

Electrochemical and Spectrofluorometric Behaviors of Eu(III) Complexes in Aqueous Solution

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Eu(III) exhibits one electron-transfer reduction at $E_{1/2} = -0.617$ V *vs.* Ag/AgCl and the hypersensitive peak at 618 nm corresponding to $^5D_0 \rightarrow ^7F_2$ transition in 0.10 M LiClO₄ aqueous solutions. Upon the addition of carboxylate or sulfonate anions to the Eu(III) aqueous solutions, the reduction potential shifts negatively and the reduction current decreases because of the complex formation between Eu(III) ions and the anions. However, for the case of carboxylate anion (acetate or propionate) the shift of reduction peak potential and the emission intensity at 618 nm are greater. The results are interpreted in terms of the differences in the formation constants and the hypersensitivity.

Introduction

Luminescence excitation spectroscopy is proven to be valuable in characterizing Eu(III) ion environments, particularly in biomolecular systems.^{1,2} Furthermore, since luminescence intensity emitted from the $^5D_0 \rightarrow ^7F_2$ transition (*ca.* 618 nm in aqueous solutions) is relatively intense, the condition of water molecules coordinated to Eu(III) can be determined. The environmentally sensitive transition in emission is subsequently designated as a hypersensitive transition.^{2,3} Carbonate, for example, produced an overall increase in Eu(III) fluorescence intensity by a factor of about 10 for most peaks but over 100 fold for the $^5D_0 \rightarrow ^7F_2$ transition.⁴ While most ligands are expected to produce hypersensitivity effects with respect to aquo ions, there may be some ligands for which the effect may not be observed.

The electrochemical reduction of europic (Eu(III)) to europous (Eu(II)) ion produces a well-developed wave that can be used for the determination of Eu(III) content in a rare earth mixture. For example, the wave is excellently defined in 0.1 M NH₄Cl, that is, reduction proceeds nearly reversibly and the half-wave potential is observed at -0.67 V *vs.* S.C.E.⁵ The complexes of Eu(III) with a variety of carboxylic acids were investigated by electrochemical methods.^{6,7} In acetonitrile, Eu(III) is reduced first to Eu(II) and then to Eu-amalgam. The limiting-current of the second wave is twice of the first, since *n*, the number of electrons involved in the reduction, is one for the first reduction but two for the second.⁸

This paper reports the electrochemical and fluorometric behaviors of the complexes of Eu(III) with some carboxylate and sulfonate counter anions, which are typically classified as inner sphere complexing ligand and outer sphere complexing ligand, respectively. Presented are the results of some interesting relationship between electrochemical and fluorometric aspects that can be correlated well with the variation of the reduction potential and the hypersensitivity of Eu(III) in aqueous media.

Experiment

Reagents. Europium(III) chloride hexahydrate was purchased from Aldrich (99.99% purity grade). A stock solution

was adjusted at 1.0×10^{-2} M Eu(III) in triply distilled water. Formate (Janssen), acetate (Kanto), propionate (Yakuri), benzosulfonate (Aldrich), and poly styrene sulfonate (PSS) (avg. MW=70,000: Aldrich) of sodium salts were used as received. The preparation of poly(styrene maleic acid)-Na salt (PSMA-Na) was described previously.⁹ Solution mixtures of Eu(III) and anions were purged with Ar gas for 10 min and allowed to equilibrate before fluorescence and electrochemical measurements.

