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The molten phase conductance and the thermotropic phase transition in lead(II), zinc(II) and cadmium(II) 10-hydroxyoctadecanoates

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Abstract

The electrical conductances and heats of phase changes in lead(II), zinc(II) and cadmium(II) 10-hydroxyoctadecanoates are measured. The soaps are prepared by metathesis in alcohol solution from 10-hydroxyoctadecanoic acid which in turn is prepared from the oxidation of *cis*-9-octadecenoic (oleic) acid with concentrated sulphuric acid.

The Arrhenius plot for lead(II) 10-hydroxyoctadecanoate shows a maximum, a behaviour that had earlier been interpreted to be due to complex formation. A similar plot for zinc(II) 10-hydroxyoctadecanoate is linear while that for cadmium(II) 10-hydroxyoctadecanoate presents a discontinuity which is interpreted, with the aid of the differential scanning calorimetric (DSC) spectra and optical examination, to be suggestive of the formation of an intermediate phase between the solid and the liquid phases. The low conductances of the soaps in comparison with the literature data on some metal caboxylates indicate the existence of extensive intermolecular hydrogen bonding in the molten phase. Both lead(II) and zinc(II) 10-hydroxyoctadecanoates melt directly from the solid to the liquid phase while their cadmium(II) counterpart passes through the gel-like phase before melting into the liquid. The mesophase of cadmium(II) 10-hydroxyoctadecanoate is transformed to the liquid phase with a relatively low enthalpy change and the behaviour is associated with the cylindrical micekkar structures of the liquid phase that have their formative stage from the gel-like mesophase.

Keywords: Gel-like mesophase; Molten phase conductance; Thermotropic phase transition

1. Introduction

The electrical conductances and the melting behaviour of the octadecanoates of lead(II) [1,2] zinc(II) [1,3] and cadmium(II) [3,4] have been investigated. Over the range of temperature employed, the plot of logarithm of conductivity against inverse absolute temperature was linear for zinc octadecanoate, while similar plots for lead and cadmium octadecanoates showed curvatures. On heating, lead and cadmium octadecanoates passed through meophases. The phase sequence are: crystal → G_{smectic} → liquid for the lead salt and crystal → mesophase(I) → mesophase(II) → liquid for the cadmium soap. Zinc octadecanoate, on the other hand, melted directly from the crystal to the liquid phase.

The influence of the unsaturation centre on the melting behaviour of lead(II) octadecanoate had been examined [5]. The DTA study of pure lead elaidate did not show any intermediate phase observed in the saturated counterpart while that of lead oleate did

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not produce a consistent result possibly due to the presence of an overwhelming impurity. The effect of substituting dihydroxy groups in the middle of the carbon chain of lead(II) octadecanoate had also been reported [6,7]. The Arrhenius plot for conductance of the soap showed a maximum explained to arise from complex formation. Optical examination under a polarizing microscope revealed the phase sequence: solid → mesophase → luquid for the racemic isomer and solid(I) → solid(II) → mesophase → liquid for the meso isomer.

The behaviour brought to focus the effect of stereochemical configuration on phase transitions. Many anionic surfactants (soaps) had earlier been reported to pass through liquid crystal phases before melting into the liquid states [8–15]. Recently, the phase behaviour of some cerium(III) carboxylates was studied [16]. The DSC and polariised light microscopy revealed one or more mesophases over the temperature range of 70–120 °C prior to melting at about 130 °C. The technological applications of systems exhibiting liquid crystallinity [7] seem to provide the impetus for the continuos accumulation of data on this class of amphiphiles. The present study reports the preparation of and thermodynamic data on some metal(II) 10-hydroxyoctadecanoates. The objective of the study is to prepare new compounds and examine upon heating the number and properties of the phases they exhibit prior to melting into the liquid phases. Both conductance and differential scanning calorimetric (DSC) measurements are employed as complementary techniques for the purpose of achieving our objective.

2. Experimental

2.1. Materials

All the fatty acids employed were British Drug House (BDH) grade and were stated to have minimum 99% purity by g.l.c. assay. They were used without further purification. Lead(II) nitrate, cadmium(II) chloride and zinc(II) chloride were Analar grade from BDH.

