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ELECTRICAL CONDUCTANCE, DENSITY AND VISCOSITY OF THE SYSTEM LEAD(II) DODECANOATE/DODECANOIC ACID

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ABSTRACT

Data are presented for the densities, electrical conductances and viscosities of the molten system lead(II) dodecanoate/dodecanoic acid. Over the concentration range studied, molar volumes are linear functions of concentration at any selected temperature, although there are indications of deviations from ideal behaviour over the complete composition range from pure soap to pure acid. The molar volumes of the system lead(II) carboxylate/carboxylic acid for the even chain acids C_{10} to C_{18} are linear functions of chain length. As with other lead(II) dodecanoate systems, the Arrhenius plots for the conductance of the mixtures show curvature.

Activation energies for conductance in the low temperature region show a steady decrease with increasing mole fraction of the acid. It is suggested that this arises largely from the increased mobility of the Pb^{2+} ion. The activation energies for viscous flow in the mixtures are similar to that of pure lead dodecanoate. Studies of the viscosities of the system lead(II) carboxylate/carboxylic acid as a function of temperature for the even chain length acids C_{10} to C_{18} suggest a slight decrease in size of the unit of viscous flow when acid is present.

INTRODUCTION

In a previous paper [1] data were presented on the thermal behaviour of the system lead(II) dodecanoate/dodecanoic acid. The most significant feature of the results is that the total entropy change accompanying the transformation crystal → liquid phase is the same for all compositions of the mixture, which suggests that the addition of dodecanoic acid to lead dodecanoate does not affect the degree of order of the hydrocarbon chains, either in the solid or liquid phases.

In addition, information has been obtained on the thermal behaviour of the system lead(II) dodecanoate/lead acetate [2] and lead(II) dodecanoate/lead(II) oxide [3], and on the electrical conductance, density, and viscosity of the molten system lead(II) dodecanoate/lead acetate [4]. Addition of lead acetate to lead dodecanoate again appears to have no effect on the state of aggregation of the soap in the liquid phase [2]. In contrast, it is suggested that addition of lead oxide to lead dodecanoate changes the structure of the

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liquid phase from small, essentially spherical micelles in the pure lead dodecanoate to long, cylindrical micelles in the mixture [3].

Viscosity studies on lead dodecanoate/lead acetate indicate that the unit of flow is the same as in the pure soap, while conductivity measurements suggest that Pb^{2+} is the major charge carrier in the pure soap [4].

In an attempt to investigate further the effect of dodecanoic acid upon the physical properties of lead(II) dodecanoate, the densities, electrical conductances, and viscosities of some molten lead(II) dodecanoate/dodecanoic acid mixtures have been measured.

EXPERIMENTAL

Materials

Dodecanoic acid was obtained from B.D.H. with stated minimum purity of 99% by GLC assay. This was recrystallised from ethanol before use. The preparation of lead(II) dodecanoate has been described elsewhere [5].

Mixtures were prepared by weighing the appropriate amounts of the components into a quick-fit conical flask. The flask was then evacuated and the mixture melted on a hot-plate. The acid dissolved readily in lead dodecanoate.

Physical measurements

The procedures for the measurement of density, viscosity, and electrical conductance were the same as previously described [5,6]. Attempts to determine the conductance of pure dodecanoic acid were not successful, as any conductance was too small to be measured by our apparatus.

RESULTS AND DISCUSSION

Density and molar volume

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

$$\rho_T = \rho_0 - aT \tag{1}$$

and molar volumes to

$$V_m(T) = V_0 + bT \tag{2}$$

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

At any given temperature, the densities of the mixtures do not vary by more than 2%. On the other hand, there is a steady decrease in molar volume with increasing mole fraction of dodecanoic acid. Over the concentration

TABLE 1

Densities and molar volumes of lead(II) dodecanoate/dodecanoic acid mixtures

$X_{CH_3(CH_2)_{10}CO_2H}$	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	Standard error (%)	$a \times 10^3$	Error in a (%)	V_0	Standard 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	427–450	1.595	0.06	0.72	6.9	351.0	0.11	0.265	6.8
0.06	398–442	1.654	0.70	0.90	3.3	320.0	0.15	0.320	3.5
0.10	407–448	1.692	0.77	1.00	3.0	295.2	0.15	0.354	3.0
0.14	426–450	1.736	0.28	1.13	1.8	265.7	0.08	0.403	2.3
0.18	406–447	1.786	0.85	1.22	2.5	247.1	0.22	0.406	3.0
0.22	425–453	1.662	0.45	0.97	3.1	273.1	0.09	0.329	2.8
1.00	334–411	1.005	0.19	0.40	0.1	193.0	0.29	0.110	7.4