Apparatus. A Hitachi 650-60 fluorescence spectrophotometer was used to obtain the emission spectra of Eu(III) and its complexes at room temperature. Absorption spectra were measured with a Hewlett Packard 8452A diode array spectrophotometer. An EG & G Princeton Applied Research Co. (PARC) 273 potentiostat/galvanostat, an EG & G PARC 303A static mercury drop electrode (SMDE), and a cell system were used for the measurements of DC and differential pulse polarography and cyclic voltammetry. This cell was suited for sample volumes of about 10 mL, and the top of the cell allowed for the introduction of three electrodes and a deaeration tube. The SMDE and HMDE (hanging mercury drop electrode) modes of the 303A system were served as working electrodes for electrochemical measurements. A mercury-drop under each mode was characterized by the weight of 1.2 mg and the surface area of 0.96×10^{-2} cm². A reference electrode, Ag/AgCl, was encased in a bridge tube connected to the test solution by means of a Vycor-tip. All potentials are cited against the Ag/AgCl reference electrode.

Results and Discussion

Fluorometric Analysis. Typical fluorescence emission spectra of 1.0×10^{-4} M Eu(III) ions in the presence of 0.10 M counter anions were obtained at $\lambda_{ex} = 395$ nm and are shown in Figure 1. In the emission spectra three separate peaks are observed at 595, 618, and 697 nm, corresponding to $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, and $^5D_0 \rightarrow ^7F_4$ transitions of Eu(III), respectively. The peak positions of Eu(III) are unchanged in the presence of the counter anions. It is noted that the peak at 618 nm in the mixed solutions of Eu(III) and ligands is strongly increased relative to the other peaks. The enhancement is particularly strong in the acetate and propionate solutions (Figure 1(d) and (e)). This phenomenon of strong

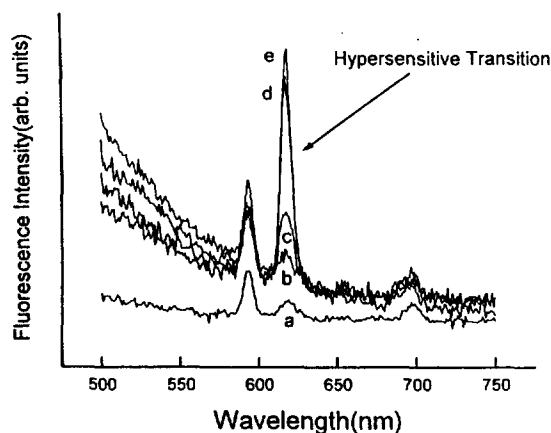


Figure 1. Emission spectra ($\lambda_{ex}=395$ nm) of 1.0×10^{-4} M Eu(III) in various 0.10 M solution of anions: (a) none; (b) perchlorate; (c) formate; (d) propionate; (e) acetate.

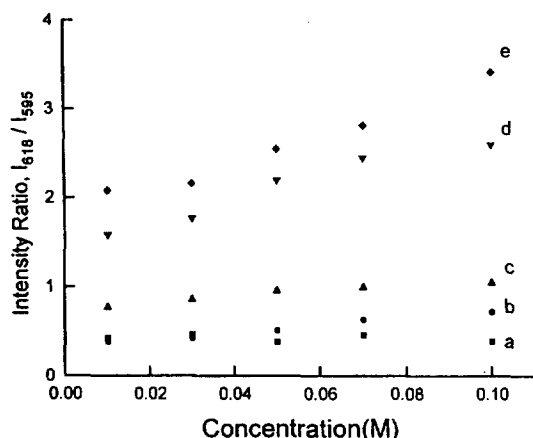


Figure 2. Plots of I_{618}/I_{595} of Eu(III) vs. concentration of counter anion: (a) benzosulfonate; (b) perchlorate; (c) formate; (d) propionate; (e) acetate.

enhancement of fluorescence emission is termed as the hypersensitive transition due to the destruction of the centrosymmetry of the aquo-Eu(III) ion (D_{3h}). To elucidate a relationship between the hypersensitive transition and the nature of the Eu(III) complexes, we utilized the intensity ratio (I_{618}/I_{595}) of the intensity of the hypersensitive transition at 618 nm to the intensity at 595 nm. The latter is weakly dependent on the environment around Eu(III) ions.