2.1.1. Preparation of 10-hydroxyoctadecanoic acid

10-Hydroxyoctadecanoic acid was prepared by the oxidation of *cis*-9-octadecenoic (oleic) acid with concentrated sulphuric acid as reported by Vesely and Majtl [17]. The crude product obtained was re-crystallised thrice in hot propan-1-ol. It melted at 354 K in good agreement with the reported value [17,18] of 355 K. Further re-crystallisation did not change this value and so, the acid was considered pure enough for the preparation of the soaps. Theoretically, two possible oxidation products, 9,10-hydroxyoctadecanoic acids could be obtained from the reaction of oleic acid with concentrated H_2SO_4. The mixture of both was also a possibility. However, Tomecko and Adams [18], using the condensation method, obtained pure 9,10-hydroxyoctadecanoic acids which melted at 348–349 and 354–355 K, respectively. They showed that 10-hydroxyoctadecanoic acid prepared by the oxidation of *cis*-9-octadecenoic acid with concentrated sulphuric acid was free of traces of 9-hydroxyoctadecanoic acid, as a little quantity of the 9-hydroxy isomer in the 10-hydroxy product was found to reduce the melting point of the latter from 354 to 348 K. Many other workers [19–24] confirmed the accuracy of the melting point values.

2.1.2. Preparation of soaps

Lead(II), zinc(II) and calcium(II) 10-hydroxyoctadecanoates [$M(OHA)_2$, M = metal] were prepared by the metathesis in alcohol solution [1,25]. The prepared 10-hydroxyoctadecanoic acid was dissolved in hot absolute propan-2-ol and a stoichiometric amount of potassium hydroxide was added with stirring according to the equation.

$$\mathrm{RCOOH} + \mathrm{KOH} \rightarrow \mathrm{RCOOK} + \mathrm{H_2O}$$

where $R = CH_3(CH_2)_7CH(OH)CH_2(CH_2)_{7}$–. A stoichiometric amount of the appropriate salt, $Pb(NO_3)_2$, $ZnCl_2$ or $CdCl_2$ was dissolved in a minimum amount of hot distilled water and the salt solution was added slowly, with stirring, to the alcohol solution. The resulting mixture was left overnight to ensure complete precipitation. A typical reaction equation using the lead salt is

$$2\mathrm{RCOOK} + \mathrm{Pb(NO_3)_2} \rightarrow \mathrm{(RCOO)_2Pb} + 2\mathrm{KNO_3}$$

The precipitate was then filtered, washed with copious quantities of propan-2-ol followed by distilled water and petroleum ether. The white crystals obtained were dried under vacuum at 332 K and finally re-crystallised

Table 1
Melting points and elemental composition of soaps, $Pb(OHA)_2$, $Zn(OHA)_2$ and $Cd(OHA)_2$

Metal carboxylate	Melting point (°C)	Elements determined	Theory (%)	Found (%)
$Pb(OHA)_2$	390–391	Carbon	53.6	53.2
		Hydrogen	8.7	8.5
		Lead	25.7	26.5
$Zn(OHA)_2$	409–410	Carbon	65.2	65.7
		Hydrogen	10.6	10.3
		Zinc	9.8	10.1
$Cd(OHA)_2$	405–406	Carbon	60.9	60.7
		Hydrogen	9.9	9.8
		Cadmium	15.8	16.2

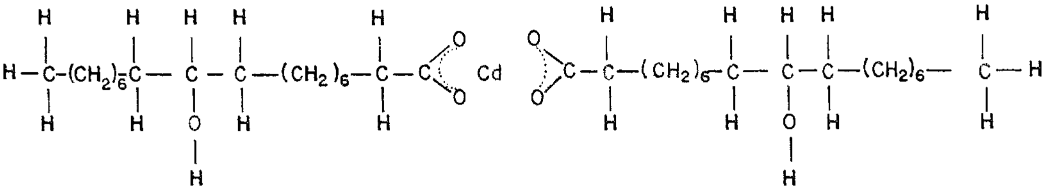


Fig. 1. Structure of cadmium 10-hydroxyoctadecanoate.

in hot propan-2-ol. The infra red spectra showed them to be free of excess organic acid. Results of elemental analyses for the metal, carbon, hydrogen and the melting points are presented in Table 1.

The NMR spectra of the 10-hydroxy soaps were run on a Varian VRX 300 spectrometer operating at 300 MHz in dimethyl sulphoxide heated and maintained at 50 °C. Fig. 1 shows a typical structure of one of the soaps. Six types of protons in different chemical environments are expected. The ratio of splitting is envisaged to be 2:2:4:8:48:6, but the observed ratio is 2:4:8:48:6 at the δ-values of 3.4, 2.1, 1.5, 1.3 and 0.9, respectively. The integration of the hydroxylic proton was not observed and so, the number of protons for this group was not distinguished. However, the combination of NMR data, the IR spectra, the melting points and the percentage composition appeared to resolve, perhaps unambiguously, the identity of the soaps to be metal(II) 10-hydroxyoctadecanoates.

