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THE ELECTRICAL CONDUCTANCE OF SOME MOLTEN CARBOXYLATE MIXTURES

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ABSTRACT

Data are presented for the electrical conductivities in the melt for lead(II) octadecanoate/lead(II) decanoate, lead(II) hexadecanoate/lead(II) decanoate, lead(II) hexadecanoate/zinc hexadecanoate and lead(II) hexadecanoate/cadmium hexadecanoate mixtures over their complete composition ranges. The electrical conductivities are measured as a function of temperature from just above the melting point to just below the decomposition point of the mixtures. The Arrhenius plots for the mixtures are linear in all cases and the activation energies are determined. While the activation energies for lead(II) octadecanoate/lead(II) decanoate and lead(II) hexadecanoate/lead(II) decanoate mixtures are mole fraction independent over the concentration range studied, rendering support to previous models advanced by other workers that the major charge carrier is the free metal cation, the other systems show no such simple behaviour. In these systems there are indications of deviations from ideal behaviour, suggesting that entropy and enthalpy of mixing might be important.

INTRODUCTION

The temperature dependence on the molar volume, density and electrical conductivity of some molten divalent metal carboxylates has been extensively studied [1—5] in our laboratories. These studies have indicated that the metal ions were solely responsible for electrical conduction, while the carboxylate moiety, usually an aggregate of approximately three or four carboxylate molecules, was responsible for viscous flow. The model presented to explain the conductance behaviour proposes that a dissociation equilibrium of the type

$$MA_2 \rightleftharpoons MA^+ + A^- \rightleftharpoons M^{2+} + 2A^-$$

where M is the metal and A, the carboxylate moiety, existed in the melt.

It has been demonstrated that in these types of metal carboxylates, mesophases were present between the solid and isotropic liquid phases [6]. Furthermore, Adeosun [7] has shown that the addition of a common metal ion such as lead, in the form of lead acetate to lead(II) decanoate, did not alter the phase sequence observed in lead decanoate [6] and also did not

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alter the state of aggregation of the soap molecules in the liquid phase [7]. However, the addition of lead oxide to lead(II) decanoate changed the structure of the liquid phase from small, essentially spherical micelles in the pure soap, to long cylindrical micelles in the mixture [8]. The conductivity behaviour of some of these mixed systems [9,10] was proposed to fit the model advanced to explain the conductivity of the pure molten soap; namely, that the cation was the main current carrier. More recently, Ellis and Adeosun [11] have shown, from DTA evidence, that the addition of zinc octadecanoate to lead(II) octadecanoate up to 0.3 mole fraction did not alter the degree of order of the hydrocarbon chains in either the solid or liquid phase. Clearly then, the hydrocarbon chains of the two soaps were arranged in the same manner in the crystal lattice as well as in the liquid phase.

The work reported in this paper is an extension of the work begun in our laboratories to investigate the effect on conductivity of the addition of a common ion or carboxylate moiety to the pure soap at higher concentrations than previously studied.

EXPERIMENTAL

Materials

The soaps were prepared by metathesis in alcohol solution [12—14], purified and characterised as previously described [1,2]. The elemental analysis and melting point data were consistent with those described in the literature.

The binary mixtures were prepared using the following mole fractions of one of the components: 0.1, 0.5, 0.7 and 0.9 by adding the appropriate weight of one of the components to the other in a quick-fit conical flask which was then evacuated to minimise decomposition of the soaps on heating. During melting, the mixture was shaken periodically to effect proper mixing. The heating of the mixture was carefully monitored to ensure that the temperature did not exceed the decomposition temperature.

Conductivity measurements

The conductivities of the mixtures were measured as described by Sime and co-workers [1] in the temperature range 10 K above the melting point to just below the decomposition temperature (~430 K) of the mixtures. All runs were repeated using fresh samples. Measurements were taken upon heating and cooling the sample. The values obtained for heating and cooling the sample were the same within experimental error. Duplicate runs were also within experimental error.