Figure 2 presents the dependence of I_{618}/I_{595} of Eu(III) on the ligand concentration obtained from the fluorescence emission spectra such as shown in Figure 1. The intensity ratio of Eu(III) in benzosulfonate solution essentially remains the same as the anion concentration is varied up to 0.10 M. For the cases of formate and perchlorate, the increase in the intensity ratio is small but clearly discernible with the increase in the respective anion concentration. However, the mixed solutions of Eu(III) with acetate and propionate show substantial increase in the intensity ratio. The results indicate that benzosulfonate ($pK_a=0.70$), perchlorate ($pK_a=1.77$), and formate ($pK_a=3.75$) destruct the symmetry of hydrated Eu(III) less than propionate ($pK_a=4.87$) and acetate

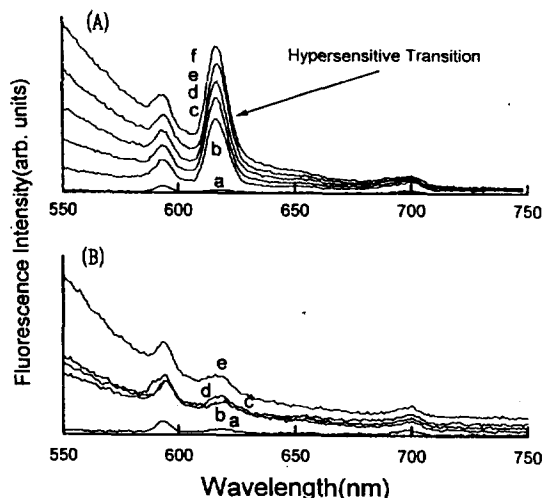


Figure 3. (A) Emission spectra ($\lambda_{ex}=395$ nm) of 1.0×10^{-4} M Eu(III) in PSMA-Na solutions. Concentration of PSMA-Na in carboxylate unit: (a) 0; (b) 1.4×10^{-4} ; (c) 2.1×10^{-4} ; (d) 5.2×10^{-4} ; (e) 1.8×10^{-3} ; (f) 9.0×10^{-3} M. (B) Emission spectra ($\lambda_{ex}=395$ nm) of 1.0×10^{-4} M Eu(III) in PSS-Na solutions. Concentration of PSS-Na in sulfonate unit: (a) 0; (b) 1.4×10^{-4} ; (c) 2.1×10^{-4} ; (d) 5.2×10^{-4} ; (e) 1.8×10^{-3} M.

($pK_a=4.75$) counter anions. Benzosulfonate and perchlorate anions with small pK_a values behave as soft conjugate bases, whereas acetate and propionate anions with large pK_a values act as hard conjugate bases. Eu(III) ion, typically, acts as a hard acid and interacts well with a hard base. For this reason acetate and propionate anions affect greatly the environment around the Eu(III) ion. In the solution of Eu(III) and acetate (Figure 2(e)), the hypersensitivity appears to show the largest change among the simple ligands used in the present system. See the discussion below.

In Figures 3(A) and (B), the effect of polymers containing different pendant anions $-\text{COO}^-$ and $-\text{SO}_3^-$ ions, respectively, on the fluorescence emission is compared. To the short wavelength region below 550 nm the fluorescence emission comes from the tail of $\pi \rightarrow \pi^*$ transition of styrene unit in the polymers. From the figures, it is quite obvious that the polymer containing pendant carboxylate ions exhibits the hypersensitivity more than the sulfonate containing polymer. The intensity ratio is enhanced linearly from 0.3 of aquo-Eu(III) without PSMA-Na to 4.4 with PSMA-Na at 9.0×10^{-3} M carboxylate unit. In comparison with acetate ions above, this enhancement of the intensity ratio is enormous at such a small concentration of PSMA-Na. However, in the PSS-Na and Eu(III) mixture, the intensity ratio essentially remains constant at approximately 0.6 with the increase of PSS-Na concentration up to 9.0×10^{-3} M sulfonate unit, although both of the Eu(III) intensities at 595 nm and 618 nm are increased in the presence of the polymer. The intensity ratio of Eu(III) with PSS-Na is almost comparable with that of benzosulfonate, indicating that the pendant sulfonate groups do not show any additional improvement over simple sulfonate ions with respect to the hypersensitivity. From the differences in the hypersensitivity, one can conclude that the carboxylate polymer, PSMA containing maleic acid ($pK_{a1}=1.83$, $pK_{a2}=6.07$) breaks the symmetry of aquo-Eu(III) more effectively

