

Voltammetric studies of Cadmium ion at the Mercury Electrode in the presence of L-Cysteine

W.T.Tan*, L.L.Ooi and E.B.Lim

Department of Chemistry, Universiti Putra Malaysia
43400 UPM Serdang Selangor D.E., Malaysia

Abstract: Voltammetric behaviours of cadmium (II) ion in the presence of a ligand with sulphur bearing group, such as cysteine ($\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COOH}$) were studied using mainly Osteryoung square wave voltammetry (OSWV) and cyclic voltammetry (CV) on a mercury electrode. Assessment of the chemical and physical conditions that may favour optimum current enhancement was done by studying the effect of varying pH, concentration of metal and ligand, pulse amplitude, scan rate and supporting electrolyte. The presence of 2 – 5 mM cysteine in a weakly complexing supporting electrolyte at pH 5-6 caused a 2-5 fold increase in the reduction current of Cd(II) and a slight negative shift in peak position. The current enhancement observed in different electrolytic media varied in the following order : perchlorate > nitrate > sulphate > chloride . An anion-induced adsorption mechanism can be used to account for the observed current enhancement of Cd(II) ion in the presence of cysteine.

Abstrak: Tingkahlaku voltametri bagi ion kadmium(II) dalam kehadiran ligan yang mempunyai kumpulan sulfur seperti sistena telah dikaji dengan menggunakan teknik voltametri gelombang segi empat sama Oesteryoung (OSWV) dan voltametri siklik (CV) pada elektrod merkuri. Penilaian keadaan kimia dan fizikal yang cenderung terhadap penambahan arus optima telah dilakukan dengan mengkaji kesan-kesan perubahan pH, kepekatan ion logam dan ligan, amplitud denyut, kadar imbasan dan elektrolit penyokong. Kehadiran 2-5 mM sistena di dalam elektrolit penyokong yang berkompleks sedikit pada pH 5-6 telah menghasilkan penambahan arus penurunan Cd(II) sebanyak 2-5 kali ganda dan sedikit anjakan kedudukan keupayaannya ke arah negatif. Penambahan arus di dalam media elektrolit yang berlainan berubah mengikut tertib berikut : perklorat > nitrat > sulfat > klorida. Mekanisma “penjerapan anion-teraruh” boleh diguna untuk menerangkan penambahan arus Cd(II) di dalam kehadiran sistena.

Received 12.4.00; accepted 24.11.00

Introduction

The use of ligands containing sulphur atoms as potential anchoring groups to induce the adsorption of metal complexes at a mercury electrode is well documented [1-7]. By using proper electrochemical techniques such as cathodic stripping voltammetry and pulse voltammetry [6], current enhancement was observed for the electrochemical oxidation or reduction of sulphur-bearing organic compounds and/or the metal ion. Interest in metal complex systems that involve the divalent and a simple thiol group such as cysteine or thiourea is still apparent in recent years. However it involved mainly the use of electrocatalysis process of cysteine in the presence of Cu(II) or Ni(II) for the determination of cysteine and related thiol compounds or for the analysis of metal ion [1-7]. The ability of cysteine to form complexes with Cd (II) in aqueous solutions has been investigated in constant ionic medium of NaCl [8]. However only the stability constants between the two species ($\log \beta_1 = 4.97$ and $\log \beta_2 = 9.92$ in 1.0 M NaCl) and the protonation constants ($\log k_1 = 10.26$, $\log k_2 = 8.22$ and $\log k_3 = 2.04$ in 1.0 M NaCl) of cysteine were reported [8]. Thus far there is no report on the current enhancement behaviour of divalent metal ion, Cd(II) in the presence of cysteine at a mercury electrode . It is therefore our

intention to report the work done on Cd (II)-cysteine system using fast sweep square wave voltammetry, cyclic voltammetry, chronocoulometry and chronoamperometry.

Experimental

Reagents

All chemicals used were of reagent grade purity and were used as received. 1000 $\mu\text{g/ml}$ Cd(II) was prepared as a stock solution from cadmium nitrate salt. A stock solution of L-cysteine (BDH) was usually prepared fresh in doubly distilled water and used within a few hours after preparation. 0.03M sodium acetate buffer was used, with adjustment to pH 4 and 6 by either an addition of acetic acid or nitric acid or NaOH. 0.04M triethanolamine was used for pH 7 while 0.04 M $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ buffer was used for pH 8 - 10. Unbuffered solution of pH < 4 was used with the addition of nitric acid.

