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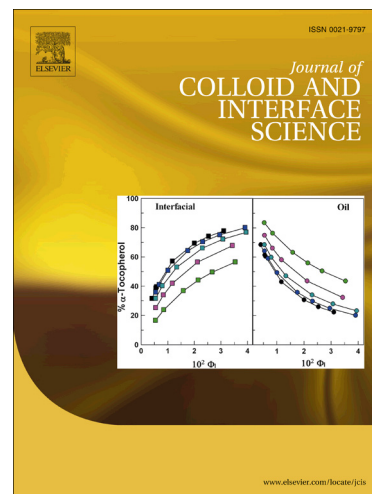Rui F.P. Pereira, Artur J.M. Valente, Hugh D. Burrows

The interaction of long chain sodium carboxylates and sodium dodecylsulfate with lead(II) ions in aqueous solutions

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ABSTRACT

The interaction of sodium octanoate, decanoate or dodecanoate with lead(II) has been studied in aqueous solutions using potentiometry, electrical conductivity, turbidity and ICP-OES measurements. These show an alkyl chain length dependence on the behaviour. At the lead(II) concentration used (1.0 mM), relatively strong interactions are observed with the decanoate and dodecanaote, leading to formation of the lead carboxylates (soaps) as insoluble complexes. All techniques show 1:2 (metal:carboxylate) stoichiometry corresponding to charge neutralization. With sodium octanoate and lead(II), a rather weaker interaction is seen, and complexation is only observed at metal:carboxylate ratios > 0.5. However, in contrast to our previous work on octanoate and calcium(II) in aqueous solutions [1], precipitation does occur at higher concentrations. This difference between the behaviour of the metal ions is probably due to the more covalent nature of the bonds of the carboxylate with Pb^{2+} than with Ca^{2+}. Association constants of the complexes have been determined from potentiometric measurements and are consistent with data on solubility products. A comparison is made of the effect of surfactant head group on the interactions with lead(II) using two surfactants with the same chain length: dodecanoate and dodecylsulfate. Differences in their interactions with this metal ion in aqueous solutions are interpreted in terms of greater covalency of the bond between the metal and the carboxylate than with the sulfate group.

1. INTRODUCTION

The interaction of metal ions with anionic surfactants in aqueous solutions is of both theoretical [2-6] and practical [7, 8] importance. Over the last decades, there have been a considerable number of scientific reports regarding the interaction between mono- or higher valent ions and ionic surfactants, with particular attention to the phase separation which occurs in these systems [9-11]. Precipitation of surfactants, as metal salts, can be desirable in some applications (e.g., catalysis [12] and wastewater treatment [13, 14]) but can be also detrimental in others, including detergency, and enhanced oil recovery, due to loss of surfactant activity [15].

Although these systems have been widely studied and reviewed [16-20], most of the publications are relatively old. In addition, there is not much information about the phase separation mechanism, or the structures of the solutions, which complicates the development of models of such systems.

The study of lead(II)-containing solutions is of particular interest due to its industrial, environmental and biological impact. Lead salts are toxic, and human exposure can result in the damage of the central nervous system, kidney, liver and reproductive system, basic cellular processes and brain functions. The toxic symptoms are anaemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damage [21], and there is interest in developing new methods for removing this metal from the environment. This is a global problem, and low cost routes, such as precipitation, are particularly important for remediation. The systems discussed in this article may be relevant to this problem.

In general, unbuffered aqueous solutions of soluble lead (II) salts, such as the nitrate, are slightly acidic [22]. The hydrolysis of Pb^{2+} may be written as

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$$xPb^{2+} + 2yH_2O \underset{\longleftarrow}{\overset{K_{h,i}}{\longrightarrow}} Pb_x(OH)_y^{(2x-y)+} + yH_3O^+ \tag{1}$$
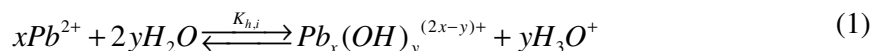
where $K_{h,i}$ is the equilibrium constant for the ith hydrolysis, with the $K_{h,1}$ value equal to 6.3×10^{-8} (in a solution with ionic strength zero), and the most prominent hydrolysed species are $Pb_4(OH)_4^{4+}$ and $Pb_6(OH)_8^{4+}$ [23].

The long chain carboxylates of divalent metal ions (metal soaps) are an important group of compounds, which find applications as emulsifiers, paint driers, grease thickeners, dispersant agents, etc [24-27]. They are also used in solvent extraction procedures [28], and are starting to find interesting material applications in metal–organic mesogen systems [29-31]. We have become particularly interested in the interaction of lead(II) with alkanoates. This is relevant to corrosion inhibition [32-34], but also plays an important role in areas as diverse as studies on the lipid organization in human hair [35], and art conservation, where lead carboxylates have been shown to slowly form through the reaction between lead pigments and drying oils in historic paintings and other art works [36, 37]. In addition, long chain lead carboxylates show a rich, and chain length dependent thermotropic phase behavior [38-42], and an understanding of the driving forces for the precipitation of these systems from solution is likely to be important for interpreting phase stability.

In this work we focus on the interaction in aqueous solutions at 25 ℃ between lead(II) ions and carboxylates with three different alkyl chain lengths (octanoate, decanoate and dodecanoate). Our aim is to obtain a detailed insight into the mechanism of their interaction by using conductimetric, potentiometric and turbidity techniques. This complements our previous work on the precipitation of carboxylates by the more ionic calcium(II) ion [1]. The effects of metal ion hydration, covalent (hard/soft) character and of surfactant alkyl chain length on the interaction process will be

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discussed. In addition, for the C_{12} (dodecanoate) chain, the effect of head group acidity will be considered by comparison with the behaviour of the homologous surfactant: the dodecylsulfate.

2. MATERIALS AND METHODS

2.1 Reagents and Sample preparation

Lead nitrate tetrahydrate (98 %) was purchased from Riedel-de Haën. Sodium octanoate (99 %), sodium decanoate (98 %), sodium dodecanoate (99-100 %) were purchased from Sigma. For the sake of simplicity these carboxylate surfactants ($C_nH_{2n+1}COONa$) will be designated as C_7COONa, C_9COONa and $C_{11}COONa$, respectively. All the experiments with sodium carboxylates have been carried out at concentrations below their critical micelle concentration: 340 mM, 94 mM and 24 mM, respectively [43]. Sodium dodecylsulfate ($\geq$ 98 %) was purchased from Sigma. These reagents were used as received, and all solutions were prepared using Millipore-Q water. No control was made on the pH, which was the natural value for each solution.

2.2 Conductance measurements

Electrical conductance measurements were carried out with a Wayne-Kerr model 4265 automatic LCR meter at 1 kHz, through recording of solution electrical resistances, measured by a conductivity cell with a constant of 0.1178 cm^{-1} (uncertainty 0.02 %) [44]. The cell constant was determined from electrical resistance measurements with KCl (reagent grade, recrystallized, and dried) using the procedure and data of Barthel et al [45]. Measurements were made at 25.00 ($\pm$0.02) ºC in a Thermo Scientific Phoenix II B5 thermostat bath. Solutions were always prepared

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immediately before the experiments. In a typical experiment, 20 mL of lead(II) solution (1 mM) was introduced in the conductivity cell; aliquots of the surfactant solution were then added at 4 minute intervals from a Gilson Pipetman micropipette. The specific conductance of the solution was measured after each addition and corresponds to the average of three ionic conductances (uncertainty less than 0.2%), determined using house-made software. The specific electrical conductance of the solutions, κ, is calculated from the experimental specific conductance, κ_{exp}, and corrected for the specific conductance of water, κ_0: $\kappa = \kappa_{exp} - \kappa_0$.

