

Voltammetric Studies on Composition and Stabilities of Complexes of Tetracycline and Oxytetracycline with Some Metal Ions in Aqueous Medium

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Summary. The composition and stability of complexes of tetracycline and oxytetracycline with Cu(II), Cd(II), Pb(II) and UO₂(II) have been studied polarographically (direct current and differential pulse polarographic techniques) at 25 ± 0.1°C. Differential pulse polarographic studies have been particularly helpful in deciding the nature of metal-drug interactions at low concentrations. The reduction of Cu(II)-tetracycline has been found to be irreversible and diffusion controlled with the presence of an adsorption component. In the system uranyl(II)-tetracycline the complex formed has a stoichiometry of 1 : 1 and log K_{ox} = 4.04 which is very close to that obtained by potentiometric measurements. The peak half width $W_{1/2}$ of the Pb(II)-OTC system is 60–70 mV indicating that the process is reversible and two electrons are consumed. The log β' is 10.30 in 0.1 mol dm⁻³ NaClO₄. In the Cu(II)-OTC system two complexes were formed with log $\beta_1' = 8.50$ and log $\beta_2' = 14.10$. Cyclic voltammograms were recorded using a hanging dropping mercury electrode for the systems Cu(II), Cd(II), Pb(II) and UO₂(II)-OTC to examine the irregularities in both peak potentials and peak currents during the polarographic investigations.

Keywords. Voltammetric studies; Complexes; Tetracycline; Oxytetracycline.

Voltammetrische Untersuchungen zur Zusammensetzung und Stabilität von Komplexen von Tetracyclin und Oxytetracyclin mit einigen Metallionen in wäßrigem Medium

Zusammenfassung. Es wurden Zusammensetzung und Stabilität von Tetracyclin- und Oxytetracyclin-Komplexen mit Cu(II), Cd(II), Pb(II) und UO₂(II) polarographisch mittels Direktstrom- und differentieller Pulspolarographie-Technik bei 25 ± 0.1°C bestimmt. Zur Aufklärung der Metall-Substrat-Wechselwirkungen bei geringen Konzentrationen waren insbesondere differentielle Pulspolarographie-Untersuchungen erfolgreich. Es wurde festgestellt, daß die Reduktion von Cu(II)-Tetracyclin irreversibel und diffusionskontrolliert verläuft. Im System Uranyl(II)-Tetracyclin hat der Komplex eine Stöchiometrie von 1 : 1 und ein log K_{ox} von 4.04; dieser Wert ist dem aus potentiometrischen Messungen erhaltenen sehr ähnlich. Die Peak-Halbwertsbreite des Pb(II)-OTC-Systems ist 60–70 mV und zeigt damit einen reversiblen Prozess bei Verbrauch von zwei Elektronen an. In 0.1 mol dm⁻³ NaClO₄ ist log β' 10.30. Im Cu(II)-OTC-System werden zwei Komplexe mit log $\beta_1' = 8.50$ und log $\beta_2' = 14.10$ gebildet. Die cyclischen Voltammogramme wurden unter Verwendung einer hängenden tropfenden Quecksilberelektrode für die Systeme Cu(II), Cd(II), Pb(II) und UO₂(II)-OTC aufgenommen, um die Unregelmäßigkeiten der Peak-Potentiale und der Peak-Ströme während der polarographischen Untersuchung zu überprüfen.

Introduction

Tetracyclines are a family of broad-spectrum antibiotics of known prophylactic and therapeutic values. The phenomenon of complex formation between tetracycline analogues and various cations is well documented [1–16]. The mechanism of antibacterial activity has not been definitely established, though it is believed to be associated with the formation of mixed complexes of antibiotic, ribosomes and a metal ion [17]. These findings have stimulated work on the behaviour of tetracyclines with metal ions. In the present paper the complexation of tetracycline (TC) and oxytetracycline (OTC) with Cu(II), Pb(II), Cd(II), and UO₂(II) has been studied polarographically (dc and DPP techniques). Cyclic voltammograms were recorded using HMDE for the systems Cu(II), Cd(II), Pb(II) and UO₂(II)-OTC.

