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ELECTRICAL CONDUCTANCE, DENSITY, VISCOSITY AND THERMAL BEHAVIOUR OF LEAD(II) AND ZINC(II) SALTS OF SOME UNSATURATED FATTY ACIDS

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ABSTRACT

Data are presented for the electrical conductance, density, viscosity and differential thermal analysis of the lead(II) and zinc(II) salts of *cis*-9-octadecenoic, *trans*-9-octadecenoic and 9,12-octadecadienoic acids. The data are compared with those of lead(II) and zinc(II) octadecanoates. The activation energies for conductance in these soaps are similar to those of the corresponding octadecanoates which suggest that the charge carriers are the metal ions. However, the activation energies for viscous flow in these soaps are much smaller than for the corresponding lead and zinc octadecanoates which suggest that the structure of the carboxylate anions is important in determining viscous flow.

The soaps do not form mesophases but melt directly into the isotropic liquid. The values of the entropy changes accompanying the fusion of the zinc salts suggest either that zinc 9,12-octadecadienoate is more ordered in the liquid phase or more disordered in the crystal phase than zinc octadecanoate or the zinc salts of *cis*- and *trans*-9-octadecenoic acids.

INTRODUCTION

In previous papers[1, 2] data were presented for the density, electrical conductance and viscosity of some even chain length lead(II) and zinc(II) carboxylates from hexanoate to octadecanoate inclusive. It was shown that the metal ions were responsible for electrical conduction while the carboxylate moiety was responsible for viscous flow. Further, it was proposed that the unit of viscous flow in the lead and zinc soaps is an aggregate of approximately 3 or 4 carboxylate molecules. In another paper[3], the thermal behaviour of some even chain length lead(II) carboxylates was reported. We showed that the lead soaps pass through a number of mesophases before finally melting into the isotropic liquid. On the other hand, the zinc soaps do not form mesophases but melt directly into the isotropic liquid[4].

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Several studies have shown that the physical properties of metal carboxylates, either in solution[5-12] or in the pure melt[1-4, 13-22], depend crucially on the nature of the metal ion. However, there had been very little study of the effect of modifying the structure of the hydrocarbon portion of the metal carboxylates on the physical properties of the soaps in the molten state. In the work reported in this paper we have examined the effect of unsaturation of the hydrocarbon chains on the physical properties of some lead(II) and zinc(II) carboxylates. We have, therefore, obtained data on the density, viscosity, electrical conductivity and thermal properties of lead(II) and zinc(II) salts of *cis*-9-octadecenoic, *trans*-9-octadecenoic and 9,12-octadecadienoic acids with a view to comparing them with the behaviours of the corresponding lead(II) and zinc(II) saturated fatty acid salts of the same chain length, i.e. lead and zinc octadecanoate.

EXPERIMENTAL

Materials

All the fatty acids employed were B.D.H. grade and were stated to have minimum 99% purity by GLC assay. They were used without further purification. Lead nitrate and zinc sulphate were "Analar" B.D.H. grade.

The soaps were prepared by metathesis in alcohol solution as previously described[1]. All the zinc salts were recrystallised from benzene. The lead salt of *trans*-9-octadecenoic acid was also recrystallised from benzene while the lead salt of *cis*-9-octadecenoic acid was recrystallised from chloroform. The IR spectra of the compounds showed that they were free from water and excess acid. Elemental analyses of the compounds for carbon and hydrogen gave satisfactory results. However, the lead salt of 9,12-octadecadienoic acid could not be recrystallised from any solvent and elemental analysis of the crude product did not give satisfactory results hence this compound was not used in any of the physical measurements.

Measurements

The procedures for the measurement of density, viscosity and conductance have been described elsewhere[1, 2]. DTA measurements were made on a Mettler TA 2000 Analyser. About 20 mg of the sample were sealed into the standard aluminium crucibles of the DTA equipment and scanned at a heating rate of 1 K min^{-1}. Measurements were made in duplicate on at least three separate samples. Peak areas were measured by cutting and weighing.