2.3 Potentiometric Measurements

Potentiometric measurements were carried out with a pH Radiometer PHM 240. The ion concentration present in solution was measured using a lead selective electrode (WTW, Pb 500) and an Ag/AgCl reference electrode (Ingold). Calibration was carried out before each set of measurements using freshly prepared lead(II) standard solutions. No ionic strength adjustment buffer has been added; however, the electrode shows a Nernst-like response in the working concentration range.

The pH measurements were carried out with a combined glass/reference electrode (Ingold U457-K7); the pH was measured on fresh solutions, and the electrode was calibrated immediately before each experimental set of measurements using IUPAC-recommended pH 4 and 10 buffers.

In a typical experiment, aliquots of the surfactant solution were added, using a Gilson Pipetman micropipette, to 20 mL of metal divalent solution. The electrode potential was recorded after signal stabilisation, and all measurements were carried out at 25.00 (±0.02) ºC.

2.4 Turbidity Measurements

Turbidity changes were studied by measuring the change in solution transmittance at 550 nm with a Shimadzu UV-2450 spectrophotometer. In a typical experiment, different amounts of surfactant were added to a 1 mM lead nitrate solution, with continuous stirring for about five minutes before each measurement.

2.5 Inductively coupled plasma optical emission spectrometry (ICP-OES)

The ICP-OES analysis was performed using a Horiba Jobin-Yvon JY 2000 instrument. In a typical experiment, different amounts of sodium dodecylsulfate (from 0 to 20 mM) were added to a 1 mM metal ion solution. Twenty samples were prepared in the surfactant concentration range of interest. All samples were continuously stirred during six hours and then left to equilibrate for twelve hours (in the samples where flocculation occurs, a clear two phase separation can be observed). Aliquots for ICP-OES analysis were taken from the supernatant after samples were centrifuged at 3500 rpm during 15 minutes. Solutions were pipetted into a polypropylene tube and thoroughly mixed with an yttrium internal standard solution. They were then diluted with 2 % (w/w) aqueous nitric acid (HNO_3, purum p.a. from Fluka) solution to obtain the necessary final analytical metal concentration. Before each set of measurements, calibration was carried out using metal-containing standard solutions; an aqueous solution of 2 % (w/w) HNO_3 was used both as a blank and for rinsing the instrument after the highest concentration standard solution measurement. Each sample was injected in triplicate and the reported value corresponds to an average value of three measurements.

3. RESULTS AND DISCUSSION

The interaction between divalent (or higher valent) metal ions and alkanoates in aqueous solution generally leads to precipitation of metal carboxylates (metal soaps) [26, 46, 47]. These interactions depend on the nature of the metal ion, the surfactant chain length [48] and the bulk conditions (pH, temperature, etc). The effect of these factors in the case of lead(II) will be discussed in the following sections.

3.1 Interaction between sodium alkanoates and lead(II)

Fig. 1 shows the turbidity (as measured by optical transmittance) of a 1 mM Pb^{2+} aqueous solution in the presence of varying concentrations of sodium carboxylates (C_nCOONa, n = 7, 9 and 11). Upon adding C_9COONa or $C_{11}COONa$, the optical transmittance of solutions sharply decreases as a consequence of the formation of an insoluble complex. The minimum transmittance is reached for molar ratios (r = $[C_nCOONa]/[Pb^{2+}]$) *ca.* 2 (see Table 1). Similar values are observed by electrical conductivity (Fig. 2) and potentiometry (Fig. 3) with these two carboxylates. Electrical conductivity is particularly valuable for the assessment of the effect of ionic [49, 50] or non-ionic surfactants [51] on the structure of ionic solutions, because it follows modifications of complex electrolyte solutions, resulting from changes in the size and shape of moving particles and/or in the effective charge [52]. Since the specific conductance is a measure of the overall ion concentration in solution, the decrease in the specific conductance up to r equals 1.9 and 2.0, respectively, upon addition of sodium deca- and dodecanoates to 1 mM Pb^{2+} aqueous solutions indicates a strong (probably mainly electrostatic) interaction between lead(II) and the carboxylate. For molar ratios

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greater than 2, the specific conductance of Pb^{2+}:C_nCOONa solutions increases through the increase of the concentration of sodium carboxylates, since when all the Pb^{2+} has been "consumed" by the complexation it can no longer affect the electrical properties of the solutions. This behaviour has been confirmed by pH measurements, since the pH values of carboxylate/Pb^{2+} mixtures for C_7COONa, C_9COONa and $C_{11}COONa$ at high r (5.80, 6.47, 6.92, respectively) are in agreement with the pK_a values for the hydrolysis of these sodium salts (9.11, 9.1, and 8.7, respectively [53]).
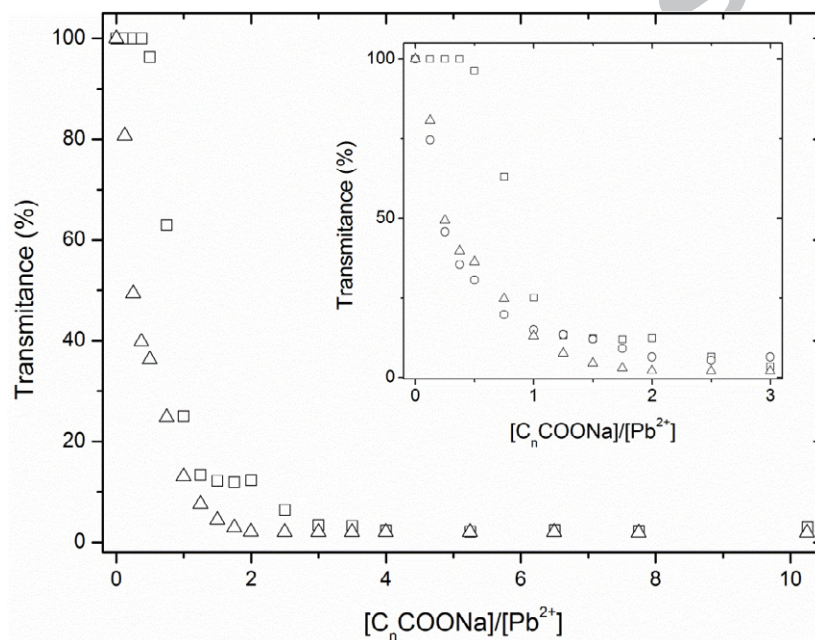
Fig. 1. Effect of the addition of sodium octanoate (□), sodium decanoate (○) and sodium dodecanoate (Δ) to 1 mM Pb^{2+} aqueous solution transmittance, at 25 ºC. Inset figure shows a zoom for low molar ratios.
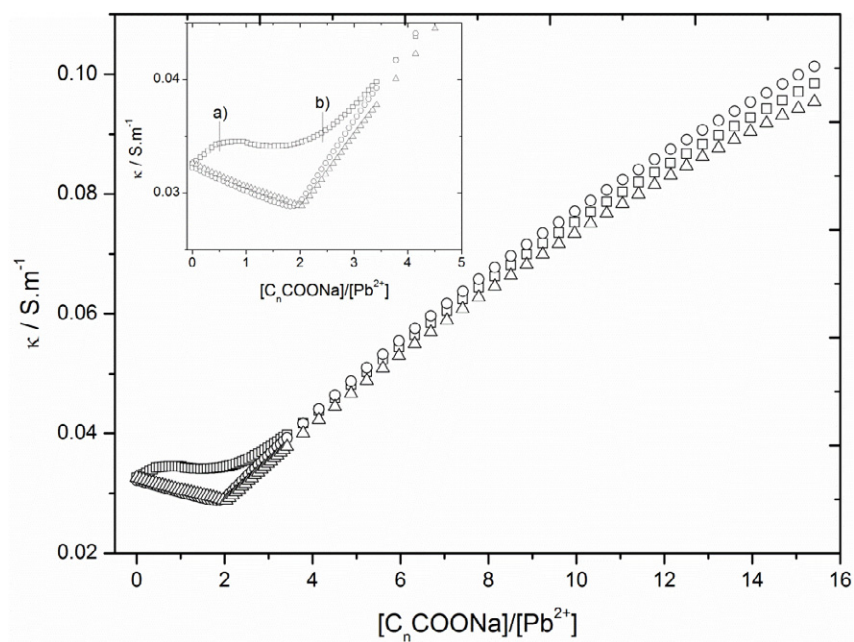
Fig. 2. Effect of Pb^{2+} 1 mM on the specific conductivity of sodium octanoate (□, n=7), sodium decanoate (○, n=9) and sodium dodecanoate (△ n=11) at 25 ºC.