Experimental Part

Tetracycline and oxytetracycline were obtained as hydrochlorides and used without purification as fresh solutions in bidistilled water to avoid decomposition of the antibiotics. All other chemicals used were of analytical grade.

The direct current polarographic measurements were carried out with a Tacussel PRG 5 in conjunction with a TV 11 GD built in potentiometer and an EPL 1 B recorder equipped with three Tacussel RM 06 electrodes and a thermostated cell. A saturated calomel electrode served as the reference electrode. The dropping mercury working electrode had the following characteristics : $m = 2.10 \text{ mg s}^{-1}$ and $t = 4.11 \text{ s/drop}$ in 0.1 mol dm^{-3} KCl (open circuit) and the height of the mercury column was adjusted at a level of 50 cm allowing a proper drop.

Before polarography, the solutions were deaerated by passage of purified nitrogen. The gas was purified by allowing it to pass through the following solutions:

- (a) A vanadous solution (prepared as recommended by Meites [18]) was placed in a tall cylinder provided with a coarse-porosity sintered pyrex gas dispersion disc. The cylinder contains also about 25 gm heavily-amalgamated zinc which serves mainly to reduce the oxidized vanadium formed by reaction of the vanadous solution with oxygen (contaminating the inert gas);
- (b) a copper sulphate solution, prepared from a BDH product;
- (c) a 0.1 mol dm^{-3} silver nitrate solution, prepared from a BDH product;
- (d) 1% sodium plumbite solution, obtained by adding a solution of sodium hydroxide dropwise to another of pure lead nitrate;
- (e) twice distilled water.

The adjustment of the *pH* of the solutions was made using a corning 601 A precision research ionalyzer digital *pH* meter with a combined glass-calomel electrode.

DPP measurements were carried out with a PAR 264 A polarographic analyzer coupled with a RE 0089 *x-y* recorder. The working electrode was a PAR 303 A SMDE (medium size drop) equipped with a platinum auxiliary electrode and a Ag/AgCl saturated KCl reference electrode. The following parameters have been imposed: pulse amplitude = 25 mV, drop time = 1 s and scan rate = 5 mV s^{-1} .

DPP measurements for the investigation of the formation of cadmium(II), lead(II), Copper(II) and uranyl(II) complexes with oxytetracycline were carried out in sodium perchlorate-perchloric acid (*pH* = 2.6) and sodium acetate-acetic acid (*pH* = 4.6) as supporting electrolytes and $t = 25^\circ\text{C}$.

Cyclic voltammograms were recorded with an EG & G Princeton Applied Research Corp. micro-processor-controlled, coupled with a PAR 303 A SMDE (drop size: medium), area of the drop 0.014 cm^2 . The polarographic cell bottom (PAR Model K 0060) was fitted with an Ag/AgCl reference electrode and a platinum wire served as an auxiliary electrode. A PAR Model RE 0089 *x-y* recorder was used for the collection of experimental data.

Results and Discussion

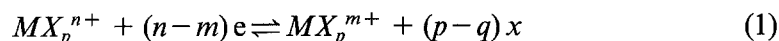
Copper(II)-Tetracycline

The polarographic electroreduction of 0.1 mmol dm^{-3} Cu(II) in presence of 0.1 mol dm^{-3} sodium nitrate and at different concentrations of tetracycline ($1 - 10 \text{ mmol dm}^{-3}$) produces a single wave due to the reduction of Cu(II). The shift in the $E_{1/2}$ values to more negative potentials on increasing the concentration of tetracycline indicates the complex formation between Cu(II) and TC. The slopes obtained from the analysis of the wave reveals that the reduction process proceeds irreversibly. However, the effect of mercury height shows that the reduction is controlled by diffusion and an adsorption component which is in contrast to those obtained by Sachan and Coworkers [7]. Polarographic characteristics for this system are given in Table 1.

Uranyl(II)-Tetracycline

In the system of uranyl(II)-tetracycline ($\mu = 0.1 \text{ mol dm}^{-3}$ NaNO_3) a single wave is observed with a slight shift ($\approx 3 \text{ mV}$) in the $E_{1/2}$ values towards more electro-negative potentials on increasing the tetracycline concentration ($\leq 6 \text{ mmol dm}^{-3}$). On further addition of tetracycline, a measurable shift is noticed. The values of slopes from $\log i/\log h$ plots show that the polarographic reduction process is diffusion-controlled with an adsorption contribution. The logarithmic analysis of the wave indicates that the nature of the reduction process is reversible and one electron is involved in the reduction step.

