of conductivity measurements, drew a distinction between magnesium oleate which gave conducting solutions in benzene and zinc oleate which did not, although their method of measurement did not permit high precision. Cady and Baldwin (*J. Amer. Chem. Soc.*, 1921, **43**, 646) concluded that copper stearate and copper oleate also were ionized in benzene. More recently Banerjee and Palit (*J. Indian Chem. Soc.*, 1950, **27**, 385) have reported relatively high dipole moments for some metal oleates.

EXPERIMENTAL

Preparation and Purification of Materials.—Oleic acid was redistilled " purissimus grade " from Schering–Kahlbaum. The preparation of the oleates involved metathesis of potassium oleate in ethanol with an aqueous solution of a salt of the metal : sulphate for zinc, copper, and

magnesium, nitrate for lead, and chloride for calcium. The precipitated soap was thoroughly washed with water, until free from excess of precipitant, and with a little ethanol to remove free acid. It was then recrystallised from benzene, where possible, and finally dried (P_2O_5) *in vacuo*. The magnesium and calcium oleates which are precipitated in the hydrated form were dried ($CaCl_2$) before the water of hydration was liberated by boiling in benzene. In all cases the last traces of benzene were removed under reduced pressure. For analysis, the oleates were hydrolysed with 2N-sulphuric acid, and the metal contents of the hydrolysates determined by standard procedures, after the oleic acid had been removed by extraction with ether.

	Zinc	Copper	Lead	Magnesium	Calcium
Metal, found %	10·43	10·07	26·55	4·22	6·85
„ calc. %	10·41	10·15	26·93	4·15	6·65

Sulphur-free toluene was dried (KOH, then Na) and distilled from sodium in an all-glass apparatus just before use. " AnalaR " chloroform was dried for two weeks (exsiccated Na_2SO_4) before distillation.

Apparatus.—Dielectric-loss measurements were made in the frequency range 50 c./s. to 300 kc./s. with a capacitance bridge (General Radio Type 716–*c*) in conjunction with a resistance–inductance bridge-type oscillator and a stabilised high-gain, wide-band amplifier and cathode-ray oscilloscope indicator. Conductivities were calculated from the loss data by equation (1). The conductivity of some of the solutions was also measured by a direct-current method. The results thus obtained were in good agreement with those calculated from the dielectric-loss data.

The dielectric cell consisted of two concentric stainless-steel cylindrical electrodes, the top of the outer electrode being tapered and ground to accommodate a B40 Pyrex ground-glass cone through which was sealed a 2-mm. tungsten rod. This rod was plug-sealed into a steel rod which was firmly screwed to the inner, live, electrode. This inner electrode was hollowed to reduce its weight. The tungsten rod served as the lead to the live electrode, and a steel rod soldered to the case of the outer electrode served as the lead to ground. A side-arm fitted with a B9 stopper was sealed into the B40 cone. The air capacity of the cell was 32·9 $\mu\mu$F and the loss at 100 c./s. was not greater than tan $\delta = 0.001$. A similar cell of smaller air capacity (8·2 $\mu\mu$F) was used with the more highly conducting solutions. The temperature was controlled to $\pm0.02°$ in a liquid-paraffin bath.

Viscosity measurements at 25° were made by the capillary flow method.

Conductivity Results.—Conductivity data at 25° for solutions of zinc, copper, lead, magnesium, and calcium oleates are shown in Fig. 1, where the equivalent conductivity is plotted against the square root of the concentration. In dilute solutions the conductivity at equivalent concentrations increases in the order zinc, copper, lead, magnesium, calcium. All the metal oleates in the concentration range studied, with the exception of copper, show a rise in equivalent conductivity with increasing concentration. This effect is particularly striking for magnesium and lead oleates. Of the five soaps studied, solutions of calcium oleate alone showed a fall in equivalent conductivity with increase in concentration in the higher concentration range. This decrease in equivalent conductivity is accompanied by a marked increase in viscosity (Fig. 2) and is probably a direct result of reduced mobility of the charge-carriers. The viscosities of magnesium oleate solutions are included in Fig. 2 for comparison.