3. Measurements

The procedure for the measurement of electrical conductance and the heat of phase transition had been described elsewhere [1,7]. The difference in technique is that in the present study, peak areas were integrated for the automatic evaluation of heats of phase transitions instead of the previous method of cutting peak areas and weighing.

4. Results

The Arrhenius plots for conductance for pure lead(II), zinc(II) and cadmium(II) 10-hydroxyoctadecanoates are shown in Fig. 2. While the plot for $Pb(OHA)_2$ exhibited a maximum, that for $Zn(OHA)_2$ was linear. For $Cd(OHA)_2$, a clear discontinuity which gave rise to two linear portions occurred in the plot at 407 K. At low temperature, where the degree of dissociation is small, the slopes of the plots are equal to $\Delta H_k^\# + \Delta H/3$ [1,6,26], where $\Delta H_k^\#$ and ΔH are the enthalpies of activation for the movement of M^{2+} and for dissociation, respectively. In Table 2, values of $\Delta H^* = (\Delta H_k^\# + \Delta H)$ are presented as calculated by a least-squares method from the plots together with the correlation coefficients.

Typical DSC curves for the soaps are shown in Fig. 3. Thermogram A for $Pb(OHA)_2$ gave a single

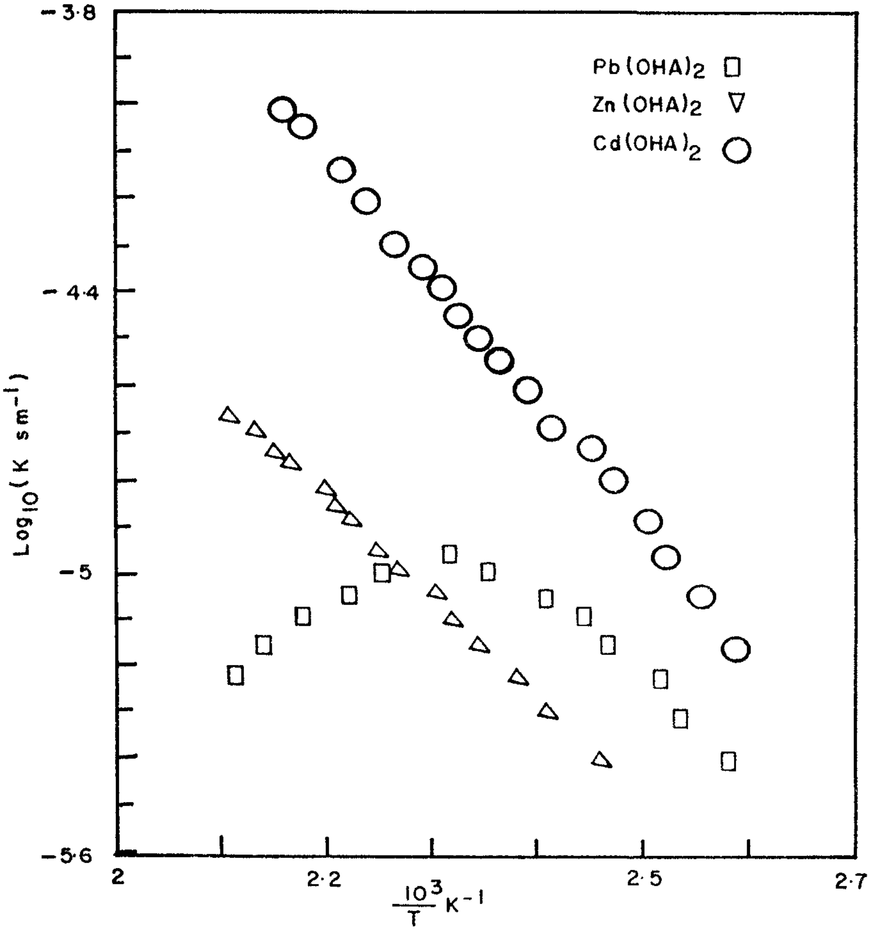


Fig. 2. Logarithm of specific conductivity (K) against inverse absolute temperature for pure lead(II) 10-hydroxyoctadecanoate ($Pb(OHA)_2$), zinc(II) 10-hydroxyoctadecanoate ($Zn(OHA)_2$) and cadmium(II) 10-hydroxyoctadecanoate ($Cd(OHA)_2$).