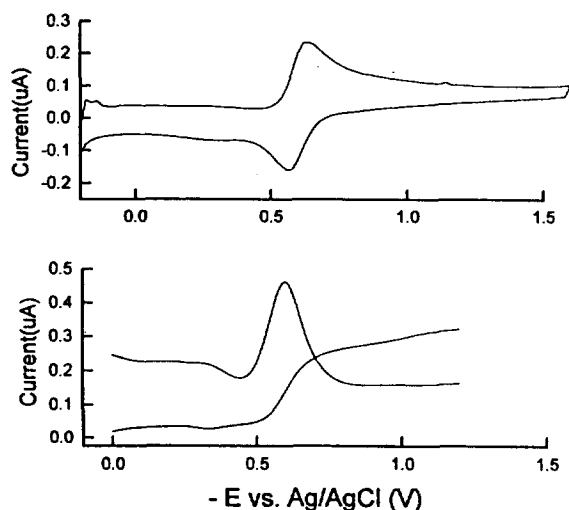


Figure 4. Differential pulse and DC polarograms and cyclic voltammogram of 1.0×10^{-4} M Eu(III) in 1.0×10^{-2} M LiClO_4 .

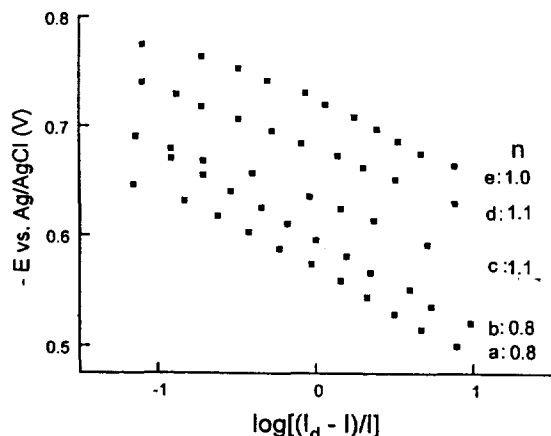


Figure 5. Plots of $-E$ vs. $\log[(I_d - I)/I]$ for the reduction of Eu(III) in 0.01 M anions of (a) benzosulfonate; (b) perchlorate; (c) formate; (d) propionate; and (e) acetate. n is the electron number.

than simple carboxylate ligands and the sulfonate polymer containing 4-styrenesulfonic acid.

Voltammetric Analysis. Voltammetric methods are also useful tools in investigating complexes of metal ions. In order to obtain additional information concerning with the formation constants of Eu(III) and carboxylate and sulfonate complexes, we employed several voltammetric techniques.

Figure 4 shows representative differential pulse and DC polarograms, and a cyclic voltammogram of 1.0×10^{-4} M Eu(III) in 1.0×10^{-2} M LiClO_4 . In the cyclic voltammogram there is a reversible wave, in which the one electron transfer reduction/oxidation processes, $\text{Eu(III)} + e^- \rightleftharpoons \text{Eu(II)}$, occur at $E_{pc} = -0.632$ V and $E_{po} = -0.562$ V at a scan rate of 50 mV/s, and electrochemical half-wave potential $E_{1/2} = -0.602$ V. Well defined polarographic waves are also obtained for all of the other Eu(III) solution containing 0.10 M anions.