Relaxation Effects in Concentrated Calcium Oleate Solutions.—At very high concentrations the loss data for solutions of calcium oleate failed to conform to equation (1), indicating the presence of an absorption in addition to the direct current losses. The departure from a conductivity plot which is shown in Fig. 3 (where both curves should be parallel to the broken line corresponding to $\varepsilon'' \propto 1/f$) might be explained on the basis of a restricted movement of ions in a viscous medium (Whitehead and Marvin, *Trans. Amer. Inst. Elect. Eng.*, 1929, **48**, 313; cf. Gemant, *Trans. Faraday Soc.*, 1935, **31**, 1582) or by the formation of ionic dipoles (Murphy and Lowry, *J. Phys. Chem.*, 1930, **34**, 617). Moreover, the presence of a Maxwell–Wagner type of absorption in these systems, arising from inhomogeneities in the dielectric, cannot be ruled out. In any case it is significant that such departures were observed only in very viscous solutions. This effect was not investigated further.

Effect of Water and Other Additives as Impurities.—The possibility that the conductivity observed in the metal oleate–toluene solutions might be due to traces of impurity was examined by noting the effect on the conductivity of adding known amounts of water, inorganic precipitant, and oleic acid. Small amounts of water had a negligible effect except with magnesium and calcium oleates where a considerable lowering of the conductivity was observed. These oleates

form insoluble hydrates and the reduction in conductivity in these solutions may be explained in terms of reduced solubility.   Inorganic precipitant had little effect except in the presence of water when a small increase in conductivity was observed.   Similarly, the presence of free oleic acid could in no way account for the magnitude of the observed conductivities.   No increase
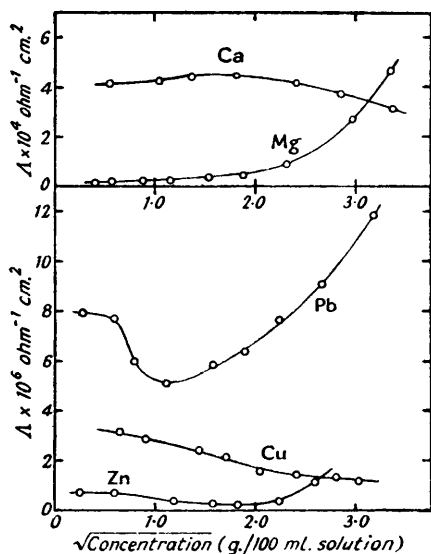
FIG. 1.   *Effect of concentration on conductivity.*
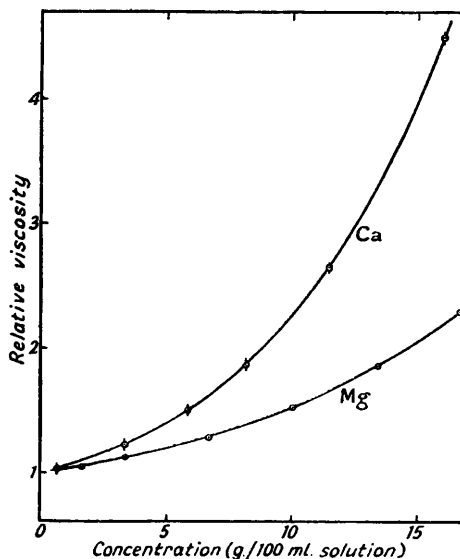
FIG. 2.   *Effect of concentration on viscosity.*

√Concentration (g./100 ml. solution)

Concentration (g./100 ml. solution)

FIG. 3.   *Effect of frequency on dielectric loss factor of calcium oleate solutions.*

log f (cycles/sec.)

Concn. : *A*, 0·31% ; *B*, 22·4%.
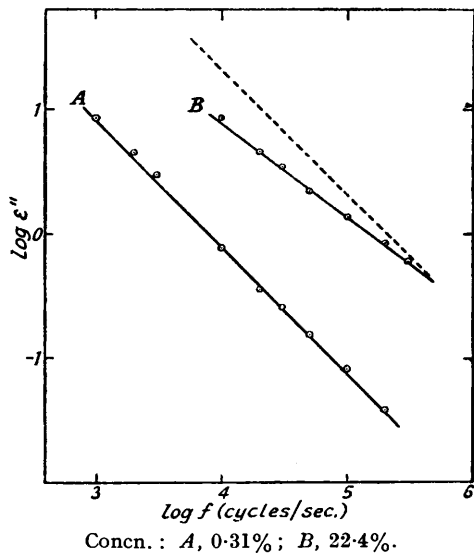
FIG. 4.   *Effect of temperature on specific conductance of magnesium oleate solutions.*

