

Complexing power of alkanesulfonate ions: the lead-methanesulfonate system

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The interaction between lead(II) and methanesulfonate ions was studied by conventional d.c. polarography at 2.0 M ionic strength and pH 4.0. Two stepwise lead complexes are formed in solution: $[\text{Pb}(\text{CH}_3\text{SO}_3)]^+$, $\beta_1 = 1.76 \pm 0.03 \text{ M}^{-1}$ and $[\text{Pb}(\text{CH}_3\text{SO}_3)_2]$, $\beta_2 = 0.25 \pm 0.05 \text{ M}^{-2}$ which are reversibly reduced at the DME. At high ligand concentrations, above 1.0 M, a third lead complex, $[\text{Pb}(\text{CH}_3\text{SO}_3)_3]^-$, $\beta_3 = 0.30 \pm 0.07 \text{ M}^{-3}$, is formed.

1. Introduction

Tin and tin–lead alloys are extensively employed in surface finishing processes and in the electrical/electronic industries due to their good solderability to bond electronic components, in addition to their superior corrosion resistance. For a long time fluoroborate electroplating baths have been used to commercially plate tin, lead and tin–lead alloys [1–3]. Alternatives to electrodepositing lead from nonfluoroborate systems have been sought such as sulfamate, fluorosilicate, gluconate and lead sulfate in acidic ammonium acetate [4, 5]. Fluoroboric acid undergoes hydrolysis in acidic media producing hydrofluoric and boric acids with formation of insoluble lead fluoride [6, 7]. The hydrolysis of sulfamate baths, resulting in an insoluble lead sulfate, caused them to be impractical for continuous processes [8–10]. The less conventional fluorosilicate, gluconate and pyrophosphate baths are employed mainly for tin–lead alloy plating; they are, however, more expensive than the fluoroborate-based electrolytes [5].

In the 1940s Proell and coworkers demonstrated the feasibility of plating many metals, including nickel, zinc, cadmium, lead and silver, from alkanesulfonate baths [11, 12]. Surprisingly, only from the early 1980s have these baths gained commercial interest [13–21]. The primary advantages claimed for the methanesulfonic acid (MSA)-based plating process are: less toxic electrolyte, wider operating window, higher conductivity, and the ease of treating MSA effluents. The metals plated from methanesulfonate baths are highly adherent and less porous, which are important factors in the tinplate and electronic industries [5]. These advantages have stimulated efforts in its gradual application on the industrial scale, substituting the traditional electroplating baths.

Hitherto the electrochemistry of the lead(II)-methanesulfonate electrolyte has not been fully elucidated. Hsueh and Wan [22] studied the electro-dissolution of metallic lead in dilute MSA solutions by voltammetric techniques. The effect of methanesulfonate concentration on the polarographic half-wave potential for Pb(II) ion reduction at the dropping mercury electrode (DME) was observed without ionic strength control. The $E_{1/2}$ shift observed was only 2 mV when the methanesulfonate concentration changed from 0 to 0.01 M. It was concluded that the sulfonate ion was not involved in the electrodic step. On the other hand, the concentrations of methanesulfonate species in operating electrodeposition processes are orders of magnitude higher than those studied by Hsueh and Wan and certainly the lead(II) and methanesulfonate ions could be associated. Hence the aim of this paper is to report the polarographic behaviour of lead ions in more concentrated methanesulfonate solutions, up to 2 M at constant ionic strength, and to investigate the possible formation of lead methanesulfonate complexes.

2. Experimental details

All polarographic measurements were carried out with an EG&G–PARC model 264A polarographic analyser coupled to model 303A static mercury drop electrode (SMDE) assembly. A small drop size with 1 s drop time was selected. The polarograms were traced at 2 mV s^{-1} and recorded on a model 7090A Hewlett–Packard X–Y plotter. The electrode potentials were measured against an Ag/AgCl, NaCl (0.1 M) reference electrode separated from the working solutions by a 2.0 M NaCH_3SO_3 salt bridge. For IR drop corrections, the ohmic resistances of the solutions in the polarographic cell were measured with a Micronal B330 conductivimeter.

Sodium perchlorate 4.0 M and sodium methanesulfonate 4.0 M stock solutions were prepared by

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stoichiometric reaction between sodium hydroxide p.a. (Merck) and perchloric acid p.a. (Merck) methanesulfonic acid (MSA) (Aldrich), respectively. The NaCH_3SO_3 solution was stirred with activated charcoal, filtered and stored in an amber bottle. The final neutral solutions were standardized by conventional acid-base titration after passing aliquots through a 50 mL capacity column packed with a Fisher strongly acid ion exchange resin. A ca. 0.01 M lead(II) perchlorate stock solution was prepared by dissolution of lead oxide p.a. (Mallinckrodt) with HClO_4 . The solution acidity was adjusted to pH 4.0 and standardized by potentiometric EDTA titration in acetate buffer 0.5 M pH 4.75 using a mercury film indicator electrode.