Apparatus

An electrochemical workstation (Model BAS 100A) was used to perform square wave voltammetry (OSWV), cyclic staircase voltammetry (CV), chronocoulometry (CC) and chronoamperometry (CA). It was used together with SMDE (Model PARC 303),

Controlled Growth Mercury Electrode (CGME, BAS) and a DME cell system (Model AMEL 291). For the latter, a 5 seconds delay time was used before the commencement of the potential scan. The DME was assumed to approximate a stationary electrode at high scan rate. An electrode area of 0.028 cm^2 was employed in SMDE which was used in the studies of CC and CA. All potentials were measured against the Ag/AgCl (3M NaCl) reference electrode. A platinum wire was used as a counter electrode. The experiments were carried out at $25 \pm 1^\circ \text{C}$.

Results

Fig. 1 demonstrates the effect of cysteine on the square wave voltammograms of Cd(II) ion in different electrolytes namely KClO_4 (pH 5.2) KNO_3 (pH 5.2) and $(\text{NH}_4)_2\text{SO}_4$ (pH 4.9) using mercury electrode based on different electrode assemblies of SMDE and CGME in acetate buffer.

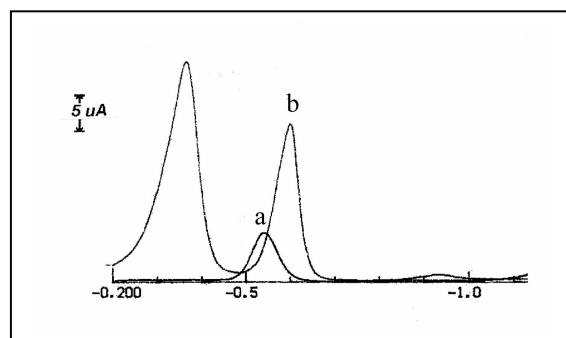


Fig.1. Square wave voltammograms:
(i) $10 \mu\text{g/ml}$ Cd(II) in 0.5 M $(\text{NH}_4)_2\text{SO}_4$, 3 mM acetate buffer, pH 4.9, in SMDE,
(a) without cysteine (b) with 10 mM cysteine spike.

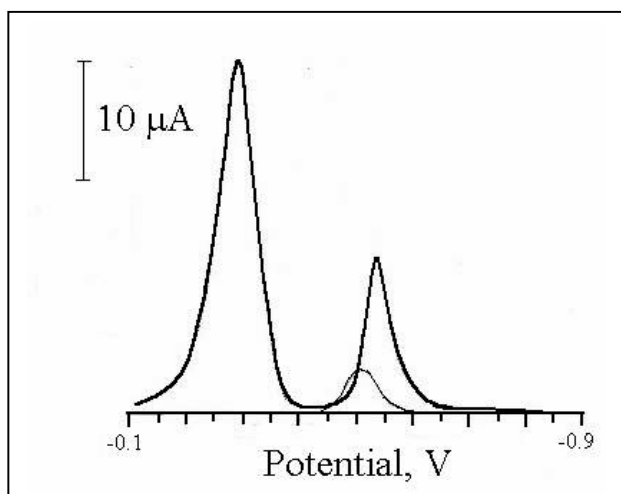


Fig. 1. (ii) $5.62 \mu\text{g/ml}$ Cd(II) in 1.0 M KNO_3 , 3 mM acetate buffer, pH 5.2, in CGME,
(a) without cysteine
(b) with 2 mM cysteine spike.

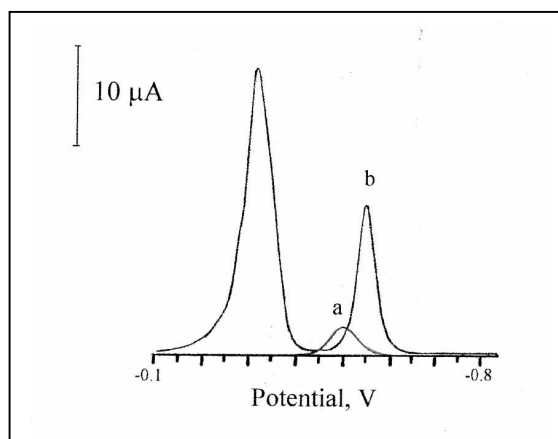


Fig.1. (iii) $5.62 \mu\text{g/ml}$ Cd(II) in 0.1 M KClO_4 , 3 mM acetate buffer, pH 5.2, in CGME, (a) without cysteine (b) with 2 mM cysteine spike.

