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ELECTRICAL CONDUCTANCE, DENSITY, AND VISCOSITY OF THE MOLTEN SYSTEM LEAD(II) DODECANOATE/LEAD(II) OXIDE

(The late) S. OLUYEMI ADEOSUN, M. SHOLA AKANNI and HUGH D. BURROWS *

Department of Chemistry, University of Ife, Ile-Ife (Nigeria)

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ABSTRACT

Data are presented for densities, electrical conductances, and viscosities of the molten system lead(II) dodecanoate/lead(II) oxide for concentrations up to 0.22 mole fraction of the oxide. Values of ρ_0 obtained from extrapolation of graphs of density against temperature are seen to decrease on adding small quantities of PbO, but to increase on adding further PbO. Results from thermal analysis suggest that this may be due to a change in structure of the liquid phase from small, spherical to long, cylindrical micelles. Over the concentration range studied, molar volumes are linear functions of concentration at any particular temperature. The molar volumes of the system lead(II) carboxylate/lead(II) oxide for the even chain acids C_{10} to C_{18} are linear functions of chain length. Arrhenius plots for the electrical conductance of the mixtures show curvature, as in other lead(II) dodecanoate systems. The activation energies for conductance in the low temperature region show a steady decrease with increasing PbO concentration and it is proposed that this arises from increased mobility of the charge carrier. The specific conductance at any temperature decreases with increasing mole fraction of oxide, indicating the oxide to be essentially undissociated in the melt. The activation energy for viscosity shows a dramatic increase on adding small amounts of PbO. This is suggested to arise from a change in the structure of the melt. Studies of the viscosites of the system lead(II) carboxylate/lead oxide as a function of chain length for the even chain acids C_{10} to C_{18} suggest a slight decrease in the size of the unit of viscous flow when oxide is present.

INTRODUCTION

Previous studies from this laboratory have provided information on the electrical conductance, density, and viscosity of pure lead(II) dodecanoate [1,2] and of mixtures of it with lead acetate [3] or dodecanoic acid [4]. In addition, quantitative DTA has provided valuable information on the phase changes occurring on heating lead dodecanoate, either alone [5] or in mixtures with lead acetate [6], dodecanoic acid [7], hendecane [8], and lead(II) oxide [8]. It is found that, whilst addition of lead acetate [6] or dodecanoic acid [7] to lead dodecanoate appears to have no effect on the state of aggregation of the soap in the liquid phase, addition of lead oxide seems to change the structure of the liquid phase from small, essentially spherical micelles in

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* To whom all correspondence should be addressed.

the pure soap to long, cylindrical micelles in the mixture [8]. It would thus be valuable to study the physical properties of molten mixtures of lead dodecanoate with lead oxide. We have, accordingly, measured the densities, electrical conductances, and viscosities of this system.

EXPERIMENTAL

Materials

The preparation and purification of lead(II) dodecanoate and other lead carboxylates has been described in detail elsewhere [1]. Lead(II) oxide was Hopkin and Williams general purpose grade and was dried at 120°C under vacuum and stored in a dessicator over silica gel before use.

Mixtures were prepared by weighing the appropriate amounts of the components into a quick-fit conical flask. The flask was then evacuated to prevent decomposition of the mixture, which was then melted on a hot plate. The problems associated with dissolving lead oxide in lead dodecanoate have been described previously [6].

Physical measurements

The procedures for the measurement of density, viscosity, and electrical conductance were the same as described in earlier papers [1,2].

RESULTS AND DISCUSSION

Density and molar volume

Plots of densities and molar volumes against temperature were linear and were fitted by least squares to the equations

$$\rho_T = \rho_0 - aT \quad (1)$$

and

$$V_m(t) = V_0 + bT \quad (2)$$

where a and b are constants. Least squares parameters for the fits with standard errors and the range of measurement are given in Table 1.