DSC peak with the transition temperature of 390 K. Cooling the melt on optical microscope produced an anisotropic texture which had cracks suggesting that the liquid just cooled to a solid phase. On reheating, the soap again passed directly to the liquid phase. Like $Pb(OHA)_2$, $Zn(OHA)_2$ melted to a clear liquid at about 412 K, curve B. There appeared to be formation of crystalline phase when a sample was heated and viewed on a polarising microscope fitted with a hot stage. The phase was fairly fluid and had anisotropic texture typical of smectic phase at two or three degrees below the melting point. Calorimetric heating, cooling and reheating did not give a clear identification of the crystalline phase. On heating a fresh sample of $Cd(OHA)_2$, two peaks were observed, curve C. Observation on optical microscope confirmed the existence of an intermediate phase at about 392 K. This phase could be deformed but with great difficulty which

Table 2
Values of low temperature limiting slopes of conductance

Metal 10-hydoxyoctadecanoate	$\Delta H_k^{\#} + \Delta H$ (kJ mol^{-1})	Correlation coefficient
Lead	41.7 ± 3.1	0.998
Zinc	40.5 ± 1.5	0.999
Cadmium	62.8 ± 3.4	0.999
Cadmium[a]	49.0 ± 1.8	0.998

[a] Second linear portion of the graph.

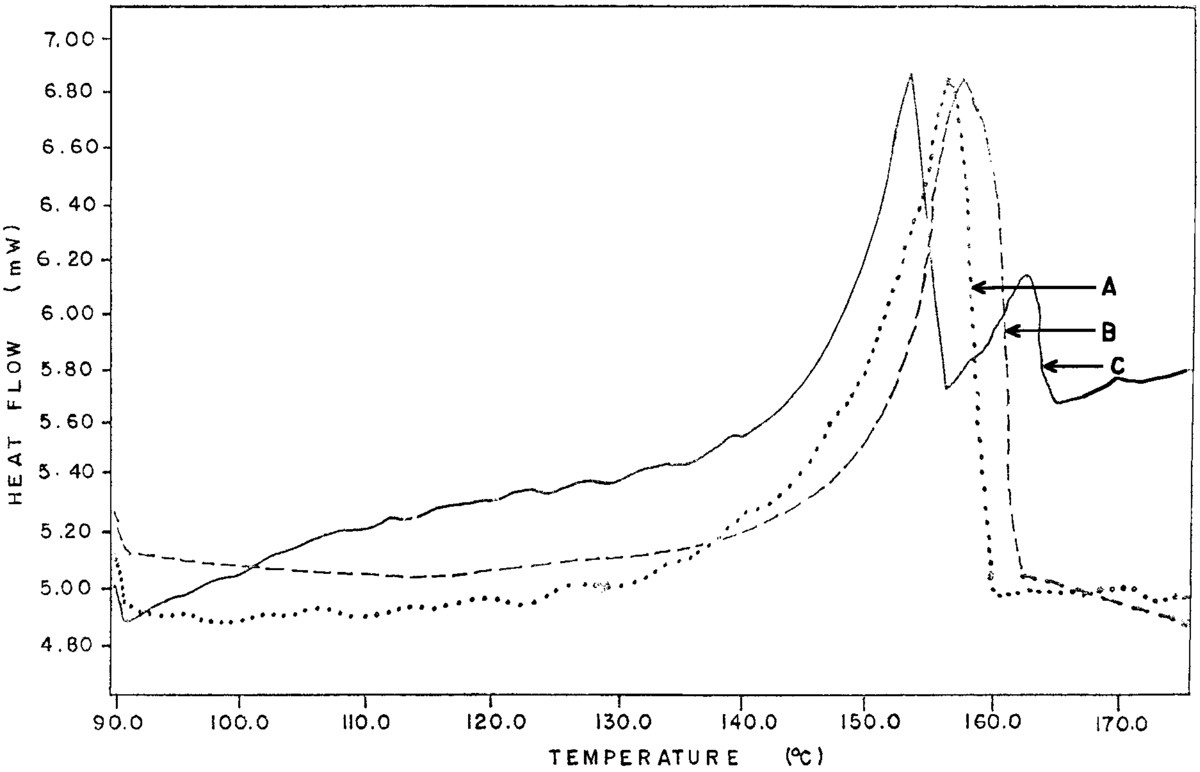


Fig. 3. Plot of heat flow against temperature (°C): A = $Pb(OHA)_2$; B = $Zn(OHA)_2$; C = $Cd(OHA)_2$.