Temperature

Concn. : *A*, 8·06% (L.H. scale) ;
          B, 0·014% (R.H. scale).
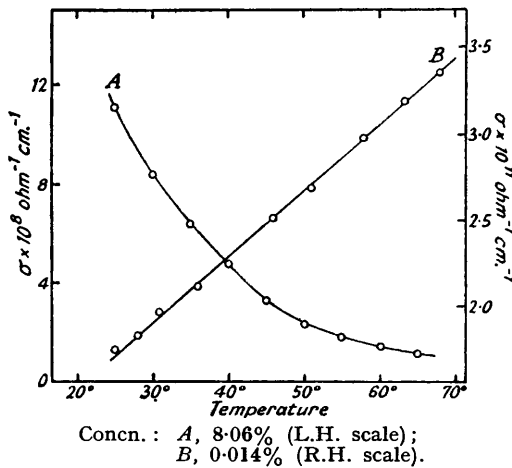
whatever in dielectric loss over that of the pure solvent was observed even in concentrated solutions of oleic acid in toluene.   Different preparations of the same soap were sometimes found to have slightly different conductivities in toluene but the effects of varying concentration and temperature were in all cases essentially the same.

Temperature Effects.—The conductivity was found to vary with temperature in a manner

depending on the particular soap and its concentration. Two opposing effects appear to operate consequent on a change of temperature. In concentrated magnesium oleate solutions, for example, the conductivity falls rapidly as the temperature is raised whereas in very dilute solutions an increase in conductivity with temperature is observed (Fig. 4).

A characteristic feature of the more concentrated solutions is the slow approach to an equilibrium conductivity following a change in concentration or temperature. This effect is shown clearly in Fig. 5 which illustrates the approach to an equilibrium conductivity at 30° of an 8·06% magnesium oleate solution from a lower (25°) and a higher (35°) temperature. Similarly, it was found that after dilution of a concentrated solution the final equilibrium conductivity might not be reached until after several hours or even days. Such changes were, however, fully reversible.
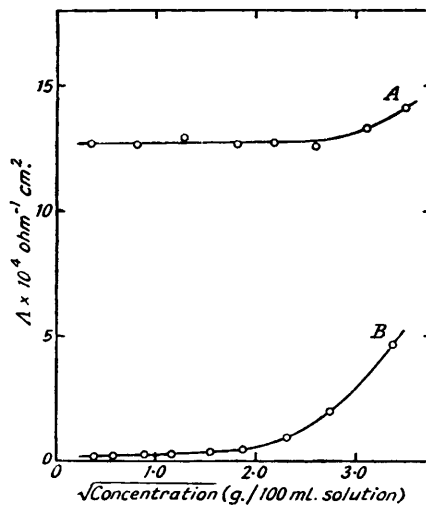
Measurements in Chloroform as Solvent.—Conductivity data for magnesium oleate in chloro-

Fig. 5. *Approach of specific conductance to equilibrium value.*
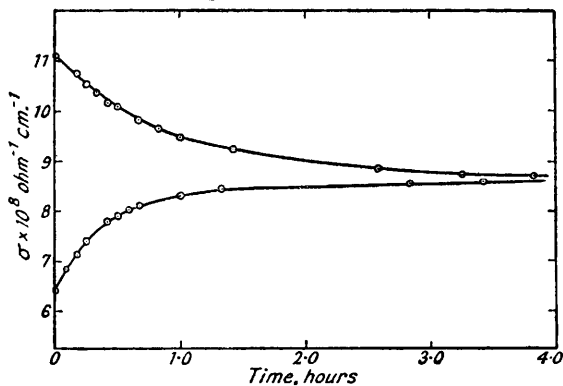
Upper and lower curves refer to σ at 25° and 35° respectively.