The initial result shows that the presence of $2 - 10 \text{ mM}$ cysteine caused a 2-5 fold increase in the peak height and a negative shift in the peak position of the reduction peak of 0.05 mM ($5.62 \mu\text{g/ml}$) Cd(II) in KClO_4 and KNO_3 as well as 0.089 mM ($10 \mu\text{g/ml}$) Cd(II) ion in $(\text{NH}_4)_2\text{SO}_4$ electrolytes. As the enhancement in its reduction current was considerable in differential mode Fig.1(iii) as well as in individual current components (measurement made prior to the pulse and on top of the pulse in the square wave) Fig.1(iv) during OSWV, it justified further investigation concerning the chemical and physical conditions under which optimum current enhancement can be obtained and the possible mechanism involved.

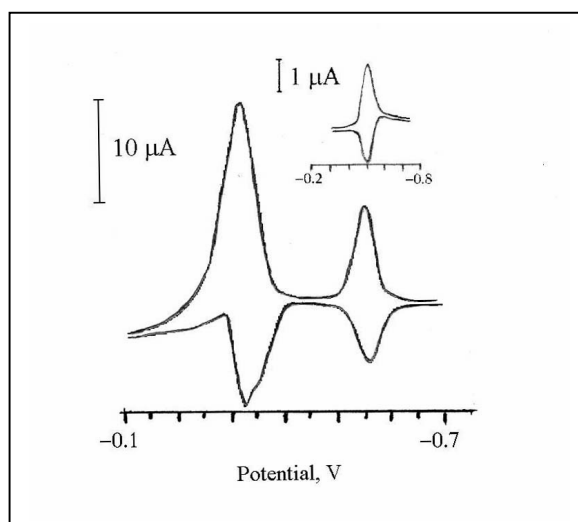


Fig. 1. (iv) Individual current components of (iii);
(a) without cysteine
(b) with 2 mM cysteine spike.

Table 1

Effect of supporting electrolyte on I_p and E_p of 5.62 $\mu\text{g/ml}$ Cd(II) with and without 2.0 mM cysteine (Cyst) during square wave voltammetry using CGME as a working electrode.

Supporting Electrolyte	$I_p/\mu\text{A}$		E_p/V		Enhancement
	No Cyst.	Cyst.	No Cyst.	Cyst.	
1.0 M KCl	2.55	5.88	-0.564	-0.608	2.3
1.0 M Na_2SO_4	1.58	4.07	-0.532	-0.608	2.6
0.5 M $(\text{NH}_4)_2\text{SO}_4$	2.58	5.22	-0.536	-0.540	2.0
1.0 M KNO_3	3.49	12.24	-0.512	-0.540	3.5
0.1 M KClO_4	2.77	14.70	-0.504	-0.552	5.3

Square Wave Voltammetry (OSWV)

Table 1 represents the effect of supporting electrolyte on the electrode reduction of Cd(II) including the peak current (I_p) and peak potential (E_p) in the absence and presence of cysteine. Potassium perchlorate provided the largest (5.3 fold) and potassium nitrate produced the second largest current enhancement (3.5 fold) for Cd(II)-cysteine system. In general the current enhancement observed in different media varied in the following order : perchlorate > nitrate > sulphate > chloride.