probably suggests it to be the gel type. The phase transformed to the liquid phase at about 407 K. However, on cooling, the intermediate phase was lost and the melt supercooled directly to the solid phase. The temperatures, enthalpies and entropies of these phase changes on heating and cooling are presented in Table 3. The entropies were calculated at the solid–liquid or mesophase–liquid equilibrium temperatures with

Table 3
Temperature (K), enthalpies ($kJ\,mol^{-1}$) and entropies ($J\,mol^{-1}$) for phase transition in $Pb(OHA)_2$, $Zn(OHA)_2$ and $Cd(OHA)_2$

Metal 10-hydroxyoctadecanoate	Heat treatment	Thermodynamic parameters (solid → liquid)		
		T	ΔH	ΔS
Lead	Heating fresh sample	390	102 ± 1.8	263.8
	Cooling	389	−72.5 ± 1.3	−186.4
Zinc	Heating fresh sample	410	49.7 ± 2.5	121.2
	Cooling	403	−30.5 ± 1.2	−75.7
Cadmium	Heating fresh sample[a]			
	Cooling	393	−43.2 ± 1.4	−109.9

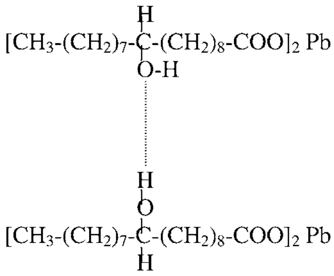
ΔH_T and ΔS_T are the total enthalpy change and entropy change, respectively, for the transition from the solid through a mesophase to the liquid state. The percentage error in ΔH for any phase transition is not more than 5%.

[a] The values of solid → mesophase (T, ΔH, ΔS); mesophase → liquid (T, ΔH, ΔS); and solid → liquid (ΔH_T, ΔS_T) are 394, 60.2 ± 1.1, 152.8; 403, 16.5 ± 0.8, 40.9; and 76.7 ± 1.9, 190.3, respectively.

the assumption that the free energy change at equilibrium, $\Delta G = 0$. The calculated entropies are mere compensatary energy terms and little significant thermal interpretation is placed on them. Five values of enthalpy of phase transitions were obtained for each sample using fresh sample for each run and the standard error of measurement was not more than 5%. This thus suggests a fairly reproducible DSC data.

5. Discussion

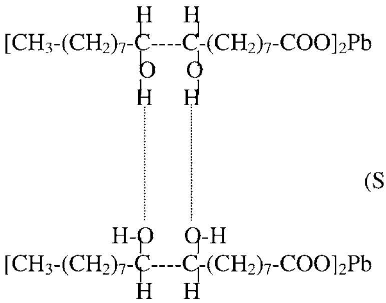
The electrical conductance of lead(II) 10-hydroxyoctadecanoate, $Pb(OHA)_2$ is found to be low in comparison with those of two different lead soaps earlier studied in our laboratory, lead 9,10-dihydroxyoctadecanoate, $Pb(OH)_4A_2$ and lead(II) octadecanoate, PbA_2. The order of conductance is $Pb(OHA)_2 < Pb(OH)_4A_2 < PbA_2$ (Fig. 4). The composite activation enthalpy, $\Delta H^* = (\Delta H_k^{\#} + \Delta H)$ is $43.6 \pm 1.7\,kJ\,mol^{-1}$ for PbA_2 [26], $38.3 \pm 1.5\,kJ\,mol^{-1}$ for $Pb(OH)_4A_2$ [6] and $41.7 \pm 3.1\,kJ\,mol^{-1}$ for $Pb(OHA)_2$ (present study). These values are approximately constant upon the incorporation of the error margin and suggest that the Pb^{2+} ions which move by a simple activated process are the major charge carrier in the melts [1,6,26]. The low values of conductance of $Pb(OHA)_2$ and $Pb(OH)_4A_2$ relative to those of PbA_2 can be associated with the existence of extensive hydrogen bonding. Evidence for this comes from the IR data of $Pb(OHA)_2$ and $Pb(OH)_4A_2$ which gave broad bands at 3100–3400 cm^{-1} (Figs. 5 and 6). $Pb(OHA)_2$ can form intermolecular hydrogen bond in the liquid phase thus:



$[CH_3\text{-}(CH_2)_7\text{-}\overset{H}{\underset{O\text{-}H}{C}}\text{-}(CH_2)_8\text{-}COO]_2\,Pb \cdots [CH_3\text{-}(CH_2)_7\text{-}\overset{\overset{H}{O}}{\underset{H}{C}}\text{-}(CH_2)_8\text{-}COO]_2\,Pb$

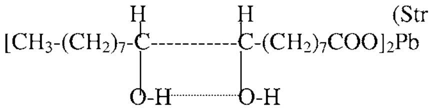
More molecules can be involved in the bonding thereby converting the molten soap to a net work of hydrogen bonded *n*-mer.

