

Electrochemical Study of Complex Formation of Cerium (IV) Ion with Glycyl-Glycine and Glycyl-Valine

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Abstract: Cyclic voltammetry can be used to determine the relative stability of $Ce^{4+/3+}$ complexes which has been less accessible by other techniques. Shifts in the anodic and cathodic peak potentials of $Ce^{4+/3+}$ -L and the reversibility of the electrochemical processes were studied as a function of concentration of the ligands. The cyclic voltammograms of $Ce^{4+/3+}$ obtained at different scan rates are quasireversible with a formal redox potential of $E_{1/2} = 0.95975$ V in 0.5 M H_2SO_4 solution. The voltammograms of $Ce^{4+/3+}$ -glycyl-glycine ($Ce^{4+/3+}$ -gly gly) and $Ce^{4+/3+}$ -glycyl-valine ($Ce^{4+/3+}$ -gly val) show a reduction wave negatively shifted relative to the reduction wave of $Ce^{4+/3+}$. The reversibility of the Ce^{4+}/Ce^{3+} couple improved with the increase of scan rates.

Key words: Cyclic Voltammetry % Stability Constant % Half-Wave Potential % Glycyl-valine and Glycyl-Glycine

INTRODUCTION

Peptides are an amazing class of compounds. Although they are all constructed from relatively simple building blocks (the amino acids), they exhibit a remarkable range of biological properties: peptides can act as antibiotics, hormones, food additives, poisons, or pain-killers and it is primarily because of their medicinal properties that the study of peptides has become one of the most active areas of current research. When two amino acids are covalently linked together by amide bonds, the resulting molecules are called dipeptides [1]. The interaction between amino acids, peptides and proteins with metal ions plays an important role in biochemistry and biology and has been studied extensively during the last three decades. Complexes of amino acids and oligopeptides are involved in the exchange and transport mechanism of some trace metal ions in the human body [2-5]. The Ce^{4+}/Ce^{3+} couple was chosen as the positive electrolyte of cerium (Ce^{4+}/Ce^{3+}) redox flow cell [6,7] mainly for the high potential of Ce^{4+}/Ce^{3+} couple.

The reduction of Ce^{4+} at Pt, Au, Ir [8,9] highly boron-doped conductive diamond electrodes [9,10] and the oxidation of Ce^{3+} on Au, GC [11,12], PbO_2 [13,14], SnO_2 [15] electrodes were investigated. Klekens *et al.* [16] reported that the reduction of Ce^{4+} was independent of the electrode materials; the charge-transfer coefficient (α) and the heterogeneous rate constant (k_c) were similar for different electrodes, for instance, at Pt, Au, GC electrodes the k_c was 3.7×10^4 cm.sG⁻¹ [19], 4.8×10^4 cm.sG⁻¹ [20], 3.8×10^4 cm.sG⁻¹ [17] and α was 0.21 [17], 0.35 [18], 0.28 [19], respectively. But, as to the oxidation of Ce^{3+} , the various electrodes had different effects on the following reaction:



Here, H_2SO_4 was chosen as the acid media mainly because:

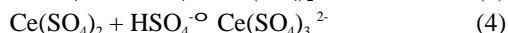
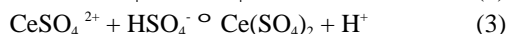
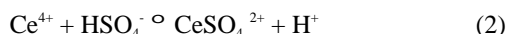
- In $HClO_4$ or HNO_3 solution, the potential of Ce^{4+}/Ce^{3+} couple is high and far above the over-potential for oxygen evolution and the Ce^{4+}/Ce^{3+} couple is not stable in $HClO_4$ or HNO_3 solution [19,20]. Although

the potential of the Ce^{4+}/Ce^{3+} couple is also high in H_2SO_4 solution, Kunz [21] proved that $Ce(SO_4)_2$ could stably exist in H_2SO_4 solution, redox reaction seldom took place and the stability of the electrochemical active material is especially important in a redox flow cell.