It can be noted that the value of ρ_0 decreases dramatically on adding the smallest quantity of PbO. Following this, there is a progressive increase in ρ_0 on adding more PbO. A similar trend, but in the opposite direction, is observed with the molar volumes. The calculated density at temperatures close to the melting point again shows a decrease on adding the smallest amounts of PbO, followed by an increase on adding more oxide. However, at higher temperatures, only a steady increase in density is observed on adding PbO. Interpretation of thermal data on this system [8] provides an insight into

TABLE 1

Densities and molar volumes of the system lead (II) dodecanoate/lead (II) oxide

X_{PbO}	Temp. range (K)	$\rho = \rho_0 - aT$ (10^3 kg m^{-3})				$V_m = V_0 + bT$ (10^{-6} m^3 mole^{-1})			
		ρ_0	Stnd. error (%)	$a \times 10^3$	Error in a (%)	V_0	Stnd. error (%)	b	Error in b (%)
0.00	421—471	1.680	0.08	0.89	3.4	330.3	0.15	0.330	3.1
0.02	412—476	1.544	0.03	0.55	1.8	371.0	0.05	0.211	1.8
0.06	407—454	1.614	0.03	0.70	1.4	342.0	0.04	0.234	1.3
0.10	413—470	1.636	0.02	0.71	1.4	327.3	0.04	0.229	1.0
0.14	413—476	1.689	0.03	0.81	1.2	303.1	0.05	0.250	0.9
0.18	422—475	1.728	0.03	0.84	1.2	286.5	0.06	0.245	1.3
0.22	421—474	1.742	0.03	0.82	1.2	278.1	0.07	0.224	1.8

what is happening. Addition of PbO is suggested to change the structure of the liquid phase from small, essentially spherical micelles into long, cylindrical micelles. The addition of PbO may thus decrease the density by causing a structural change to a less tightly packed liquid system. On adding further lead oxide, however, the increased mole fraction of the more dense PbO causes the observed increase.

As with previous studies of mixtures of lead dodecanoate with lead acetate [3] or dodecanoic acid [4], plots of molar volume of the lead dodecanoate/lead oxide system against mole fraction of oxide at one particular temperature are linear, indicating that, within the accuracy of these measurements, there is no excess volume of mixing over the concentration range studied (Fig. 1).

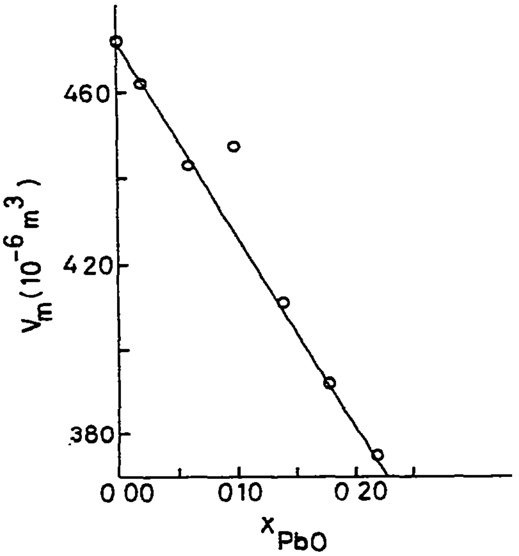

Fig. 1. Plot of molar volume at 400 K against mole fraction of lead oxide.

TABLE 2

Densities and molar volumes of the system lead (II) carboxylate/lead (II) oxide (0.10 mole fraction)

Carbon chain length	Temp. range (K)	$\rho = \rho_0 - aT$ (10^3 kg m^{-3})				$V_m = V_0 + bT$ (10^{-6} m^3 mole^{-1})			
		ρ_0	Stnd. error (%)	$a \times 10^3$	Error in a (%)	V_0	Stnd. error (%)	b	Error in b (%)
10	415—470	1.698	0.02	0.743	1.3	287.1	0.05	0.205	1.4
12	413—470	1.636	0.02	0.708	1.4	327.3	0.04	0.229	1.0
14	408—469	1.480	0.02	0.490	2.0	404.3	0.02	0.189	0.8
16	408—471	1.424	0.01	0.513	1.9	452.7	0.02	0.242	0.7
18	407—476	1.374	0.05	0.495	2.0	504.7	0.06	0.266	1.6

Previous studies [1,4,9] have shown that valuable information can be obtained by studying the molar volumes of metal carboxylate systems as a function of chain length. The densities and molar volumes were determined for the system lead(II) carboxylate/lead oxide for the even chain length acids C_{10} to C_{18} at a constant mole fraction (0.10) of the oxide. These were fitted by least squares treatment to eqns. (1) and (2) and the parameters for these fits are given in Table 2.

