

THE EFFECT OF CETYL TRIMETHYLAMMONIUM BROMIDE ADDITIVE ON THE ELECTRICAL CONDUCTANCES OF MOLTEN ZINC(II), CADMIUM(II) AND LEAD(II) OCTADECANOATES

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ABSTRACT

Data are presented for the electrical conductances of systems of molten zinc(II) octadecanoate, cadmium(II) octadecanoate and lead(II) octadecanoate with cetyl trimethylammonium bromide (CTAB), at concentrations of up to 0.22 mole fraction of CTAB ($X_{\text{CTAB}} = 0.22$).

In all the mixtures, the conductance at any temperature decreases with increasing X_{CTAB} . The Arrhenius plots for the conductances of zinc(II) octadecanoate–CTAB are linear, while those for cadmium(II) octadecanoate–CTAB show curvature similar to that observed for the pure soap. For lead(II) octadecanoate–CTAB at $X_{\text{CTAB}} < 0.10$, the plots also show curvature. However, for $X_{\text{CTAB}} \geq 0.10$, the plots show maxima. Conductances in these cases are reproducible up to the maximum but show a permanent decrease beyond this. The maximum can be interpreted in terms of dipole–dipole interaction between the polar ends of the soap and CTAB, leading to the formation of a complex.

The activation energies for dissociation and conductance in the low temperature region show a steady decrease with increasing X_{CTAB} for the lead and cadmium octadecanoates, but give constant values for the zinc octadecanoate–CTAB system. This behaviour is linked to the degree of ideality of the liquid mixtures. Plots of molar volume vs. absolute temperature reinforce our conception of the different ways in which CTAB interacts with the soaps. The size of the ionic radii of the metal ions would seem to dictate the extent of ion interaction in the molten mixtures.

INTRODUCTION

Previous studies from this laboratory have provided information on the temperature dependence of electrical conductance, density and molar volume of some pure molten, divalent metal carboxylates [1–4] and their binary mixtures [5–7]. The Arrhenius plot for pure zinc(II) octadecanoate (ZnC_{18}) gives a straight line, while those for pure cadmium(II) and lead(II) octadecanoates (CdC_{18} , PbC_{18}) show curvature. Maxima have been observed in similar plots for several molten inorganic salts [8]. Recently, a maximum has

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been observed in the Arrhenius plot for pure, molten lead(II) 9,10-dihydroxy-octadecanoate and its binary mixtures [9]. This observation has been interpreted in terms of the charge carrier reacting with the dihydroxy groups of the soap.

The objective of the present study is to examine the effect of the additive cetyl trimethylammonium bromide (CTAB) on the electrical conductances of some pure metal carboxylates. Metal organic ionic melts (such as soaps) provide a picture of a class of liquids which have intermediate conductances, lower than those at which ionic forces determine the behaviour and higher than those at which aliphatic chains dominate the properties [2]. They are used as simple electrolytes. This important use stimulates our interest in attempting to find ways of enhancing the conductances of some pure soaps by doping them with a material which provides highly mobile ions upon dissociation. The choice of CTAB as our doping agent arose from the observations that it is completely soluble in the molten soaps at fairly low temperatures, and the bromide ions produced on dissociation carry a high proportion of currents in concentrated inorganic salt solutions [10,11]. New areas of use may be opened up for metal carboxylates if the thermal [12] and electrolytic [13,14] properties of these soap-additive systems can be enhanced. As will be seen in the following sections, this objective was not achieved; instead, an equally interesting result (almost the exact opposite of that which we expected) was obtained.

EXPERIMENTAL

Materials

The CTAB used was a B.D.H. product with stated minimum purity of 99% by GLC assay. It was dried at 100 °C under vacuum for several days before use. The fatty acid used for preparing the soaps was also a B.D.H. product with minimum 99% purity by GLC assay. Lead nitrate, zinc and cadmium chlorides were AnalaR grade, also from B.D.H.