C ClO_4^- and NO_3^- can not form stable complexes with Ce^{4+} and Ce^{3+} (this is also the reason that the potential of this couple is higher than that in H_2SO_4 solution). However, SO_4^{2-} can form a complex with Ce^{4+} , in the form of $CeSO_4^{2+}$, $Ce(SO_4)_2$ and $Ce(SO_4)_3^{2-}$ [10]. Because of the formation of a stable complex, it was generally accepted that the Ce^{4+} and Ce^{3+} would not undergo hydrolysis in H_2SO_4 solution.

C If trying to take HCl as the acid media, then Ce^{4+} would oxidize Cl^- to Cl_2 . Mills [22] used the Ru, Ir oxide as the catalyst to accelerate this reaction, which demonstrated that the Ce^{4+}/Ce^{3+} couple was unstable in HCl solution.

In H_2SO_4 solution, the Ce^{4+} could form the following complexes with SO_4^{2-} :



In this study, the shifts in the anodic and cathodic peak potentials of $Ce^{4+/3+}$ -L and the reversibility of the electrochemical processes were studied as a function of concentration of the ligands. The cyclic voltammograms of $Ce^{4+/3+}$ obtained at different scan rates are quasireversible with a formal redox potential of $E_{1/2} = 0.95975$ V in 0.5 M H_2SO_4 solution. The voltammograms of $Ce^{4+/3+}$ -glycyl-glycine ($Ce^{4+/3+}$ -gly gly) and $Ce^{4+/3+}$ -glycyl-valine ($Ce^{4+/3+}$ -gly val) show a reduction wave negatively shifted relative to the reduction wave of $Ce^{4+/3+}$. The reversibility of the Ce^{4+}/Ce^{3+} couple improved with the increase of scan rates.

Experimental Section

Reagents: All the chemicals used were of analytical reagent grade. Glycyl-glycine ($C_4H_8N_2O_3$), (gly gly), glycyl-L-valine ($C_7H_{14}N_2O_3$), (gly val), sulfuric acid and ceric ammonium sulfate dihydrate were obtained from Merck and Sigma, respectively. The aqueous stock solutions of the peptides were freshly prepared daily.

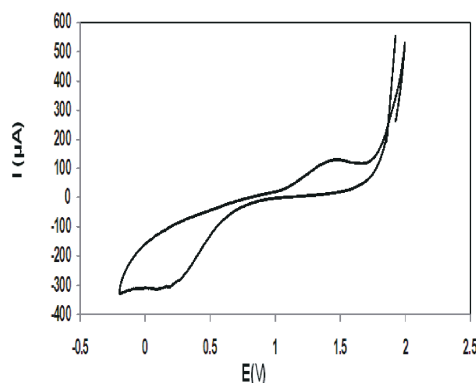


Fig. 1: Cyclic voltammograms at a scan rate of 40 mV/s for a glassy carbon electrode in a solution containing $Ce^{3+/4+}$ 0.1 M in aqueous 0.5 M H_2SO_4 .

Electrode Preparation: A one-compartment electrochemical cell was used with a three-electrode configuration. Glassy carbon electrode was used as working electrode. The reference electrode was Ag/AgCl (saturated KCl) and the platinum gauze was used as the counter electrode. The working electrode was polished using 0.5 μm of alumina for 2 min and rinsed with distilled water prior to each measurement.

Electrochemical Experimental: In cyclic voltammetry, CV, a cyclic voltammeter, Solartron 270, connected to a computer for automated data acquisition was used for current versus potential measurements. First, cyclic voltammogram of $Ce^{4+/3+}$ 0.1 M in H_2SO_4 0.5 M was determined as shown in Figure 1. Then, the complexation of $Ce^{4+/3+}$ by glycyl-valine and glycyl-glycine has been studied in different concentrations of the ligands [5×10^{-4} , 8×10^{-4} , 11×10^{-4} , 14×10^{-4} , 17×10^{-4} and 0.01] M in the same mixture of solvents accompanied by a gentle stirring and an nitrogen purge for 10 min prior to each measurement. All measurements were made at scan rates (20, 40, 60, 100 and 250) mV \cdot s $^{-1}$. The half wave potential ($E_{1/2}$) values reported here are defined as the numerical average of the cathodic and anodic peak potentials. All electrochemical potentials measurements are expressed relative to the Ag/AgCl electrode.