The molar volume at a specific temperature (450 K) was plotted against total carbon chain length and the data was found by least squares to fit the equation

$$V_m(450) = [62.55 + 31.03n] \times 10^{-6}\ \mathrm{m^3\ mole^{-1}} \tag{3}$$

The correlation coefficient was 0.9982. Taking the total number of carbon atoms per molecule as $2n$ [9] gives an increase in volume per methylene group of 15.5×10^{-6} m^3 mole^{-1}. Not suprisingly, considering the volume which must be occupied by the lead oxide component, this is smaller than the volume increase observed with pure lead(II) carboxylates (18.3×10^{-6} m^3 mole^{-1}) [1] or with the system lead(II) carboxylate/carboxylic acid (0.10 mole fraction)(16.5×10^{-6} m^3 mole^{-1}) [4]. The molar volume of the system can be related to the partial molar volumes of lead carboxylate, $V_m(\mathrm{PbC}_x)$, and lead oxide, $V_m(\mathrm{PbO})$.

$$V_m = V_m(\mathrm{PbC}_x)(1 - X_{\mathrm{PbO}}) + V_m(\mathrm{PbO})\, X_{\mathrm{PbO}} \tag{4}$$

Assuming, as suggested by Fig. 1, that ideal behaviour is observed over the concentration range studied, the partial molar volumes can be equated to the molar volumes of the pure components. Since the molar volume of pure lead carboxylates are related to the carbon chain length by the equation [1]

$$V_m(450) = [53.01 + 36.53n] \times 10^{-6}\ \mathrm{m^3\ mole^{-1}} \tag{5}$$

the molar volume of the lead oxide can be calculated, and is found to have a value of 145.6×10^{-6} m^3 mole^{-1}. This is considerably higher than the value obtained by extrapolating the high temperature data for PbO [10] to this temperature (extrapolated $V_m = 25.5 \times 10^{-6}$ m^3 mole^{-1}). This discrepancy may arise from the facts that extrapolation of lead oxide data to temperatures below its melting point is not strictly justified, and that the values used in eqn. (5) for the pure soaps may no longer be justified because of the structural change in the melt.

Electrical conductance

Electrical conductances were determined for the molten system lead(II) dodecanoate/lead(II) oxide for oxide mole fractions between 0 and 0.22. Values of the logarithm of the specific conductance were plotted against the reciprocal of the absolute temperature for each mixture studied (Fig. 2). As is common in lead carboxylate systems [1,3,4], curvature was observed at high temperatures.

The major charge carrier in the system is thought to be Pb^{2+}, which moves by a simple activated process. This ion may arise from two equilibria

$$PbA_2 \rightleftharpoons Pb^{2+} + 2\,A^- \tag{6}$$

$$PbO \rightleftharpoons Pb^{2+} + O^{2-} \tag{7}$$

However, like the case of the system lead(II) dodecanoate/dodecanoic acid [4], but unlike the system lead(II) dodecanoate/lead(II) acetate [3], the specific conductance at any temperature decreases with increasing mole fraction of lead oxide. This strongly suggests that the extent of dissociation according to eqn. (7) is small in this system and that the only significant contribution to the conductance arises from Pb^{2+} ions produced in the dissociation of lead(II) dodecanoate. Analysis of the dissociation of lead dode-