Preparation of soaps

The methods used for preparation, purification and characterization of zinc(II), cadmium(II) and lead(II) octadecanoate have been described elsewhere [1,2]. The mixtures were prepared by weighing appropriate amounts of the components into a Quick-Fit conical flask fitted with a vacuum tap. The flask was evacuated before melting to prevent decomposition of the mixture. The melt was allowed to cool and then ground and remelted several times, until homogeneous mixtures were obtained.

Measurements

The procedures used for measurement of molar volume and conductance have been described in our previous papers [2,6].

RESULTS

The Arrhenius plots for ZnC_{18} -CTAB are shown in Fig. 1. The plots are similar to that obtained for pure ZnC_{18} , which can be explained in terms of a simple theory in which the soap dissociates according to the scheme



If it is assumed that the M^{2+} ion is the major charge carrier in the melt, and that it moves by a simple activated process, then

$$\log k = \log Q - \frac{\Delta H_k^* + \Delta H/3}{2.303RT} \quad (2)$$

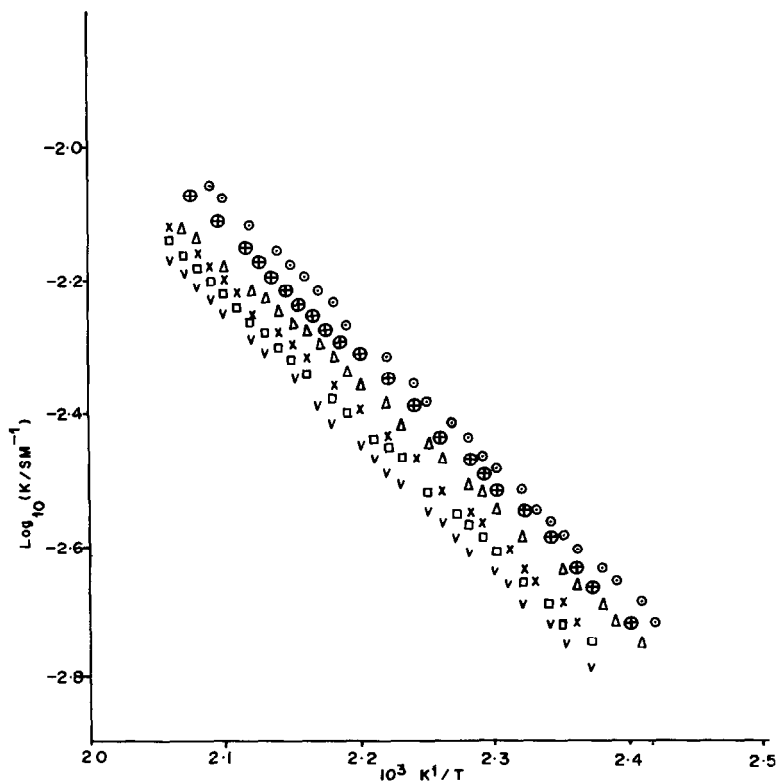


Fig. 1. Semi-logarithmic plot of conductivity vs. inverse absolute temperature for mixtures of zinc(II) octadecanoate with cetyl trimethylammonium bromide: \odot , $X_{\text{CTAB}} = 0.02$; \oplus , $X_{\text{CTAB}} = 0.06$; Δ , $X_{\text{CTAB}} = 0.10$; \times , $X_{\text{CTAB}} = 0.14$; \square , $X_{\text{CTAB}} = 0.18$; ∇ , $X_{\text{CTAB}} = 0.22$.