RESULTS

According to the model proposed by Sime and co-workers [1] to explain the conductance behaviour of divalent metal carboxylates, the metal carboxylate is envisaged to dissociate according to the scheme

$$\mathrm{MA_2} \rightleftharpoons \mathrm{MA^+} + \mathrm{A^-} \rightleftharpoons \mathrm{M^{2+}} + 2\mathrm{A^-}$$

If the assumption is made that the main current carrier is the M^{2+} ion rather than the more bulky A^- ion, and that it moves by a simple activated process then

$$\log \kappa = \log Q - \frac{\Delta H_\kappa^\ddagger + \Delta H/3}{2.303R} \cdot \frac{1}{T}$$

where $\Delta H_\kappa^\ddagger$ and ΔH are the enthalpies of activation for movement of the M^{2+} ion and for dissociation, respectively.

$$Q = \log(NeA/2V_\mathrm{m}) + \frac{1}{2.303R}\,(\Delta S_\kappa^\ddagger + \Delta S/3)$$

where $\Delta S_\kappa^\ddagger$ and ΔS are the entropies of activation and dissociation, respectively, and V_m is the molar volume of the soap mixture.

The logarithms of the specific conductivities of the mixtures are shown in Figs. 1—4 as a function of inverse temperature. It should be noted that in

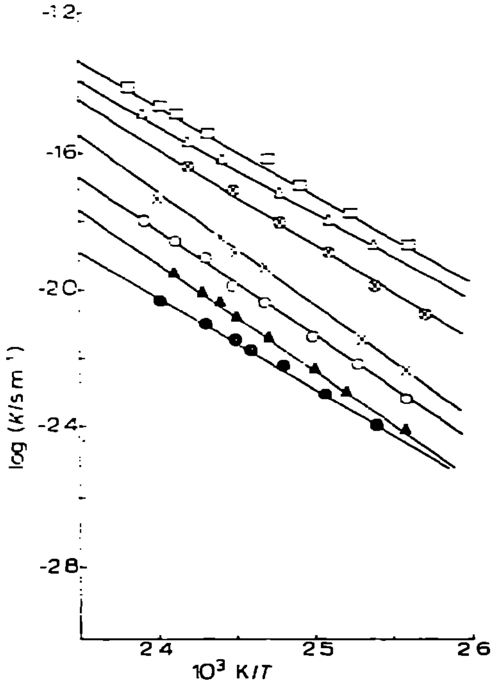


Fig. 1. Semilogarithmic plots of specific conductivity vs. inverse temperature for lead octadecanoate/lead decanoate mixtures: □, pure lead decanoate; △, $X_{\mathrm{PbC}_{10}} = 0.9$; ⊗, $X_{\mathrm{PbC}_{10}} = 0.7$; x, $X_{\mathrm{PbC}_{10}} = 0.5$; ○, $X_{\mathrm{PbC}_{10}} = 0.3$; ▲, $X_{\mathrm{PbC}_{10}} = 0.1$; ●, pure lead octadecanoate.

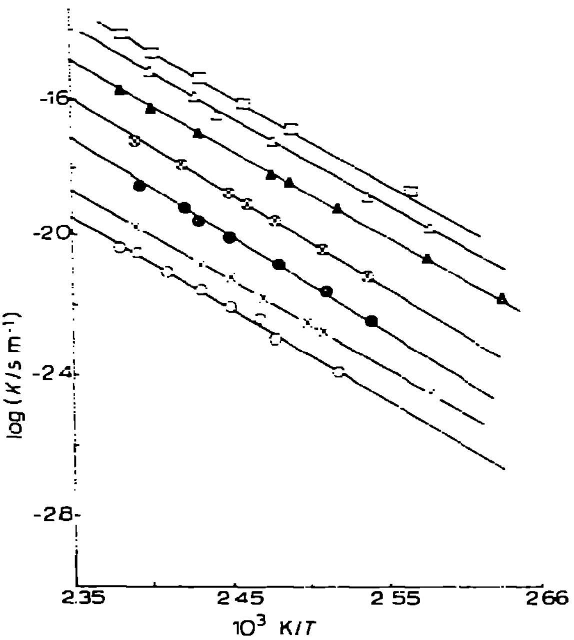
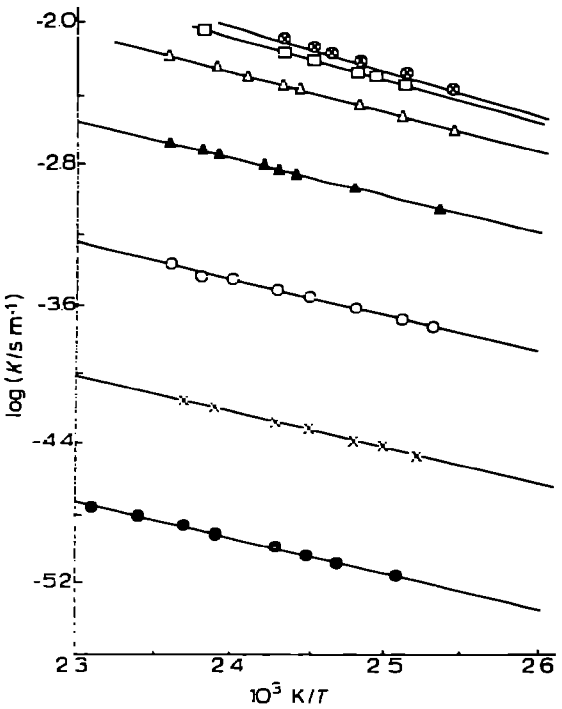


