

### 344. Dielectric Properties and Electrical Conductivity of Some Fused Metal Carboxylates.

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Dielectric data and derived electrical conductivities are reported for a series of molten metal carboxylates. In fused zinc carboxylates and lead stearate the measured loss is due solely to direct-current conductivity but in magnesium and copper oleates relaxation effects are imposed on the direct-current conduction loss. In the melts the electrical conductivity increases exponentially with temperature. The very low conductivities of the melts may be explained on the assumption that fusion incompletely destroys the crystal lattice and that the charge carriers are aggregates bearing a limited number of charges in proportion to their mass. A contribution to the conductivity may also be made by simple unassociated ions but the proportion of these ions in the melts must be very small.

ALTHOUGH some of the properties of long-chain metal carboxylates, *e.g.*, their solubility in non-polar solvents and their low melting points,<sup>1</sup> suggest that they are essentially covalent compounds, measurements of dipole moments<sup>2</sup> and electrical conductivity in non-polar solvents<sup>3</sup> indicate that some of them are ionic. We have now investigated the dielectric properties and electrical conductivity of a series of bivalent metal carboxylates both in the molten and in the solid state, in order to provide experimental evidence on this point. No previous investigation of the electrical properties of these compounds in the molten state has been reported.

#### EXPERIMENTAL

*Materials.*—The metal carboxylates chosen were magnesium, zinc, and copper oleate, zinc laurate and decanoate, and lead stearate. They were prepared and purified as described elsewhere.<sup>3</sup>

*Apparatus.*—Dielectric-constant and dielectric-loss measurements were made in the frequency range 30 c./sec. to 300 kc./sec. 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 as indicator. The dielectric cell consisted of two partially silvered concentric Pyrex cylinders closed at the bottom and sealed at the top with a B24 joint. The air capacity of this cell was  $\sim 25$  pF and its loss angle ( $\tan \delta$ ) at 60 c./sec. was  $> 0.001$ . Its volume was about 3 ml. Finely powdered samples of the carboxylates were melted into it under dry oxygen-free nitrogen and before the electrical measurements were made bubbles of gas were removed by careful pumping. Under these conditions an analytical check indicated negligible decomposition of the samples during the period required by the measurements. The temperature of the cell was controlled to  $\pm 0.2^\circ$  in an electrically heated aluminium block thermostat.

*Dielectric Loss.*—The dependence of dielectric loss factor  $\epsilon''$  on frequency for fused zinc laurate, decanoate, and oleate and lead stearate at the temperatures indicated is shown in Fig. 1. Where the whole of the loss in a dielectric is due to direct-current conduction it can be shown from a consideration of the voltage-current vectors that the dielectric-loss factor is inversely proportional to frequency, and the specific conductance  $\sigma$  can then be calculated from eqn. (1) where  $f$  = frequency in cycles per second. It is clear from Fig. 1. that this condition

$$\sigma = 5.5 \times 10^{-13} \epsilon'' f \text{ (ohm}^{-1} \text{ cm.}^{-1}\text{)} \quad \dots \quad (1)$$

is met in the case of the fused zinc carboxylates and lead stearate and that in these cases the whole of the measured loss in this frequency range is due to direct-current conductivity. With copper oleate, however, inverse proportionality between loss factor and frequency was found

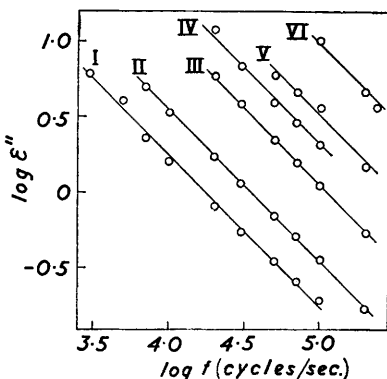
<sup>1</sup> Koenig, *J. Amer. Chem. Soc.*, 1914, **36**, 951.

<sup>2</sup> Banerjee and Palit, *J. Indian Chem. Soc.*, 1950, **27**, 385.

<sup>3</sup> Nelson and Pink, *J.*, 1954, 4412.