TABLE 1

Least-squares parameters for conductances for the system $\text{ZnC}_{18}\text{-CTAB}$

X_{CTAB}	$\log Q$	$\Delta H_k^* + \Delta H$ (kJ mol^{-1})	Correlation coefficient
0.00	—	39.7 ± 1.3^a	—
0.02	2.1792	38.8 ± 1.0	0.9982
0.06	2.2191	39.4 ± 1.0	0.9996
0.10	1.7848	36.0 ± 1.9	0.9995
0.14	2.1919	39.8 ± 1.0	0.9854
0.18	1.8748	37.3 ± 1.9	0.9989
0.22	2.1019	39.5 ± 1.0	0.9980

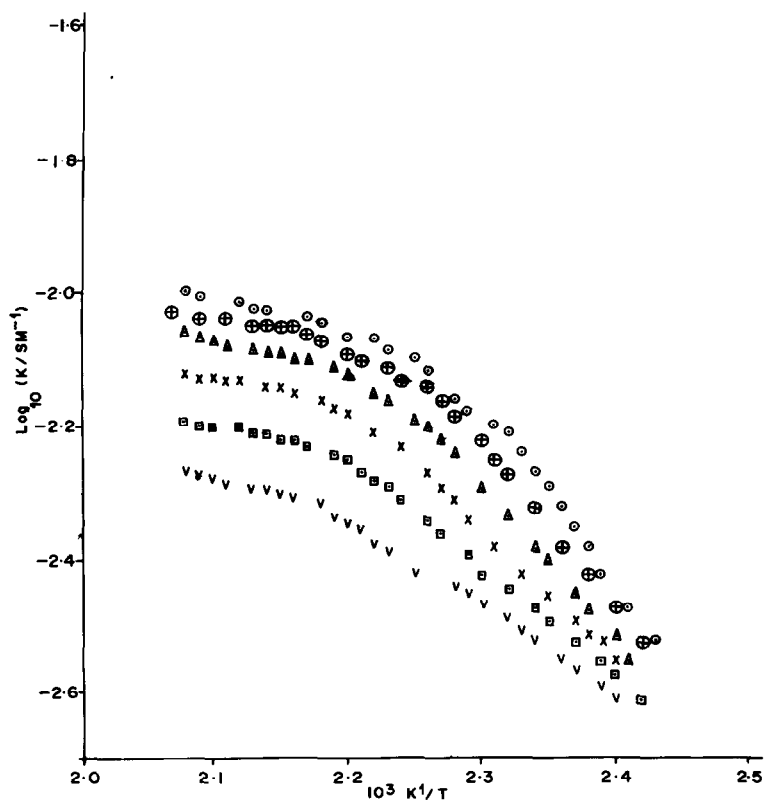
^a Ref. 2.

Fig. 2. Semi-logarithmic plot of conductivity vs. inverse absolute temperature for mixtures of cadmium(II) octadecanoate with cetyl trimethylammonium bromide: \odot , $X_{\text{CTAB}} = 0.02$; \oplus , $X_{\text{CTAB}} = 0.06$; Δ , $X_{\text{CTAB}} = 0.10$; \times , $X_{\text{CTAB}} = 0.14$; \square , $X_{\text{CTAB}} = 0.18$; ∇ , $X_{\text{CTAB}} = 0.22$.

TABLE 2

Least-squares parameters for conductances for the system CdC₁₈-CTAB

X_{CTAB}	$\log Q$	$\Delta H_k^* + \Delta H$ (kJ mol ⁻¹)	Correlation coefficient
0.00	—	69.0 ± 5.0 ^a	—
0.02	4.8616	58.2 ± 3.0	0.9746
0.06	3.3754	46.6 ± 4.0	0.9995
0.10	3.0697	44.6 ± 3.5	0.9963
0.14	1.9266	35.7 ± 3.8	0.9993
0.18	1.3868	31.6 ± 4.2	0.9937
0.22	0.8217	27.4 ± 4.8	0.9977

^a Ref. 1.

where ΔH_k^* and ΔH are the enthalpies of activation for movement of M²⁺ and for dissociation, respectively, and

$$\log Q = \log \frac{NeA}{2V_m} + \frac{\Delta S_k^* + \Delta S/3}{2.303R} \quad (3)$$