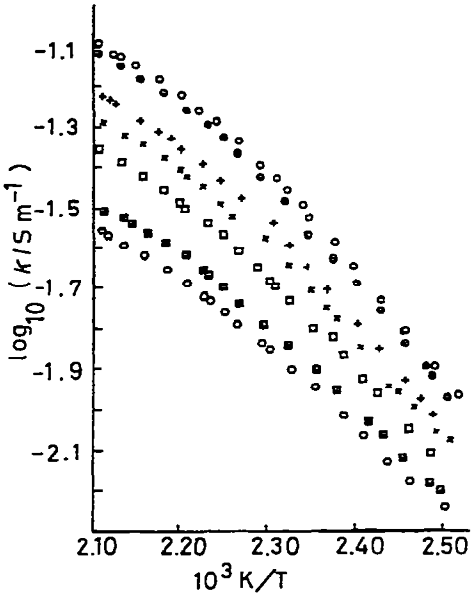

Fig. 2. Semilogarithmic plot of specific conductivity against inverse temperature for lead(II) dodecanoate/lead oxide mixtures. ○, Pure lead dodecanoate; ●, $X_{PbO} = 0.02$; +, $X_{PbO} = 0.06$; ×, $X_{PbO} = 0.10$; □, $X_{PbO} = 0.14$; ▪, $X_{PbO} = 0.18$; o, $X_{PbO} = 0.22$.

TABLE 3

Low temperature limiting slopes and conductances for the system lead (II) dodecanoate/lead (II) oxide

X_{PbO}	$\log_{10}Q$	Stnd. error in $\log_{10}Q$	$(\Delta H_\kappa + \Delta H/3)$ (kJ mole^{-1})
0.00	5.161	0.008	54.4 ± 1.4
0.02	4.892	0.013	52.5 ± 2.2
0.06	4.452	0.004	49.7 ± 0.7
0.10	4.107	0.003	47.3 ± 0.5
0.14	3.633	0.006	44.1 ± 1.1
0.18	3.162	0.004	41.1 ± 0.6
0.22	2.899	0.013	39.4 ± 1.9

canoate has shown [1] that the conductance behaviour can be described by the equations

$$\log \kappa = \log Q - \frac{\Delta H_\kappa^\ddagger + \Delta H/3}{2.303RT} \qquad (8)$$

and

$$\log Q = \log(NeA/2V_m) + \frac{\Delta S_\kappa^\ddagger + \Delta S/3}{2.303R} \qquad (9)$$

where $\Delta H_\kappa^\ddagger$, $\Delta S_\kappa^\ddagger$, ΔH, and ΔS are the enthalpies and entropies of activation for movement of Pb^{2+} and for dissociation, respectively. At low temperatures, where the degree of dissociation is small, plots of log κ against $1/T$ should be linear with slope $(\Delta H_\kappa^\ddagger + \Delta H/3)/2.303$. Values of $(\Delta H_\kappa^\ddagger + \Delta H/3)$ calculated by least squares from these plots are given in Table 3.

As in the case of the system lead dodecanoate/dodecanoic acid [4], the enthalpy is seen to show a steady decrease with increase in oxide concentration. It is difficult to see how addition of oxide will affect the enthalpy of the dissociation reaction, so that the main effect of adding oxide must be to decrease $\Delta H_\kappa^\ddagger$. In the lead dodecanoate/dodecanoic acid system [4], it was suggested that the decrease in $\Delta H_\kappa^\ddagger$ resulted largely from increased mobility of the Pb^{2+} ion. In the present system, the macroscopic viscosity at any temperature decreases with increasing mole fraction of the oxide and it is reasonable in this case, too, that the decrease in activation energy arises from the increased mobility of the Pb^{2+} ion.

Viscosity

The viscosity data were fitted by least squares to the equation

$$\log \eta = \log \eta_0 + \frac{\Delta H_\eta^\ddagger}{2.303RT} \qquad (10)$$

where η is the viscosity in Pa s and $\Delta H_\eta^\ddagger$ is the activation energy for viscous flow. Data for the fits are presented in Table 4.

TABLE 4

Least squares parameters for viscous flow in the system lead (II) dodecanoate/lead (II) oxide

X_{PbO}	Temp. range (K)	$\log_{10}\eta_0$	ΔH_η (kJ mole^{-1})	Correlation coefficient
0.00	406—460	−6.897	70.4 ± 4.4	0.9974
0.02	407—458	−7.289	80.2 ± 2.1	0.9983
0.06	405—451	−7.762	83.3 ± 1.3	0.9994
0.10	396—447	−7.970	84.7 ± 2.4	0.9979
0.14	400—446	−8.166	85.4 ± 3.3	0.9971
0.18	396—450	−8.282	86.0 ± 2.8	0.9980
0.22	396—445	−8.580	88.3 ± 5.3	0.9909

The one striking thing about the results is the dramatic increase in activation energy on adding small amounts of lead oxide. This has been confirmed by other workers in our laboratory [11]. The change seems to parallel the suggested change in structure of the melt [8].