RESULTS AND DISCUSSION

Density and molar volume

The densities were fitted, by the method of least squares, to the equation

$$\rho(T) = \rho_0 - aT$$

TABLE 1

DENSITIES AND MOLAR VOLUMES

Compound		$\rho = \rho_0 - aT$ (10^3 kg m^{-3})				$V_m = V_0 + bT$(10^6 m^3)			
	Temp. range (K)	ρ_0	*Std. error (%)*	$a \times 10^3$	*% error in a*	V_0	*Std. error (%)*	*b*	*% error in b*
Lead carboxylates									
Lead octadecanoate*	400–450	1.515	0.10	0.942	1.9	444.3	0.12	0.589	1.5
Lead *cis*-9-oxtadecenoate	326–366	1.670	0.12	1.089	1.5	434.0	0.30	0.597	1.8
Lead *trans*-9-octadecenoate	382–430	1.639	0.25	1.148	1.3	439.4	0.25	0.618	2.5
Zinc carboxylates									
Zinc octadecanoate*	432–462	1.206	0.10	0.702	2.4	456.2	0.18	0.565	2.1
Zinc *cis*-9-octadecenoate	380–457	1.323	0.23	0.848	1.9	439.7	0.25	0.574	1.9
Zinc *trans*-9-octadecenoate	410–450	1.272	0.18	0.789	2.1	442.8	0.29	0.544	2.5
Zinc 9,12-octadecadienoate	340–380	1.304	0.28	0.837	1.5	433.9	0.20	0.526	2.3

* Values are from ref. 1.

and molar volumes to

$$V_m(T) = V_0 + bT$$

The parameters for the fits are summarised in Table 1 together with the standard error, probable error in slope and temperature range of measurements. The values earlier reported[1] for lead and zinc octadecanoate have been included for comparison.

The molar volumes of both the lead and zinc salts of the unsaturated fatty acids differ by at most 3% from each other and from those of the octadecanoates. Thus it would appear as if unsaturation of the hydrocarbon chains does not significantly affect the molar volume of the soaps and that it is the length of the hydrocarbon chain that determines the molar volume of a metal carboxylate regardless of whether it contains one or more double bonds. Also, the fact that the molar volumes of the salts of *cis*-9-octadecenoic acid and *trans*-9-octadecenoic acids are essentially the same, suggests that the molar volumes of the soaps do not depend on the configuration of the geometric isomers.

Electrical conductance

Figure 1 shows semi-logarithmic plots of specific conductivity against inverse temperature for the zinc carboxylates studied. It can be seen that the plots are linear. This behaviour is similar to what was observed for the zinc salts of some alkanoic acids[1]. The corresponding plot for zinc octadecanoate is also included in Fig. 1 for comparison. The data shown in Fig. 1 were fitted to least squares lines of the form