Fig. 2. Semilogarithmic plots of log specific conductivity vs. inverse temperature for lead hexadecanoate/lead decanoate mixtures: □, pure lead decanoate; △, $X_{\mathrm{PbC}_{10}} = 0.9$; ▲, $X_{\mathrm{PbC}_{10}} = 0.7$; ⊗, $X_{\mathrm{PbC}_{10}} = 0.5$; ●, $X_{\mathrm{PbC}_{10}} = 0.3$; x, $X_{\mathrm{PbC}_{10}} = 0.1$; ○, pure lead hexadecanoate.



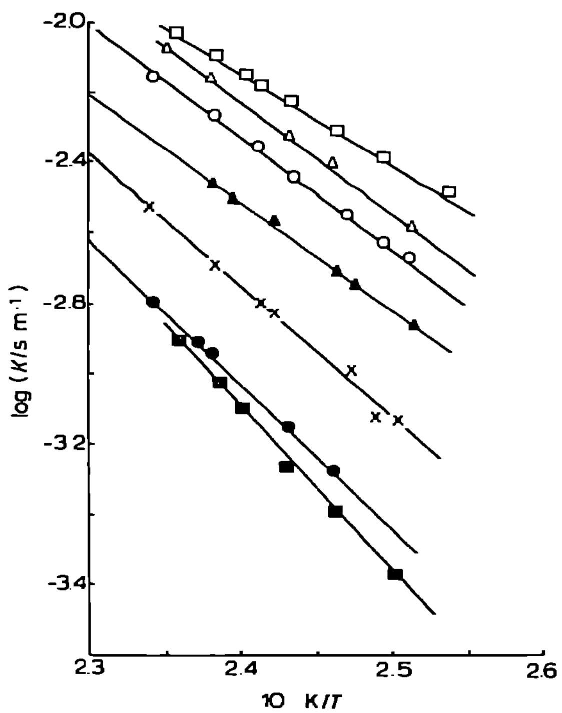


Fig. 3. Semilogarithmic plots of log specific conductivity vs. inverse temperature for lead hexadecanoate/zinc hexadecanoate mixtures; ⊗, pure lead hexadecanoate; □, $X_{ZnC_{16}} = 0.1$, △, $X_{ZnC_{16}} = 0.3$; ▲, $X_{ZnC_{16}} = 0.5$: ○, $X_{ZnC_{16}} = 0.7$; ×, $X_{ZnC_{16}} = 0.9$; ●, pure zinc hexadecanoate.

Fig. 4. Semilogarithmic plots of log specific conductivity vs. inverse temperature for lead hexadecanoate/cadmium hexadecanoate mixtures: □, pure lead hexadecanoate, △, $X_{CdC_{16}} = 0.1$; ○, $X_{CdC_{16}} = 0.3$; ▲, $X_{CdC_{16}} = 0.5$; ×, $X_{CdC_{16}} = 0.7$; ●, $X_{CdC_{16}} = 0.9$: ■, pure cadmium hexadecanoate.

most cases, the plots for the pure soaps show curvature at high temperatures and therefore only their low temperature data are analysed here. As the low temperature limiting slopes for the pure soaps and the slopes for the mixtures show no sign of curvature, the experimental data shown in Figs. 1—4 were fitted to least squares lines of the form

$$\log \kappa = \log Q - \frac{\Delta H_{\kappa}^{\ddagger} + \Delta H/3}{2.303R} \cdot \frac{1}{T}$$

to obtain values for the coefficients log Q and ($\Delta H_{\kappa}^{\ddagger} + \Delta H/3$). These values are tabulated in Tables 1—4.