The effect of pH was studied in 0.5M $(\text{NH}_4)_2\text{SO}_4$. There was no obvious increase in peak current of Cd(II)-cysteinate complex species below pH 4.5. However, as pH increased from 4.5 onwards, a rapid increase in peak current was observed until pH of about 6. From pH 6 onwards, the peak current decreased sharply. The optimum pH range appears to be between pH 5 to pH 5.5. The effect of varying cysteine concentration at a constant Cd(II) concentration on the peak current and potential of Cd(II)-cysteinate complex was also assessed during OSWV. I_p value increased gradually with increasing concentration of cysteine until 5 mM of cysteine concentration was reached. I_p remains constant until 10 mM cysteine. It is noted that the individual current components of square wave voltammograms Figs.1(iv), 2(a-c) show significant increase in its cathodic peak components but not the anodic peak component with an increase in ligand concentration. Both current components of cadmium-cysteine peaks gradually become more symmetrical with an increase in ligand concentration. The optimum ligand concentration for maximum sensitivity is between 2 to 5

mM. Figure 3 shows the effect of varying Cd(II) ion concentration in the presence of 2 mM cysteine at pH 5.2 using CGME as a working electrode in single drop square wave voltammetry. Linearity exists below 3 ppm of Cd(II) ion concentration in the Cd(II)-cysteine system. Above this concentration, the plot of I_p vs Cd(II) ion concentration assume a smaller gradient. Under similar experimental conditions, linearity was extended to 20 ppm but with much lower current output for a simple system, ie Cd(II) in supporting electrolyte without ligand. Similar calibration and enhancement results were observed when DME was used as a working electrode.

The optimum pulse amplitude, ΔE range for well defined and enhanced peak current for Cd(II) reduction wave of OSWV in the presence of cysteine was between 25 - 50 mV. According to Barker and Gardner (1958) [9], the half-width ($W_{1/2}$) for 1, 2 and 3 electron transfer are 90.4, 45.2 and 30.1 mV respectively at 25 °C for small amplitudes of the order of 5 or 10 mV. Our results show that the Cd(II)-cysteine system produced differential waveforms having a $W_{1/2}$ of 37 - 52.mV at ΔE between 10 and 35 mV. Hence an electron transfer of 2 is indicated. $W_{1/2}$ increased with an increase in ΔE . Peak broadening became obvious at $\Delta E > 50$ mV. The peak potential for Cd(II)-cysteine wave shift anodically as the pulse amplitude was raised. Scan rate is equal to the product of frequency and the potential step in OSWV. There is no advantage of increasing the scan rate by varying the potential step while maintaining a constant frequency, as peak broadening becomes acute at higher step potential (> 20 mV).