Since the reduction of the $\text{UO}_2(\text{II})$ ion occurs in successive steps, a $\text{UO}_2(\text{II})$ complex is reduced to a lower valency state from a higher valency state, and the process may, therefore, be represented as follows:



where n and m are the valencies of the metal ion in the oxidised and reduced states, p and q are the corresponding coordination numbers of the two states and x is the ligand. The complexed species $\text{UO}_2(\text{II})$ and $\text{UO}_2(\text{I})$ differ by only one electron.

Table 1. Polarographic characteristics of 0.1 mmol dm^{-3} Cu(II) in different concentrations of tetracycline

[TC] mol dm^{-3}	$-E_{1/2}$ Volt	$\frac{0.0591}{an}$	$\log \frac{i_l}{h}$	an
0.000	+0.010	0.031	0.500	—
0.001	0.0263	0.0471	0.800	1.254
0.002	0.0363	0.0565	—	1.046
0.004	0.0375	0.0476	0.966	1.255
0.005	0.0463	0.050	0.848	1.182
0.006	0.0475	0.0438	—	1.349
0.008	0.0488	0.050	0.741	1.182
0.01	0.0500	0.0588	0.741	1.005

Thus, in order to determine the characteristics of the possible complexed species in solution, it may readily be shown that the shift in half-wave potential for the above system (with the assumption that the diffusion coefficient of MX_p and MX_q are approximately equal) with increasing antibiotic concentration is given by:

$$E_{1/2} = (E_{1/2})_s - (E_{1/2})_c = (p - q) \frac{RT}{F} \ln [x] - \frac{RT}{F} \ln \frac{\beta \text{UO}_2(\text{I})}{\beta \text{UO}_2(\text{II})} \quad (2)$$

This equation suggests that a plot of $E_{1/2}$ against $-\log [x]$ may provide information on the difference in the number of ligand molecules bound in the oxidised and reduced forms, and also that the value of each one of the stability constants cannot be determined for this system (i. e. that only the ratio of stability constants can be calculated).

From the $\log [TC]$ vs. $E_{1/2}$ plot linear relations are found with a break at $[TC] = 6 \text{ mmol dm}^{-3}$. The first linear portion is almost parallel to the $\log [TC]$ axis whereas the second one exhibits a limited slope. This may be interpreted on the basis of the following:

(a) The value of $p - q$ in the first portion equals zero. This means that the oxidized and the reduced form each have the same coordination number, i. e., $p = q$.

(b) The second linear section observed at concentration higher than 6 mmol dm^{-3} , has a slope of 0.085. This value reveals that $p - q = 1.2$ and the value of $\log (K_{ox}/K_{red}) = 4.04$.

Therefore, it is considered that the value of q is practically zero [5] and that of p is 1. In other words, the complex formed by the $\text{UO}_2(\text{II})$ ion with tetracycline has a stoichiometry of 1 : 1 and $\log K_{ox} = 4.04$ which is very close to that obtained by potentiometric measurements [19] and that reported by Mahgoub et al. [20] by spectrophotometric method. However, Chandel et al. [5] reported that $\text{UO}_2(\text{II})$ forms a 1 : 1 complex with tetracycline with $\log K = 8.29$. Their very much higher value may be due to the argument concerning the protonated ligand species whether it is LH_2^- or LH^{2-} . Our data depend on the total ligand concentration where the ligand is present in excess. Polarographic characteristics of the $\text{UO}_2(\text{II})$ -TC system are given in Table 2.

