

ELECTRICAL CONDUCTANCE, DENSITY AND VISCOSITY OF MOLTEN LEAD DODECANOATE/LEAD ACETATE MIXTURES

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ABSTRACT

Data are presented for the densities, electrical conductances and viscosities of the system lead dodecanoate/lead acetate. The molar volumes are linear functions of composition. The Arrhenius plots for the conductance of the mixtures show curvature. Activation energies for conductance in the low temperature region are independent of composition and similar to that of pure lead dodecanoate, suggesting that the major charge carrier is the same i.e. Pb^{2+} ions. The observed increase in the conductance of the mixtures with increasing concentration of lead acetate is probably due to an increase in the Pb^{2+} concentration.

The activation energies for viscous flow in the mixtures are similar to that of pure lead dodecanoate. Evidence is presented to show that the size of the unit of viscous flow in the mixtures is the same as in the pure soap.

INTRODUCTION

In a previous paper¹, data were presented for the heats and entropies of phase changes for the system lead dodecanoate/lead acetate. The results showed that addition of lead acetate to lead dodecanoate does not alter the phase sequence observed in lead dodecanoate² i.e. crystal $\rightarrow G_{(\text{smectic})} \rightarrow V_{2(\text{cubic isomorphous})} \rightarrow$ liquid. The magnitude of the entropy change for the $V_2 \rightarrow$ liquid transition also suggested that addition of lead acetate to lead dodecanoate does not affect the state of aggregation of the soap molecules in the liquid phase. These observations were rationalised in terms of the R theory³ of fused micellar phases.

In an attempt to investigate further the effect of lead acetate upon the physical properties of lead dodecanoate, we have measured the densities, electrical conductances and viscosities of some molten lead dodecanoate/lead acetate mixtures.

EXPERIMENTAL

Materials

All the fatty acids employed were “specially pure” B.D.H. grade and were

stated to have minimum 99% purity by GLC assay. They were used without further purification. The preparation of anhydrous lead acetate, lead dodecanoate and the mixtures has been described elsewhere^{1, 4}.

Measurements

The procedures for the measurement of density, viscosity and conductance were the same as previously described^{4,5}.

RESULTS AND DISCUSSION

Density and molar volume

Plots of densities and molar volumes against temperature were linear. The densities were fitted by least squares method to the equation

$$\rho_{(T)} = \rho_0 - aT$$

and molar volumes to

$$V_{m(T)} = V_0 + bT$$

where a and b are constants. The parameters for the fits are presented in Table 1 with their standard errors and the range of measurement.

Plots of the molar volumes of the mixtures at some selected temperatures against mole fraction of lead acetate (Fig. 1) are linear, indicating that there is no excess volume of mixing, at least within the accuracy of these measurements.

Electrical conductance

The electrical conductance data are presented in Fig. 2 where values of log specific conductance are plotted against inverse absolute temperatures. The plots show curvature which is similar to the behaviour of pure lead dodecanoate⁴. The curvature

TABLE I

DENSITIES AND MOLAR VOLUMES

$X_{Pb(CH_3COO)_2}$	Temperature range (K)	$\rho = \rho_0 - aT/10^3$ (Kg m ⁻³)				$V_m = V_0 + bT/10^{-6}$ (m ³)			
		ρ_0	Std. error (%)	$a \times 10^3$	Error in a (%)	V_0	Std. error (%)	b	Error in b (%)
0.00	390-455	1.787	0.10	1.216	2.0	315.0	0.10	0.387	3.7
0.02	408-457	1.753	0.14	1.103	4.5	298.2	0.16	0.395	4.1
0.04	418-451	1.693	0.21	0.911	1.2	325.6	0.09	0.319	2.5
0.06	413-453	1.793	0.18	1.136	1.9	319.1	0.13	0.305	1.7
0.08	413-453	1.672	0.12	0.852	4.7	321.3	0.12	0.289	4.6
0.10	418-458	1.656	0.08	0.813	3.5	314.0	0.21	0.272	2.8
0.12	425-460	1.730	0.15	0.991	3.0	287.0	0.15	0.305	3.6