Information on the unit of flow can be obtained by studying viscosity as a function of chain length [2]. The viscosities of the system lead(II) carboxylate/lead oxide (0.10 mole fraction) were studied as a function of temperature for the even chain acids C_{10} to C_{18}. Data obtained using eqn. (10) are presented in Table 5.

For the system lead carboxylate/lead oxide (0.10 mole fraction), a plot of $\Delta H_\eta^\ddagger$ against carbon chain length is fairly linear (least squares correlation coefficient 0.9853) with slope 2.3 kJ mole^{-1} (C atom)$^{-1}$ (Fig. 3) close to that observed in the system lead carboxylate/carboxylic acid (0.1 mole fraction) [2.4 kJ mole^{-1} (C atom)$^{-1}$] [4], but considerably lower than the values of 4.2 and 4.0 kJ mole^{-1} (C atom)$^{-1}$ observed with the systems lead carboxylate/lead acetate (0.1 mole fraction) [3] and pure lead carboxylate [2], respectively. This suggests that the unit of viscous flow in the system lead

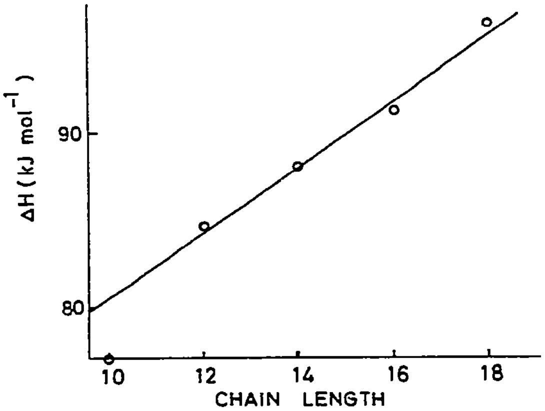

Fig. 3. Plot of $\Delta H_\eta^\ddagger$ against chain length for the system lead(II) carboxylate/lead oxide (0.1 mole fraction).

TABLE 5

Least squares parameters for viscous flow in the system lead (II) carboxylate/lead (II) oxide (0.10 mole fraction)

Carbon chain length	Temp. range (K)	$\log_{10}\eta_0$	ΔH_η (kJ mole^{-1})	Correlation coefficient
10	412—453	—7.139	77.0 ± 2.9	0.9973
12	396—447	—7.970	84.7 ± 2.4	0.9994
14	400—449	—8.460	88.1 ± 1.5	0.9994
16	394—448	—8.805	91.3 ± 4.1	0.9959
18	402—447	—9.439	96.2 ± 1.3	0.9998

carboxylate/lead oxide is somewhat smaller than in the pure lead carboxylate case, where aggregates of between 3 and 5 molecules are supposed to be responsible for viscous flow [2]. This result appears to conflict with the observed increase in activation energy on adding lead oxide (Table 4). However, the activation energy depends on both the unit of flow and the structure of the bulk liquid and the suggested change in structure to long cylindrical micelles may cause an increase in viscous drag, so increasing the activation energy for viscous flow. In addition, there may also be contributions from undissociated PbO molecules. If the unit of flow was a single soap molecule, it would be expected that there would be an increase in activation energy of about 1.6 kJ mole^{-1} (C atom)$^{-1}$. The fact that the observed increase is somewhat higher, but is lower than in the pure soap, suggests that the unit of flow may consist of small aggregates sheared off of the fairly bound long cylindrical micelles. A similar example of the unit of flow being smaller than the main structural unit in a liquid is observed with carboxylic acids, which consist of hydrogen bonded dimers, but whose mobile units are suggested to be the simple acid monomers, with the hydrogen bond being broken during viscous flow [2,12].

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