Table 2. Polarographic characteristics of 0.1 mmol dm^{-3} $\text{UO}_2(\text{II})$ in different concentrations of tetracycline

$[TC]$ mol dm^{-3}	$-E_{1/2}$ Volt	$\frac{0.0591}{n}$	$\log \frac{i_l}{h}$
0.000	0.178	0.060	0.500
0.001	0.262	0.068	0.722
0.002	0.265	0.068	0.667
0.006	0.268	0.062	0.702
0.008	0.278	0.061	0.739
0.010	0.283	0.055	0.846

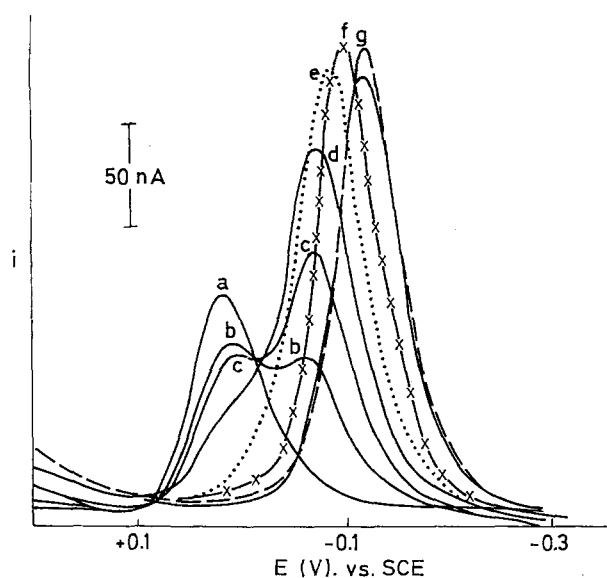


Fig. 1. Differential pulse polarograms for $1 \cdot 10^{-5} \text{ mol dm}^{-3}$ Cu(II) in 0.04 mol dm^{-3} NaClO₄ + 0.01 mol dm^{-3} sodium acetate + 0.04 mol dm^{-3} acetic acid ($pH=4.4$) and at different [OTC]. a Cu(II) alone, b $0.5 \cdot 10^{-5}$, c $1.5 \cdot 10^{-5}$, d $2.5 \cdot 10^{-5}$, e $4 \cdot 10^{-5}$, f $6 \cdot 10^{-5}$, g $8 \cdot 10^{-5}$, h $10 \cdot 10^{-5} \text{ mol dm}^{-3}$ OTC

Copper(II)-Oxytetracycline

Figure 1 shows the differential pulse polarograms for $1 \cdot 10^{-5} \text{ mol dm}^{-3}$ Cu(II) in absence and in presence of different concentrations of oxytetracycline in 0.04 mol dm^{-3} NaClO₄ + 0.01 mol dm^{-3} sodium acetate + 0.04 mol dm^{-3} acetic acid ($pH=4.40$) as supporting electrolyte. By increasing the OTC concentration, a more electronegative peak was observed and the simple Cu(II) reduction peak diminishes whereas the height of the new peak increases on further addition of OTC. The new peak was shifted to more electronegative potential by increasing the OTC concentration. The polarographic characteristics for this system are given in Table 3. The peak-half width ($W_{1/2}$) of the reduction peak of the Cu(II)-OTC system is in the range of 60 – 70 mV using a pulse amplitude of 50 mV. This indicates that the process is reversible and two electrons are consumed which is in good agreement with theoretical values calculated by Parry and Osteryoung [21]. The current of simple Cu(II) is lower than that in presence of OTC. Increase in the current was observed on the addition of the ligand, due to the adsorption of Cu(II)-OTC complexes. Then, the current is constant when the surface coverage is reached. Therefore, the shift in peak potential may be due to the complex formation and slight adsorption component.

On plotting the peak potential of the Cu(II)-OTC complex vs. $\log [\text{OTC}]$, two linear sections are obtained. It is concluded that two complexes are formed between Cu(II) and OTC with stoichiometry 1:1 and 1:2; this is in accordance with that reported by Sachan and Gupta [7].