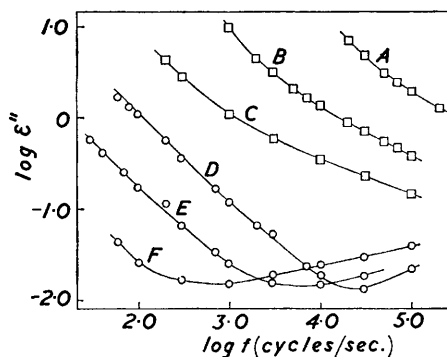
only at lower frequencies, and with magnesium oleate the results departed from a conductivity plot over the whole range (Fig. 2). Since fused magnesium oleate is exceptionally viscous, the departure from a conductivity plot indicated in Fig. 2 may possibly be explained on the basis of restricted movements of ions in a viscous medium.<sup>4</sup> It is possible that the dielectric absorption observed in copper oleate at higher frequencies is associated with a molecular orientation process but if this is so it is surprising that evidence of absorption at these frequencies was not obtained in the other carboxylates. Dielectric absorption in this frequency range, observed in

FIG. 1. Effect of frequency on loss factor of molten carboxylates.



- (I) Zinc oleate (73°)  
 (II) " (93.5°)  
 (III) " (133°)  
 (IV) Zinc laurate (127°)  
 (V) Lead stearate (113.5°)  
 (VI) Zinc decanoate (131.5°)

FIG. 2. Effect of frequency on loss factor of molten carboxylates.



- Magnesium oleate: A 185.5°, B 155°, C 135°.  
 ○ Copper oleate: D 122.5°, E 93°, F 63°.

long-chain alcohols, has been attributed by Dalbert, Magat, and Surdut to the duration of life of molecular aggregates but it is not clear from their discussion how this could lead to dielectric loss.<sup>5</sup>

**Electrical Conductivity.**—Specific conductivities calculated from eqn. (1) are shown in the Table together with data for some other fused salts.<sup>6,7</sup>

Compound	Temp. range	$\sigma$ (ohm <sup>-1</sup> cm. <sup>-1</sup> )	$E\sigma$ (kcal./mole)	$A$
Zinc decanoate .....	131.5—154°	$5.56 \times 10^{-7}$ — $1.04 \times 10^{-6}$	9.6	$8.02 \times 10^{-2}$
„ laurate .....	127—151	$1.15 \times 10^{-7}$ — $2.57 \times 10^{-7}$	11.4	$1.71 \times 10^{-1}$
„ oleate .....	73—133	$9.3 \times 10^{-9}$ — $6.03 \times 10^{-8}$	8.7	$2.89 \times 10^{-3}$
Copper oleate .....	63—122.5	$1.95 \times 10^{-10}$ — $5.89 \times 10^{-9}$	15.2	1.34
Lead stearate .....	105—115	$5.52 \times 10^{-8}$ — $2.63 \times 10^{-7}$	—	—
KHSO <sub>4</sub> <sup>6</sup> .....	211.8—300.5	0.049—0.141	6.2	33
NaHSO <sub>4</sub> <sup>6</sup> .....	190.0—310.2	0.079—0.256	5.7	38
KCl <sup>7</sup> .....	768	2.12	2.3	6.5
AgCl .....	600	4.48	—	—

**Effect of Temperature.**—The effect of temperature on the conductivity is shown in Figs. 3 and 4 (cooling curves). With the possible exception of lead stearate, a simple exponential relation was found in every case between conductivity and temperature. The high apparent dielectric constant of lead stearate prevented accurate loss measurements except over a limited temperature range. A feature of the result in the case of the zinc carboxylates was the time-lag in the establishment of equilibrium conditions when the temperature of the sample was changed.

<sup>4</sup> Whitehead and Marvin, *Trans. Amer. Inst. Elect. Engrs.*, 1929, **48**, 313; Gemant, *Trans. Faraday Soc.*, 1935, **31**, 1582.

<sup>5</sup> Dalbert, Magat, and Surdut, "Polarisation de la Matière," Colloques Internationaux, Paris, 1949, 14.

<sup>6</sup> Rogers and Ubbelohde, *Trans. Faraday Soc.*, 1950, **46**, 1051.

<sup>7</sup> Biltz and Klemm, *Z. anorg. Chem.*, 1926, **152**, 267.