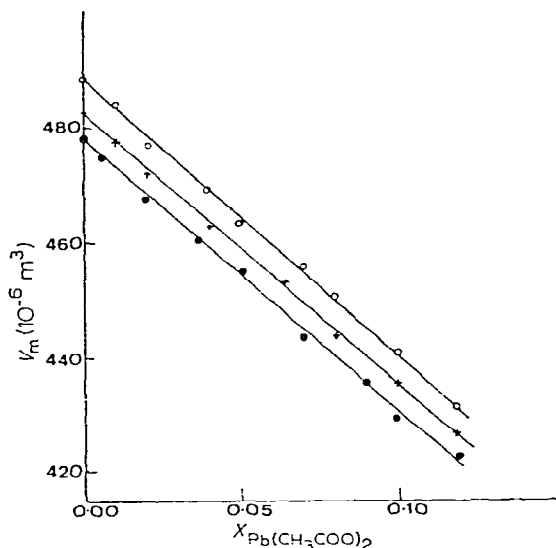
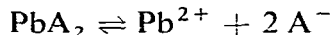


Fig. 1. Plots of molar volume at different temperatures against mole fraction of lead acetate. \circ , 450 K; $+$, 440 K; \bullet , 430 K.

in the conductance behaviour of lead dodecanoate has been interpreted in terms of a simple dissociation theory in which the carboxylate dissociates according to the scheme



Assuming that the major charge carrier is the Pb^{2+} ion and that it moves by a simple activated process, then we obtain the following expressions⁴

$$\log \kappa = \log Q - \frac{\Delta H_{\kappa}^{\ddagger} + \Delta H/3}{2.303 RT} \quad (1)$$

and

$$\log Q = \log (NeA/2V_m) + \frac{1}{2.303 R} \left(\Delta S_{\kappa}^{\ddagger} + \frac{\Delta S}{3} \right) \quad (2)$$

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

At low temperatures, where the degree of dissociation is small, plots of $\log \kappa$ against $1/T$ should be linear with slopes of $(\Delta H_{\kappa}^{\ddagger} + \Delta H/3)/2.303 R$.

Table 2 shows values of $\Delta H_{\kappa}^{\ddagger} \pm \Delta H/3$ calculated from these plots by least squares method. It can be seen that these values are reasonably constant within the limits of experimental error. This suggests that the major charge carrier in these mixtures is the same, most certainly the Pb^{2+} ions.

Inspection of Fig. 2 shows that the conductivity of the mixtures increases with increasing concentration of lead acetate at any given temperature. The increase in conductivity with increasing lead acetate concentration may be seen from eqns. (1) and (2) to arise from an increase in the entropy term i.e. $(\Delta S_{\kappa}^{\ddagger} + \Delta S/3)$ with increasing