The overall electrode reaction may be represented as

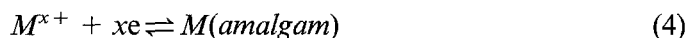
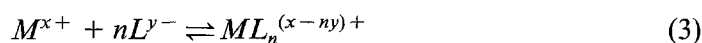


Table 3. Differential pulse polarographic characteristics for the Cu(II)-OTC system at $25 \pm 0.1^\circ\text{C}$

[OTC]·10 ⁵ mol dm ⁻³	0.05 mol dm ⁻³ NaClO ₄ + 0.007 mol dm ⁻³ NaAc + 0.008 mol dm ⁻³ acetic acid			0.04 mol dm ⁻³ NaClO ₄ + 0.01 mol dm ⁻³ NaAc + 0.04 mol dm ⁻³ acetic acid		
	-E _p , V	-W _{1/2} , mV	i _p , nA	-E _p , V	-W _{1/2} , mV	i _p , nA
0	+0.015	80	115	+0.015	70	110
0.5	-	-	-	0.060	70	97.5
1	0.068	70	125	0.068	65	127.5
1.5	0.072	70	138	0.070	70	147.5
2	0.075	68	170	0.075	70	175.0
2.5	0.075	70	190	0.078	62	197.5
3	0.085	70	210	0.085	65	215
3.5	0.090	68	220	-	-	-
4	-	-	-	0.092	65	222.5
4.5	0.095	68	235	-	-	-
5	-	-	-	0.098	60	222.5
6	0.105	65	240	0.105	60	250
7	-	-	260	0.110	60	232.5
8	0.115	65	240	0.115	60	235
9	0.115	65	230	0.120	60	225
10	0.120	60	215	-	-	-
11	-	-	-	125	60	215
12	0.122	65	210	-	-	-
13	-	-	-	-	-	-
14	0.125	65	200	-	-	-
15	0.126	68	195	-	-	-

for a reversible diffusion controlled process Parry and Osteryoung [21] have shown that, within the limits of experimental accuracy and in accord with theory [21–22], the peak potential of a d. p. polarographic wave (E_p) and the half-wave potential of a conventional d. c. polarographic wave ($E_{1/2}$) are related by the expression

$$E_p = E_{1/2} - \frac{1}{2} \Delta E \quad (5)$$

where E is the magnitude of the applied pulse. It follows from Eq. (5) that the shift in the d. p. peak potential on the addition of a complexing agent at a constant pulse amplitude will be the same as the shift in the d. c. halfwave potential. That is:

$$(E_{1/2})_s - (E_{1/2})_c = (E_p)_s - (E_p)_c \quad (6)$$

where the subscripts s and c refer to the simple and complexed ions, respectively.

Thus, the basic relationship expressed by Lingane [23] can be rewritten in the form

$$(E_p)_c - (E_p)_s = \frac{0.0591}{n} \log K_f - \frac{0.0591}{n} p \log [x] \quad (7)$$

where K_f is the apparent formation constant. The calculated apparent logarithmic constants were 8.5 and 14.1 for the 1:1 and 1:2 complexes formed in the Cu(II)-OTC system.

Lead(II)-Oxytetracycline

The differential pulse polarograms for $1 \cdot 10^{-5} \text{ mol dm}^{-3}$ Pb(II) in absence and in presence of different concentrations of oxytetracycline in 0.1 mol dm^{-3} NaClO₄ are shown in Fig. 2.

The current of simple Pb(II) is lower than that observed in presence of the ligand. This may be attributed to the adsorption of lead complexes. The shift in peak potentials may, therefore, be due to complex formation and adsorption. At higher concentration of OTC, it is assumed that Pb(II)-OTC complex and OTC are accumulated at the electrode surface. At $3.5 \cdot 10^{-5} \text{ mol dm}^{-3}$ OTC the surface coverage is attained during the drop life. Further addition of OTC brings about an equilibrium of adsorbed material at the electrode-solution interface. For this reason no shift in the potential is observed and the reverse effect is observed, namely a shift to less negative potentials. The slope of the straight line obtained in plotting E_p vs. $\log [\text{OTC}]$ in 0.1 mol dm^{-3} NaClO₄ is 0.053 at the concentration of OTC $(1 - 3.5) \cdot 10^{-5} \text{ mol dm}^{-3}$. The corresponding coordination number can be approximated to 2, this means that the stoichiometry metal:ligand is 1:2 and the logarithmic stability constant calculated using Eq. (7) is 10.30. The polarographic characteristics for the Pb(II)-OTC system are given in Table 4.