Apparent activation energies for conduction  $E_{\sigma}$  and values of  $A$  calculated from the equation (2) are also shown.

$$\sigma = A \exp (-E_{\sigma}/RT) \quad \dots \quad (2)$$

*Dielectric Constant.*—In all the carboxylates the apparent dielectric constant of the melt increased very rapidly at low frequencies. The behaviour of fused zinc laurate which was typical of the group is shown in Fig. 5 which also gives results for the solid phase at several temperatures. There is a sharp fall in dielectric constant when solidification takes place. At

FIG. 3. Effect of temperature on conductivity.

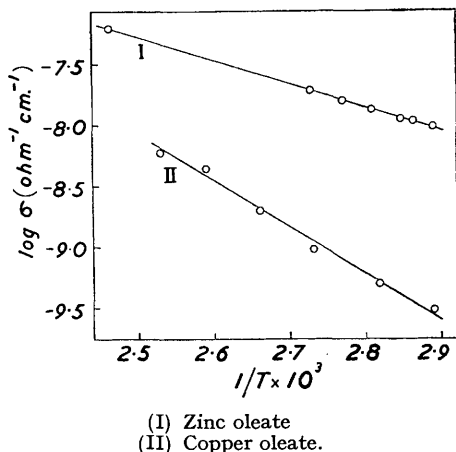


FIG. 4. Effect of temperature on conductivity.

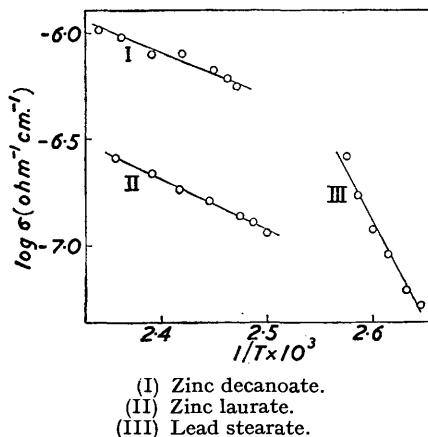
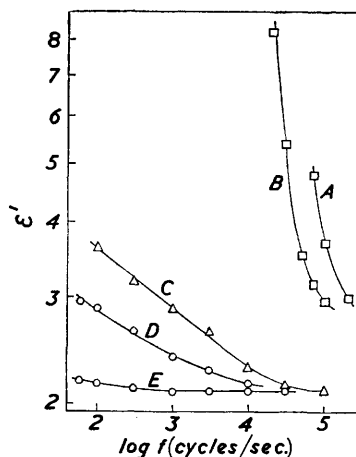


FIG. 5. Effect of frequency on dielectric constant.

- Molten zinc laurate: A 151°, B 129°.
- △ Solid zinc laurate immediately after solidification: C 120°.
- Solid zinc laurate after storage for 18 hours: D 121°, E 109.5°.



high frequencies the value for the solids tended to a value between 2 and 3. Just below the m. p. the dielectric constant at low frequencies immediately after solidification was found to be considerably greater than the value after the solid had been stored overnight at the same temperature (Fig. 5). This decrease may be due to a gradual increase in ordering in the lattice with time. A very similar effect has been reported in other long-chain compounds by Meakins and Mulley.<sup>9</sup>

In view of the relatively high conductivity of the melt the sharp rise in apparent dielectric constant observed in the melt as the frequency falls may be accounted for largely by electrode polarisation or possibly by the development of a space charge in the neighbourhood of the electrode surfaces. If ionic micelles are present in these systems their discharge at the electrodes

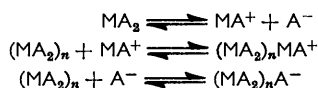
<sup>8</sup> Lowry, *Phil. Mag.*, 1928, **5**, 1072.

<sup>9</sup> Meakins and Mulley, *Austral. J. Sci. Research*, 1951, **A**, **4**, 365.

may present considerable steric difficulties since it may be assumed that the electrical charge will be located inside a micelle and be surrounded effectively by an insulating layer of hydrocarbon chains. Johnston and Cole<sup>10</sup> found that the apparent dielectric constant of liquid formic acid which has a specific conductance at 25° of  $6 \times 10^{-5}$  ohm<sup>-1</sup> cm.<sup>-1</sup> did not differ from  $\epsilon$  at 10 kc./sec. but was approximately ten times as great at 20 c./sec. They showed that this apparent large increase could be accounted for satisfactorily by the combined effects of direct current conduction and electrode polarisation.