$Pb(OH)_4A_2$, on the other hand, can form both *inter*- and *intra*-molecular hydrogen bonds.



$[CH_3\text{-}(CH_2)_7\text{-}\overset{H}{\underset{O\text{-}H}{C}}\text{----}\overset{H}{\underset{O\text{-}H}{C}}\text{-}(CH_2)_7\text{-}COO]_2Pb \cdots [CH_3\text{-}(CH_2)_7\text{-}\overset{H\text{-}O}{\underset{H}{C}}\text{----}\overset{O\text{-}H}{\underset{H}{C}}\text{-}(CH_2)_7\text{-}COO]_2Pb$

(Structure with intermolecular hydrogen bonds)



$[CH_3\text{-}(CH_2)_7\text{-}\overset{H}{\underset{O\text{-}H}{C}}\text{-----------}\overset{H}{\underset{O\text{-}H}{C}}\text{-}(CH_2)_7COO]_2Pb$

(Structure with intra-molecular hydrogen bonds)

It is assumed in writing the structures that the extent of hydrogen bonding between the OH and COO groups is small relative to that between two OH groups because of the delocalisation of electrons within the carboxylate head group. The carbon–carbon bond length in a soap molecule is also small compared to the proximity of two or more soap molecules entangled in a melt micellar aggregate such that the hydrogen bonded intra-molecular structure in $Pb(OH)_4A_2$ predominates over the intermolecular bonded structure. If this view is plausible, then the micellar units of $Pb(OH)_4A_2$ formed predominantly by intra-molecular hydrogen bonds will be smaller in size than the micellar units of