In the present work one complex is formed with a stoichiometry of 1:2 for metal:ligand. In the previous potentiometric measurements [19] the ratio was 1:1. The higher ratio in the polarographic measurements may be due to the adsorption of the ligand which leads to excess complexation. Sachan and Gupta [7] reported

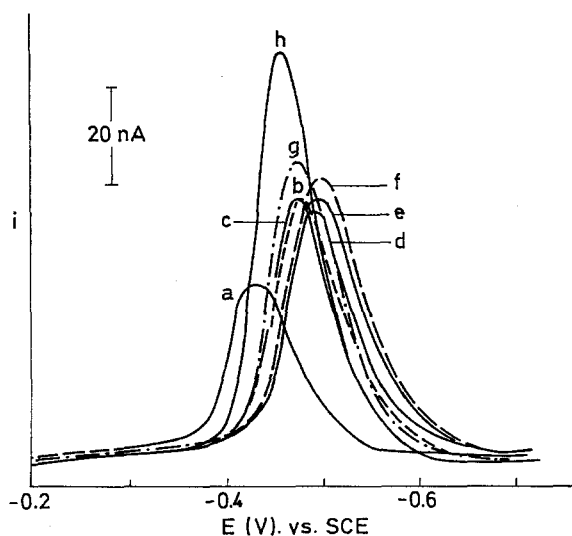


Fig. 2. Differential pulse polarograms for $1 \cdot 10^{-5} \text{ mol dm}^{-3}$ Pb(II) in 0.1 mol dm^{-3} NaClO₄ and at different [OTC]. a Pb(II) alone, b $1.5 \cdot 10^{-5}$, c $2.5 \cdot 10^{-5}$, d $3.5 \cdot 10^{-5}$, e $4 \cdot 10^{-5}$, f $5 \cdot 10^{-5}$, g $6 \cdot 10^{-5}$, h $8 \cdot 10^{-5} \text{ mol dm}^{-3}$ OTC

Table 4. Differential pulse polarographic characteristics for the Pb(II)-*OTC* system at $25 \pm 0.1^\circ\text{C}$

$[\text{OTC}] \cdot 10^5$ mol dm^{-3}	$0.05 \text{ mol dm}^{-3} \text{ NaClO}_4$			$0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$		
	$-E_p$, V	i_p , nA	$-W_{1/2}$, mV	$-E_p$, V	i_p , nA	$-W_{1/2}$, mV
0.0	0.378	50	75	0.430	50	75
0.5	0.378	50	—	0.468	55	60
1.0	0.378	50	75	0.475	61.5	65
1.5	0.420	65	75	0.482	52	62
2.0	0.428	62.5	75	0.485	52	60
2.5	0.438	65	75	0.488	50	65
3.0	0.442	75	65	0.495	50	70
3.5	0.448	85	65	0.495	48	75
4.0	0.450	65	60	0.498	50	70
4.5	—	—	—	0.498	49	72
5.0	—	—	—	0.498	54	72
6.0	0.46	68	68	0.485	64	72
8.0	0.462	65	60	0.470	86	60
10.0	—	—	—	0.470	88	62

that two complexes, 1:1 and 1:2 for Pb(II)-*TC* ratios can be detected using direct current polarography which differs from our results.