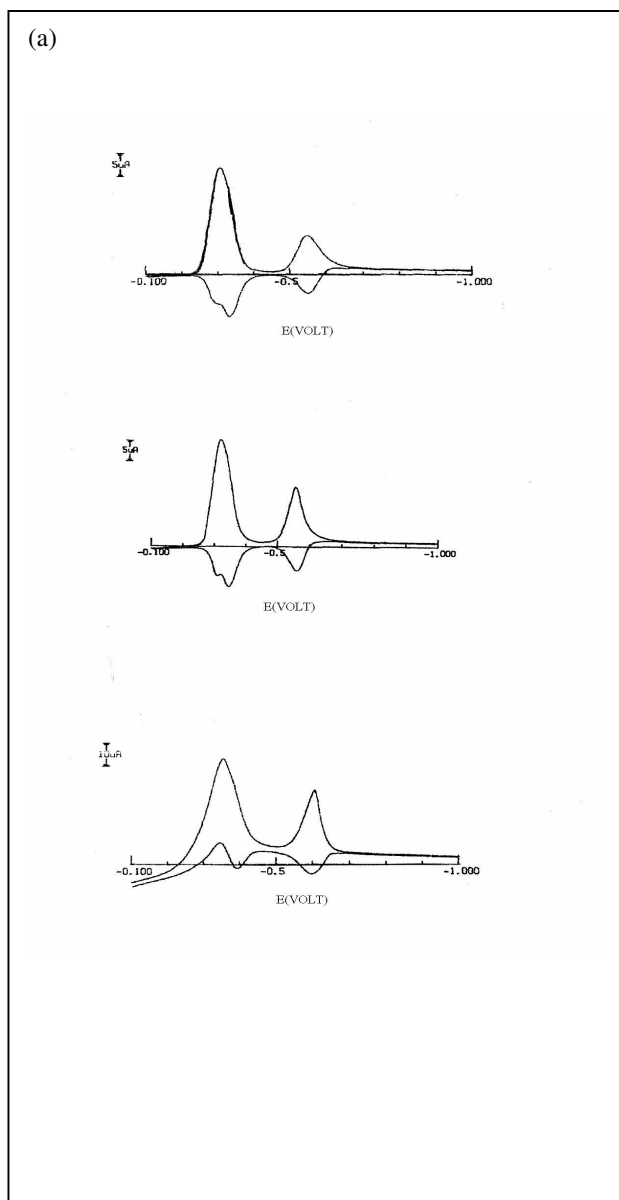


Fig.2 Square wave voltammograms showing individual current components of 10 µg/ml Cd(II) in 0.5 M $(\text{NH}_4)_2\text{SO}_4$, 3 mM acetate buffer, pH 5.1 with varying cysteine concentration of (a) 0.2 mM (b) 0.5 mM (c) 5 mM; 80 cycle/s, 4 mV step potential, 5 sec. delay time, DME as a working electrode.

In this study, scan rate was varied by varying frequency while maintaining potential step constant at 4 mV. If all experimental parameters are held constant except scan rate (varied by varying frequency at constant potential step), a plot of $\ln(I_p)$ vs $\ln(\text{scan rate}, \nu)$ should have a slope of one-half for diffusion control and unity for adsorption control [10]. Based on this theory, the dependence of I_p on scan rate of Cd(II)-cysteine,

simple system of Cd(II), i.e. the one without ligand were investigated by OSWV. A close to one-half (0.49) power dependence of scan rate on I_p was observed for simple system of Cd(II) indicating a diffusion controlled process. The experimental value of I_p for Cd(II)-cysteine system depicting scan rate dependence by a power of 0.81 which is closer to one than to 0.5 indicating the presence of a mixed mode of mass transport i.e. diffusion and adsorption.

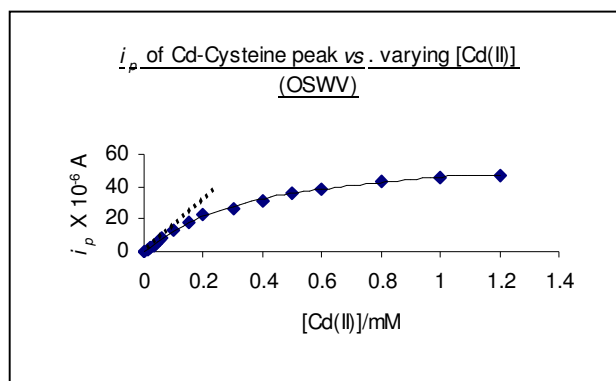


Fig. 3. Calibration curve of varying Cd(II) at 2.0 mM cysteine, 0.5 M $(\text{NH}_4)_2\text{SO}_4$, 3 mM acetate buffer, pH 5.2 using square wave voltammetry: 80 cycle/s, 4 mV step potential and CGME as a working electrode.

Cyclic Voltammetry (CV)

Fig. 4 is an example of the cyclic voltammogram performed for Cd(II)-cysteine system at a mercury electrode. Formation of multiple peak components with a spike was observed at a more positive potential ($E_p = -0.4 \text{ V}$) while a well defined redox couple was observed at a more negative potential ($E_p = -0.6 \text{ V}$). The former can be attributed to the formation and subsequent stepwise reduction of mercury cysteinate species, $\text{Hg}_x(\text{RS})_2$ (to be elaborated further under discussion) while the latter can be attributed to the electrochemical reaction of cadmium cysteinate complex species at the mercury electrode. Wopschall and Shain [10] have theorized that in Cyclic Voltammetry, adsorption of reactants leads generally to an enhancement of the cathodic peak current (I_{pc}) to a greater extent than the reverse scan of the anodic peak current (I_{pa}). This was also observed in this study.

In the absence of complexing agent, such as cysteine, cyclic voltammograms of simple system of Cd(II) ion in 0.5M $(\text{NH}_4)_2\text{SO}_4$ supporting electrolyte showing cathodic and anodic current possess the shape of a diffusion peak for all pH range; the ratio of cathodic to anodic peak current are nearly equal to 1.