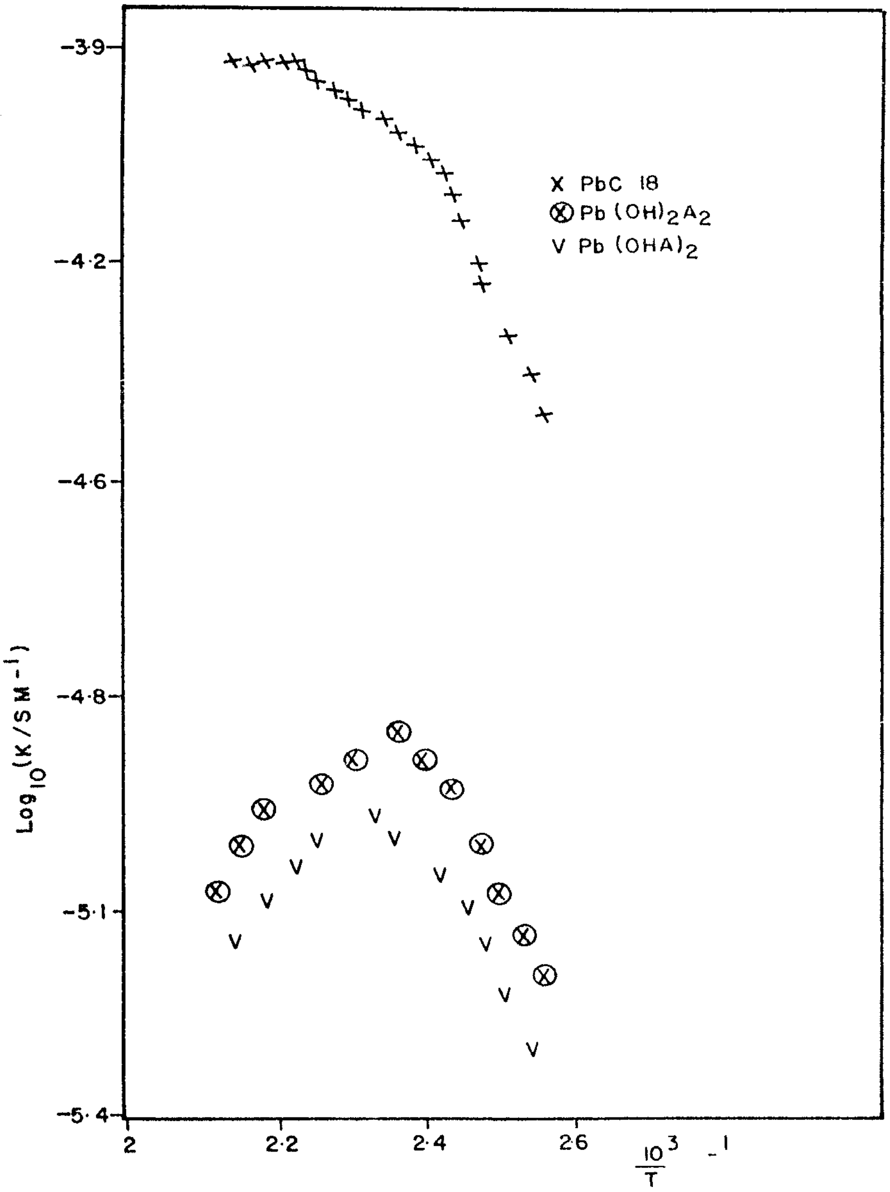


Fig. 4. Semi-logarithmic plots of specific conductivity against inverse absolute temperature for lead(II) octadecanoate (PbA_2), lead(II) 9,10-dihydroxyoctadecanoate ($Pb(OH)_4A_2$) and lead(II) 10-hydroxyoctadecanoate ($Pb(OHA)_2$).

$Pb(OHA)_2$ formed mainly by inter-molecular hydrogen bonds. Consequently, molten $Pb(OHA)_2$ should offer a higher resistance than molten $Pb(OH)_4A_2$ to the mobility of the common charge carriers, the Pb^{2+} ions. This assertion is made attractive by the visual observation which found the molten $Pb(OHA)_2$ to be more viscous than the molten $Pb(OH)_4A_2$ within the range of our working temperature.

It may be tempting to generalise that the higher the resistance to the motion of the charge carriers, the lower the actual conductance and hence the greater the activation energy. Consequently, the approximate

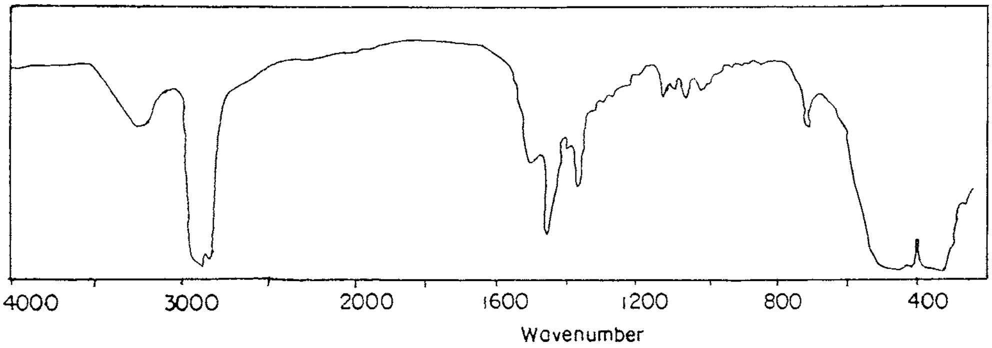


Fig. 5. IR spectrum for lead(II) 9,10-dihydroxyoctadecanoate (product from oleic acid).

constant activation energy, ΔH^* obtained for PbA_2, $Pb(OH)_4A_2$ and $Pb(OHA)_2$ (barring error margin) should invalidate the above explanation. However, ΔH^* is a composite energy term whose value involves contributions from both the conduction and dissociation/association equilibria [26] and the trend of how ΔH^* varies with the actual conductance could be clearly understood only if $\Delta H_k^\#$ can be separated from ΔH^*. At a high temperature region where dissociation is expected to have reached completion, the slope of the Arrhenius plot in this region should correspond to $\Delta H_k^\#$ [1]. Before this temperature region that was to give rise to a second linear portion is reached, the Pb^{2+} ions had started to react with the hydroxy groups to form complexes [6,27] leading to a decrease of conductance. This explains the observed maximum in the Arrhenius plot for $Pb(OHA)_2$ in Fig. 2 or 4. For PbA_2, a case for which the Arrhenius plot gave a curvature [1,26] (Fig. 4), the melt started to decompose before the second linear portion is reached.