Cadmium(II)-Oxytetracycline

In presence of sodium perchlorate ($pH \sim 7$), the complex formation between Cd(II) and *OTC* has been studied at different ionic strengths viz; 0.02, 0.05 and 0.1 mol dm^{-3} . The differential pulse polarograms in $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ are displayed in Fig. 3. The shift in E_p to more electronegative values was observed in the range $(1.5-6) \cdot 10^{-5} \text{ mol dm}^{-3} \text{ OTC}$ at ionic strengths 0.02 and 0.05. In $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ the shift in peak potential was covering the range $(1.5-9.0) \cdot 10^{-5} \text{ mol dm}^{-3} \text{ OTC}$. It should be noticed that the shift in peak potential is slightly increased by increasing the ionic strength (2–5 mV). On drawing the relationship between E_p versus $\log[\text{OTC}]$, the linear relation is not covering all ranges of *OTC* concentration in the three ionic strengths. It is observed that at lower concentrations, viz. $< 1.5 \cdot 10^{-5} \text{ mol dm}^{-3} \text{ OTC}$, no shift was observed indicating that no complexes were formed between Cd(II) and *OTC*. However, at $6 \cdot 10^{-5} > [\text{OTC}] > 1.5 \cdot 10^{-5} \text{ mol dm}^{-3}$, there is a linear relation with a definite slope, viz. 0.04. At concentrations higher than $6 \cdot 10^{-5} \text{ mol dm}^{-3} \text{ OTC}$, the value of the peak potential is constant in the presence of $(6-8) \cdot 10^{-5} \text{ mol dm}^{-3}$ ($\mu = 0.02$ and 0.05 mol dm^{-3}) and at $(9-12) \cdot 10^{-5} \text{ mol dm}^{-3} \text{ OTC}$ ($\mu = 0.1 \text{ mol dm}^{-3}$), then the shift in peak potential reversed its direction. At higher concentration of *OTC*, it is assumed that the Cd(II)-*OTC* complex and *OTC* are accumulated at the electrode surface. At $6 \cdot 10^{-5} \text{ mol dm}^{-3} \text{ OTC}$ ($\mu = 0.02$ and 0.05 mol dm^{-3}) and $9 \cdot 10^{-5} \text{ mol dm}^{-3} \text{ OTC}$ ($\mu = 0.1 \text{ mol dm}^{-3}$) the surface coverage is reached during

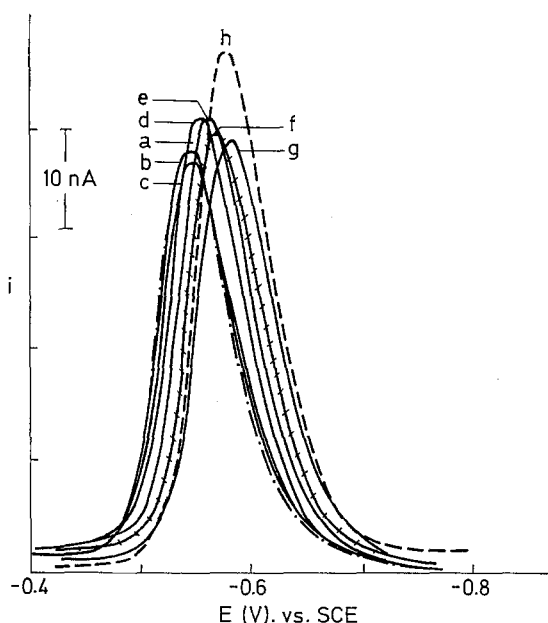


Fig. 3. Differential pulse polarograms for $1 \cdot 10^{-5} \text{ mol dm}^{-3} \text{ Cd(II)}$ in $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ and at different $[\text{OTC}]$. *a* Cd(II) alone, *b* $0.5 \cdot 10^{-5}$, *c* $1.5 \cdot 10^{-5}$, *d* $2.5 \cdot 10^{-5}$, *e* $4 \cdot 10^{-5}$, *f* $6 \cdot 10^{-5}$, *g* $9 \cdot 10^{-5}$, *h* $12 \cdot 10^{-5} \text{ mol dm}^{-3} \text{ OTC}$

the drop life (one second). Therefore, no shift in E_p was observed. On further addition of OTC, the shift occurs in positive direction due to the equilibrium at the electrode-solution interface.

The half-peak width values in the three different ionic strengths are 60–78 mV (pulse amplitude = 50 mV), indicating that the reduction is reversible and two electrons are consumed in the reduction process. The current of simple Cd(II) is lower than that observed in presence of ligand, viz. 0.02 and 0.1. On plotting i_p against $\log [\text{OTC}]$, it is visualized that the current (being constant in the concentration of OTC less than $1.5 \cdot 10^{-5} \text{ mol dm}^{-3}$) increases in both solutions. The enhancement in peak current is due to adsorption. Generally, the plots exhibit maxima and minima according to the variation in the concentration of the ligands and of the metal complex. This behaviour is mainly due to the complication arising from the adsorption at the electrode surface. The stoichiometry of the complexes formed was 1:2 for metal to ligand in both 0.02 and $0.05 \text{ mol dm}^{-3} \text{ NaClO}_4$ while the logarithmic values of the apparent stability constant were 6.95 and 6.90, respectively. At higher ionic strength $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$, one 1:1 complex with $\log \beta' = 6.30$ is formed. This is in good agreement with our potentiometric studies ($\mu = 0.1$) [19]. However, Sachan and Gupta [7] reported that two complexes (with tetracycline) were formed between Cd(II) and tetracycline using direct current polarography at $\mu = 0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$. They reported the values of $\log K_1 = 3.2$ and $\log \beta_2 = 5.72$ for the two complexes formed in solution. The polarographic characteristics for Cd(II)-OTC are reported in Table 5.