Rather different behaviour is observed with the least hydrophobic alkanoate, the sodium octanoate, in the presence of lead(II) nitrate. The formation of insoluble complexes only takes place at *r* values above 0.48 (±0.03), as seen by turbidity, suggesting that a critical minimum concentration for interaction, the so-called critical aggregation concentration (*cac*), is required (see inset Fig. 1). This is likely to be related to the higher solubility of this complex in water [54]. Furthermore, the minimum optical transmittance is only reached at *r* = 2.3 (±0.1).

Similar results are observed by electrical conductance; that is, interaction between lead(II) and octanoate only occurs at *r* values greater than 0.48 (±0.02) (see Fig. 2 inset). These interactions continue up to *r* = 2.45 (±0.04), corresponding to the maximum interaction concentration, *mic* (b in Fig. 2). It should be noted that such behavior has also been observed for solutions of trivalent metal ions with sodium

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dodecylsulfate [55, 56]. As with the other carboxylates, at higher molar ratios, the electrical conductance of octanoate-lead(II) solutions increases upon increasing sodium octanoate concentration, since above the *mic*, sodium octanoate is in excess and the neutral lead(II) complexes do not contribute significantly to the overall ionic conductivity. As was previously observed with calcium(II),[1] these results show that although interactions between alkanoates and lead(II) are probably driven by electrostatic interactions through charge neutralization [26], and by changes in ion hydration, the effect of the alkyl chain length cannot be neglected. However, Pb^{2+} is a much softer Lewis acid than Ca^{2+} [57], and there is evidence from X-ray crystallography [58, 59], and ^{207}Pb NMR spectroscopy [40, 60] that the lead(II) carboxylate bond has appreciable covalent character. This justifies the observation of interactions between octanoate and lead(II), whereas no interaction is observed for the same carboxylate with the more ionic Ca^{2+} [1]. This is in agreement with stability data on the metal acetates, where the stability constant for the 1:1 complex is higher with Pb^{2+} than with Ca^{2+} [61].

Turbidity (as given by minimum optical transmittance) and electrical conductance also indicate an association stoichiometry of 2:1 between C_nCOO^- (n = 9 and 11) and lead(II). For the $C_7COO^-:Pb^{2+}$ association, the stoichiometry can be calculated as the difference between the *mic* and *cac*, which also gives a value of 2, consistent with charge neutralization. A summary of molar ratios at stoichiometric interaction, as obtained for the different techniques, is given in Table 1.
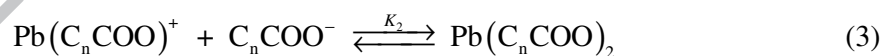
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Table 1. Interaction stoichiometries for the interaction between sodium carboxylates and lead(II), as seen by different techniques.

	$[C_nCOO^-]/[Pb^{2+}]$		
	Turbidity	Conductivity	Pb^{2+} selective electrode
Pb^{2+}/ C_7COONa	$1.80\pm0.10^*$	$2.06\pm0.04^*$	2.35 ± 0.05
Pb^{2+}/ C_9COONa	2.00	1.88 ± 0.01	1.90 ± 0.20
$Pb^{2+}/ C_{11}COONa$	2.00	2.03 ± 0.01	2.08 ± 0.05

* Value obtained by the difference between *mic* and *cac* – see text for further details;

3.2 Modeling the Association Process

From the above discussion, it is reasonable to treat the interaction between carboxylates and lead(II) in terms of formation of a 2:1 complex. Assuming that the association occurs in a two-step fashion, the following two equilibrium equations can be presented:

$$Pb^{2+} + C_nCOO^- \xrightleftharpoons{K_1} Pb(C_nCOO)^+ \qquad (2)$$

$$Pb(C_nCOO)^+ + C_nCOO^- \xrightleftharpoons{K_2} Pb(C_nCOO)_2 \qquad (3)$$

Equation (2) is written assuming that hydrolysed Pb^{2+} species can be neglected. This is reasonable since at the experimental pH of 1 mM aqueous solutions of lead(II) nitrate (around 5), the only significant species present in solution is non-hydrolysed Pb^{2+} [23, 62, 63].

For simplicity with these relatively dilute solutions we will use concentration instead of activities for the ions in solution. The stability of the complexes $Pb(C_nCOO)^+$, $Pb(C_nCOO)_2$ can then be described in terms of the association constants, K_1 and K_2:

$$K_1 = \frac{\left[Pb(C_nCOO)^+ \right]}{\left[Pb^{2+} \right]\left[C_nCOO^- \right]} \tag{4}$$

$$K_2 = \frac{\left[Pb(C_nCOO)_2 \right]}{\left[Pb(C_nCOO)^+ \right]\left[C_nCOO^- \right]} \tag{5}$$

Conservation of mass gives

$$\left[Pb^{2+} \right]_f = \left[Pb^{2+} \right]_T - \left[Pb(C_nCOO)^+ \right] - \left[Pb(C_nCOO)_2 \right] \tag{6}$$

$$\left[C_nCOO^- \right]_f = \left[C_nCOO^- \right]_T - \left[Pb(C_nCOO)^+ \right] - 2\times\left[Pb(C_nCOO)_2 \right] \tag{7}$$

where the subscripts f and T represent the free and total concentration of species. Combination of Eqs. (4)–(7) gives, after some algebraic manipulations, the following expressions:

$$2K_2K_1\left[Pb^{2+} \right]\left[C_nCOO^- \right]^2 + \left(1 + K_1\left[Pb^{2+} \right]\right)\left[C_nCOO^- \right] + \left[C_nCOO^- \right]_T = 0 \tag{8}$$

and

$$\left[Pb^{2+} \right] = \frac{\left[Pb^{2+} \right]_T}{1 + K_1\left[C_nCOO^- \right] + K_2K_1\left[C_nCOO^- \right]^2} \tag{9}$$

