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Effect of pH on the Polarographic Behavior of Pb(II) in the Presence of Acetates

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The polarographic properties of Pb(II) dissolved in 1 mol dm^{-3} acetate solutions with $2.5 \leqslant pH \leqslant 14$ were investigated at 25°C. All DC polarograms of the Pb(II) manifested a single reduction wave and their half-wave potentials, $E_{1/2}$, began to decrease at pH 8.5 from -0.5 to -0.8V because of the formation of Pb(II) hydroxo complexes. Similar investigations were also carried out for Pb(II) in strongly acidic and nearly neutral solutions containing 1 mol dm^{-3} in the total concentration of NO_3^- and OAc^-, varying in the NO_3^-/OAc^- ratio. Pb(II) in the acetate solution would form monomers of aqua, acetato, and hydroxo complexes beyond the range $8.5 < pH < 12$, whereas polynuclear complexes with oxo and hydroxo bondings within this pH range. From the polarographic data, the formation constants of these complexes are also estimated.

KEY WORDS: Lead(II) acetate hydroxide/ Lead(II) hydroxide oxide/ Lead (II) oxides/ Lead(II) hydroxo complexes/ Lead(II) aqua complexe/ Diffusion current/Half-wave potential/

INTRODUCTION

Our previous paper discribed that a white precipitate formed by mixing aqueous solutions of NaOH and $Pb(OAc)_2$(lead(II) acetate) in the presence of 1M(1M=1 mol dm^{-3}) OAc^- ions transformed itself gradually at 25°C into a crystalline precipitate in the form of one of lead(II) acetate hydroxide($Pb_3(OAc)_2(OH)_4$), hydroxide oxide($Pb_5O_3(OH)_4$), yellowish oxide, or reddish oxide depending mainly on the pH of the suspension and that the fewer became the kinds of products, the higher the aging temperature or the lower the OAc^- concentration.[1)]

Such a variety in the product formation at 25°C in the presence of OAc^- ions is probably attributable to the formation of different lead(II) complexes in the suspension media prior to the formation of the crystalline precipitate. Research on the formation of Pb(II) acetato complexes in perchlorate solutions containing OAc^- ions has already been published.[2),3)]

The purpose of this paper is to discuss our investigation results of the polarographic properties at 25°C of Pb(II) in the presence of 1M OAc^- ions with different pH values.

EXPERIMENTAL

Extremely pure water free from dissolved oxygen and carbon dioxide which had

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been prepared by distilling conductivity water in a nitrogen atmosphere was used in the present work. Two kinds of stock solutions, each containing 2 mM $Pb(OAc)_2$ and 2 M OAc^-, were prepared by dissolving $Pb(OAc)_2\ 3H_2O$ and either HOAc or NaOAc (both analytical grade) in required amounts into water contained in 5 dm^3 polyethylene vessels.

To each of a number of 100 cm^3 stock solutions contained in 250 cm^3 poly(tetrafluoroetylene) bottles, a NaOH solution whose concentration had been suitably controlled was added to obtain desired OH^-/OAc^- ratios and then, each mixture was diluted with water to 200 cm^3. These bottles each containing 200 cm^3 solutions of varying pH values were installed in a rotating drum immersed in a large water bath kept at 25°C. These solutions were stirred up for homogeneity by slowly rotating the drum for many hours.

The pH value of each sample was measured with a Horiba-Hitachi glass electrode pH meter, Model F-7DE, at 25°C. The DC polarograms were recorded with a Yanagimoto XY recorder, Model WX 4402, associated with a model PA 1000 polarograph of the same manufacturer.

The dropping mercury electrode(DME) was set to conditions as follows: The rate of mercury flow from the DME, m, was 2.30 mg/s, and the drop time, t, was 3.71 s at the mercury-column height, h, of 90 cm with the polarograph open-circuited. Occasionally, the DME conditions were deliberately changed to $h=60$ cm and $m=1.50$ mg/s to find how electrolysis proceeds. The results indicated that the electrolysis process was governed by the Pb(II) diffusion velocity toward the electrode. All potentials were measured by reference to the saturated calomel electrode(SCE). The viscosity of each sample was measured at 25°C by use of an Ubbelohde's viscometer.

The preparation and measurements of all samples were carried out in a nitrogen atmosphere.

RESULTS AND DISCUSSION

All samples were clear and colorless, except that some with $10 \leqslant pH \leqslant 12$ were slightly whitish and turbid. All DC polarograms of Pb(II) in the presence of 1M OAc^- ions manifested a single reduction wave within the potential range -2 to 0V. The half-wave potential, $E_{1/2}$, obtained from each of these DC polarograms is plotted against pH in Fig. 1.