$$\log \kappa = \log Q - \frac{\Delta H^*}{2.303RT} \tag{1}$$

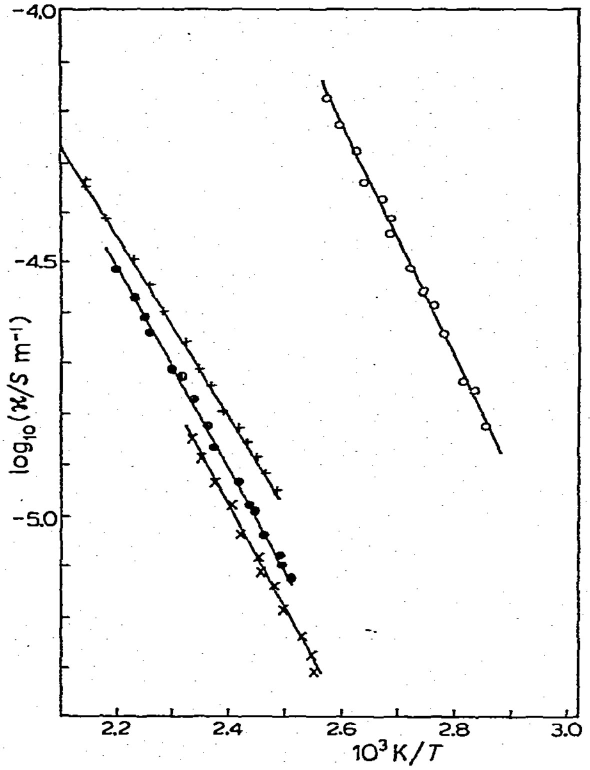

Fig. 1. Semilogarithmic plots of specific conductivity against inverse temperature for zinc soaps. +, Zinc octadecanoate; ×, zinc *cis*-9-octadecenoate; ●, zinc *trans*-9-octadecenoate; ○, zinc 9,12-octadecadienoate.

TABLE 2

LEAST SQUARES PARAMETERS FOR THE ARRHENIUS PLOTS FOR CONDUCTANCE FOR THE ZINC SOAPS

Compound	*Temp. range (K)*	log*Q*	$\sigma_{\log Q}$	ΔH^* *(kJ mole*$^{-1}$*)*	$\sigma_{\Delta H^*}$
Zinc octadecanoate*	406–480	−0.081	0.006	37.86	0.05
Zinc *cis*-9-octadecenoate	390–430	−0.024	0.008	39.53	0.12
Zinc *trans*-9-octadecenoate	400–455	−0.151	0.012	41.01	0.08
Zinc 9,12-octadecadienoate	350–390	2.155	0.011	38.98	0.10

* Values are from ref. 1.

and the values of the coefficients, log Q and ΔH^* are shown in Table 2 together with their least squares deviations (σ).

It can be seen from Table 2 that the values of ΔH^* for the zinc salts of the unsaturated fatty acids are the same within the limits of experimental error. It is also interesting to note that this value is the same as for zinc octadecanoate. In the model[1]

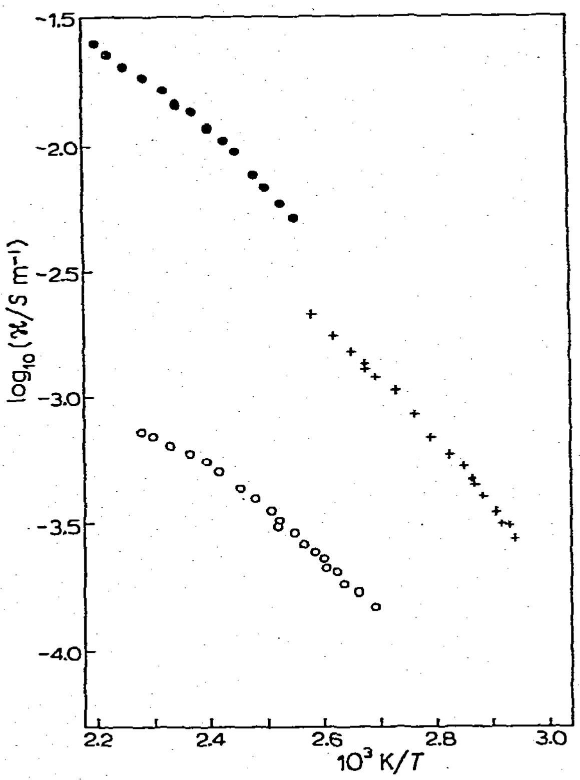

Fig. 2. Semilogarithmic plots of specific conductivity against inverse temperature for lead soaps. ●, Lead octadecanoate; +, lead *cis*-9-octadecenoate; ○, lead *trans*-9-octadecenoate.

proposed to explain conductance of some lead and zinc alkanoates, it was proposed that a dissociation equilibrium of the type