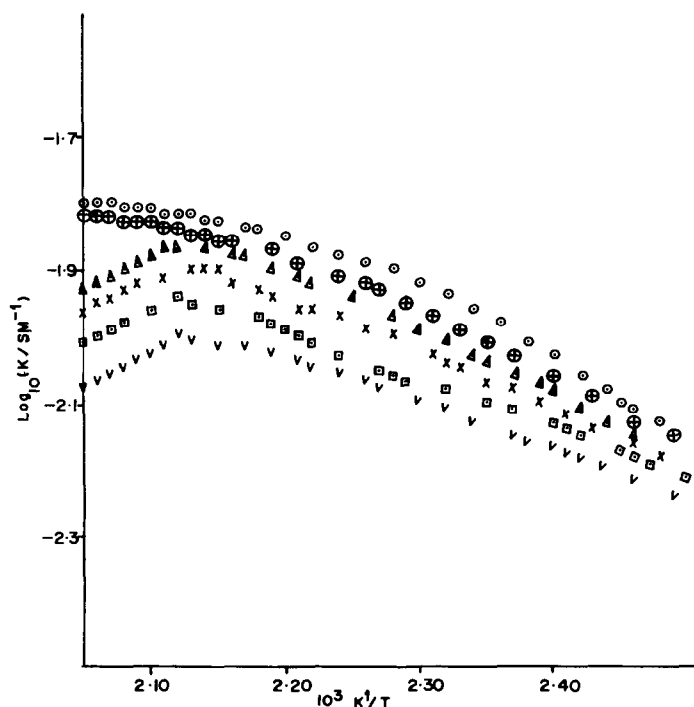


Fig. 3. Semi-logarithmic plot of conductivity vs. inverse absolute temperature for mixtures of lead(II) octadecanoate with cetyl trimethylammonium bromide: \odot , $X_{\text{CTAB}} = 0.02$; \oplus , $X_{\text{CTAB}} = 0.06$; Δ , $X_{\text{CTAB}} = 0.10$; \times , $X_{\text{CTAB}} = 0.14$; \square , $X_{\text{CTAB}} = 0.18$; ∇ , $X_{\text{CTAB}} = 0.22$.

TABLE 3

Least-squares parameters for conductances for the system $\text{PbC}_{18}\text{-CTAB}$

X_{CTAB}	$\log Q$	$\Delta H_k^* + \Delta H$ (kJ mol^{-1})	Correlation coefficient
0.00	—	43.6 ± 3.5^a	—
0.02	0.7931	22.5 ± 1.5	0.9977
0.06	0.4220	19.8 ± 1.2	0.9991
0.10	0.3068	19.1 ± 1.1	0.9992
0.14	0.3576	16.3 ± 1.2	0.9995
0.18	0.4407	13.5 ± 1.3	0.9957
0.22	0.3794	12.8 ± 1.5	0.9929

^a Ref. 2.

where e is the charge on an electron, N is Avogadro's number, A is a pre-exponential factor in the relationship between the electrical mobility of M^{2+} and the absolute temperature, ΔS_k^* and ΔS are the entropies of