TABLE 2

Densities and molar volumes of even chain length lead(II) carboxylate/carboxylic acid (0.1 mole fraction) systems

Carbon chain length	Temp. range (K)	$\rho = \rho_0 - aT^3$ (10^3 kg m^{-3})				$V_m = V_0 + bT$ (10^{-6} m^3 mole^{-1})			
		ρ_0	Standard error (%)	$a \times 10^3$	Error in a (%)	V_0	Standard error (%)	b	Error in b (%)
10	415–471	1.677	0.11	0.75	4.0	286.2	0.20	0.215	4.6
12	407–448	1.692	0.77	1.00	3.0	295.2	0.15	0.354	3.0
14	417–470	1.509	0.08	0.71	2.8	381.3	0.15	0.310	3.2
16	425–471	1.446	0.08	0.62	4.8	437.8	0.14	0.308	4.5
18	411–456	1.310	0.02	0.44	2.3	537.0	0.11	0.254	3.9

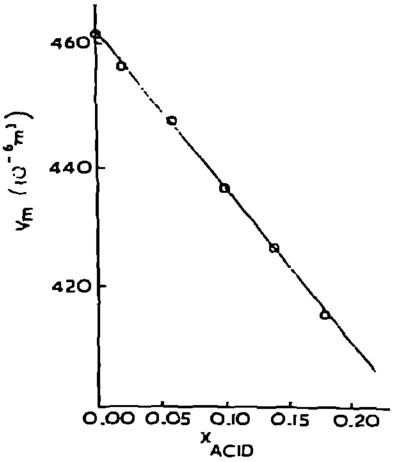
range studied, plots of V_m vs. mole fraction at any selected temperature are linear (Fig. 1), indicating little excess volume of mixing within the accuracy of these measurements. This is similar to the behaviour observed with the system lead dodecanoate/lead acetate [4]. Pure dodecanoic acid was found to have a molar volume of 237.0 m^3 $mole^{-1}$ at 400 K, which is somewhat higher than the value obtained by extrapolation of Fig. 1 (192 m^3 $mole^{-1}$), suggesting that there is slight deviation from ideal behaviour.

In addition, the densities and molar volumes were determined for the system lead(II) carboxylate/carboxylic acid for the even chain length acids C_{10} to C_{18} at a constant mole fraction of the acids. These were fitted by least squares method to eqns. (1) and (2), and the parameters for the fits are presented in Table 2.

For comparison with previous studies [5,7] the molar volumes at 450 K were fitted by least squares method as a function of the total carbon chain length of the acid, n, by

$$V_m(450) = (56.17 + 32.93n) \times 10^{-6}\ m^3\ mole^{-1} \qquad (3)$$

The correlation coefficient for the fit was 0.9991. It can be noted that the total number of carbon atoms per molecule is $2n$ [7]. The increase in volume



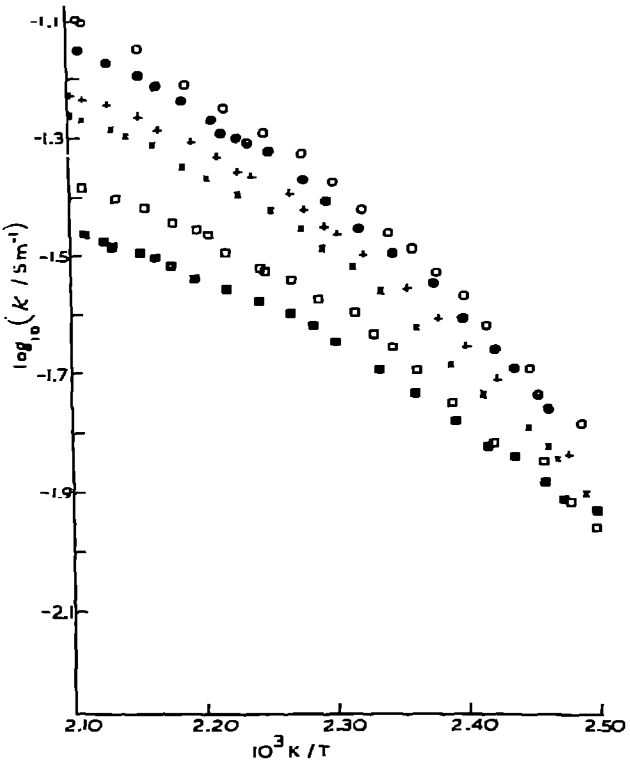


Fig. 1. Plot of molar volume at 400 K as a function of mole fraction of dodecanoic acid.