Fig. 6. *Effect of solvent on equivalent conductivity.*

Magnesium oleate in (*A*) chloroform, (*B*) toluene.

form are shown in Fig. 6. It will be noted that the conductivities are considerably greater and that the anomalous rise in equivalent conductivity occurs at a much higher concentration in this solvent.

DISCUSSION.

The most striking features of the results are, first, the relatively high conductivities of the soaps in such a non-polar solvent as toluene and, secondly, the unusual form of the equivalent conductivity–concentration and conductivity–temperature relations. The occurrence of ionic conduction in the metal soap–hydrocarbon systems contrasts strongly with other physical properties such as the solubility of the metal soaps in organic solvents and their low melting points (Koenig, *loc. cit.*). These contrasting properties which are characteristic of ionic and covalent compounds respectively may be reconciled by a consideration of the amphipathic nature of the metal soap molecule. The properties characteristic of covalent compounds are those which are conferred by the long hydrocarbon chains while the ionic conduction is a consequence of the highly polar or, probably in some cases, ionic nature of the metal–carboxylate bond.

As might be expected there is a rough correlation between the equivalent conductivities of the metal soaps in dilute solution and the magnitude of the ionization potential for the process $M \longrightarrow M^{++}$. This is shown in the Table below which also includes Banerjee and Palit's (*loc. cit.*) values for the dipole moments of the corresponding oleates.

These different lines of evidence indicate increasing polarity of the metal–carboxylate

bond in the approximate order zinc, copper, lead, magnesium, calcium. The dipole moment of lead oleate is anomalous; too much emphasis, however, need not be placed on this apparent anomaly, since the data appear to have only qualitative significance (Gilmour, Nelson, and Pink, *Nature*, 1953, **171**, 1075). The order of polarity of the soaps is, however, probably correct. The magnetic properties of the copper soaps provide additional evidence for the relatively covalent character of the copper–carboxylate bond. For example, in copper laurate the copper atoms are sufficiently close to permit strong quantum-mechanical exchange forces to come into play so that at very low temperature copper laurate is actually anti-ferromagnetic (Gilmour and Pink, *J.*, 1953, 2198). At the other end of the series there seems to be little reason to doubt that the metal–carboxylate bond in the case of magnesium and calcium soaps is almost wholly ionic in nature. Lawrence (*Trans. Faraday Soc.*, 1938, **34**, 660) has previously drawn attention to the gradation in properties of the metal soaps with change of cation.

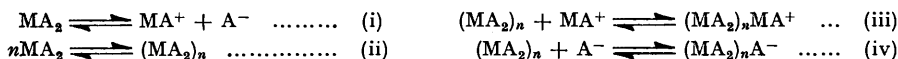| Oleate	$10^6\Lambda$ (ohm^{-1} cm.^{2})	Ionization potential * (v)	Dipole moment (D)
Zinc	0·75	27·2	0·29
Copper	3·25	28·2	1·20
Lead	7·50	—	4·29
Magnesium	20·0	22·58	1·66
Calcium	401	17·91	4·49

* International Critical Tables, 1929, **6**, 70—72.
The values of Λ refer, in all cases, to 0·004M-solutions.

An unusual feature of the results is the sharp rise in equivalent conductivity with increasing concentration observed in solutions of zinc, lead, magnesium, and calcium oleates (Fig. 1). Any explanation of this effect must embrace a consideration of the well-established fact that the metal soaps are associated in non-polar solvents to micelles of various sizes. In dilute solutions the size of the aggregate is a function, first, of the polarity of the metal–carboxylate bond, the more polar soaps forming larger aggregates, and secondly, of the chain-length of the carboxylic acid (Nelson and Pink, *J.*, 1952, 1744).

On simple Stokes's law considerations an increase in equivalent conductivity is to be expected with increasing micelle size for spherical micelles. The magnitude of the increase reported in the present paper, however, is too great to be explained on this basis alone. In dilute solutions there is no reason to believe that the micelles are other than roughly spherical but little can be said about the structure and shape of the much larger micelles which occur in more concentrated solutions. There is, of course, a limit to the number of molecules which can be accommodated in a spherical micelle and, by analogy with aqueous solutions of colloidal electrolytes, it would seem reasonable to assume that the larger micelles are either lamellar or rod-like.