Like $Pb(OHA)_2$, the IR spectra also indicate the existence of hydrogen bonds in $Cd(OHA)_2$ and $Zn(OHA)_2$. While $Pb(OHA)_2$ and $Zn(OHA)_2$ melted directly from the solid to the liquid phases, $Cd(OHA)_2$ passed through a mesophase. One noteworthy feature of the study is that the Arrhenius plot for $Cd(OHA)_2$ showed a marked discontinuity at about 407 K (Fig. 2). Such discontinuity has been interpreted to be a consequence of phase changes [28]. At the temperature between 392 and 408 K, a linear graph with the correlation coefficient of 0.9990 was obtained. The activation energy, ΔH^* in this region is 62.8 kJ mol^{-1}. The second linear portion starts from 415 to 463 K with the correlation coefficient of

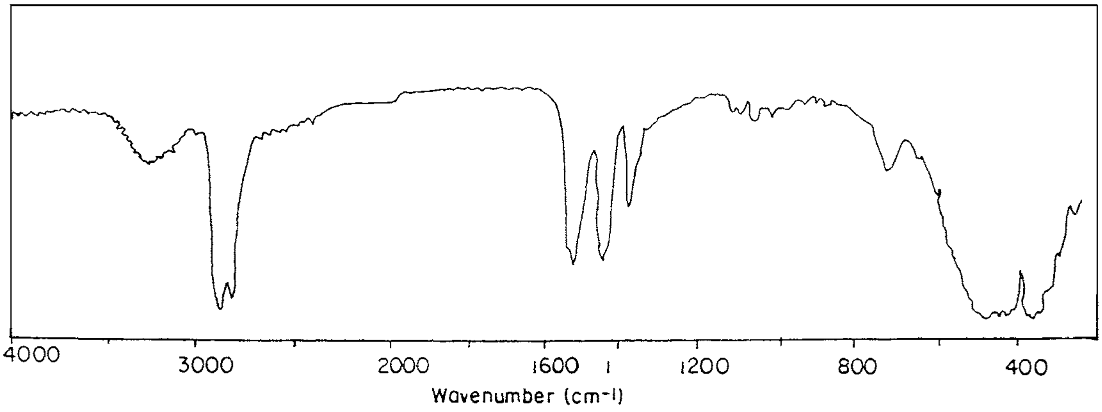


Fig. 6. IR spectrum for lead(II) 10-hydroxyoctadecanoate.

0.9980 and ΔH^{*} of 49.0 kJ mol^{-1}. The DSC study of $Cd(OHA)_2$ gave a clear insight into the observed discontinuity obtained from the electrical conductance data. The phase sequence obtained for the soap is, solid → mesophase → liquid. The lower transition temperature is 394 K and the mesophase → liquid one is 406 K. Thus the initial linear portion corresponds to conductance in the mesophase (optical observation suggests this phase to be gel-like), while the second linear portion depicts conductance in the liquid phase. As earlier said, the composite energy term is $\Delta H^{*} = (\Delta H_k^{\#} + \Delta H)$. It is difficult to see how the activation enthalpy for dissociation (ΔH) will vary significantly from the intermediate phase to the liquid phase such that the difference between $\Delta H^{*} = 62.8$ kJ mol^{-1} in the mesophase and $\Delta H^{*} = 49.0$ kJ mol^{-1} in the liquid phase would stem mainly from the difference in the activation enthalpy for conductance ($\Delta H_k^{\#}$) in the two phases. It has been reported [29] that partial melting involving mainly the paraffin chains of an amphiphile occurs at the low transition temperature, while the carboxylate head group subsequently melts at a higher temperature to give the liquid. The incomplete rupture of the crystal structure should offer a relatively high resistance to the mobility of the charge carriers and hence bring about higher ΔH^{*} or by implication higher $\Delta H_k^{\#}$ in the mesophase than in the more mobile liquid phase.

Optical examination on a polarising microscope suggests the intermediate phase of $Cd(OHA)_2$ to be gel-like but the complete identification of the structure of the phase must await the result of X-ray photograghic analysis. The total enthalpy change obtained for the phase transition (crystal → liquid) is 76.7 kJ mol^{-1} (Table 3). This value is close to 68.2 kJ mol^{-1} reported for CdA_2, the liquid of which was proposed to consist of cylindrical micellar structure [3]. Optical examination tends to suggest the liquid phase of $Cd(OHA)_2$ to consist of hexagonal arrangement of cylindrical micelles that are possibly stabilised by the monohydroxy group via hydrogen bonding. The IR and conductance data lend weight to the existence of extensive hydrogen bonding in the liquid phase. The primordial stage of the cylindrical micelles is presumed to be from the gel-like intermediate phase and this may explain the relative ease with which this phase is transformed to the liquid phase as the transition enthalpy, 16.5 kJ mol^{-1}, is somewhat close but significantly lower than the value of 26.2 kJ mol^{-1} reported for the mesophase liquid in CdA_2.

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