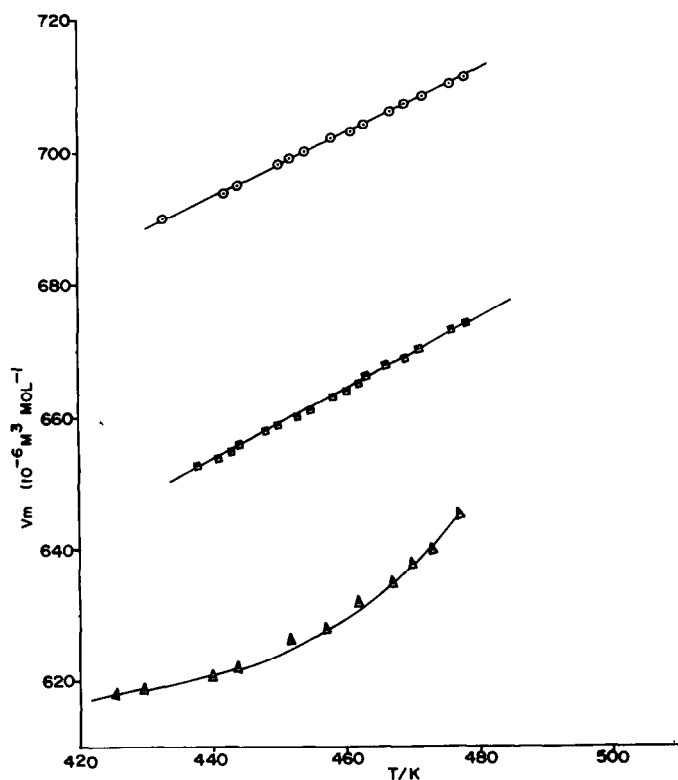


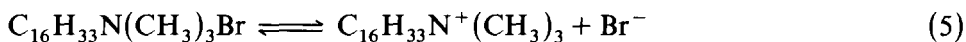
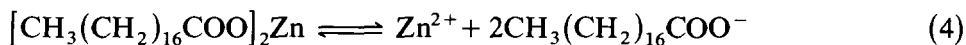
Fig. 4. Plot of molar volume vs. absolute temperature for $X_{\text{CTAB}} = 0.10$ in lead(II), cadmium(II) and zinc(II) octadecanoates: \odot , zinc(II) octadecanoate-CTAB mixture; \square , cadmium(II) octadecanoate-CTAB mixture; \triangle , lead(II) octadecanoate-CTAB mixture.

activation for movement of M^{2+} and for dissociation, respectively, and V_m is the molar volume of the pure soaps or the mixtures.

At low temperatures where the degree of dissociation is small, plots of $\log k$ against $1/T$ should be linear (Fig. 1), with slope equal to $(\Delta H_k^* + \Delta H/3)/2.303R$. Table 1 presents values of $(\Delta H_k^* + \Delta H)$ as calculated by the least-squares method from these plots, together with the correlation coefficients. The Arrhenius plots for CdC_{18} -CTAB and PbC_{18} -CTAB (at mole fractions of CTAB $X_{CTAB} < 0.10$ for the latter case) show curvature (Figs. 2 and 3, respectively). Again, this behaviour is similar to that observed for pure CdC_{18} and PbC_{18} , and can be explained in terms of complete dissociation of the soaps at relatively high temperatures [1,2]. However, the Arrhenius plots for PbC_{18} -CTAB at $X_{CTAB} \geq 0.10$ show maxima (Fig. 3). Values of the enthalpy terms $(\Delta H_k^* + \Delta H)$ for CdC_{18} -CTAB and PbC_{18} -CTAB are shown in Tables 2 and 3, respectively. The molar volumes of the three soaps were measured at $X_{CTAB} = 0.10$. Figure 4 shows the plots of molar volume vs. absolute temperature obtained for the three systems.

DISCUSSION

Conductance values for ZnC_{18} -CTAB at any particular temperature decrease with increasing X_{CTAB} (Fig. 1). This is consistent with the behaviour of some metal carboxylate-additive systems previously studied in our laboratory [6,9] and has been attributed to the relatively low level of dissociation of the additives. If the dissociation equilibria in the ZnC_{18} -CTAB melt are



then the major charge carriers in the system should be Zn^{2+} and Br^- . The fall in conductance with increasing X_{CTAB} suggests that the extent of dissociation according to eqn. (5) is small. Since the classical concept of "ion exchange" is only meaningful in consideration of ionic solid states where ions are in fixed positions in the lattice and where conductance occurs mainly as a result of lattice defects (Frenkel, Schottky, etc.), it is reasonable to assume here that the only significant contribution to conductance in this molten state arises from Zn^{2+} ions produced in the dissociation of ZnC_{18} (eqn. (4)).