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

exists in the melt where the MA_2 and A^- species may be highly aggregated. Assuming that the major current carrier is the M^{2+} ion and that it moves by a simple activated process, then one obtains for the specific conductivity at low degrees of dissociation the expression[1]

$$\log \kappa = \log Q - \frac{\Delta H^{\ddagger} + (\Delta H/3)}{2.303\,RT} \qquad (2)$$

where $\Delta H^{\ddagger}$ and ΔH are the enthalpies of activation for movement of the metal ion and for the dissociation reaction respectively. Thus

$$\Delta H^{*} = \Delta H^{\ddagger} + (\Delta H/3) \qquad (3)$$

It is difficult to evaluate the separate contributions of $\Delta H^{\ddagger}$ and $\Delta H/3$ to ΔH^{*}. However, the value of ΔH would not be expected to vary significantly for the three soaps examined in this study as the major contribution is the breaking of the zinc–carboxylate bond which should not be significantly affected by unsaturation of the carboxylate chains. Indeed, it has been shown[1] that the value of ΔH for the lead carboxylates of even numbered chain lengths from hexanoate to octadecanoate inclusive does not vary by more than 5%. Thus it is reasonable to suggest that the similar ΔH^* values observed here for the zinc soaps also implies that the $\Delta H^{\ddagger}$ values are the same for these soaps. This conclusion would be perfectly reasonable if the charge carriers are the Zn^{2+} ions. The ΔH^* values for the even chain length zinc carboxylates from hexanoate to octadecanoate inclusive, do not vary by more than 4% and this had been interpreted as showing that the charge carriers in these systems are the Zn^{2+} ions. Thus, it is reasonable to conclude that Zn^{2+} ions are responsible for conductance in the melts of both the zinc alkanoates and the zinc salts of the unsaturated fatty acids studied in this work.

Figure 2 shows plots of log κ against inverse temperature for the lead soaps studied. It can be seen that the plots show curvature. This behaviour is similar to that observed for some even chain length lead alkanoates[1]. The plot for lead octadecanoate has been included in Fig. 2 for comparison. The curvature observed in the Arrhenius plots of the lead soaps has been explained in terms of the dissociation theory. At low degrees of dissociation, plots of log κ against $1/T$ will be linear with slope $\Delta H^{\ddagger} + (\Delta H/3)$. Table 3 shows the values for the limiting slopes at low temperatures for the lead soaps studied. The corresponding value for lead octadecanoate is also included. The values for the lead salts of *cis*-9-octadecenoic and *trans*-9-octadecenoic acids are the same within the limits of experimental error and also similar to that of lead octadecanoate.

In terms of the proposed model, the curvature at higher temperatures results from an appreciable degree of dissociation making the approximation used in deriving eqn. (2) invalid. In this case, the plot should tend to a second linear region with slope corresponding to $\Delta H^{\ddagger}$. For the soaps studied in this work, this region was not reached before the compounds started to decompose. Hence independent estimation of $\Delta H^{\ddagger}$ for these soaps cannot be made.

It has been shown[1] that the value of ΔH for the lead alkanoates from hexanoate to octadecanoate is constant (~ 84 kJ mole^{-1}). It is reasonable to assume that the value of ΔH for the lead salts of *cis*-9-octadecenoic and *trans*-9-octadecenoic acids will also be close to 84 kJ mole^{-1} since the major contribution to the enthalpy of dissociation is the breaking of the lead–carboxylate bond. Thus if a value of 84 kJ

TABLE 3

LOW TEMPERATURE LIMITING SLOPES FOR CONDUCTANCE FOR THE LEAD SOAPS

Compound	$\Delta H^{\ddagger} + \Delta H/3$ *(kJ.mole^{-1})*
Lead octadecanoate*	43.0 ± 1.5
Lead *cis*-9-octadecenoate	45.3 ± 2.0
Lead *trans*-9-octadecenoate	42.9 ± 1.5

* Value is from ref. 1.