The NaCH_3SO_3 concentration varied from 0 to 2 M maintaining the ionic strength at 2.0 M with NaClO_4 . The analytical Pb(II) concentration was fixed at 1.0 mM. Typically 5.0 mL of the working solutions at pH 4.0 were polarographed after 15 min deaeration with oxygen-free nitrogen. The half-wave potentials were obtained by interpolation of the corresponding IR-corrected log-plots [23]. All measurements were carried out at $25 \pm 0.5^\circ\text{C}$. The performance of the polarographic circuit was checked with a 0.5 mM cadmium chloride in 1.0 M hydrochloric acid supporting electrolyte as suggested by Meites [23]. The cadmium half-wave potential obtained was -0.679 V in 1.0 M HCl and -0.740 V in 1.0 M MSA. In both solutions the slopes from the log-plots were the same and around $-30\text{ mV}(\text{dec})^{-1}$ being an indication of the suitability of the polarographic setup. This checking showed that the methanesulfonate ion is a stronger complexing agent than chloride ion.

3. Results and discussion

The overall stability constants of the lead(II)-methanesulfonate complexes were determined by the conventional DeFord and Hume methodology [24] applied to d.c. polarography, as was done to other lead(II)-ligand-supporting electrolyte systems [25–28]. The complexing function defined as [29, 30]:

$$F_0(L) = \frac{C_M}{[M]} \quad (1)$$

where C_M is the total analytical concentration of the metallic ion, $[M]$ its equilibrium concentration and L represents the ligand, which in the present case is the CH_3SO_3^- ion, is related to the overall stability constants of the stepwise complexes and the ligand concentration by the well known Leden function [30]. The $F_0(L)$ function can be determined by a number of experimental techniques such as spectrophotometry, partition and electroanalytical methods. Polarography is a powerful and versatile technique to estimate qualitatively and quantitatively the stepwise complex formation of metal ions, mainly those which undergo reversible reduction at the DME. The polarographic determination of the complexing

function is related to the shift in the half-wave potential as a function of the ligand equilibrium concentration:

$$F_0(L) = \text{antilog} \left(\frac{nF}{2.303 RT} \Delta E_{1/2} + \log \frac{I_s}{I_L} \right) \quad (2)$$

where $\Delta E_{1/2}$ is the difference between the reduction half-waves for the metallic ion in the absence and presence of the complexing agent, respectively. I_s and I_L are the corresponding limiting diffusion currents for the electrodic processes. The constants n , F , R and T have their usual meanings. For the $F_0(L)$ dependence on the ligand concentration, a series of subsidiary $F_j(L)$ functions ($j = 1, 2, 3, \dots$) can be calculated and the overall stability constants graphically/numerically determined. This DeFord–Hume methodology has been applied since its proposal to a wide number of complex formation systems with further improvements on the numerical data treatment as, for example, computer-aided polynomial regression. Once the overall stability constants β_j have been determined, the distribution of each complex species can be plotted as a function of ligand concentration giving a view of the metal–ligand system in the concentration range investigated. The fraction α_j of a given complex ML_j is defined as the relation between its equilibrium concentration and the total metal ion concentration added, which, combined with the corresponding overall stability constant expression, gives

$$\alpha_j = \frac{\beta_j [L]^j}{F_0(L)} \quad (3)$$

In all methanesulfonate concentrations the corresponding log-plots were linear and showed reversible lead(II) reduction processes with slopes ranging from -29.8 to $-30.1\text{ mV}(\text{dec})^{-1}$. A linear relation between the diffusion current and Pb(II) concentration in all methanesulfonate solutions was obtained indicating the diffusion-controlled reduction process at the DME. At a constant total Pb(II) concentration, as the MS^- ion concentration is increased, the diffusion current increases, reaching a maximum at 0.37 M, as can be seen in Fig. 1. Above this ligand concentration, only above 1.0 M the current decreases linearly. This apparent abnormal behaviour can be understood in terms of a tensoactive effect of the MS^- ion decreasing the surface tension of the solution, resulting in a corresponding increase of the diffusion coefficient of the electroactive species. After the maximum, these effects are counterbalanced by two main factors: (a) the lowering of the diffusion coefficient by complex formation and (b) the increase in the solution viscosity.