Fig. 2. Semilogarithmic plot of specific conductivity vs. inverse temperature for lead(II) dodecanoate/dodecanoic acid mixtures: (○) pure lead dodecanoate; (●) X_{acid} = 0.05; (+) X_{acid} = 0.10; (×) X_{acid} = 0.14; (□) X_{acid} = 0.18; (■) X_{acid} = 0.22.

per methylene group is thus 16.5×10^{-6} m^3 mole^{-1}. This is somewhat smaller than that observed with pure lead(II) carboxylates (18.3×10^{-6} m^3 mole^{-1}) [5].

Electrical conductance

Electrical conductances were determined for the molten system lead(II) dodecanoate/dodecanoic acid for acid mole fractions between 0 and 0.22. Pure dodecanoic acid was found to be non-conducting within the capabilities of our experimental method. Values of the logarithm of the specific conductance for any particular mole fraction were plotted against the reciprocal of the absolute temperature (Fig. 2). As with other lead dodecanoate systems [4,5], curvature was observed at high temperatures.This behaviour has been interpreted [5] in terms of a simple theory in which the carboxylate dissociates according to

$$PbA_2 \rightleftharpoons Pb^{2+} + 2A^- \qquad (4)$$

The major charge carrier is assumed to be Pb^{2+}, which moves by a simple activated process. The following expressions have been obtained to describe this behaviour [5]

$$\log \kappa = \log Q - \frac{\Delta H_\kappa^\ddagger + \Delta H/3}{2.303\,RT} \qquad (5)$$

and

$$\log Q = \log(NeA/2V_\mathrm{m}) + \frac{1}{2.303R}(\Delta S_\kappa^\ddagger + \Delta S/3) \qquad (6)$$

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 $\log \kappa$ vs. $1/T$ should be linear, with slopes $(\Delta H_\kappa^\ddagger + \Delta H/3)/2.303$. In Table 3, values of $(\Delta H_\kappa^\ddagger + \Delta H/3)$ are given as calculated by least squares method from these plots.

In contrast to the lead dodecanoate/lead acetate system [4] where $(\Delta H_\kappa^\ddagger + \Delta H/3)$ is independent of lead acetate concentration up to 0.12 mole fraction, the enthalpy term in the lead dodecanoate/dodecanoic acid case is seen to show a steady decrease with increasing mole fraction of the acid. It seems unlikely that addition of acid will significantly affect the enthalpy term for the dissociation reaction, such that the main effect should be on $\Delta H_\kappa^\ddagger$. Two different effects are possible on increasing the acid concentration: it may either increase the mobility of Pb^{2+} ions, or it may affect the ionic atmosphere or free volume around the cation. In studies on molten alkali metal carboxylates, Ubbelohde and co-workers [8] have shown that specific conductivity is considerably reduced in salts with large anions, and they have suggested that the free volume around each cation is probably playing a critical role. Results of DTA studies [1] indicate that addition of dodecanoic acid to lead dodecanoate does not affect the degree of order of the hydrocarbon chains, although viscosity studies suggest that the unit of flow in the

TABLE 3

Values of intercept and low temperature limiting scopes for conductance

$X_{CH_3(CH_2)_{10}CO_2H}$	log Q	$(\Delta H^{\ddagger}_{\kappa} + \Delta H/3)$ (kJ $mole^{-1}$)
0.00	4.453	54 ± 2
0.05	4.212	46 ± 2
0.10	3.936	45 ± 1
0.14	3.292	40 ± 2
0.18	2.105	31 ± 3
0.22	1.984	30 ± 1

presence of acid may be somewhat smaller than with the pure soap. It is not clear whether such arguments can be extended to the case of the degree of order round the Pb^{2+} ion in the presence of an electric field. However, results of the present study indicate that the actual viscosity at a particular temperature decreases with increasing mole fraction of acid, and, while extrapolation of these results for macroscopic flow to the microscopic case of Pb^{2+} ion in an electric field is not without risk, it certainly seems reasonable that the decrease in $\Delta H^{\ddagger}_{\kappa}$ with increasing mole fraction of acid stems in large part from an increase in mobility of the Pb^{2+} ion.

It is possible to actually calculate the Pb^{2+} ion concentration in the different mixtures at any temperature by a method described previously for the pure *n*-alkanoates [5]. However, this requires data in the high temperature region where the Arrhenius plots tend to a second linear portion with slope corresponding to $\Delta H^{\ddagger}_{\kappa}$, and, unfortunately, the mixtures started to decompose before these temperatures were reached. Hence, it was not possible to compare the Pb^{2+} concentrations in the different mixtures.