RESULTS AND DISCUSSION

Cyclic voltammetry can be used to qualify the comparative stability of $Ce^{4+/3+}$ complexes which has been less available by other techniques. Shifts in the anodic and cathodic peak potentials of $Ce^{4+/3+}$ -L and the

Table 1: Values of formation complex cerium ion with Glycyl-Glycine in deferent scan rates and concentrations of ligand

$I_c(\mu A)$	$I_a(\mu A)$	$E_c(v)$	$E_a(v)$	$E_{1/2}(v)$	$\langle(mV/S)$	C ligand M
-264	96.3	0.182	1.57	0.876	20	0
-391	219	0.023	1.9	0.961	60	0
-511	286	0.0744	1.89	0.982	100	0
-239	50.4	0.106	1.39	0.748	20	0.01
-355	197	0.122	1.63	0.876	60	0.01
-490	182	0.0845	1.62	0.852	100	0.01
-734	208	0.0303	1.67	0.850	250	0.01
-249	90.2	0.42	1.44	0.93	20	0.0005
-452	159	0.0702	1.56	0.815	60	0.0005
-537	246	0.102	1.58	0.841	100	0.0005
-838	307	0.0354	1.65	0.842	250	0.0005
-253	107	0.268	1.36	0.814	20	0.0008
-400	212	0.16	1.54	0.85	60	0.0008
-509	290	0.249	1.54	0.894	100	0.0008
-776	365	0.128	1.62	0.874	250	0.0008
266	67.7	0.0846	1.52	0.8023	20	0.0011
-443	143	0.0836	1.59	0.836	60	0.0011
-308	173	0.294	1.41	0.852	100	0.0011
-267	71.2	0.113	1.51	0.811	20	0.0014
-435	171	0.0842	1.6	0.842	60	0.0014
-558	155	0.0416	1.6	0.820	100	0.0014
-262	72.5	0.14	1.53	0.835	20	0.0017
-434	165	0.0859	1.64	0.862	60	0.0017
-36	196	0.113	1.67	0.891	100	0.0017

Table 2: Values of formation complex cerium ion with Glycyl-valine in deferent scan rates and density of ligand

$I_c(\mu A)$	$I_a(\mu A)$	$E_c(v)$	$E_a(v)$	$E_{1/2}(v)$	$\langle(mV.SG^1)$	C ligand M
-264	96.3	0.182	1.57	0.876	20	0
-391	219	0.023	1.9	0.961	60	0
-511	286	0.0744	1.89	0.982	100	0
-175	96.9	0.137	1.31	0.723	20	0.01
-287	144	0.0911	1.47	0.780	60	0.0005
-184	110	0.403	1.28	0.841	20	0.0008
-416	118	0.0382	1.58	0.722	60	0.0008
-211	70	-0.0605	1.47	0.704	20	0.0011
-374	175	0.134	1.55	0.842	60	0.0011
-434	244	0.0996	1.55	0.824	100	0.0011
-214	95.9	0.123	1.49	0.806	20	0.0014
-331	163	0.0243	1.53	0.777	60	0.0014
-421	249	0.0657	1.62	0.842	100	0.0014
-207	112	0.255	1.32	0.787	20	0.0017
-295	169	0.0739	1.51	0.791	60	0.0017
-409	218	0.0594	1.52	0.789	100	0.0017

Table 3: Values of formation complex cerium ion with Glycyl-Glycine in deferent concentrations of ligand in scan rate 40 mV/s