In fact, CTAB does not melt below 500 K even though it dissolves in the soap to give a homogeneous melt at a much reduced temperature. All our measurements were taken below 493 K, and the decomposition temperature of CTAB is greater than 503 K*. Conductances were measured for the

* Value of decomposition obtained from Aldrich Chemical Co. Ltd., Catalogue No. 85, 1983-4, 582-0.

systems upon both heating and cooling, and the results were found to be reproducible. This confirms that no decomposition occurred and hence there were no decomposition fragments in the melt to complicate the analysis of our data. Thus the addition of CTAB serves to decrease the concentration of the current-carrying Zn^{2+} ions, and consequently, the conductance falls. This decrease can be attributed to a decrease in the entropy terms ($\Delta S_k^* + \Delta S$) with increasing X_{CTAB} . Such a decrease could arise either from a decrease in ΔS_k^* or from a decrease in ΔS . The two effects cannot be unambiguously separated. However, it is difficult to see how addition of CTAB could significantly alter ΔS_k^* , and so the main effect is probably due to a decrease in ΔS . It is possible to estimate the size of the decrease in the entropy of dissociation $\delta \Delta S$ by examining the separation between the Arrhenius plots for two different compositions of a given mixture at the same temperature. If the increase in the concentration of the second component is 0.04, the solution of the relation [7]

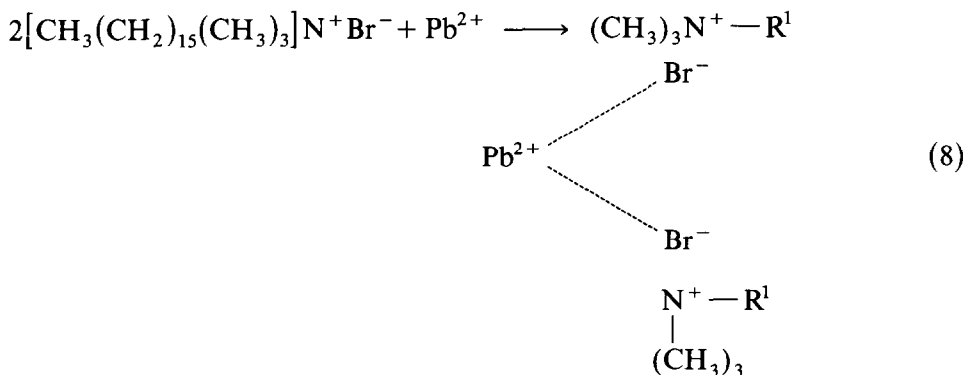
$$\log k_x - \log k_{x+0.04} = \frac{\delta \Delta S}{2.3033R} \quad (6)$$

gives a value of $\delta \Delta S$ of approximately $1.4 \text{ J mol}^{-1} \text{ K}^{-1}$ per increase of 0.04 in X_{CTAB} . This suggests that the undissociated carboxylate chain becomes less disordered with respect to the dissociated chain by a factor of approximately $1.4 \text{ J mol}^{-1} \text{ K}^{-1}$ per increase of 0.04 in X_{CTAB} . It is therefore logical to infer that the decrease in conductance may be due to a decrease in the concentration of Zn^{2+} ions arising from a decrease in ΔS on the addition of more CTAB. The situation in the CdC_{18} -CTAB system is not very different from that of the ZnC_{18} -CTAB system, except that the Arrhenius plots showed curvature which was similar to that obtained in the plots for pure CdC_{18} . The Arrhenius plots for PbC_{18} -CTAB at $X_{\text{CTAB}} < 0.10$ show curvature similar to that obtained for pure PbC_{18} , while at $X_{\text{CTAB}} \geq 0.10$, maxima are observed. Conductances in the latter cases are reproducible at temperatures cycling up to the maximum, but show permanent decrease when cycled beyond the maximum. Arrhenius plots displaying a maximum of this kind are common, and have been reported for a number of inorganic salts [15,16] and for some binary mixtures of lead(II) octadecanoate with lead 9,10-dihydroxy-octadecanoate (PbC_{18} - $\text{Pb}(\text{OH})_2\text{C}_{18}$) [9]. Explanations for the maximum are often based on chemical reaction or formation of complexes, especially at high temperatures. For example, the conductance maximum observed for Al_2Cl_6 has been explained in terms of a chemical reaction in which traces of water react with Al_2Cl_6 to produce HCl [15]. Similarly, the maximum observed for the system PbC_{18} - $\text{Pb}(\text{OH})_2\text{C}_{18}$ has been explained in terms of the Pb^{2+} ion reacting with the dihydroxy groups to form a cyclo-bridged product at high temperatures [9]. It has also been suggested that the maximum observed in the plot of log conductivity vs. inverse temperature for some molten inorganic salts might be due to the cation-an-