In general, $E_{1/2}$ values of Pb(II) dissolved in aqueous solutions of varying ligand concentration, C_X, as plotted against log C_X manifest a slope of $-0.059p/2$ at 25°C, wherein the mean coordination number, p, of the ligand can be estimated from the slope value.[4] Figure 1 demonstrates that the Pb(II) begins to form the hydroxo complexes at $pH=8.5$ and that the p value of OH^- increases gradually to 4 with increasing pH. In our preceding paper, it was indicated that Pb(II) in the presence of 1M OAc^- ions mostly precipitates as lead(II) hydroxide oxide with its minimum solubility as small as $10\ M^{-3}$ or less at pH of about 12.[1] Accordingly, it is presupposed that the hydroxo complexes are cationic($p<2$) at pH below 12, and anionic($p>2$) at pH above 12.

The properties of Pb(II) in aqueous solutions of nitrate or perchlorate have been studied by various techniques—polarographic, potentiometric, spectrophotometric, and X-ray diffraction methods.[5~9] Let us elucidate the properties of Pb(II) dissolved in the

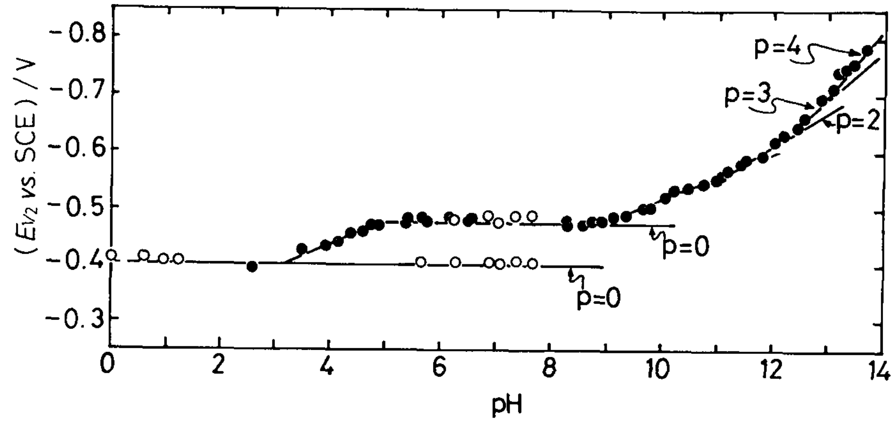

Fig. 1. Half-wave potential, $E_{1/2}$, of Pb(II) in acetate(●) or nitrate(○) solutions as a function of pH.

acetate solutions with pH<8.5 by comparing the properties with those of Pb(II) dissolved in nitrate or perchlorate solutions with pH<8.5. Similar experiments were conducted by use of lead(II) perchlorate and $HClO_4$, or lead(II) nitrate and HNO_3 in place of lead(II) acetate and HOAc. To our regret, the $E_{1/2}$ values of Pb(II) in the presence of perchlorates manifested poor reproducibility, probably due to the reaction of K^+ ions in the SCE with ClO_4^- to form a $KClO_4$ precipitate at an interface between the SCE and the sample solution, as pointed out by Hershenson.[5]

The polarograms of Pb(II) dissolved in nitrate solutions with pH<6 and $6 \leqslant pH \leqslant 7.8$ manifested the single wave with $E_{1/2} = -0.400$ V and the double wave with $E_{1/2} = -0.400$ and -0.475 V, respectively(Fig. 1). These results readily reveal that Pb(II) forms only one kind of aqua complex for pH<6, whereas it forms two kinds of complexes for

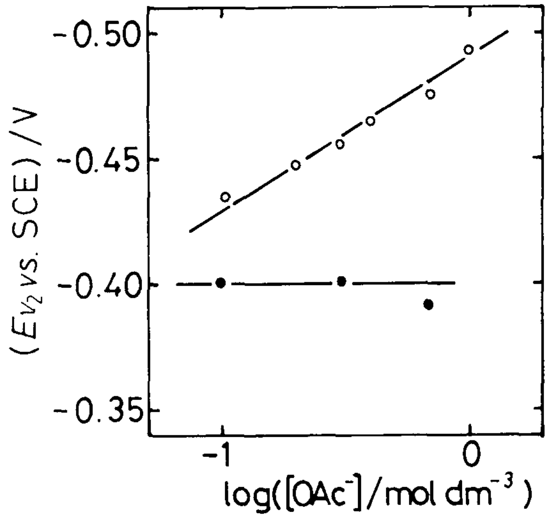

Fig. 2. Half-wave potential, $E_{1/2}$, of Pb(II) in mixed solutions of acetate and nitrate with pH 6.5(○) and 0.65(●) as a function of the acetate concentration.