$I_c(\mu A)$	$I_a(\mu A)$	$E_c(v)$	$E_a(v)$	$E_{1/2}(v)$	$\langle(mV.SG^1)$	C ligand M
-320	91.3	0.067	1.49	0.77	40	0.0005
-354	82.5	0.0887	1.56	0.824	40	0.0008
-302	157	0.261	1.42	0.840	40	0.0011
-322	177	0.294	1.42	0.857	40	0.0014
-311	185	0.337	1.43	0.883	40	0.0017
-335	104	0.0997	1.58	0.839	40	0.01
-272	111	0.23	1.49	0.86	40	0.05

Table 4: Values of formation complex cerium ion with Glycyl-valine in different density of ligand

$I_c(\mu A)$	$I_a(\mu A)$	$E_c(v)$	$E_a(v)$	$E_{1/2}(v)$	$\langle(mV.SG^1)$	C ligand M
-344	156	0.197	1.56	0.878	40	0.0005
-334	187	0.296	1.42	0.858	40	0.0008
-349	135	0.127	1.51	0.818	40	0.0011
-322	185	0.333	1.4	0.866	40	0.0014
-353	182	0.133	1.41	0.771	40	0.0017
-367	104	0.0871	1.44	0.755	40	0.01
-44	163	0.197	1.43	0.813	40	0.05

Table 5: Average values of the formation constants of Ce-gly gly and Ce-gly val at 25°C and constant ionic strength

Species	log \$_{101}^*\$
Ce-gly gly	5.685
Ce-gly val	8.742

$$^* \$_{pqr} = [M_p H_q L_r^{(4p+q-r)}] / [M^{+4}]^p [H^+]^q [L^-]^r \quad [23]$$

reversibility of the electrochemical processes were determined as a function of concentration of the ligands. The cyclic voltammograms of Ce^{4+/3+}-gly gly and Ce^{4+/3+}-gly val obtained at different scan rates are quasireversible with an average formal redox potential of $E_{1/2} = 0.893$ V and $E_{1/2} = 0.834$ V as shown in Tables 1 and 2, respectively. On the basis of the cyclic voltametry measurements described above, the electron transfer process is attributed to the Ce^{4+/3+}-L redox couple. The effect of the scan rate on the shape of the cyclic voltammograms is shown in Figure 2 for Ce^{4+/3+}-gly gly (the cyclic voltammograms Ce^{4+/3+}-gly val have not shown). In the whole scan rate range, the cathodic peak potential is slightly shifted toward more cathodic potentials with increasing scan rate. The decrease of the cathodic peak potential (a few mV) could be due to a small error provoked by ohmic drop corrections and the uncertainty of the R_s measurement. It can be mentioned that most of the other actinides have shown a reversible behavior at low scan range. The voltammograms of Ce^{4+/3+}-gly val and Ce^{4+/3+}-gly gly show a reduction wave negatively shifted relative to the reduction wave of Ce^{4+/3+} in deferent concentrations of ligand which as shown in Figures 3 and 4. The half-wave potential, $E_{1/2}$, of Ce^{4+/3+}-gly val and Ce^{4+/3+}-gly gly was found to be somewhat dependent on concentration of the ligands and these results can be simply explained by their interaction between the metal ion and each ligand which this results reported in Tables 3 and 4 at below. In Figures 3 and 4, a shift of $E_{1/2}$ of the Ce^{4+/3+}-gly gly and Ce^{4+/3+}-gly val couples to less negative values is observed when the concentration of each ligand is increased. The half-wave potentials, $E_{1/2}$, of the Ce^{4+/3+}, Ce^{4+/3+}-gly val and Ce^{4+/3+}-gly gly couples were determined according to the following equation:

$$E_{1/2} = E_{pa} -) E_p / 2 \quad (5)$$

where, E_{pa} is the anodic peak potential and $) E_p$ is the difference between the anodic and cathodic peak potentials $() E_p = (E_{pa} - E_{pc})$. The stability constants of Ce^{4+/3+}-gly val and Ce^{4+/3+}-gly gly were determined at 25°C by plotting equation 6 to give m and the stability constant, log \$, from the slope and the intercept, respectively.