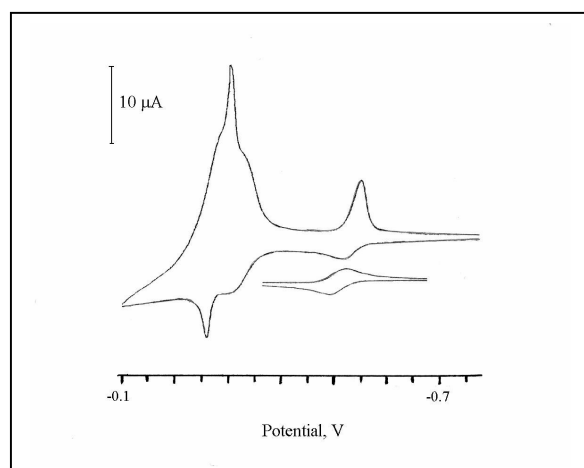


Fig.4. Cyclic staircase voltammogram of 5.62 $\mu\text{g/ml}$ Cd(II), 1.0 M KNO_3 , 3 mM acetate buffer, pH 5.2 (a) without cysteine (b) with 2.0 mM cysteine; 1000 mV/s; CGME as a working electrode.

However, when ligand was added, i_{pc} / i_{pa} ratio increased and was greater than one with an enhanced and more symmetrical cathodic peak current (I_{pc}) while the anodic peak current (I_{pa}) did not show significant enhancement (Table 2).

Cysteine Concentration / mM	I_{pc} / I_{pa}
0.05	0.7
0.01	0.8
1.00	1.2
3.00	2.0
5.00	1.9
10.00	1.9

Table 2

Effect of varying cysteine concentration on the ratio of I_{pc} to I_{pa} for Cd(II)-cysteine system during Cyclic Voltammetry. 1.0 $\mu\text{g/ml}$ Cd(II) in 0.5M $(\text{NH}_4)_2\text{SO}_4$ was used.

The characteristic of the current components observed in CV (as represented by Fig.4) with enhanced current component matches well with those observed in OSWV (as represented by Fig. 2 (b-c)) as it should be. The enhanced reduction current shows a scan rate dependence by a power of 0.8 similar to those observed in OSWV technique mentioned above.

A current enhancement of 2 - fold was observed at the optimum pH of 5 and similar trend continues until pH 7. However, from pH 7 onwards, I_{pc} gradually decreased. Both cathodic and anodic peak potential of Cd(II) ion were shifted cathodically with increasing pH in the presence of cysteine. This indicates the formation of increasingly more stable complex species with an increase in pH. Effect of varying cysteine concentration on the CV voltammogram of Cd(II) was also studied. The result shows that the cathodic peak current, I_{pc} of Cd(II) in the presence of cysteine increased until the cysteine concentration reached 3 mM. In the presence of 3 mM cysteine, I_{pc} was about 3.2 times as large as that observed in the absence of cysteine. Above this concentration (3 mM), I_{pc} decreased slightly as was observed in OSWV and for the same reason as mentioned above.

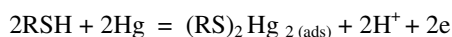
Based on the result obtained from double potential step chronocoulometry, cysteinate anion such as Hg(I/II)-cysteinate complex species appears to contribute the most (about 80%) as compared to a much smaller contribution (about 20%) of Cd-cysteinate complex species towards the total surface coverage ($80 \mu\text{C}/\text{cm}^2$) of the Cd(II)-cysteinate-Hg(I/II) system (see discussion). A monotonic rising but enhanced current transient of the reduction of cadmium ion was also observed during chronoamperometry in the presence of cysteine indicating the presence of an adsorption controlled process.

Discussion

Evidence gathered from cyclic voltammetric studies on the i_c / i_a ratio which is greater than one, the concentration isotherm obtained from fast scan square wave voltammetry and the chronocoulometric and chronoamperometric studies of Cd(II)-Cysteine system using DME as a working electrode all pointed to the adsorption of the reactants of Cd(II)-cysteinate complex species at the surface of mercury electrode as a controlling process which is responsible for the current enhancement of the peak current of Cd(II) ion in the presence of excess amount of cysteine under weakly acidic condition. The slightly less than power one (0.8) current dependence on scan rate obtained from square wave and cyclic voltammetry can be attributed to the adsorption as being not as strong and/or the mixed mode of transport was involved.