TABLE 4

LEAST SQUARES PARAMETERS FOR VISCOUS FLOW

$$\log_{10}\eta = \log_{10}\eta_0 + \frac{\Delta H_\eta^*}{2.303RT}$$

Compound	*Temp. range (K)*	*$\log_{10}\eta_0$*	*ΔH_η^* (kJ mole^{-1})*	*Error in ΔH_η^**	*Std. dev.*	*Corr coeff.*
Lead carboxylates						
Lead octadecanoate*	395–449	−11.252	89.4	0.9	0.011	0.9999
Lead *cis*-9-octadecenoate	355–390	− 1.879	35.9	2.8	0.056	0.9981
Lead *trans*-9-octadecenoate	380–420	− 1.968	32.6	1.8	0.042	0.9950
Zinc carboxylates						
Zinc octadecanoate*	431–498	− 8.243	66.6	0.8	0.018	0.9998
Zinc *cis*-9-octadecenoate	374–422	− 0.596	39.5	1.5	0.042	0.9931
Zinc *trans*-9-octadecenoate	412–451	− 1.518	37.9	2.1	0.061	0.9988
Zinc 9,12-octadecadienoate	349–400	− 1.618	41.8	2.8	0.057	0.9979

* Values are from ref. 2.

mole^{-1} is substituted for ΔH in eqn. (3), $\Delta H^{\ddagger}$ can be shown to be equal to 15 kJ mole^{-1} which is within the range 15–18 kJ mole^{-1} reported for the lead alkanoates. The fact that the value of $\Delta H^{\ddagger}$ is constant for the lead carboxylates from hexanoate to octadecanoate inclusive has been suggested to imply that lead ions are the charge carriers in the melts of these soaps. Thus, it would also be reasonable to conclude that Pb^{2+} ions are responsible for electrical conduction in the lead salts of the unsaturated fatty acids studied in this work.

Viscosity

Viscosities were fitted, by the method of least squares, to the equation

$$\log_{10}\eta = \log_{10}\eta_0 + \frac{\Delta H_\eta^*}{2.303RT} \tag{4}$$

where η is the viscosity in Pa and ΔH_η^* is the activation energy for viscous flow. The results of these fits are shown in Table 4 where $\log_{10}\eta_0$, ΔH_η^*, the probable error in ΔH_η^*, the standard error and the correlation coefficients of the fits are listed. The corresponding values for lead and zinc octadecanoates have been included in Table 4 for comparison.

The most striking feature of the data in Table 4 is that the activation energies for viscous flow for the salts of the unsaturated fatty acids are much smaller than for the octadecanoates. It has been observed[2] that for the lead and zinc even chain length carboxylates from hexanoate to actadecanoate, ΔH_η^* varies significantly with chain length. This has been interpreted to imply that the unit of flow is the carboxylate anion. If viscous flow is determined by the carboxylate anion, then changes in the

TABLE 5

THERMODYNAMIC PARAMETERS FOR PHASE TRANSITIONS IN THE LEAD AND ZINC SOAPS

Error in ΔH values are within $\pm$ 2%.

Compound	*Transition temperature (K)*	ΔH *(kJ mole^{-1})*	ΔS *(J mole^{-1} K^{-1})*
Lead *trans*-9-octadecenoate	372.5	113.2	304 ± 8
Zinc *cis*-9-octadecenoate	362.7	65.2	179 ± 6
Zinc *trans*-9-octadecenoate	384.4	69.5	180 ± 5
Zinc 9,12-octadecadienoate	345.7	34.2	99 ± 2

structure of the carboxylate anion would be expected to affect the activation energy for viscous flow. It is therefore consistent that the introduction of one or more double bonds into the hydrocarbon chains of the soaps significantly alters the value of ΔH_η^*.