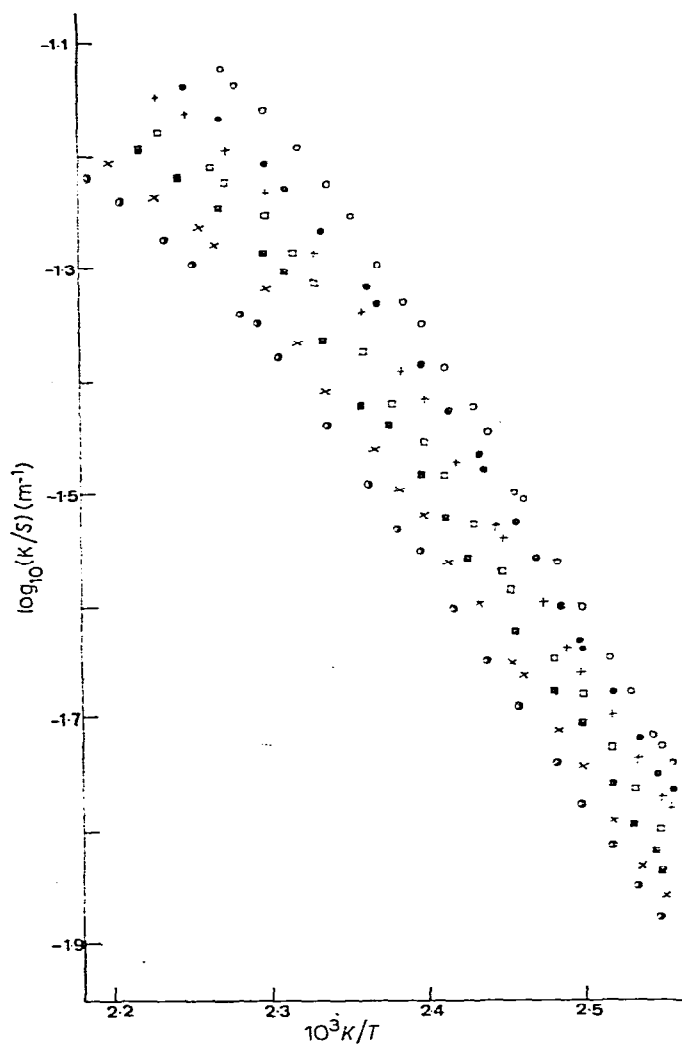


Fig. 2. Semilogarithmic plots of specific conductivity against inverse temperature for the lead dodecanoate-lead acetate mixtures. \circ , $X_{\text{Pb}(\text{CH}_3\text{COO})_2} = 0.12$; \bullet , $X_{\text{Pb}(\text{CH}_3\text{COO})_2} = 0.10$; $+$, $X_{\text{Pb}(\text{CH}_3\text{COO})_2} = 0.08$; \square , $X_{\text{Pb}(\text{CH}_3\text{COO})_2} = 0.06$; \blacksquare , $X_{\text{Pb}(\text{CH}_3\text{COO})_2} = 0.04$; \times , $X_{\text{Pb}(\text{CH}_3\text{COO})_2} = 0.02$; \ominus , pure lead dodecanoate.

TABLE 2

LOW TEMPERATURE LIMITING SLOPES FOR CONDUCTANCE

$X_{\text{Pb}(\text{CH}_3\text{COO})_2}$	$(\Delta H_{\text{K}}^{\ddagger} + \Delta H/3)$ (kJ mole^{-1})
0.00	47 ± 3
0.02	47 ± 3
0.04	50 ± 4
0.06	49 ± 3
0.08	50 ± 3
0.10	48 ± 2
0.12	48 ± 2

lead acetate concentration. Thus the increase in κ could arise either from an increase in $\Delta S_{\kappa}^{\ddagger}$ or from an increase in ΔS . It is impossible to unambiguously distinguish between these two effects. However, as little is known about the conduction process in these melts, it seems more useful to try and rationalise the changes in terms of ΔS that may arise on addition of lead acetate and assume that $\Delta S_{\kappa}^{\ddagger}$ is effectively constant for the different mixtures.

We may estimate the size of the increase in the entropy of dissociation (ΔS) by examining the separation of conductance curves for mixtures with 0.02 difference in the mole fraction of lead acetate. Evaluation of $\delta(\Delta S)$ from the relation

$$\log \kappa_{(x)} - \log \kappa_{(x+0.02)} = \frac{\delta(\Delta S)}{2.303 \times 3 R} \quad (3)$$

corresponds to a change of approximately $2 \text{ J mole}^{-1} \text{ K}^{-1}$ per 0.02 increase in the mole fraction of lead acetate, which suggests that the dissociated carboxylate chain becomes more disordered with respect to the undissociated chain by a factor of about $2 \text{ J mole}^{-1} \text{ K}^{-1}$ per 0.02 increase in the mole fraction of lead acetate. Thus the increase in conductivity is probably due to an increase in the Pb^{2+} concentration corresponding to the increase in ΔS .

It is possible to actually calculate the Pb^{2+} ion concentration in the different mixtures at any temperature by a method previously described for the pure *n*-alkanoates⁴. However, this requires data at high temperatures where the Arrhenius plot tends to a second linear portion with slope corresponding to $\Delta H_{\kappa}^{\ddagger}$. Unfortunately this region was not reached in the mixtures before the onset of decomposition. Hence we could not calculate and compare the Pb^{2+} ion concentrations in the different mixtures.

Viscosity

The viscosity data were fitted by least squares to the equation

$$\log_{10} \eta = \log_{10} \eta_0 + \frac{\Delta H_{\eta}^{\ddagger}}{2.303 RT} \quad (4)$$

where η is the viscosity in Pa s and $\Delta H_{\eta}^{\ddagger}$ is the activation energy for viscous flow. The results of the fits are shown in Table 3 where $\log_{10} \eta_0$, $\Delta H_{\eta}^{\ddagger}$, the probable error in $\Delta H_{\eta}^{\ddagger}$ and the correlation coefficients are listed. The corresponding values for pure lead dodecanoate are also included in Table 3. The value of $\Delta H_{\eta}^{\ddagger}$ obtained in this work for pure lead dodecanoate is significantly higher than the value of 54 kJ mole^{-1} earlier reported by Ekpe and Sime⁵. The reason for this discrepancy is not clear to us, especially when 1 mm capillary viscometers were used for the two sets of experiments. However we are confident that the present data are reliable as they have been confirmed by other workers in our laboratory^{6, 7}.