Viscosity

The viscosity data were fitted by least squares method to the equation

$$\log \eta = \log \eta_0 + \frac{\Delta H^{\ddagger}_{\eta}}{2.303RT} \qquad (7)$$

where η is the viscosity in Pa s, and $\Delta H^{\ddagger}_{\eta}$ is the activation energy for viscous flow. The results for these fits are shown in Table 4, where log η_0, $\Delta H^{\ddagger}_{\eta}$, the probable error in $\Delta H^{\ddagger}_{\eta}$ and the correlation coefficients are listed. Data are also included for the pure soap and pure acid. As has been noted previously [4], the value of $\Delta H^{\ddagger}_{\eta}$ obtained for pure lead dodecanoate is significantly higher than that of 54 kJ $mole^{-1}$ reported by Ekpe and Sime [6]. However, the present value is probably more reliable, and has been confirmed by other workers in this laboratory [4,9].

It can be seen from Table 4 that the activation energies for viscous flow in the mixtures and in pure lead dodecanoate are the same within the limits of experimental error. This is similar to the behaviour observed in the lead dodecanoate/lead acetate system [4], suggesting similar units of flow. In

TABLE 4

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

$X_{CH_3(CH_2)_{10}CO_2H}$	Temp. range (K)	log η_0	Standard error in log η_0	$\Delta H^{\ddagger}_{\eta}$ (kJ mole^{-1})	Error in $\Delta H^{\ddagger}_{\eta}$	Corr. coeff.
0.00	406—460	−6.897	0.028	70.4	4.4	0.9974
0.02	413—453	−7.663	0.056	71.2	6.1	0.9897
0.06	416—456	−7.256	0.023	75.4	2.4	0.9982
0.10	414—452	−6.821	0.033	76.0	3.8	0.9951
0.14	411—446	−5.211	0.030	71.8	3.8	0.9927
0.18	406—445	−7.245	0.058	78.0	6.5	0.9864
0.22	411—443	−6.981	0.029	74.5	6.6	0.9953
1.00	358—430	−2.115	0.013	19.5	0.6	0.9979

pure dodecanoic acid, however, the activation energy for viscous flow is very much smaller, indicating a smaller unit of flow in that case, as has been noted with various *n*-alkanoic acids [10].

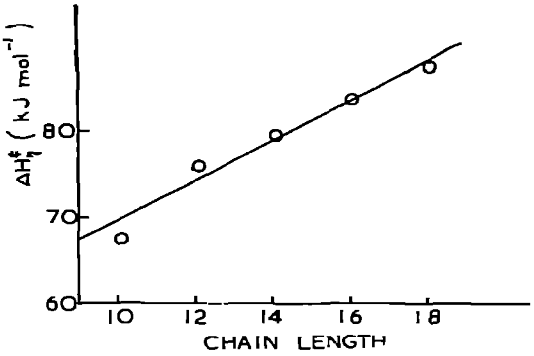
Ekpe and Sime [6] have shown that the species responsible for viscous flow in lead dodecanoate are the charged ions PbA^+ and A^-. Their work also revealed that the unit of flow in the pure soap contains approximately 3—5 molecules. To gain some insight into the unit of flow in the present case, we have investigated the viscosities of the system lead(II) carboxylate/carboxylic acid (0.1 mole fraction) as a function of temperature for the even chain acids C_{10} to C_{18}. Data, obtained from least squares analysis using eqn. (7), are given in Table 5.

As has been previously shown [6], information on the unit of flow can be obtained from the rate of increase of $\Delta H^{\ddagger}_{\eta}$ with carbon chain length. A plot of $\Delta H^{\ddagger}_{\eta}$ vs. chain length for the system lead carboxylate/carboxylic acid is linear, with slope 2.4 kJ mole^{-1} C atom^{-1} (Fig. 3). This is markedly lower than the slopes of 4.2 and 4.0 kJ mole^{-1} C atom^{-1} obtained with the systems lead alkanoate/lead acetate (0.1 mole fraction) [4], and pure lead *n*-alkanoate [6], respectively. This probably reflects a slightly smaller unit of flow in

TABLE 5

Least squares parameters for viscous flow in the systems lead(II) carboxylate/(0.1 mole fraction) carboxylic acid