The $[C_nCOO^-]_f$ value is estimated through an analytical solution of the real solution of a second-degree equation, by using the using the quadratic formula. Association constants, K_1 and K_2 are obtained from a least-squares fit of Eqs. (8) and (9) to experimental free (non-complexed) concentration of Pb^{2+}. These values have been obtained by potentiometric methods, using a lead(II) ion selective electrode and results are shown in Fig. 3.
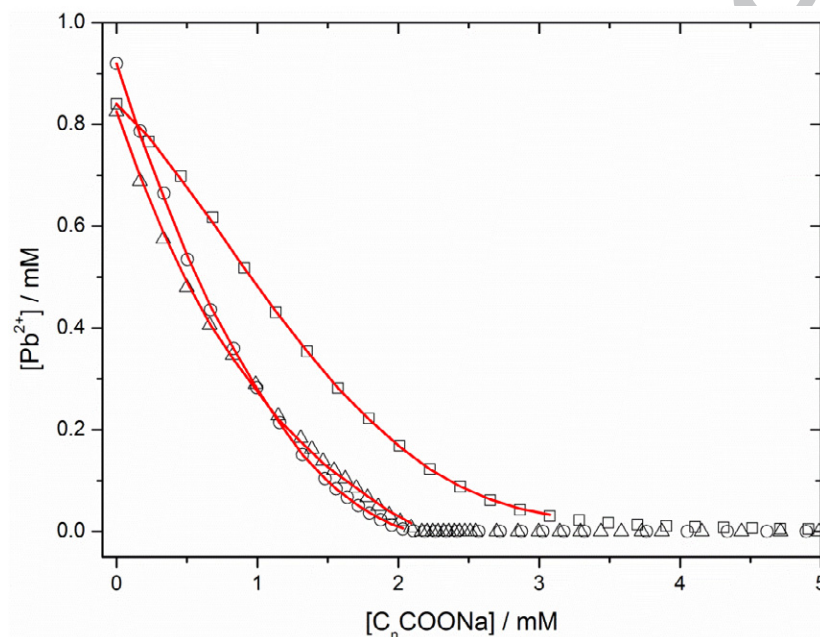
Fig. 3. Effect of sodium octanoate (□), decanoate (○) and dodecanoate (Δ) in the Pb^{2+} metal concentration of supernatant, at 25 ℃. Solid lines are obtained by fitting the experimental data to equations (8) and (9).

Before discussing the calculated association constants, a brief comment will be made concerning Fig. 3. In general, the data in this figure are in agreement with the behaviour seen by electrical conductivity and turbidity, and discussed in the previous sections. From the potentiometric data, two observations are worth noting:

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a) for all carboxylates, the association with Pb^{2+} leads to a complex with a 2:1 stoichiometry (see Table 1), which is consistent with charge neutralization [58, 64];

b) potentiometry seems to be more sensitive to study the detailed interaction of Pb^{2+} with C_7COO^- than the other techniques.

Table 2 presents the first and second association constants for C_nCOO^-:Pb^{2+} interactions, obtained by minimization of the root mean squared error (RMSE) between calculated and observed values of free lead concentration.

Table 2. Association constants for systems Pb^{2+}:C_nCOONa.

	K_1 / M^{-1}	K_2 / M^{-1}	K_1K_2 / M^{-2}	RMSE / M^*
Pb^{2+}:C_7COONa	15	5.0×10^5	7.4×10^6	4.1×10^{-6}
Pb^{2+}:C_9COONa	1.4×10^4	1.1×10^4	1.5×10^8	3.7×10^{-6}
Pb^{2+}:$C_{11}COONa$	5.2×10^3	3.4×10^3	1.8×10^7	6.9×10^{-6}

$^* \text{RMSE} = \left[\sum_{i=1}^{n} \left(y_i - \widehat{y}_i \right)^2 / n \right]^{1/2}$

In all cases, the low root mean squared error (RMSE), between the calculated and the observed values of free metal concentration, indicate that the proposed model fits the experimental data very well.

It is interesting that K_1 for Pb^{2+}:C_7COONa system is significantly lower than all other equilibrium constants, possibly reflecting the difficulty in the formation of the complex $Pb(C_7COO)^+$, which is consistent with the initial need for more surfactant to induce the formation of precipitate. It is also worth noting that the smallest global association constant ($K_0 = K_1K_2$) is found with this system, in agreement with a weaker interaction. Although direct comparison may be misleading, the trend of the global

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association constants is consistent with reported solubility products for lead(II) octanoate and decanoate [54]. K_1 and K_2 have the same order of magnitude in both the $Pb^{2+}:C_9COONa$ (10^4), and $Pb^{2+}:C_{11}COONa$ (10^3) systems, while the global association constant is an order of magnitude higher for decanoate system than for dodecanoate. This is somewhat surprising, but may reflect complications in determination of the constants arising from precipitation in the $Pb^{2+}:C_{11}COONa$ system, such that caution is needed with the absolute values of the association constants in this case.

### 3.3 Lead(II) interactions with SDS

We have previously shown that the interaction between divalent or trivalent metal ions and alkanoates in aqueous solutions is quite different from that observed with sodium dodecylsulfate (SDS) [1, 50]. With SDS, the maximum interaction concentration is not reached at charge neutralization, but at higher r values. This leads to formation of a lamellar solid [65], which redissolves in excess surfactant due to preferential hydrophobic interactions between the alkyl chains of the surfactant, destabilizing the aggregates of dodecylsulfate (DS^-)/metal ion. The fact that lead(II) alkanoates do not redissolve in the presence of excess alkanoate is in agreement with the lead(II)-carboxylate bond having some covalent character, and with the interaction also being driven by weak interactions between the alkyl chains of the carboxylates.

We have extended these studies to obtain further insight into the importance of head group/metal ion interactions by looking at the interaction between Pb^{2+} and SDS, and comparing the behaviour with the dodecanoate. These both have twelve carbon atom chains, but differ in having sulfate $(R\text{-}OSO_3^-)$ and carboxylate $(R\text{-}COO^-)$ head groups. This important difference will play a role on metal:surfactant interactions related to their proton (and Lewis) acid strengths: sodium dodecanoate is the conjugate

base salt of a weak acid while SDS is that of the corresponding strong acid [66]. These acid-base properties are used in common cation ion-exchange processes, where strongly acidic resins have sulfonic or sulfate acid groups while weakly acid ones use carboxylic acid [14]. In agreement with this, DFT calculations have shown that the carboxylate group acts as a stronger Lewis base than the sulfate one [67], consistent with carboxylate binding more strongly with metal ions. Turbidity, electrical conductometry and ICP data are presented below for Pb^{2+}:SDS system and compared with Pb^{2+}:$C_{11}COONa$.