It is interesting to note that the values of ΔH_η^* for the lead and zinc salts of *cis*-9-octadecenoic and *trans*-9-octadecenoic acids are the same. This value is also similar to that obtained for zinc 9,12-octadecadienoate. Thus the value of the activation energy for viscous flow in the salts of the unsaturated fatty acids studied in this work is independent of the number of double bonds in the carboxylate chains and the configuration of the geometric isomers.

It has been suggested that, from the rate of change of ΔH_η^* with chain length of the lead and zinc alkanoates[2], the unit of flow consists of 3 or 4 carboxylate molecules. However, it would be difficult to speculate on the size of the unit of flow in the soaps studied in this work until a study of the viscosity of several soaps of the same homologous series is undertaken.

Quantitative DTA

All the soaps studied gave a single DTA peak which showed that the compounds melted directly into the isotropic liquid. Reliable DTA curves could not be obtained for lead *cis*-9-octadecenoate as the recrystallised product was a gummy semi-liquid compound at room temperature and our DTA equipment has no facility for low temperature work. Hence the only lead soap studied was lead *trans*-9-octadecenoate. The absence of mesophases in lead *trans*-9-octadecenoate contrasts with the behaviour of the lead alkanoates which form mesophases. The dodecanoate and lower chain length lead soaps have been shown[3] to pass through the phase sequence

crystal → G(smectic) → V_2(cubic isomorphous) → liquid

while the tetradecanoate and higher chain length lead soaps show the sequence

crystal → G(smectic) → liquid

Thus the presence of the double bond in lead *trans*-9-octadecenoate results in the suppression of mesophase formation. This result suggests that the structure of the lipophilic portion of the amphiphiles is crucial in determining formation of mesophases.

The thermodynamic data for the phase changes as well as the temperatures of phase transitions are summarised in Table 5. The entropy change accompanying the melting of lead *trans*-9-octadecenoate is 304.2 J mole^{-1} K^{-1} which is reasonably close to a value of 311 ± 5 J mole^{-1} K^{-1} reported[3] for the total entropy change accompanying the process crystal → liquid for lead octadecanoate. This probably suggests that the state of order of the hydrocarbon chains in lead *trans*-9-octadecenoate is the same as in lead octadecanoate both in the crystal and liquid phases.

The zinc soaps studied do not form mesophases but melt directly into the isotropic liquid. This is similar to the behaviour of the zinc alkanoates[4]. A notable feature of the thermodynamic data obtained for the zinc salts of the unsaturated fatty acids is that they show smaller entropy changes for the fusion process compared with zinc octadecanoate. The ΔS value reported[4] for zinc octadecanoate is 256 + 17 J mole^{-1} K^{-1} which is significantly greater than the value of 180 J mole^{-1} K^{-1} obtained in this study for both zinc *cis*-9-octadecenoate and zinc *trans*-9-octadecenoate. These results probably show that the hydrocarbon chains of zinc *cis*-9-octadecenoate and zinc *trans*-9-octadecenoate are either more ordered in the liquid phase or more disordered in the crystal lattice than zinc octadecanoate. It is interesting to note that the ΔS values for both zinc *cis*-9-octadecenoate and zinc *trans*-9-octadecenoate are the same. This suggests that the configuration of the hydrocarbon chains of these geometric isomers does not appreciably affect the degree of order of the hydrocarbon chains either in the crystal or liquid phases.

The ΔS value obtained for the fusion of zinc 9,12-octadecadienoate is about half the value for the zinc salts of *cis*- and *trans*-9-octadecenoic acids. Thus the presence of two double bonds in the hydrocarbon chains of the zinc soaps results in much smaller entropy change for the fusion process than for zinc soaps which contain one double bond. This suggests either that zinc 9,12-octadecadienoate is considerably more ordered in the liquid phase or considerably more disordered in the crystal phase than zinc octadecanoate or the zinc salts of *cis*- and *trans*-9-octadecenoic acids.

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