Carbon chain length	Temp. range (K)	log η_0	Standard error in log η_0	$\Delta H^{\ddagger}_{\eta}$ (kJ mole^{-1})	Error in $\Delta H^{\ddagger}_{\eta}$	Corr. coeff.
10	410—446	−6.320	0.020	67.4	2.1	0.9981
12	414—452	−6.821	0.033	76.0	3.8	0.9951
14	402—446	−7.083	0.022	79.7	1.7	0.9988
16	403—443	−7.881	0.027	83.9	2.7	0.9985
18	402—438	−8.422	0.029	87.6	3.1	0.9975



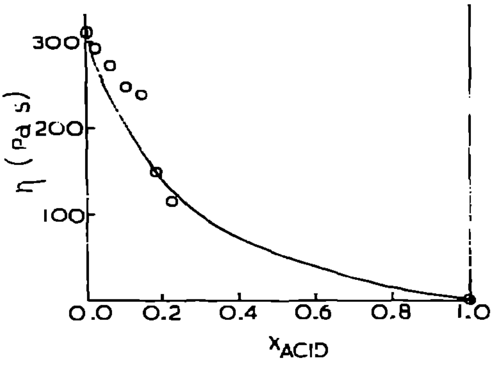


Fig. 3. Plot of $\Delta H^{\ddagger}_{\eta}$ vs. chain length for the systems lead(II) carboxylate/carboxylic acid (0.1 mole fraction).

Fig. 4. Plot of viscosity at 430 K vs. acid mole fraction for the system lead(II) dodecanoate/dodecanoic acid.

the lead carboxylate/carboxylic acid system than in the pure lead carboxylate case, where the unit of flow is suggested to be an aggregate of between 3 and 5 molecules [6]. Thus, addition of *n*-alkanoic acid probably causes a slight decrease in the size of the unit of flow. It can be noted that with the pure *n*-alkanoic acids [10] the slope of the corresponding plot is 0.8 kJ mole^{-1} C atom^{-1}, suggesting that in this case the mobile units are the simple acid monomers.

The actual viscosity at any particular temperature is observed to decrease with increase in the acid concentration. Values of viscosities of the mixtures of lead dodecanoate and dodecanoic acid at 430 K are given in Table 6.

The Laidler—Eyring theory of viscosity [11] gives the viscosity as

$$\eta = (h/v) \exp(-\Delta S^{\ddagger}_{\eta}/R) \exp(\Delta H^{\ddagger}_{\eta}/RT) \qquad (8)$$

where *h* is Planck's constant and *v* is the volume occupied by the unit of flow. Thus, values of $\Delta S^{\ddagger}_{\eta}$ can also be evaluated. The values calculated for $\Delta S^{\ddagger}_{\eta}$ at 430 K are also reported in Table 6. It can be seen that there is a steady increase in $\Delta S^{\ddagger}_{\eta}$ with increasing mole fraction of the acid. Thus, the

TABLE 6

Viscosities and $\Delta S^{\ddagger}_{\eta}$ values for the system lead dodecanoate/dodecanoic acid at 430 K

$x_{CH_2(CH_2)_{10}CO_2H}$	Viscosity (Pa s)	$\Delta S^{\ddagger}_{\eta}$ (J K^{-1} mole^{-1})
0.00	310.6	8.9
0.02	292.0	10.5
0.06	273.0	11.7
0.10	249.6	13.6
0.14	240.7	15.0
0.18	150.2	18.5
0.22	115.8	20.6
1.00	1.78	

decrease in viscosity of the lead dodecanoate/dodecanoic acid mixture with increasing mole fraction of the acid arises from the increasing value of the activation entropy.

From the viscosities of the pure soap and pure dodecanoic acid at 430 K, it can be seen that the viscosities of the lead dodecanoate/dodecanoic acid systems are lower than predicted on the basis of simple additivity of the two components (Fig. 4). This probably indicates that addition of acid modifies the unit of flow of the lead dodecanoate, rather than having additive contributions to the flow from separate lead dodecanoate, and dodecanoic acid units. Since the viscosity is less than predicted, this supports the idea, gained from the studies of $\Delta H_\eta^\ddagger$ as a function of chain length, that in the lead dodecanoate/dodecanoic acid system the unit of flow is smaller than in the pure soap. Probably, on increasing the acid concentration there is a continuous decrease in the size of the unit of flow from about 3—5 molecules in the pure soap to 1 molecule in the pure acid. It should be noted that $\Delta H_\eta^\ddagger$ is relatively unaffected by addition of dodecanoic acid up to 0.22 mole fraction (Table 4). However, $\Delta H_\eta^\ddagger$ may be expected to be a composite term involving contributions from both the flow, and the dissociation/association equilibria of the lead dodecanoate/dodecanoic acid system to give the unit of flow.

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