That the enhancement effect which is pH dependent was greatly felt only under weakly acidic condition strongly indicates that the presence of cysteinate anion

(RS⁻) is a precondition for the specific adsorption of Cd(II)-cysteine complex species to take place. It can be inferred from the pK_a values of cysteine (2.04, 8.22, 10.26) [8]. Cysteinate anion species predominate only at pH > 2. It is also a well known fact that sulphur bearing group has strong affinity for mercury as sulphur forms strong bond with mercury (pK_f(Hg-S) = 14.4) [12]. Peak at ca. -0.4 V (Figs. 1 - 4) was associated with the reversible oxidation of L-cysteine (RSH) to mercury(I) cysteinate by reaction with the electrode material [13]:

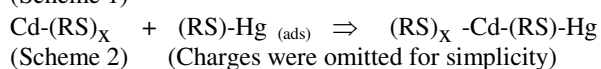
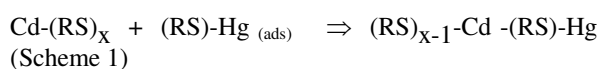


The spikes reported previously by Ralph et al. [13] was also observed in the present study at above 0.3 mmole cysteine (Fig. 4) and were assigned to the formation of a tight mercury cysteinate film formed after monolayer coverage, via lateral interaction between adsorbed molecules.

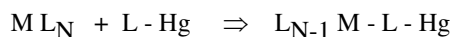
At lower pH, proton can compete with metal ion for ligand in solution. An increase in pH will reduce the concentration of hydrogen ion, thus allowing greater complex formation between Cd(II) and cysteine. This effect accounts for the negligible enhancement in the pH range between 1 and 3. In this pH range, proton is expected to be predominant.

Also any species that competes with cysteinate anion for the surface of the electrode would inevitably interfere in the adsorption of metal cysteinate complex species hence leading to a decrease in the enhancement effect. This explains why supporting electrolyte such as perchlorate and nitrate which are weakly complexing produce higher current enhancement as compared to chloride which exhibit complexing ability at concentration of 0.1 M or higher was capable of competing with cysteinate anion for electrode surface (Table 1). Some work done using chronocoulometry and chronoamperometry have shown that more than 80 percent of the total surface coverage of Cd(II)-cysteine complex species at the surface of the mercury electrode was contributed by cysteine while the remaining by cadmium-cysteinate species

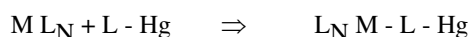
The above findings prove that the adsorption process which causes the enhancement effect of Cd(II) peak current in the presence of cysteine was probably due to the anion-induced adsorption, in which a specifically adsorbed substance (cysteine) bonds to the mercury on the electrode surface via its strong mercury mercaptide bonding and thus promotes specific adsorption of the Cd(II)-cysteine on the mercury electrode. It is possible that the following reaction schemes occurred:



Scheme 1 is in accordance with the mechanism suggested by O'Dom and Murray [14] who assumed that the interaction between one particular complex species present in the solution ML_N with an anion L already adsorbed on the mercury surface is such that it produces an adsorbed species with the same chemical composition as shown below:



The scheme 2 is in accordance with the mechanism proposed by Anson and Barclay [15] which differs from the above in that interaction with anions already on the mercury occurs according to the following reaction:



Chronocoulometric data have shown that about 80 percent of the total surface coverage of Cd(II)-cysteine complex species at the surface of the mercury electrode was contributed by cysteinate ion while the remaining ~ 20 % by cadmium-cysteinate species. The latter was probably an uncharged species such as cadmium biscysteinate complex, Cd(RS)₂ as reflected by a smaller value of the surface charge.

Conclusions

Various evidence obtained in these studies have pointed towards the enhancement of the reduction peak current of Cd(II) observed in the presence of excess amount of cysteine at a mercury electrode during fast sweep square wave voltammetry and cyclic voltammetry as being due to adsorption controlled process. Anion induced adsorption models proposed earlier by O'Dom and Murray [14] or Anson and Barclay [15] appear suitable to explain the observed behavior. The optimum current enhancement of Cd(II) can be observed under conditions where 2 - 5 mM cysteine is used in weakly complexing electrolyte media such as potassium perchlorate or potassium nitrate adjusted to pH 5 using acetate buffer.

Acknowledgement

The authors wish to thank Universiti Putra Malaysia and the Ministry of Science and Technology, Malaysia for a research fund sponsored under IRPA research program.

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