While there was an increase in conductivity with the mole fraction of lead(II) decanoate added at any particular temperature for the systems lead(II) octadecanoate/lead(II) decanoate and lead(II) hexadecanoate/lead(II) decanoate, the converse was true for the systems lead(II) hexadecanoate/zinc hexadecanoate and lead(II) hexadecanoate/cadmium hexadecanoate. Conductivities were roughly linear functions of concentration over the composition range studied for the cases where conductivity increased with concentration. There were, however, indications of deviation from ideal

TABLE 1

Least squares parameters for the activation energy plot for the system: lead octadecanoate/lead decanoate mixtures

$X_{\mathrm{PbC}_{10}}$	log Q	$(\Delta H^{\ddagger}_{K} + \Delta H/3)$ (kJ mole^{-1})
0.0	3.93 ± 0.02	48.1 ± 1.8
0.1	4.20 ± 0.01	49.5 ± 0.6
0.3	4.67 ± 0.01	52.1 ± 1.2
0.5	4.75 ± 0.01	51.8 ± 1.0
0.7	4.80 ± 0.01	52.0 ± 1.2
0.9	5.01 ± 0.01	52.0 ± 1.0
1.0	4.72 ± 0.01	49.5 ± 0.7

X = mole fraction

TABLE 2

Least squares parameters for the activation energy plot for the system: lead hexadecanoate/lead decanoate mixtures

$X_{\mathrm{PbC}_{10}}$	log Q	$(\Delta H^{\ddagger}_{K} + \Delta H/3)$ (kJ mole^{-1})
0.0	4.30 ± 0.01	50.4 ± 0.8
0.1	5.42 ± 0.01	58.6 ± 1.4
0.3	5.62 ± 0.03	59.2 ± 4.2
0.5	5.85 ± 0.02	60.5 ± 3.2
0.7	5.63 ± 0.02	57.5 ± 3.5
0.9	4.85 ± 0.01	50.7 ± 0.7
1.0	4.74 ± 0.01	49.5 ± 0.7

TABLE 3

Least squares parameters for the activation energy plot for the system: lead hexadecanoate/zinc hexadecanoate mixtures

$X_{\mathrm{ZnC}_{16}}$	log Q	$(\Delta H^{\ddagger}_{K} + \Delta H/3)$ (kJ mole^{-1})
0.0	4.30 ± 0.01	50.4 ± 0.8
0.1	3.26 ± 0.01	42.6 ± 1.1
0.3	3.11 ± 0.01	42.9 ± 0.7
0.5	2.56 ± 0.01	42.5 ± 1.3
0.7	1.47 ± 0.01	39.3 ± 1.5
0.9	0.56 ± 0.01	38.1 ± 0.8
1.0	0.20 ± 0.01	37.8 ± 0.6

TABLE 4

Least squares parameters for the activation energy plot for the system: lead hexadecanoate/cadium hexadecanoate mixtures

$x_{\mathrm{PbC}_{16}}$	log Q	($\Delta H^{\ddagger}_{\kappa} + \Delta H/3$) (kJ mole^{-1})
0.0	4.30 ± 0.01	50.4 ± 0.8
0.1	5.06 ± 0.01	56.9 ± 1.5
0.3	5.11 ± 0.01	58.1 ± 1.0
0.5	5.31 ± 0.01	61.1 ± 2.0
0.7	6.69 ± 0.02	73.8 ± 0.6
0.9	6.72 ± 0.01	76.4 ± 0.6
1.0	8.29 ± 0.02	89.0 ± 2.5

behaviour over the composition range from pure lead(II) octadecanoate or pure lead(II) hexadecanoate to pure lead(II) decanoate. In addition, plots of log κ vs. mole fraction at any temperature, for lead(II) hexadecanoate/zinc hexadecanoate showed large deviations from ideal behaviour, although these deviations were not so large in the lead—cadmium mixtures.