The polarographic wave equation that defines the sigmoidal portion at room temperature is given by¹⁰

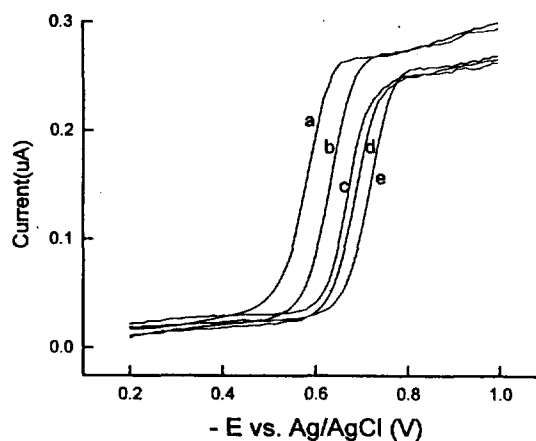


Figure 6. DC polarograms of 1.0×10^{-4} M Eu(III) in 0.1 M solutions of (a) benzosulfonate; (b) perchlorate; (c) formate; (d) propionate; and (e) acetate.

$$E = E_{1/2} - 0.05916/n \cdot \ln[(I_d - I)/I] \quad (1)$$

where n is the number of electrons in each half reaction and I_d is the diffusion current. Thus, a plot of $-E$ vs. $\log[(I_d - I)/I]$ should be linear with a slope of $59.16/n$ mV when the electrochemical reaction is reversible. Figure 5 shows the plots obtained from the polarographic study on the solutions of Eu(III) and ligands. From the figure, the values of n for the reduction of aquo- and complexes Eu(III) with various ligands are calculated to be approximately 1. Although the plots show some deviation from the expected value of unity, it is not unreasonable to conclude that the process of $\text{Eu(III)} + e^- \rightleftharpoons \text{Eu(II)}$ is a one electron transfer reaction for all the Eu(III) complexes studied.

Electrochemical half-wave potential $E_{1/2}$ of a metal ion usually shifts to a more negative value when the metal ion undergoes complex formation and changes as the concentration of the ligand varies.¹⁰ The potential shifts associated with the formation of the Eu(III)-ligand complexes at a given concentration of the ligand are measured from the sampled DC polarograms. The typical results are shown in Figure 6. From similar measurements obtained by varying the ligand concentration, the difference, $\Delta E_{1/2}$, between the half-wave potential of the aquo-Eu(III), $E_{1/2}$, and that of a Eu(III) complex, $(E_{1/2})_C$, at 25 °C is plotted as a function of the ligand concentration in Figure 7 according to^{5,10,11}

$$\Delta E_{1/2} = (E_{1/2})_C - E_{1/2} = 0.05916/n \cdot \log K - 0.05916/n \cdot p \cdot \log[L] \quad (2)$$

where K is the complex formation constant, p is the stoichiometric coefficient, and $[L]$ is the ligand concentration. The maximum ionic strength of present experiments was set to be 0.10 M, beyond which the relationship of Eq. (2) is not generally observed. From the plots in Figure 7 the stoichiometric coefficients (p) and formation constants (K) of Eu(III)-complexes are calculated and the results are summarized in Table 1. Also enclosed in the table are the formation constants measured by different techniques. Although the values are somewhat different each other because of the differences in the experimental conditions such as ligand concentration, both set of data show the same trend. In particular, the p

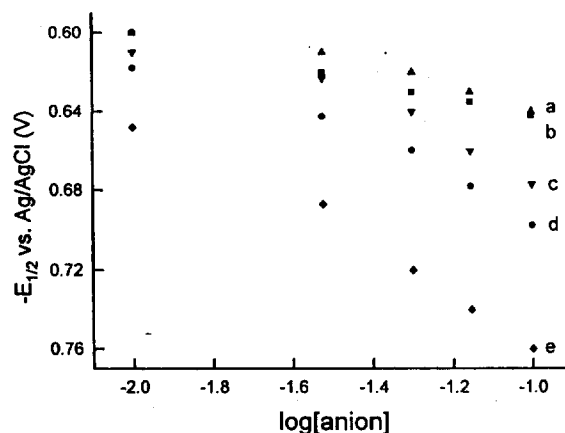


Figure 7. Plots of $E_{1/2}$ for the reduction of Eu(III) vs. $\log[\text{anion}]$ of (a) benzosulfonate; (b) perchlorate; (c) formate; (d) propionate, and (e) acetate.