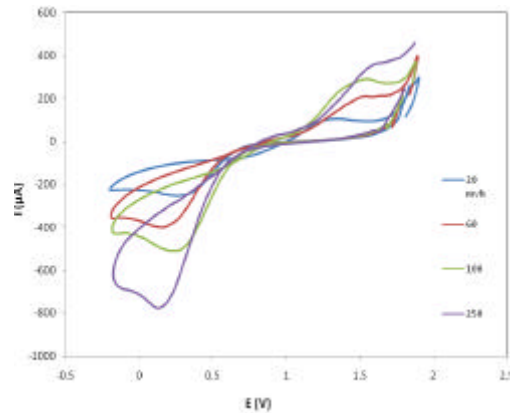


Fig. 2: Cyclic voltammograms in different scan rates for a glassy carbon electrode in a solution containing ce^{3+/4+} 0.1 M in aqueous 0.5 M H₂SO₄ 0.0008 M glycyl-glycine ligand.

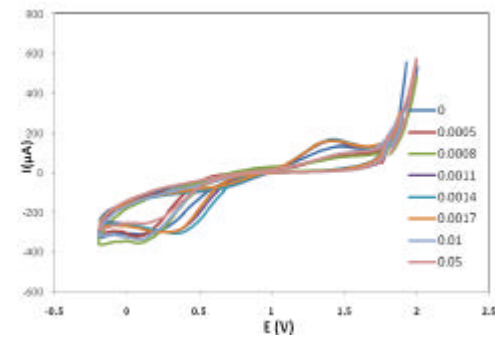


Fig. 3: Cyclic voltammograms at a scan rate of 40 mV/s for a glassy carbon electrode in a solution containing ce^{3+/4+} 0.1 M in aqueous 0.5 M H₂SO₄ and different concentrations of glycyl glycine ligand

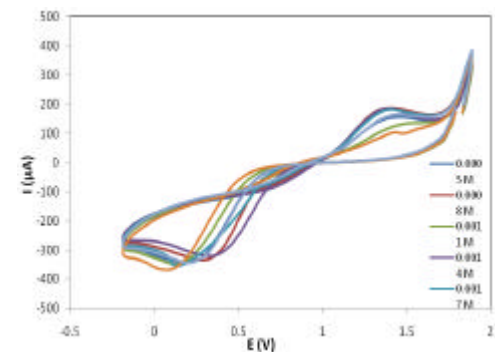


Fig. 4: Cyclic voltammograms at a scan rate of 40 mV/s for a glassy carbon electrode in a solution containing ce^{3+/4+} 0.1 M in aqueous 0.5 M H₂SO₄ and different concentrations of glycyl-Valine ligand

$$E_{1/2} = 0.0591/n (\log K + m \log[L]) \quad (6)$$

where, m and n are the ratio of each ligand in the complex species and the electron transferred, respectively. $E_{1/2}$ is the half-wave potential difference between the metal ion and the complex ($E_{1/2} = E_{1/2} - E_{1/2}(L)$). The results of the calculations and the cyclic voltammograms of $Ce^{4+/3+}$ -gly gly and $Ce^{4+/3+}$ -gly val systems are summarized in Table 5.

CONCLUSION

The stability constants of $Ce^{4+/3+}$ -gly gly and $Ce^{4+/3+}$ -gly val, the redox potentials of the Ce^{4+}/Ce^{3+} redox ion couple and the electrochemical behavior of the Ce^{4+}/Ce^{3+} redox reaction were studied at different concentration of gly gly and gly val. As shown in Table 5, the stability constant $Ce^{4+/3+}$ -gly val is more than $Ce^{4+/3+}$ -gly gly. This case can be explain due to the more nucleophilic properties glycyl valine relative to glycyl glycine, as we can observe this subject in the thorium complexes with mentioned dipeptides [23]. According to ref 23, the stability constants values of Th(IV) ion at constant temperature (25°C) and constant ionic strength (0.1 mol.dm³ sodium perchlorate) with gly gly and gly val were determined by the potentiometric and spectrophotometric titration methods.

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