DISCUSSION

The results obtained in this work are discussed in the light of the simple theory propounded by Sime and co-workers [1].

Lead(II) octadecanoate/lead(II) decanoate

The values quoted in Table 1 for ($\Delta H^{\ddagger}_{\kappa} + \Delta H/3$) are constant within experimental error. These results were consistent with those reported in the literature [9] for a comparable system such as lead(II) decanoate/lead acetate mixtures where the addition of lead acetate caused no change in the enthalpy values recovered for the pure soap. It is therefore reasonable to suggest that, as for that system, the Pb^{2+} ions are the major charge carriers in this system.

The increase in the conductivity of the mixtures is attributed to an increase in the entropy terms, ($\Delta S^{\ddagger}_{\kappa} + \Delta S/3$), with increasing concentrations of decanoate; that is with increasing Pb^{2+} concentration arising from greater dissociation of lead decanoate than lead octadecanoate. This is confirmed by the increase in log Q values (Table 1) from 4.20 for 0.1 mole fraction addition of decanoate to 5.01 for 0.9 mole fraction addition. Although it is possible to calculate the Pb^{2+} ion concentration in the different mixtures at any temperature by a method described for the pure *n*-alkanoates [1], this requires high temperature data where the Arrhenius plot tends to a second linear portion with the slope corresponding to $\Delta H^{\ddagger}_{\kappa}$. Unfortunately, this calculation could not be done because the mixtures decomposed before the required temperatures were attained.

It is unlikely that the decanoate will affect $\Delta S_\kappa^\ddagger$, and hence the main effect must be attributed to the entropy of dissociation, ΔS. An estimate of the size of increase, $\delta(\Delta S)$, of ΔS can be obtained from the separation of the Arrhenius plots for any two mixtures of different compositions of decanoate at the same temperature. If the two mixtures differ by 0.2 mole fraction of decanoate, the solution of the expression

$$\log \kappa_{(x)} - \log \kappa_{(x+0.2)} = \frac{\delta(\Delta S)}{2.303R}$$

gives $\delta(\Delta S)$ as ~8.6 J mole^{-1} K^{-1} per 0.2 increase in mole fraction of decanoate. This suggests that the dissociated carboxylate chain becomes more disordered with respect to the undissociated chain by a factor of ~8.6 J mole^{-1} K^{-1} per 0.2 increase in mole fraction of lead decanoate.

Lead(II) hexadecanoate/lead(II) decanoate

Table 2 shows that although the $(\Delta H_\kappa^\ddagger + \Delta H/3)$ values were reasonably constant for the mixtures, they were higher than those for the pure soaps. Earlier interpretations [9,10] of the conducting behaviour of similar soap mixtures, where the mole fraction of one of the components into the other did not exceed 0.3, and where the $(\Delta H_\kappa^\ddagger + \Delta H/3)$ values were nearly always the same for the mixtures and pure soaps, were based on the premise of an insignificant effect of mixing. The mixtures were therefore then treated as ideal solutions.

The results here indicate, however, an effect of mixing of the components which might be attributed to the entropy (S_m) or enthalpy (H_m) of mixing. Unfortunately, the literature on thermodynamic studies of the mixing of these soaps is sparse. However, by analogy with earlier studies where the mixtures were considered to be ideal, and where the activation energies of the mixtures were constant as in the case reported here, it seems unlikely that H_m's contribution to the increase of conductivity with concentration is significant. It is considered that the entropy term, $(\Delta S_\kappa^\ddagger + \Delta S/3)$, and S_m, are more important. This conclusion is supported by the fact that, as expected, increasing the Pb^{2+} concentration increased the entropy as shown by the increase in $\log Q$ values with increasing decanoate concentration. The increase in conductivity must arise from either an increase in $\Delta S_\kappa^\ddagger$ or ΔS. It is probable from previous arguments that ΔS is the important term here. The deviation from ideality of plots $\log \kappa$ vs. mole fraction of decanoate may therefore be ascribed to the positive entropy of mixing with some possible contribution from enthalpy of mixing as well.