Table 1 summarizes the polarographic data and the corresponding F-functions. By plotting the $F_j(L)$ functions against methanesulfonate concentration a series of curves are obtained as shown in Fig. 2. Some features can be derived from this figure related to the species formation as the ligand concentration increases. In the range 0.2–0.8 M, $F_0(L)$ is linear and

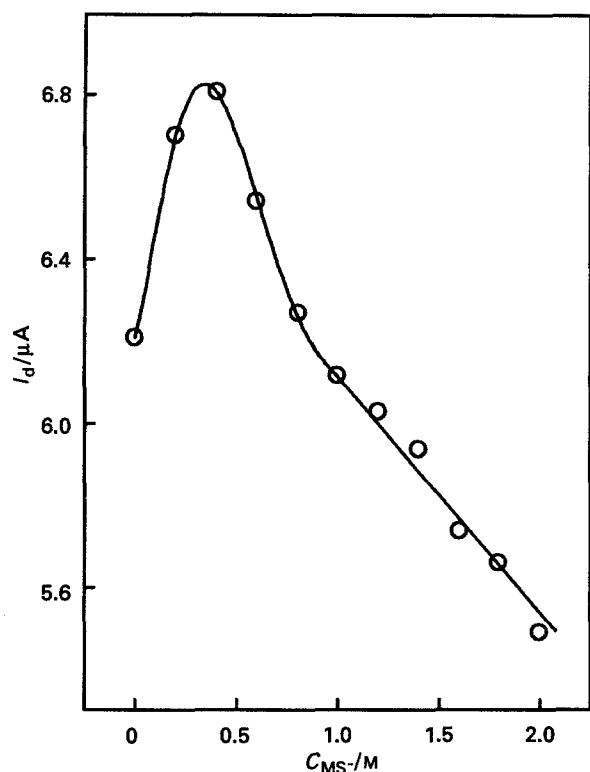


Fig. 1. Polarographic diffusion currents of 1 mM Pb^{2+} in NaCH_3SO_3 pH 4.0 solutions at 2.0 M ionic strength (NaClO_4), $25 \pm 0.5^\circ \text{C}$.

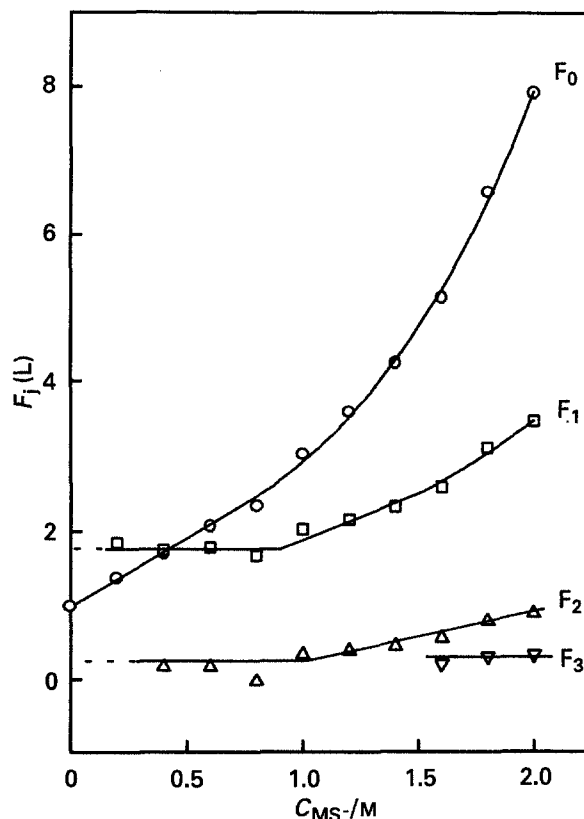


Fig. 2. Leden's $F_j(L)$ functions for the $\text{Pb(II)-CH}_3\text{SO}_3\text{-ClO}_4^-$ system at 2.0 M ionic strength pH 4.0 $25 \pm 0.5^\circ \text{C}$.

the $F_1(L)$ is independent on the methanesulfonate concentration, thus being an indication of the formation and predominance of the $[\text{Pb}(\text{CH}_3\text{SO}_3)]^+$ species. The corresponding slope of the linear part of the $F_0(L)$ function is the overall stability constant of this first lead complex, resulting in the value $\beta_1 = 1.76 \pm 0.03 \text{ M}^{-1}$. In the MS^- concentration range 0.8–1.5 M, $F_1(L)$ is linear and its slope is the second overall stability constant, $\beta_2 = 0.25 \pm 0.05 \text{ M}^{-2}$ for the neutral complex $[\text{Pb}(\text{CH}_3\text{SO}_3)_2]$. From 1.5 up to 2.0 M, evidence for the formation of the three coordinated complex, $[\text{Pb}(\text{CH}_3\text{SO}_3)_3]^-$, is seen, since a constant $F_3(L)$ function is obtained giving $\beta_3 = 0.30 \pm 0.07 \text{ M}^{-3}$. Therefore, to calculate a more precise value, measurements must be done at more concentrated ligand solutions, i.e. at least in the range 1.5–3.0 M, since the formation constant of the system is not too high. Fig. 3 illustrates the predominance of the Pb(II) species as a function of the methanesulfonate concentration in the range