#### DISCUSSION

The most interesting property of the molten carboxylates is their low conductivity in comparison with most other fused salt systems which have conductances greater by a factor of at least  $10^6$ . On the other hand the measured conductivities differ by a large factor from those of non-ionic liquids, indicating the presence in the melts of ions or charged aggregates. In view of the well-known tendency of this group of compounds to form aggregates in non-polar solvents, the simplest explanation is that fusion incompletely destroys an ionic crystal lattice and that some of the resultant aggregates or micelles carry a resultant electric charge. Ionisation processes in the system could then be represented by the equilibria (M = metal; A = acid radical):



where  $\text{MA}_2$  could be a neutral molecule or an ionic doublet. The low mobility of charge carriers of the micelle type would account for their small contribution to the conductivity. This type of aggregate is similar to that which is believed to be responsible for conduction in solutions of metal carboxylates in non-polar solvents.<sup>3</sup> The presence of micelles in these melts is supported qualitatively by their high viscosity. Lawrence<sup>11</sup> also has concluded, from a study of their melting characteristics, that many metal soaps pass through a viscous stage in which the melt consists of large aggregates or micelles. The low conductivities of the melts are no doubt accounted for partly by this high viscosity.

A contribution to the total conductivity may also be made by the kinetically free simple ions  $\text{MA}^+$  and  $\text{A}^-$  although the low measured conductivities indicate that the proportion of these present must be very small. The only comparable data are for the alkylammonium picrates,<sup>12</sup> which have specific conductivities of the order of  $10^{-2}$  ohm<sup>-1</sup> cm.<sup>-1</sup>. These relatively low conductivities have been interpreted by Greenwood and Martin<sup>13</sup> as implying limited dissociation, the average value of  $\alpha$ , the degree of ionic dissociation, for a series of primary alkylammonium picrates being estimated as 36%. These authors distinguish between ionisation which implies separation of charge within the molecule and ionic dissociation which involves the separation of a molecule into anions and cations which are free to migrate under an applied potential.

*Effect of Temperature.*—For non-associated ionic melts like the alkali halides<sup>7</sup> an exponential relation (2) has been found between electrical conductivity and temperature.

For associated melts, on the other hand, Rogers and Ubbelohde<sup>6</sup> have pointed out that a different relation (3) should hold, where  $B'$  and  $B$  are constants and  $b$  is a constant related

$$\ln \sigma = B - (B'/T) \exp (b/T) \dots \dots \dots (3)$$

to the activation energy involved in the dissociation. A similar relation would hold if simple ions were the charge carriers in a partly ionised non-associated melt and the ionisation was temperature-dependent. Since a simple exponential relation was found in every

<sup>10</sup> Johnston and Cole, *J. Amer. Chem. Soc.*, 1951, **73**, 4536.

<sup>11</sup> Lawrence, *Trans. Faraday Soc.*, 1938, **34**, 660.

<sup>12</sup> Walden, Ulich, and Birr, *Z. phys. Chem.*, 1927, **130**, 495; 1928, **131**, 1, 21.

<sup>13</sup> Greenwood and Martin, *J.*, 1953, 1431.

case between conductivity and temperature (Figs. 3 and 4) the present results appear to indicate that the carboxylate melts are simple non-associated liquids. A very similar anomaly was observed by Rogers and Ubbelohde<sup>6</sup> in the case of the alkali hydrogen sulphate melts which on the basis of viscosity measurements and on other grounds clearly contained chain-like aggregates linked by hydrogen bonds, and yet obeyed equation (2) within the limits of experimental error. If ionic micelles are actually responsible for the conductivity in the carboxylate melts the fact that equation (2) is obeyed may mean that over the temperature range of these experiments there is no redistribution of the micelles leading to a substantial change in the number of current carriers or that the redistribution of micelle size is such a slow process that only the change in conductivity due to decreased mobility is detected on lowering the temperature. Alternatively, the bulk of the current in these melts may be carried by the simple ions  $MA^+$  and  $A^-$ . Against the latter view is the magnitude of the  $E$  values found in these experiments which is much higher than in non-associated melts like the alkali halides and approximates more closely to the values found in the associated bisulphate melts. Unfortunately the paucity of data on the electrical properties of melts precludes further comparison.

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