$6 \leqslant pH \leqslant 7.8$.

Polarograms were obtained of sample solutions with pH of 0.6 ± 0.2 and of 6.5 ± 0.2, each containing 1 mM Pb(II) and a 1M total concentration of OAc^- and NO_3^- in order to study the behavior of Pb(II) in strongly acidic or neutral solutions differing in the OAc^-/NO_3^- ratio. Each polarogram manifested the single wave. Figure 2 shows a plot of $E_{1/2}$ against OAc^- concentration. In strongly acidic solutions, the dissociation of acetic acid is hindered, resulting in a decrease in ionic strength and in a slight decrease of $E_{1/2}$ value to -0.392 V, as will be evident from Fig. 2. But, the $E_{1/2}$ value remains substantially unaffected by OAc^- concentration in the strongly acidic solutions. Consequently, Pb(II) forms a single kind of aqua complex in the strongly acidic solutions. Figure 2 demonstratrates that $E_{1/2}$ value is governed by the OAc^- concentration in the neutral solutions and $p=2$ as estimated from the slope of a straight line in the figure and hence, Pb(II) exists in the form of aqua and acetato complexes.

The diffusion current, i_d, obtained from the polarograms and the viscosity, η, of the samples containing 1 mM Pb(II) and 1M OAc^- are plotted against pH in Figs, 3(a) and (b), respectively. The i_d values were compensated for $\eta = 1 \times 10^{-3}$N s m^{-2}, and the diffusion constants, D, were calculated from the compensated values, i_{dc}, using the Ilković equation. Assuming that the DME-approaching Pb(II) complexes are spherical in shape, let us calculate their radii using the Stokes-Einstein equation

$$r_s = kT/6\pi\eta D.$$

The Stokes radius, r_s(Å), is plotted against pH in Fig. 4. As a matter of course,

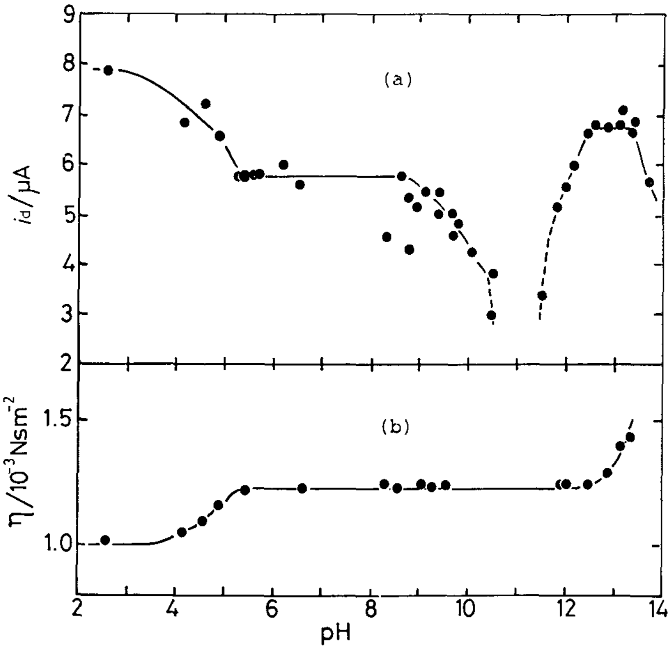

Fig. 3. Effects of pH on the diffusion current, i_d, of Pb(II) in the presence of 1 mol dm^{-3} OAc^- and their viscosity, η.

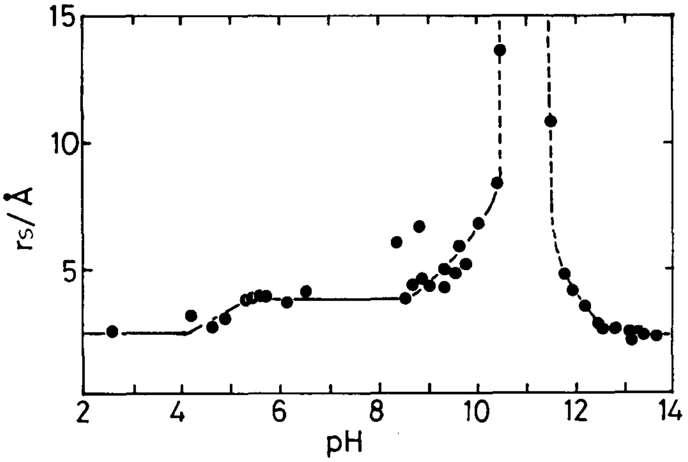

Fig. 4. Radii of Pb(II) complexes in the presence of 1 mol dm^{-3} with various pH values.