Lead(II) hexadecanoate/zinc hexadecanoate

Inspection of Table 3 shows that the enthalpy values obtained for pure zinc hexadecanoate are lower than those for pure lead hexadecanoate. Also, $(\Delta H_\kappa^\ddagger + \Delta H/3)$ values were unaffected, within experimental error, at all concentrations of zinc hexadecanoate. In addition, the conductivity of zinc hexadecanoate was less than that of lead hexadecanoate.

Over the concentration range studied, plots of $\log \kappa$ vs. mole fraction, at any temperature, indicated that the conductivity of the mixture decreased randomly as the mole fraction of zinc hexadecanoate increased. Again, this deviation from ideality may suggest an effect of mixing.

In terms of activation energy values, it would be expected that the dissociation equilibrium for the zinc soap would be more favoured than the equilibrium for the lead soap because of its lower dissociation energy and as a result, more Zn^{2+} ions would be expected in the melt. Since the Zn^{2+} ion is smaller in size than the Pb^{2+} ion, the conductivity of the zinc soap would be expected to be higher than that of the corresponding lead soap. However, because the enthalpy term is a sum of two enthalpy terms, it cannot be determined with any certainty as to which of these terms is responsible for the relatively low values of $(\Delta H_\kappa^\ddagger + \Delta H/3)$ in the zinc soap. That is, it is not possible to unambiguously calculate the contribution of each of these terms to $(\Delta H_\kappa^\ddagger + \Delta H/3)$ since this requires high temperatures where complete dissociation occurs when the main contribution to the activation energy becomes $\Delta H_\kappa^\ddagger$ [1]. This temperature cannot be obtained before the onset of decomposition.

The major explanation for the disparity between the conductivity values for these two soaps appears to be due to differences in the entropies. Such a conclusion follows from an inspection of the relative $\log Q$ values where $\log Q$ is 4.30 for the pure lead soap and 0.20 for the pure zinc soap. This clearly implies that less free Zn^{2+} ions are available for conduction in the pure melt. Therefore, as the mole fraction of zinc hexadecanoate in lead(II) hexadecanoate increased, the entropy term decreased and the concentration of undissolved zinc soap in the melt increased. The undissociated zinc carboxylate, allied with the increase in viscosity of the system due to the addition of the more viscous zinc soap [1], will affect the ionic mobilities of free Pb^{2+} and Zn^{2+} in the melt. Consequently, the conduction of the mixture decreased as the concentration of zinc carboxylate in the melt increased.

Lead(II) hexadecanoate/cadmium hexadecanoate

From an examination of Table 4, the following observations were noteworthy: the enthalpy and entropy terms increased as the mole fraction of cadmium hexadecanoate increased in the melt. Also, the $(\Delta H_\kappa^\ddagger + \Delta H/3)$ value for the pure lead soap was lower than that for the pure cadmium soap. The higher entropy value obtained for the pure cadmium soap is expected because of the higher viscosity of the cadmium melt [1,3]. Hence, the entropy of activation, $\Delta H_\kappa^\ddagger$, must be higher in cadmium than in lead and must be the main contributory factor to the activation energy.

Plots of $\log \kappa$ vs. mole fraction at any particular temperature showed a random decrease in conductivity (probably due to an effect of mixing) with increased mole fraction of cadmium soap in the melt. It is envisaged that both ΔH and $\Delta H_\kappa^\ddagger$ contribute to the decrease in conductivity with increasing concentrations of cadmium soap. Since cadmium soaps dissociate to a lesser extent than lead soaps in the melt [1,3], ΔH can reasonably be assumed to contribute to the activation energy values for the pure cadmium soap. This implies that the backward dissociation equilibrium

$Cd\,A_2 \rightleftharpoons Cd^{2+} + 2A^-$

is more favoured in the melt. Therefore, less Cd^{2+} ions will exist in the melt, probably because of the strong Cd—O bond. This would explain the relatively low conductivity values for the pure cadmium soap. As the concentration of cadmium soap increased in the melt, more undissociated cadmium species were present. However, because of the increased viscosity of the mixture with increased cadmium concentrations, the ionic mobility of Pb^{2+}, the main current carrier, must be progressively retarded and $\Delta H^{\ddagger}$ must increase. The presence of more undissociated cadmium species in the melt and the concomitant increase in viscosity and hence $\Delta H^{\ddagger}$, with increasing concentrations of cadmium in the mixture, explains the progressive decrease in conductivity with increasing mole fraction of cadmium.

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