3.3.1 Turbidity measurements

The effect of SDS on the optical transmittance of aqueous 1 mM Pb^{2+} solutions is shown in Fig. 4. Relevant differences are observed from systems with $C_{11}COONa$. Solution transmittance is only significantly affected for concentrations of SDS greater than 0.52 mM. However, upon increasing SDS concentration, a sharp decrease in transmittance is observed, due to continues formation of precipitate, which only stops when the surfactant concentration is above 2.5 mM, and then remains constant until about 7.5 mM SDS. The behaviour within this range is similar to that with dodecanoate, although with the SDS systems, the formation of precipitate does not occur immediately upon surfactant addition.
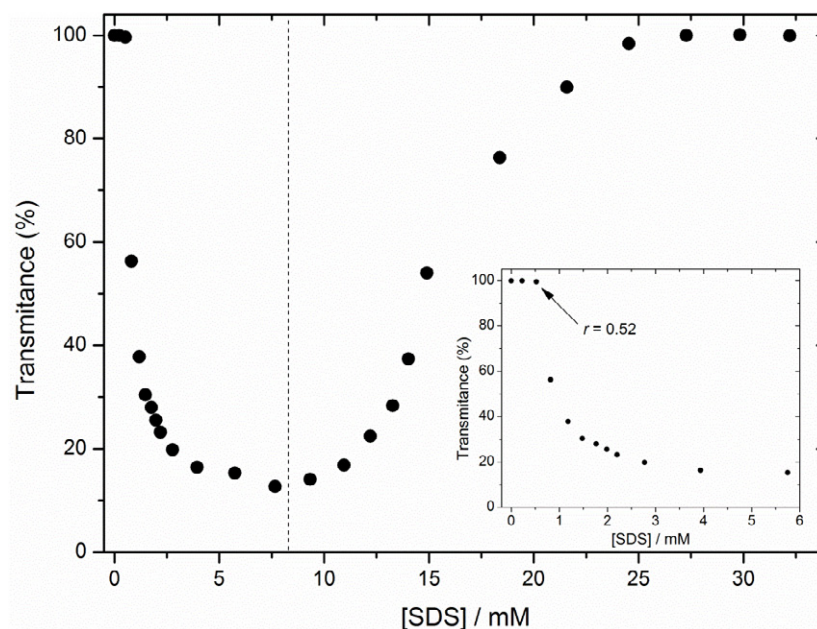
Fig. 4. Effect of the addition of sodium dodecylsulfate on 1 mM Pb^{2+} aqueous solution transmittance, at 25 ºC. Dashed line represents de *cmc* of SDS.

Upon increasing the SDS concentration above the *cmc*, redissolution of the precipitate is observed. For SDS concentrations greater than 27.3 mM, the mixed Pb^{2+}:SDS solutions are completely free of precipitate and the transmittance is 100%. With sodium dodecanoate or the other carboxylates, no redissolution of precipitate was observed with excess surfactant, indicating that the carboxylate micelles are unable to overcome the relatively strong lead(II)-carboxylate head group interactions. Thus, the redissolution of Pb^{2+}:DS^- aggregates possibly occurs due to preferential hydrophobic interactions between the alkyl chains (and possibly hydration interactions), overcoming the relatively weak lead(II) sulfate interactions in the aggregates.

This important difference between systems with SDS and sodium dodecanoate strongly supports the idea that the Pb^{2+}:$C_{11}COONa$ interaction is stronger than the Pb^{2+}:SDS one, probably because of a more covalent bond, and that hydrophobic

interactions between the SDS alkyl chains favour redissolution. This may be relevant in certain applications where it is necessary to redissolve lead(II) surfactant precipitates.

3.3.2 Electrical conductivity and hydrolysis effect

The electrical conductivity of Pb^{2+}:SDS solutions was measured and showed marked changes upon surfactant addition in the pre-micellar region, indicating alterations in the structure of solutions (Fig. 5).

In the absence of metal ions, the electrical conductivity of aqueous SDS solutions is characterized by linear behaviour with two different slopes, indicating the concentration at which a pseudophase transition takes place between unimers and micelles [49], with the transition points attributed to the surfactant critical micelle concentration (*cmc*).
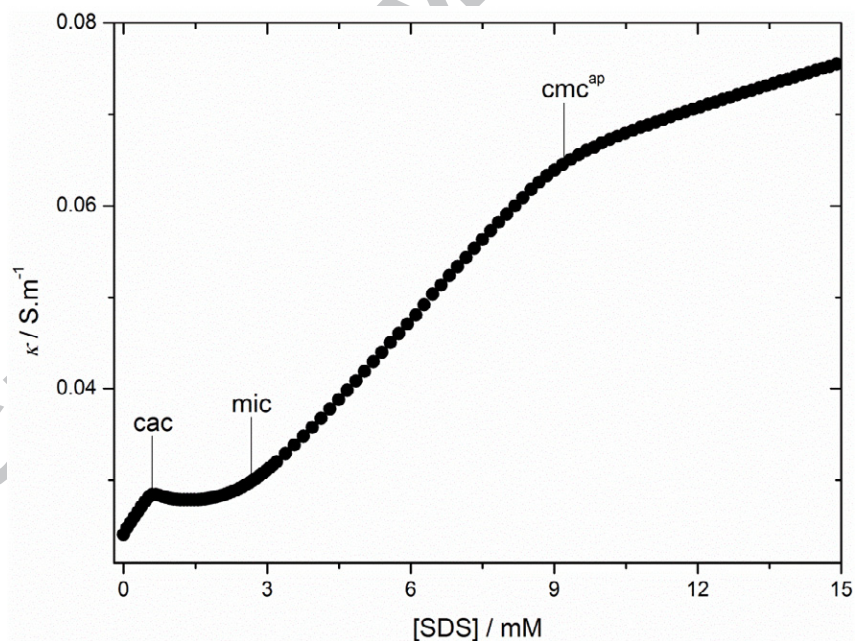
Fig. 5. Effect of lead nitrate 1 mM on the specific conductance of aqueous SDS solution at 25 ºC. Solid lines show transition points corresponding to critical aggregation concentration (*cac*), maximum interaction concentration (*mic*) and apparent critical micelle concentration (*cmc^{ap}*).

However, in the presence of Pb^{2+}, the addition of SDS leads to several modifications in the behaviour, and two further transition points can be detected (solid lines of Fig. 5). The first corresponds to the SDS concentration at which a strong interaction between Pb^{2+} and dodecylsulfate occurs; above this concentration, insoluble complexes are formed, as shown by optical transmittance measurements, and a slight decrease in electrical conductivity is observed upon addition of further surfactant until considerably higher concentrations. This solution electrical behaviour can be justified by the formation of larger charged species and/or by the charge collapse of ionic species. Both explanations are in agreement with the formation of aggregates involving Pb^{2+} and dodecylsulfate. The concentration at which aggregation takes place is called the critical aggregation concentration (*cac*) and has a value of 0.578 (±0.002) mM. This value is also in agreement with optical transmittance results ($r = 0.52$). Further evidence to support the onset of an interaction between Pb^{2+} and DS^- is found with the observation of a second transition point; at higher SDS concentrations, the shape of the plot of κ versus [SDS] is similar to that found in pure aqueous solutions, suggesting that no more Pb^{2+} is available to induce the formation of Pb^{2+}/DS^- aggregates. Consequently, SDS will be in excess, and will behave in a similar way to that in the absence of divalent salt. In other words, the SDS concentration at which all Pb^{2+} is totally consumed can be defined by the maximum interaction concentration (*mic*), which has a value of 2.64 (±0.03) mM.