It can be seen from Table 3 that the activation energies for viscous flow in the mixtures as well as in pure lead dodecanoate are the same, within the limits of experimental error. This indicates that the unit of viscous flow is the same in the

TABLE 3

LEAST SQUARES PARAMETERS FOR VISCOUS FLOW IN THE SYSTEM LEAD DODECANOATE/LEAD ACETATE

$X_{Pb(CH_2COO)_2}$	$\log_{10}\eta_0$	$\Delta H_{\eta}^{\ddagger}$ (kJ mole ⁻¹)	Error in $\Delta H_{\eta}^{\ddagger}$	Std. dev.	Corr. coeff.	Temp. range (K)
0.00	-6.897	70.4	4.4	0.038	0.9974	406-460
0.02	-7.339	73.1	5.1	0.050	0.9982	410-440
0.04	-7.829	75.3	4.5	0.049	0.9967	413-442
0.06	-7.496	72.3	4.8	0.041	0.9995	416-445
0.08	-7.378	76.1	3.0	0.036	0.9998	420-450
0.10	-7.769	74.1	4.7	0.041	0.9979	421-455
0.12	-7.467	71.4	2.3	0.022	0.9967	425-456

TABLE 4

LEAST SQUARES PARAMETERS FOR VISCOUS FLOW IN THE SYSTEMS LEAD CARBOXYLATE/(0.1 MOLE FRACTION) LEAD ACETATE

Carbon chain length	$\log_{10}\eta_0$	$\Delta H_{\eta}^{\ddagger}$ (kJ mole ⁻¹)	Error in $\Delta H_{\eta}^{\ddagger}$	Std. dev.	Corr. coeff.	Temp. range (K)
8	-5.386	53.5	2.8	0.028	0.9989	410-437
10	-5.890	62.0	3.1	0.035	0.9968	415-447
14	-8.450	80.0	3.5	0.051	0.9982	416-448
16	-9.875	85.0	2.9	0.031	0.9978	413-440
18	-10.198	98.5	4.0	0.049	0.9979	417-442

mixtures as well as in pure lead dodecanoate. This is not a surprising result since the carboxylate moiety has been shown to be responsible for viscous flow in the lead *n*-alkanoates⁵.

It has been suggested that the fact that the rate of change of $\Delta H_{\eta}^{\ddagger}$ with carbon chain length in the lead alkanoates is much greater than for the alkane series implies that the unit of flow in the lead carboxylates is not a single molecule but an aggregate consisting of between 3 and 5 molecules⁵. In an attempt to see how the addition of lead acetate affects the size of the unit of flow in lead carboxylates, we have also measured the viscosities of the even chain length lead carboxylates (from octanoate to octadecanoate inclusive) containing 0.1 mole fraction of lead acetate. The results are summarised in Table 4.

Figure 3 shows a plot of $\Delta H_{\eta}^{\ddagger}$ against chain length. The slope of this plot is 4.2 which is quite close to the value of 4.0 obtained for the pure lead *n*-alkanoates⁵. This suggests that the unit of flow in the mixtures contain the same number of soap molecules as in the pure lead carboxylates. We therefore conclude that addition of

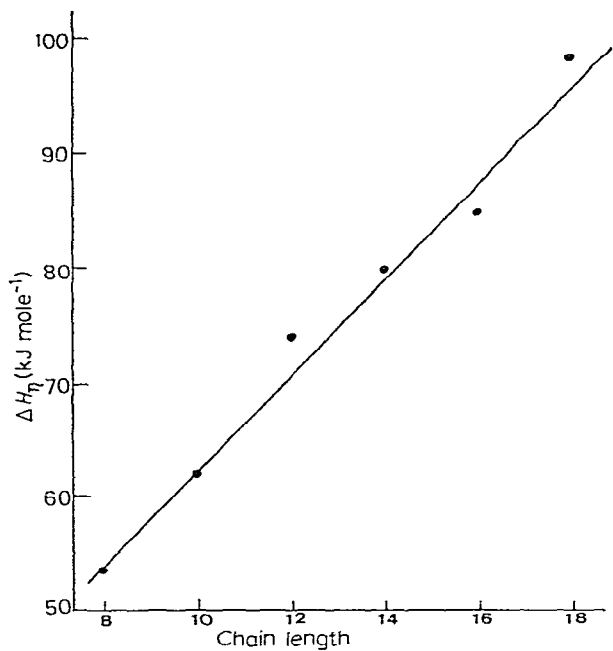


Fig. 3. Plot of $\Delta H_{\eta}^{\ddagger}$ against chain length for the systems lead carboxylate/(0.1 mole fraction) lead acetate.

lead acetate does not affect the size of the unit of flow of lead soaps, at least within the composition range studied.

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