In ionization processes in these solutions the following equilibria must be taken into account. The second stage of the ionization of the neutral soap molecule is neglected. (M = metal; A = oleate radical.)

$$MA_2 \rightleftharpoons MA^+ + A^- \quad \ldots \ldots (i) \qquad (MA_2)_n + MA^+ \rightleftharpoons (MA_2)_nMA^+ \quad \ldots (iii)$$

$$nMA_2 \rightleftharpoons (MA_2)_n \quad \ldots \ldots \ldots (ii) \qquad (MA_2)_n + A^- \rightleftharpoons (MA_2)_nA^- \quad \ldots \ldots (iv)$$

Although this picture is necessarily complex certain helpful generalisations may be made by a simple electrostatic approach. The free-energy change accompanying the separation of point charges $Z_A e$ and $Z_B e$ of opposite sign from an equilibrium distance r to infinity in a continuous medium is given by

$$\Delta F = Z_A Z_B e^2 / \varepsilon r \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ε is the dielectric constant of the medium. In the case of isolated ions or of small aggregates of the size known to exist in dilute solutions of metal oleates (Gilmour, Nelson, and Pink, *loc. cit.*) there is little hindrance to close approach of the ions so that r is necessarily small. As the concentration is increased the formation of large lamellar micelles or elongated cylindrical aggregates would lead, on the other hand, to increasingly large values of r

consequent on the shielding effect of the hydrocarbon exterior of the micelles. In contrast to aqueous solutions those micelle structures in non-polar solvents will be favoured in which the polar parts of the molecules are in the interior of the micelle. Ions so shielded are not available for recombination into neutral molecules. The position of equilibrium in the ionization process (i) is therefore moved to the right and an overall increase in ionic concentration, over that which would obtain in the absence of aggregation, results. Fuoss and Kraus (*J. Amer. Chem. Soc.*, 1935, **55**, 2387) have previously proposed the formation of triple ions to account for the minima in the conductance–concentration curves for dilute solutions of quaternary ammonium salts in solvents of low dielectric constant.

Support for the view that the rise in equivalent conductivity is a direct result of the increase in aggregate size is obtained from an examination of the conductivity–temperature plots. Since it has been established that increasing temperature leads to a reduction in micelle size (Gilmour, Nelson, and Pink, *loc. cit.*) it would be expected that the conductivity of the concentrated solutions should decrease with rise in temperature. This expectation accords with the experimental evidence. Fig. 4 shows the effect of temperature on a concentrated (8·06%) and a dilute (0·014%) magnesium oleate solution. It will be seen that the conductivity of the concentrated solution decreases whereas that of the dilute solution increases with rise in temperature. The latter effect may be partly accounted for on the basis of an increased mobility of the charged particles. In solutions of intermediate concentration both factors operate leading to a complex conductivity–temperature relation. It might be expected that the conductivity change resulting from increased mobility of the micelles would be instantaneous with change of temperature whereas the change in conductivity resulting from a redistribution of micelle sizes would be a relatively slow process. This expectation was realised with solutions of moderate concentration where increase in temperature caused an initial rise in conductivity followed by a slow decrease to an equilibrium value. Whether the net effect with increase in temperature is an increase or a decrease in conductivity depends on the particular soap and on its concentration in solution. With the less polar soaps such as copper oleate much higher concentrations must be reached before the conductivity shows a net decrease with rise in temperature.

The slow approach to an equilibrium conductivity following a change in temperature (Fig. 5) or in concentration provides additional evidence that the conductivity is strongly dependent on micelle size. The approach to equilibrium is determined by the length of time required for a redistribution of micelle sizes consequent on a change in temperature or concentration.

Fig. 6 shows the variation of equivalent conductivity at 25° with the square root of the concentration for solutions of magnesium oleate in chloroform ($\varepsilon = 4·724$) and toluene ($\varepsilon = 2·366$). In the chloroform solutions the conductivities are greater as would be expected from equation (2) and the equivalent conductivity begins to rise only at concentrations considerably higher than in toluene. This is in agreement with the experimental observation that with increase in the polarity of the solvent the metal soaps form smaller aggregates at equivalent concentrations (Nelson and Pink, *loc. cit.*).

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