The third transition point presented in Fig. 5 is related with the onset of SDS micellization. On first analysis, the micellization of SDS, in the presence of Pb^{2+}, appears to occur at SDS concentrations above the normal surfactant *cmc* (8.3 mM) [56], which cannot be justified thermodynamically. However, based on the previously

discussed interaction between Pb^{2+} and dodecylsulfate ions, this complexation will reduce the concentration of free surfactant ions and the critical micelle concentration of SDS, in the presence of divalent ions, cmc′, will be determined by: $cmc' = cmc^{ap} - mic$ = 6.56 (±0.06) mM. As can be seen, the presence of Pb^{2+} leads to a *cmc′* lower than the *cmc* of SDS [68]. The presented data cannot be compared with that for sodium dodecanoate, because, due to precipitation, it was not possible to study the effect of Pb^{2+} on its *cmc*.

The differences in the conductimetric behaviour of the Pb^{2+}:$C_{11}COONa$ and Pb^{2+}:SDS systems provides evidence that the mechanism of Pb^{2+}:surfactant interaction is also different. The fact that with $C_{11}COONa$, the interaction with Pb^{2+} occurs immediately after the addition of surfactant and, in the case of SDS, this only occurs after the *cac*, shows that the binding capacity of dodecanoate is higher than that of SDS, in agreement with the presence of a more covalent bond.

It worth noting that the conductimetric profile shown by Pb^{2+}:SDS is very similar to those observed with trivalent ions and SDS [56, 69]. However, in contrast to what is seen with other metal:SDS systems [49, 70], Pb^{2+}:DS^- interactions do not lead to any significant alterations in pH. From Fig. 6, it is possible to see that that upon increasing SDS concentration, pH increases continuously with no perceptible breaks. Furthermore, it is interesting to note that in the Pb^{2+}:DS^- interaction zone, the addition of SDS only slightly changes the pH from 5.05 (pH of 1 mM $Pb(NO)_3$ aqueous solution) to 5.39 (in *mic*).
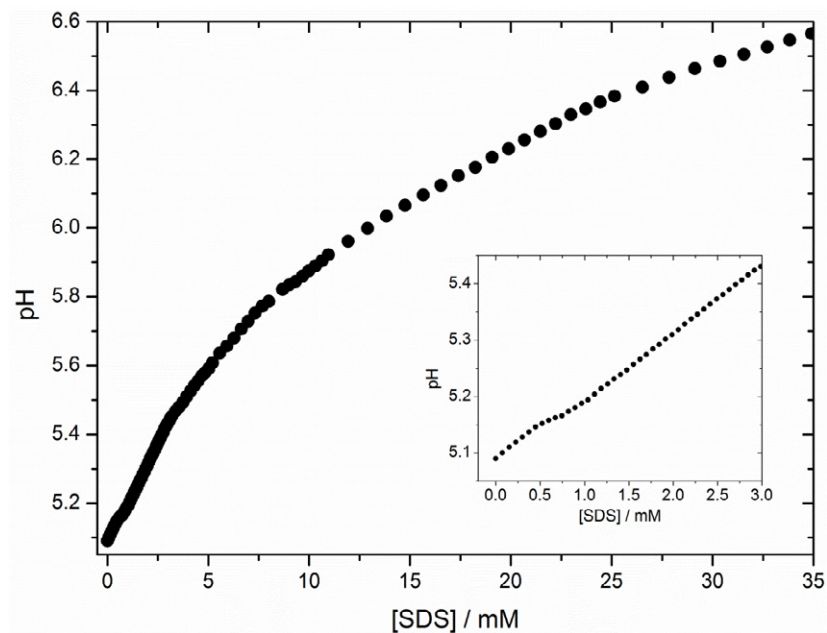
21

Fig. 6. Effect of the addition of sodium dodecylsulfate on the pH of 1 mM $Pb(NO_3)_2$ solutions, at 25 ºC.

3.3.3 ICP-OES measurements

As observed for system Pb^{2+}:$C_{11}COONa$, the addition of SDS to aqueous Pb^{2+} solution leads to the formation of a white precipitate, that consequently removes the metal ions from solution. The variation of Pb^{2+} concentration upon addition of SDS was followed by ICP-OES, and experimental results are shown in Fig. 7.

In agreement with data shown in Fig. 5 and 6, ICP-OES measurements show that upon increasing the SDS concentration, a decrease in Pb^{2+} concentration occurs in three different steps: a) an increase of SDS concentration up to around 0.25 mM leads to a decrease in the free Pb^{2+} of less than 3%; b) at higher SDS concentrations, a sharp decrease of free Pb^{2+} can be seen, with a Pb^{2+} removal of 90 % for a SDS concentration of 2.7 mM, slightly above charge neutralization; and c) at SDS concentrations greater than 6 mM, redissolution of the lead dodecylsulfate starts to be observed. This scenario

clearly suggests a strongly cooperative 1:2 association, with the first association constant significantly lower than the second one. To obtain a more quantitative insight into the Pb^{2+}:DS^- interaction, association constants were computed by using an analogous procedure to that described in section 3.3. The following association constants were computed by fitting experimental data to eqs. (8) and (9): $K_1 = 7.9$ M^{-1} and $K_2 = 1.2 \times 10^6$ M^{-1}, with a RMSE of 2.1×10^{-5} M. These results confirm our hypothesis of a cooperative association process. It can be concluded from the overall global constants that the surfactant head group has a influence on the stability of complexes, with the dodecylsulfate-based complex having a lower stability ($K_o = 9.4 \times 10^6$ M^{-2}) than the corresponding carboxylate ($K_o = 1.8 \times 10^7$), in agreement what was found for other metal ion-based systems [70].
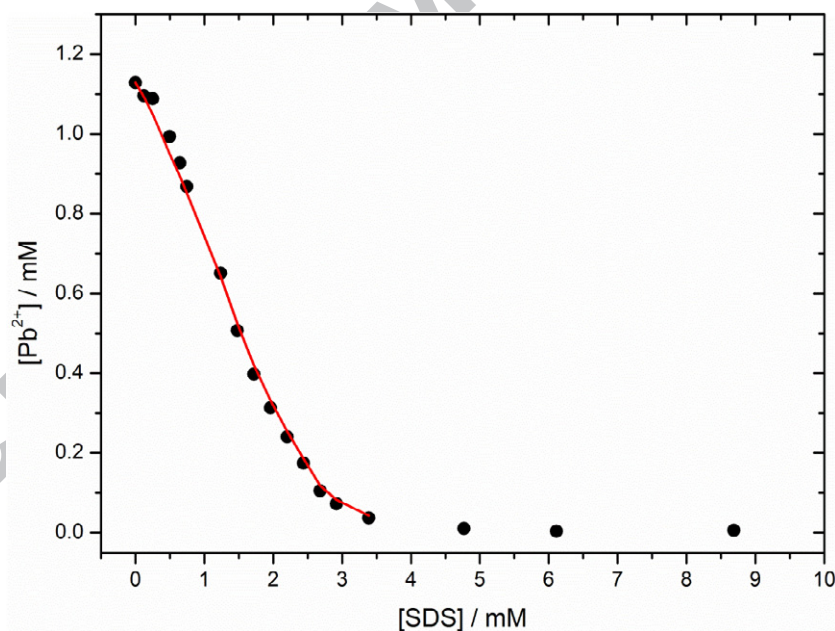
Fig. 7. Effect of SDS on the Pb^{2+} metal concentration in the supernatant part at 25 ºC, determined by ICP-OES. Solid lines are obtained by fitting equations (8) and (9) to the experimental data.