ion complexes becoming more abundant at higher temperatures [16]. To explain the maximum in the system $\text{PbC}_{18}\text{-CTAB}$ ($X_{\text{CTAB}} \geq 0.10$), it is proposed that the soap dissociates to give lead ions and carboxylate anions

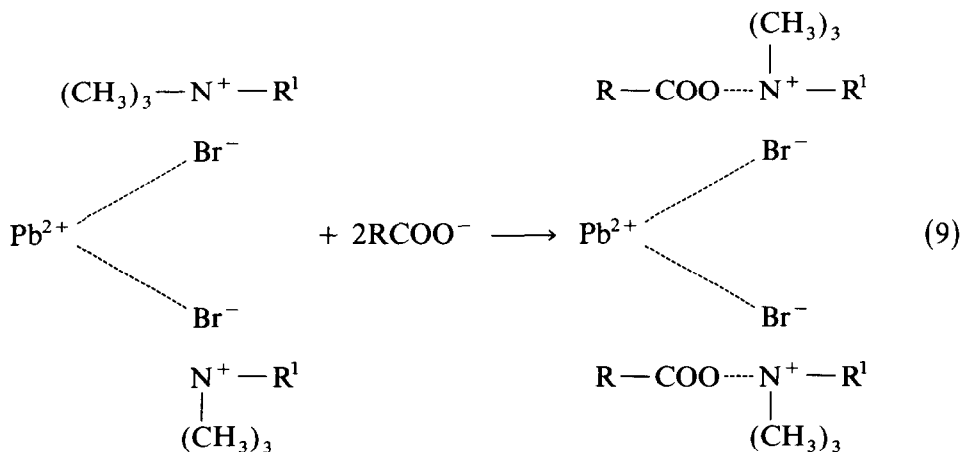
$$[\text{CH}_3(\text{CH}_2)_{16}\text{COO}]_2\text{Pb} \rightleftharpoons \text{Pb}^{2+} + 2\text{CH}_3(\text{CH}_2)_{16}\text{COO}^- \quad (7)$$

The undissociated CTAB then interacts by dipole-dipole attraction with the Pb^{2+} ions, thus



where $\text{R}^1 = \text{CH}_3(\text{CH}_2)_{15}^-$.

The carboxylate anions of the soap then interact with the intermediate product of reaction (8) to form a complex product



CTAB is believed to dissolve in the soap with the polar group of the CTAB oriented towards the polar group of the soap and the non-polar portions lying parallel to the soap hydrocarbon chains [17]. The dipole-dipole interaction presumably leads to the formation of a complex molecule. At high temperatures, reactions (8) and (9) are enhanced. This reduces the concentration of the main charge carriers, the Pb^{2+} ions, and hence brings about a fall in the conductance of the melt after the initial rise. If this proposition is valid, then the $\text{PbC}_{18}\text{-CTAB}$ melt ($X_{\text{CTAB}} \geq 0.10$) should show deviation from ideal behaviour. For an ideal isotropic liquid, the plot

of molar volume vs. absolute temperature has been shown to be a straight line, while plots for non-ideal melts show curvature [18]. It can be seen from Fig. 4 that a curve is obtained for the $\text{PbC}_{18}\text{-CTAB}$ system, as compared with the straight lines obtained for $\text{ZnC}_{18}\text{-CTAB}$ and $\text{CdC}_{18}\text{-CTAB}$. This reinforces the proposition arising from the results of the conductance measurements that some sort of interaction occurs in the molten mixtures of $\text{PbC}_{18}\text{-CTAB}$ at high temperatures.