whether the ligands are 2OH$^-$ or O^{2-} ions could scarcely be discriminated by a mere electrochemical method. Figure 4 suggests that all of Pb(II) aqua, acetato, and hydroxo complexes constitute a monomer outside the range $8.5 < pH < 12$ and that these complexes are destitute of the oxo bonds which are apt to constitute a polynuclear complex. Within this pH range, the Pb(II) would form the polynuclear complexes with the hydroxo and oxo bonds.

The formation of each complex may be described by the following general equations (to simplify representation the water ligands are omitted) ;

$$\mathrm{Pb(II)} + 2\mathrm{OAc}^- = \mathrm{Pb(OAc)}_2 \quad\cdots\cdots (1)$$

$$\mathrm{Pb(II)} + p\mathrm{OH}^- = \mathrm{Pb(OH)}_p^{2-p} \quad\cdots\cdots (2)$$

$$K = [\mathrm{Pb(OAc)}_2]/[\mathrm{Pb(II)}][\mathrm{OAc}^-]^2 \text{ or } [\mathrm{Pb(OH)}_p^{2-p}]/[\mathrm{Pb(II)}][\mathrm{OH}^-]^p.$$

The formation constants, K, of these complexes were calculated using the Lingane equation[4] from both the i_{dc} and the intercepts, $E_{1/2}$(pH 14), produced on the ordinate at pH 14 by straight lines extended in Fig. 1. Table 1 gives the K values, together with the values of i_{dc} and $E_{1/2}$(pH 14).

Table 1. Formation constants, K, of Pb(II) complexes estimated from the i_{dc} and $E_{1/2}$(pH 14) values.

Complex	i_{dc}/μA	$E_{1/2}$(pH 14)/V	log K
$\mathrm{Pb(OAc)_2}$	6.40	−0.475	2.45
$\mathrm{Pb_3(OAc)_2(OH)_4}$	4.80	−0.675	27.28
$\mathrm{Pb(OH)_2}$	3.90	−0.735	11.03
$\mathrm{Pb(OH)_3^-}$	7.55	−0.790	13.18
$\mathrm{Pb(OH)_4^{2-}}$	8.05	−0.825	14.39

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Magnetic Susceptibility of a Microbridge-Coupled Superconductor in Non-Sinusoidal Periodic Fields

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Using a weakly-connected loop model, the profile of superconducting transition of a microbridge-coupled superconductor has been generated. Applied magnetic fields to the specimen are supposed as periodic but non-sinusoidal.

KEY WORDS: Superconductivity/ ac susceptibility/ Higher-harmonic susceptibility/ Microbridge-coupled superconductor/

INTRODUCTION

The Hartshorn-type ac bridge has been widely used in the field of low-temperature physics. This method has benefited from the development of a lock-in technique and has been extensively modified from the original. The fundamental susceptibility $\chi_1'-i\chi_1''$ is conventionally measured by using a two-phase lock-in analyzer, *i.e.*, we need not make an elaborate effort to balance the bridge. In the case that a substance behaves in a non-linear manner against an external magnetic field, the higher-harmonic susceptibility $|\chi_n|$ can be obtained by applying our modification to the bridge.[1] As to an exciting magnetic field, however, the operation of the bridge has so far been limited to a sinusoidal one.

Recently, we investigated a microbridge-coupled superconductor by means of the fundamental and higher-harmonic susceptibilities.[1,2] We found the temperature-dependent and amplitude-sensitive properties of the superconducting transition. And the odd-harmonic susceptibilities were also observed to appear in the ac response of microbridge-coupled superconductor. A fine explanation of these properties was given from the standpoint of weakly-connected loop model, which implicates a non-linear process in the response. The results previously obtained lead to a further interest how the ac response would be in various kinds of non-sinusoidal periodic fields.

In the present work, we attempt to generate a superconductive profile of microbridge-coupled superconductor against nonsinusoidal exciting field with the aid of weakly-connected loop model.

CALCULATION

1. Sinusoidal Magnetic Field

In our previous works, we investigated the response of superconducting Tc with

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