4. CONCLUSIONS

Although the precipitation of long chain carboxylic acids from aqueous solutions upon addition of the heavy metal lead(II) ion has long been known and widely studied [24,26,54], there is still only limited quantitative information on the driving force for this process. This omission needs to be addressed as it is relevant to areas as diverse as corrosion inhibition [32-34], and art conservation [36, 37]. In addition, information on the phase separation mechanism and structures of the solutions will be important in the development of models of such systems.

In this study, turbidity, electrical conductivity and potentiometry have been used to obtain an insight into what drives the precipitation of long chain lead carboxylates from aqueous solution. At the Pb^{2+} ion concentration used (1.0 mM), precipitation was observed almost immediately upon addition of the decanoate and dodecanoate, while with the sodium octanoate it only started when carboxylate:metal ratios were around 0.5. This is consistent with reported low values of the solubility products of lead(II) carbooxylates [54]. The importance of the presence of the long hydrocarbon chain in the precipitation can be seen by the fact that the stability constants for short chain lead(II) carboxylates are rather modest (the 1:1 complex of lead(II) acetate has a value log K 1.93 [61]). However, complexation was more pronounced with long chain lead(II) carboxylates than in our earlier studies with calcium(II), where the octanoate did not precipitate [1]. This is likely to be associated with a more covalent nature of the metal ligand bond in lead(II) than with calcium(II). Changing the surfactant head group from carboxylate to the weaker Lewis base sulfate decreases the degree of coordination between the surfactant and lead(II) and favours redissolution. Thus, precipitation in lead(II) surfactant based systems involves a fine balance between hydrophobic factors

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(probably mainly involving interchain van der Waal's interactions), hydration effects and metal carboxylate interactions. These effects can be controlled for specific applications to lead(II) chemistry, such as environmental remediation, art conservation and corrosion protection.

REFERENCES

[1]   R.F.P. Pereira, A.J.M. Valente, M. Fernandes, H.D. Burrows, Phys. Chem. Chem. Phys. 14 (2012) 7517.
[2]   D. Stigter, J. Phys. Chem. 79 (1975) 1008.
[3]   D. Stigter, J. Phys. Chem. 79 (1975) 1015.
[4]   G. Gunnarsson, B. Jonsson, H. Wennerstrom, J. Phys. Chem. 84 (1980) 3114.
[5]   D.F. Evans, D.J. Mitchell, B.W. Ninham, J. Phys. Chem. 88 (1984) 6344.
[6]   D.F. Evans, B.W. Ninham, J. Phys. Chem. 90 (1986) 226.
[7]   K. Holmberg, B. Jönsson, B. Kronberg, B. Lindman, Surfactants and Polymers in Aqueous Solution. 2nd ed., Wiley, Chichester, U.K., 2003.
[8]   C.A. Bunton, F. Nome, F.H. Quina, L.S. Romsted, Accounts Chem. Res. 24 (1991) 357.
[9]   K.L. Stellner, J.F. Scamehorn, Langmuir 5 (1989) 70.
[10]   P.A. Kralchevsky, K.D. Danov, C.I. Pishmanova, S.D. Kralchevska, N.C. Christov, K.P. Ananthapadmanabhan, A. Lips, Langmuir 23 (2007) 3538.
[11]   S. Soontravanich, J.F. Scamehorn, J. Surfactants Deterg. 13 (2010) 1.
[12]   Y.R. Katre, G.K. Joshi, A.K. Singh, Kinet. Catal. 50 (2009) 367.
[13]   K. Al-Zboon, M.S. Al-Harahsheh, F.B. Hani, J. Hazard. Mater. 188 (2011) 414.
[14]   F.L. Fu, Q. Wang, J. Environ. Manage. 92 (2011) 407.
[15]   S. Soontravanich, S. Walsh, J.F. Scamehorn, J.H. Harwell, D.A. Sabatini, J. Surfactants Deterg. 12 (2009) 145.
[16]   N. Pilpel, Chem. Rev. 63 (1963) 221.
[17]   P.A. Winsor, Chem. Rev. 68 (1968) 1.
[18]   H.D. Burrows, The Structure, Dynamics and Equilibrium Properties of Colloidal Systems. D.M. Bloor

E. Wyn-Jones ed., Kluwer, Dordrecht, 1990.
[19]   J. Lyklema, Adv. Colloid Interface Sci. 2 (1968) 67.
[20]   A.S. Kertes, H. Gutman, Surface and Colloid Science. Plenum, New York, 1975.
[21]   R. Naseem, S.S. Tahir, Water Res. 35 (2001) 3982.
[22]   A.J.M. Valente, A.C.F. Ribeiro, V.M.M. Lobo, A. Jiménez, J. Mol. Liq. 111 (2004) 33.
[23]   C.F. Baes, R.E. Mesmer, The Hydrolysis of Cations. Wiley, New York, 1976.