The composite activation energy ($\Delta H_k + \Delta H$) for $\text{ZnC}_{18}\text{-CTAB}$ (Table 1) appears to remain constant with increasing X_{CTAB} . The values obtained are very close to the values of 38–40 kJ mol^{-1} reported for the pure alkanooates [2]. The work on the alkanooates has been interpreted in terms of the Zn^{2+} ions playing the role of the major charge carriers in the molten state. It is thus logical to speculate that the Zn^{2+} ions are the major charge carriers in molten $\text{ZnC}_{18}\text{-CTAB}$ mixtures. This speculation is encouraged by the fact that the CTAB is essentially undissociated in the melt. The values of the enthalpy terms for $\text{CdC}_{18}\text{-CTAB}$ and $\text{PbC}_{18}\text{-CTAB}$ (Tables 2 and 3) decrease with increasing X_{CTAB} . This contrasts with the case of $\text{ZnC}_{18}\text{-CTAB}$ mixtures. The values of ($\Delta H_k^* + \Delta H$) for pure CdC_{18} and PbC_{18} have been reported to be 69.0 and 43.6 kJ mol^{-1} , respectively [1,2]. Dissociation and conduction in the melts occur by an activated process with accompanying ion-ion interactions. The addition of $X_{\text{CTAB}} = 0.02$ to PbC_{18} causes the activation energy to drop to half of the value obtained for pure PbC_{18} . This significant drop in the enthalpy terms is consistent with the non-ideal behaviour proposed for $\text{PbC}_{18}\text{-CTAB}$, which only becomes apparent in the Arrhenius plots at $X_{\text{CTAB}} \geq 0.10$. Thus, the observation that the Arrhenius plots for some $\text{PbC}_{18}\text{-CTAB}$ mixtures display maxima while plots for $\text{CdC}_{18}\text{-CTAB}$ and $\text{ZnC}_{18}\text{-CTAB}$ mixtures show curvature and straight lines, respectively, may be attributable to the ionic radii of the metal ions. Earlier, Sime et al. [1–3] explained the curvatures obtained for pure lead(II) and cadmium(II) soaps in terms of complete dissociation at high temperatures. The difference between the behaviour of these soaps and that of zinc(II) soaps was ascribed to the differences in the ionic radii of the metal ions. The ionic radii show the order: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$. In molten state, the ionic atmosphere is expected to be lowest for Pb^{2+} ions, such that Pb^{2+} ions are more mobile than Cd^{2+} or Zn^{2+} ions. This trend is confirmed by the actual conductance values of the melts of the three soaps, which are in the reverse order to that of the ionic radii. This picture implies that in the molten states the Cd^{2+} and Zn^{2+} ions are in more of a 'cage' of carboxylate anions arising from relatively high electrostatic forces. Hence the Pb^{2+} ions are more exposed to the risk of interaction with charged species in the melt, and this may explain the formation of a complex in $\text{PbC}_{18}\text{-CTAB}$ mixtures with fairly high values of X_{CTAB} . Combining the results of the Arrhenius plots with those of the molar volume vs. temperature plots, we propose the relative degree of ideality to be: $\text{ZnC}_{18}\text{-CTAB} > \text{CdC}_{18}\text{-CTAB} > \text{PbC}_{18}\text{-CTAB}$.

CONCLUSIONS

The objective of finding a source of bromide with which some metal carboxylates could be doped was not achieved. Rather, the results of our study suggest that caution should be exercised in the choice of material to be used as a doping agent, especially at high temperatures, because of the possibility of complexation or formation of ion pairs. A source of positive ions with physico-chemical properties similar to those of the cations of the metal carboxylates would be better as a means of doping the soaps.

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