Table 1. Stoichiometric coefficients (p) and formation constants (K) of Eu(III) complexes

	Acetate	Propionate	Formate	Benzosulfonate	Perchlorate
p^a	1.9	1.3	1.1	0.6	0.7
$\log K^a$	1.1	1.0	0.98		
$\log K^b$	2.31	1.98	1.40		

^a Measured in this experiment. ^b Taken from Ref. 4.

value is found to be the largest in the case of acetate and decreases in the order acetate > propionate > formate > benzo-sulfonate for the range of ligand concentration over 0.010–0.10 M. This decreasing order of p value as well as K coincides qualitatively well with the increasing order of the intensity ratio.

This relationship between p value of the Eu(III) complexes and the emission intensity ratio of I_{618}/I_{595} is visually presented in Figure 8, where the intensity ratios are those obtained at the anion concentrations of 0.10 M. The correlations noted in Figure 8 is interpreted as follows.^{12,13} The complexation of Eu(III) aquo ions are assumed to proceed by a mechanism which involved initial formation of an intermediate outer sphere species separated by one or more intervening molecules of coordinated water. As the concentration of the anions increases, the inner sphere complex in direct contact with Eu(III) starts to form with the concomitant expulsion of the water molecules.

The formation of an inner sphere complex is accompanied by the following two effects. First, the dehydration of Eu(III) ions upon the formation of the inner sphere complex causes an endothermic enthalpy change. Several representative enthalpy changes for the formation of Eu(III) complexes are listed in Table 2. The enthalpies for the complexes of Eu(III) with carboxylates from acetic acid, propionic acid, and maleic acid are all endothermic. The decreasing order of the enthalpy changes are in good agreement with the increasing orders of both the p value and the formation constant in Table 1. But exothermic behaviors appear with thiocyanate, sulfonate derived from 8-hydroxyquinoline-5-sulfonic acid and 1,2-

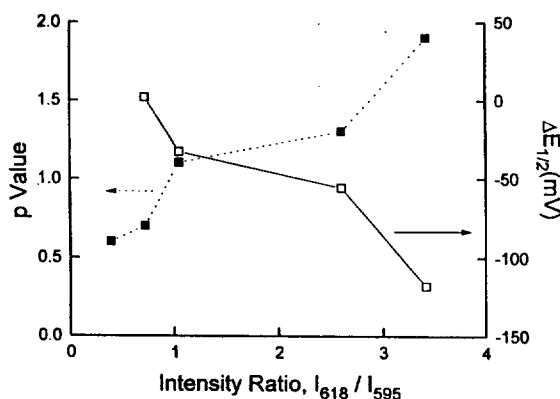


Figure 8. Relation of the p value and $\Delta E_{1/2}$ to the intensity ratio of I_{618}/I_{595} .

Table 2. Enthalpies^a of formation of Eu(III) complexes

Ligand	Enthalpy (kJ/mol)
Acetic acid	5.8
Propanoic acid	7.36
Maleic acid	14.22
Sulfate ion	15.23
8-hydroxyquinoline-5-sulfonic acid	-24.14

^a Taken from Ref. 14.

diaminoethane.¹⁴ Sulfonate ions are known to form outer sphere complexes with Eu(III). Second, the coordination of a ligand molecule directly to Eu(III) is manifested to yield an enhanced hypersensitivity because of the perturbation of the centro symmetry around Eu(III) aquo ions. Therefore it is expected that the ligand having smaller endothermic enthalpy change exhibits the larger intensity ratio. Figure 8 satisfies this expectation. Since benzosulfonate do not show any appreciable hypersensitivity the symmetry around Eu(III) is not destructed in the solution of the ligand. The exothermic enthalpy change (Table 2) supports that the nature of the weak Eu(III)-benzosulfonate complex is not an inner sphere complex.