25

[24]   F.J. Buono, M.L. Feldman, Kirk–Othmer Encyclopedia of Chemical Technology. Wiley, New York, 1979.
[25]   G.D. Parfitt, J. Peacock, Surface and Colloid Science. E. Matijevic ed., Plenum, New York, 1978.
[26]   M.S. Akanni, E.K. Okoh, H.D. Burrows, H.A. Ellis, Thermochim. Acta 208 (1992) 1.
[27]   R.G. Bossert, J. Chem. Educ. 27 (1950) 5.
[28]   H. Yamada, M. Tanaka, Adv. Inorg. Chem. 29 (1985) 143.
[29]   K. Binnemans, C. Gorller-Walrand, Chem. Rev. 102 (2002) 2303.
[30]   B. Donnio, Curr. Opin. Colloid Interface Sci. 7 (2002) 371.
[31]   R.W. Corkery, Curr. Opin. Colloid Interface Sci. 13 (2008) 288.
[32]   E. Rocca, J. Steinmetz, Corrosion Sci. 43 (2001) 891.
[33]   M. Dowsett, A. Adriaens, B. Schotte, G. Jones, L. Bouchenoire, Surf. Interface Anal. 41 (2009) 565.
[34]   K. De Wael, M. De Keersmaecker, M. Dowsett, D. Walker, P. Thomas, A. Adriaens, J. Solid State Electrochem. 14 (2010) 407.
[35]   L. Bertrand, J. Doucet, A. Simionovici, G. Tsoucaris, P. Walter, Biochim. Biophys. Acta-Gen. Subj. 1620 (2003) 218.
[36]   M.J. Plater, B. De Silva, T. Gelbrich, M.B. Hursthouse, C.L. Higgitt, D.R. Saunders, Polyhedron 22 (2003) 3171.
[37]   J. Sanyova, S. Cersoy, P. Richardin, O. Laprévote, P. Walter, A. Brunelle, Anal. Chem. 83 (2011) 753.
[38]   S.O. Adeosun, S.J. Sime, Thermochim. Acta 17 (1976) 351.
[39]   H.A. Ellis, Mol. Cryst. Liquid Cryst. 138 (1986) 321.
[40]   C.G. Bazuin, D. Guillon, A. Skoulios, M.A. Amorim da Costa, H.D. Burrows, C.F.G.C. Geraldes, J.J.C. Teixeira-Dias, E. Blackmore, G.J.T. Tiddy, Liq. Cryst. 3 (1988) 1655.
[41]   A.S. Arenas, M.V. Garcia, M.I. Redondo, J.A.R. Cheda, M.V. Roux, C. Turrion, Liq. Cryst. 18 (1995) 431.
[42]   F.J. Martínez Casado, M.V. García Pérez, M.I. Redondo Yélamos, J.A. Rodríguez Cheda, A. Sánchez Arenas, S. López-Andrés, J. García-Barriocanal, A. Rivera, C. León, J. Santamaría, J. Phys. Chem. C 111 (2007) 6826.
[43]   P. Mukerjee, K.J. Mysels, Critical Micelle Concentrations of Aqueous Surfactatns Systems. NBS, Wasington, D. C., 1971.
[44]   A.C.F. Ribeiro, A.J.M. Valente, V.M.M. Lobo, E.F.G. Azevedo, A.M. Amado, A.M.A. da Costa, M.L. Ramos, H.D. Burrows, J. Mol. Struct. 703 (2004) 93.
[45]   J. Barthel, F. Feuerlein, R. Neueder, R. Wachter, J. Solut. Chem. 9 (1980) 209.
[46]   S.L. Young, E. Matijevic, J. Colloid Interf. Sci. 61 (1977) 287.
[47]   H.D. Burrows, T.O. Chimamkpam, T. Encarnação, S.M. Fonseca, R.F.P. Pereira, M.L. Ramos, A.J.M. Valente, J. Surface Sci. Technol. 26 (2010) 197.
[48]   F.J.M. Casado, A.S. Arenas, M.V.G. Perez, M.I.R. Yelamos, S.L. de Andres, J.A.R. Cheda, J. Chem. Thermodyn. 39 (2007) 455.
[49]   A.J.M. Valente, H.D. Burrows, R.F. Pereira, A.C.F. Ribeiro, J. Pereira, V.M.M. Lobo, Langmuir 22 (2006) 5625.
[50]   R.F.P. Pereira, M.J. Tapia, A.J.M. Valente, R.C. Evans, H.D. Burrows, R.A. Carvalho, J. Colloid Interf. Sci. 354 (2011) 670.
[51]   H.D. Burrows, M.J. Tapia, S.M. Fonseca, A.J.M. Valente, V.M.M. Lobo, L.L.G. Justino, S. Qiu, S. Pradhan, U. Scherf, N. Chattopadhyay, M. Knaapila, V.M. Garamus, ACS Appl. Mater. Interfaces 1 (2009) 864.
[52]   P. Turq, J. Barthel, M. Chemla, Transport, Relaxation and Kinetic Processes in Electrolyte Solutions. Springer-Verlag, Berlin, 1992.
[53]   A. Albert, E.P. Serjeant, The Determination of Ionization Constants: A Laboratory Manual. Champman and Hall ed., Taylor & Francis Group, London, 1971.
[54]   S.P. Mauchauffee, E. Meux, M. Schneider, Ind. Eng. Chem. Res. 47 (2008) 7533.
[55]   A.C.S. Neves, A.J.M. Valente, H.D. Burrows, A.C.F. Ribeiro, V.M.M. Lobo, J. Colloid Interf. Sci. 306 (2007) 166.

[56]   R.F.P. Pereira, A.J.M. Valente, H.D. Burrows, M.L. Ramos, A.C.F. Ribeiro, V.M.M. Lobo, Acta Chim. Slov. 56 (2009) 45.

[57]   R.G. Pearson, J. Chem. Educ. 45 (1968) 581.

[58]   F. Lacouture, M. Francois, C. Didierjean, J.P. Rivera, E. Rocca, J. Steinmetz, Acta Crystallogr. Sect. C-Cryst. Struct. Commun. 57 (2001) 530.

[59]   H.A. Ellis, N.A.S. White, R.A. Taylor, P.T. Maragh, J. Mol. Struct. 738 (2005) 205.

[60]   A.M. Amorim Da Costa, H.D. Burrows, C.F.G.C. Geraldes, J.J.C. Teixeira-dias, C.G. Bazuin, D. Guillon, A. Skoulios, E. Blackmore, G.J.T. Tiddy, D.L. Turner, Liq. Cryst. 1 (1986) 215.

[61]   J.W. Bunting, K.M. Thong, Can. J. Chem. 48 (1970) 1654.

[62]   S. Sugiyama, Y. Kanda, H. Ishizuka, K.I. Sotowa, J. Colloid Interf. Sci. 320 (2008) 535.

[63]   J.J. Cruywagen, R.F. Vandewater, Talanta 40 (1993) 1091.

[64]   H.A. Ellis, N.A. White, I. Hassan, R. Ahmad, J. Mol. Struct. 642 (2002) 71.

[65]   R.F.P. Pereira, A.J.M. Valente, H.D. Burrows, V. de Zea Bermudez, R.A. Carvalho, R.A.E. Castro, RSC Adv. 3 (2013) 1420.

[66]   E.P. Serjeant, B. Dempsey, Ionization Constants of Organic Acids in Aqueous Solution. Pergamon, Oxford, 1979.

[67]   M. Remko, P.T. Van Duijnen, C.W. von der Lieth, Theochem-J. Mol. Struct. 814 (2007) 119.

[68]   P.C. Griffiths, J.A. Roe, B.L. Bales, A.R. Pitt, A.M. Howe, Langmuir 16 (2000) 8248.

[69]   R.F.P. Pereira, A.J.M. Valente, H.D. Burrows, J. Mol. Liq. 56 (2010) 109.

[70]   R.F.P. Pereira, M.J. Tapia, A.J.M. Valente, H.D. Burrows, Langmuir 28 (2012) 168.

Figure Captions

Fig. 1. Effect of the addition of sodium octanoate (□), sodium decanoate (○) and sodium dodecanoate (Δ to 1 mM Pb^{2+} aqueous solution transmittance, at 25 ºC. Inset figure shows a zoom for low molar ratios.

Fig. 2. Effect of Pb^{2+} 1 mM on the specific conductivity of sodium octanoate (□, n=7), sodium decanoate (○, n=9) and sodium dodecanoate (Δ n=11) at 25 ºC

Fig. 3. Effect of sodium octanoate (□), decanoate (○) and dodecanoate (Δ in the Pb^{2+} metal concentration of supernatant, at 25 ºC. Solid lines are obtained by fitting the experimental data to equations (8) and (9).

Fig. 4. Effect of the addition of sodium dodecylsulfate on 1 mM Pb^{2+} aqueous solution transmittance, at 25 ºC. Dashed line represents de *cmc* of SDS.

Fig. 5. Effect of lead nitrate 1 mM on the specific conductance of aqueous SDS solution at 25 ºC. Solid lines show transition points corresponding to critical aggregation concentration (*cac*), maximum interaction concentration (*mic*) and apparent critical micelle concentration (*cmc^{ap}*).

Fig. 6. Effect of the addition of sodium dodecylsulfate on the pH of 1 mM $Pb(NO_3)_2$ solutions, at 25 ºC.

Fig. 7. Effect of SDS on the Pb^{2+} metal concentration in the supernatant part at 25 ºC, determined by ICP-OES. Solid lines are obtained by fitting equations (8) and (9) to the experimental data.

Highlights

- Lead carboxylate (soap) formation in aqueous solutions has been revisited;
- Lead soap precipitation mechanism depends strongly on alkyl chain length;
- The surfactant head group acidity affects the mechanism of soap formation;
- Stability constants depend on alkyl chain length and other factors;
- Covalency of metal-oxygen bonds plays an important role in the association process.

Graphical abstract