studied. The relative average deviation, comparing calculated and experimental $F_0(L)$ values, is around 7%, indicating the reliability of the simple d.c. polarographic analysis of the lead(II)-methanesulfonate system.

4. Conclusion

Methanesulfonate ion has a tendency to form stepwise complexes with lead(II) ions in moderately acid solutions. Three lead(II)-methanesulfonate complexes were characterized as being the predominant species in the ligand concentration range 0.2–2.0 M whose overall formation constants are: $\beta_1 = 1.76 \pm 0.03 \text{ M}^{-1}$, $\beta_2 = 0.25 \pm 0.05 \text{ M}^{-2}$ and $\beta_3 = 0.30 \pm 0.07 \text{ M}^{-3}$. At methanesulfonate concentrations above 1.8 M, the three coordinated lead complex predominates. Thus in lead electroplating baths, where the concentration levels are high, various soluble

Table 1. Polarographic analysis of the lead(II)-methanesulfonate system at $25 \pm 0.5^\circ \text{C}$, $\mu = 2.0 \text{ M}$ (NaClO_4) and pH 4.0. $C_{\text{Pb(II)}} = 1 \text{ mM}$

$C_{\text{CH}_3\text{SO}_3^-} \text{ M}$	$\Delta E_{1/2}/\text{mV}$	$I_d/\mu\text{A}$	$F_0(L)$	$F_1(L)$	$F_2(L)$	$F_3(L)$
0.2	5	6.70	1.37	1.84	—	—
0.4	8	6.81	1.70	1.75	—	—
0.6	10	6.54	2.07	1.78	—	—
0.8	11	6.27	2.33	1.67	—	—
1.0	14	6.12	3.02	2.02	—	—
1.2	16	6.03	3.58	2.15	0.39	—
1.4	18	5.94	4.24	2.32	0.45	—
1.6	20	5.74	5.13	2.58	0.56	0.2
1.8	23	5.66	6.58	3.10	0.79	0.3
2.0	25	5.49	7.92	3.46	0.89	0.3

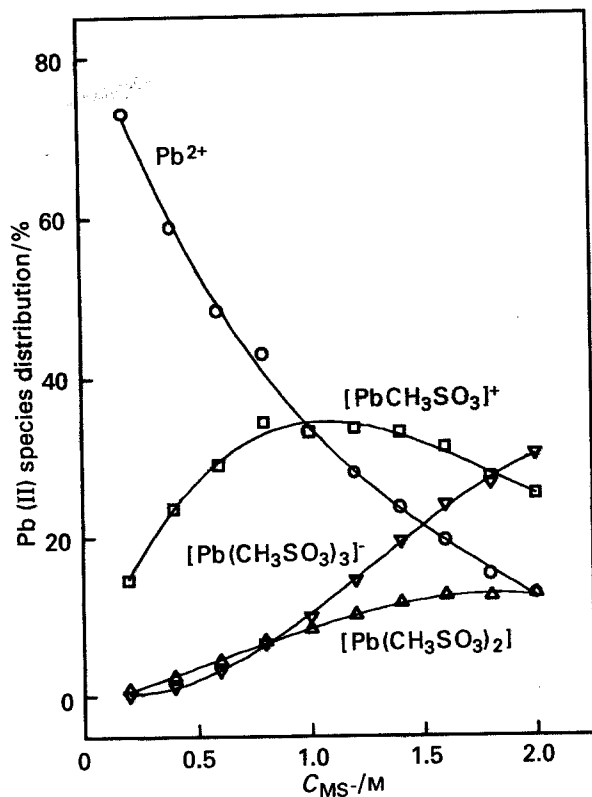


Fig. 3. Percent distribution of the Pb(II) species in methanesulfonate solutions at 2.0 M ionic strength ($NaClO_4$), pH 4.0 $25 \pm 0.5^\circ C$.

$Pb(II)-CH_3SO_3^-$ species are in equilibrium and must be considered when solution and electrochemical properties are established. On the other hand, since the total lead(II) ion concentration in the electro-deposition baths is high, the formation of polynuclear complexes is possible and must be taken into account.

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