Since the intensity ratio of Eu(III) with PSS-Na is found to be 0.5 close to that with benzosulfonate (Figure 3(B)), its p value is estimated to be about 0.6 at all concentrations of the polymers. The p value of the Eu(III) complex with PSMA-Na was not accurately evaluated due to the experimental difficulties. However, since the intensity ratio is about 4.4 at 9.0×10^{-3} M carboxylate unit from Figure 3(A), the p value of the Eu(III)-PSMA complex is estimated to be exceeding much higher than 2.0 which could not be obtained at 0.10 M acetate.

Included also in Figure 8 are the variation of the difference of the half-wave potential, $\Delta E_{1/2}$, with respect to the intensity ratio of Eu(III). The figure shows that the higher the intensity ratio of the Eu(III) complexes, the larger $\Delta E_{1/2}$, indicating that the increasing order of the intensity ratio is correlated well with the increasing order of $\Delta E_{1/2}$.

Therefore it may be concluded that a complex which shows stronger hypersensitivity possesses a larger formation

constant and a more negatively shifted half-wave potential. The hypersensitivity of Eu(III), which is easily measured from aqueous solution with a spectrofluorometer, may be served as a good indicator to estimate the relative strength of the complex formation of Eu(III) with a ligand and to understand the environment around Eu(III).

Conclusion

We have studied both electrochemical and fluorometric behaviors of aquo-Eu(III) and its complexes with carboxylate and sulfonate anions. Ligands, that are known to form inner sphere complexes such as acetate, propionate, and PSMA ions, form stronger complexes with Eu(III) and show more enhanced hypersensitivity of Eu(III). The increasing orders of the complex formation constant and the p value which are obtained by the electrochemical methods correlates well with the increasing order of the intensity ratio determined by spectrofluorometry.

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Mechanistic Studies on the Formation of Soluble Intermediate during the Electrochemical Nucleation of Lead Dioxide

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Different behavior on the formation of soluble intermediate was observed depending on the substrate employed during the nucleation of lead dioxide from plumbous ion using a rotating ring-disk electrode. It was found that no soluble intermediate was formed at glassy carbon electrode, while the presence of soluble intermediate could be detected at platinum substrate. From the different anodic behavior of two substrates, the formation of a probable Pb(III) soluble intermediate was suggested. A most probable nucleation mechanism at the platinum substrate involving a second order chemical reaction was derived on the basis of rotating disk electrode experiments.

Introduction

As mentioned in the previous paper¹, it is clear that there is a soluble intermediate during the electrochemical nucleation of lead dioxide at platinum substrate from plumbous ion. Even though some authors have suggested the nature of the intermediate, the formation mechanism of the soluble

intermediate during the nucleation has not been discussed. Fleischmann *et al.*² have suggested $\text{Pb}(\text{OH})_2^{2+}$ species as an adsorbed, not soluble, intermediate during the course of deposition of $\alpha\text{-PbO}_2$ at platinum substrate in acetate solution. Hampson *et al.*³ proposed a detailed mechanism for the formation of Pb(III) intermediate as $[\text{OH}\cdot\text{Pb}\cdot\text{OH}]^+$ during the deposition of bulk lead dioxide in perchloric acid. They also suggested $\text{PbO}_2(\text{H}^+)_2$ as an adsorbed intermediate. Recently, Chang and Johnson^{4,5} have claimed the presence of soluble species of Pb(IV) at gold electrode in perchloric acid solution.

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