Table 5. Differential pulse polarographic characteristics for the Cd(II)-*OTC* system at $25 \pm 0.1^\circ\text{C}$

[<i>OTC</i>] $\cdot 10^5$ mol dm $^{-3}$	0.02 mol dm $^{-3}$			0.05 mol dm $^{-3}$			0.1 mol dm $^{-3}$		
	$-E_p$, V	$-W_{1/2}$, mV	i_p , nA	$-E_p$, V	$-W_{1/2}$, mV	i_p , nA	$-E_p$, V	$-W_{1/2}$, mV	i_p , nA
0.0	0.550	70	80	0.550	65	85	0.552	70	73
0.5	0.550	68	82	0.552	65	68	0.552	70	73
1.0	0.550	70	82	0.554	70	84	0.554	70	72
1.5	0.550	70	82	0.555	60	86	0.556	65	71
2.0	0.552	65	83	0.558	65	76	0.558	65	76
2.5	0.555	70	80	0.560	60	76	0.560	60	78
3.0	0.560	65	80	0.562	65	90	0.565	62	76
3.5	0.565	68	98	—	—	—	—	—	—
4.0	0.568	70	99	0.565	65	76	0.570	65	79
4.5	0.568	70	100	—	—	—	—	—	—
5.0	0.570	70	99	0.570	70	77	0.576	65	78
6.0	0.572	70	94	0.575	75	72	0.580	65	76
7.0	0.572	75	88	—	—	—	0.584	68	68
8.0	0.572	75	83	0.575	75	67	—	—	—
9.0	0.570	70	88	—	—	—	0.588	65	75
10.0	0.570	78	82	0.578	75	84	0.588	68	70
12.0	0.565	75	82	0.580	70	70	0.588	65	92
14.0	0.560	65	88	0.578	65	84	0.580	65	98

Uranium(VI)-Oxytetracycline

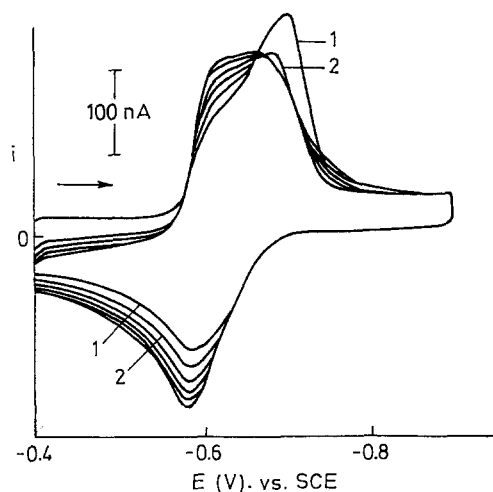
The differential pulse polarographic behaviour of $1 \cdot 10^{-5}$ mol dm $^{-3}$ UO $_2$ (II) in absence and in presence of different concentrations of oxytetracycline using 0.04 mol dm $^{-3}$ NaClO $_4$ and 0.01 mol dm $^{-3}$ HClO $_4$ ($pH \sim 2.6$) as supporting electrolyte shows a single peak which shifted to more electronegative potential by increasing the *OTC* concentration. After the surface coverage is achieved at $\sim 8 \cdot 10^{-5}$ mol dm $^{-3}$ *OTC*, the further addition of *OTC* brings about a shift in E_p towards less electronegative values due to the equilibrium at the electrode – solution interface.

The peak-half width $W_{1/2}$ of the UO $_2$ (II)-*OTC* complex is in the range 90–100 mV using a pulse amplitude 50 mV. This indicates that one electron is consumed in the reduction process and the reduction proceeds in a reversible manner. The complex formed by the UO $_2$ (II) ions and *OTC* has the stoichiometry of 1 : 1 and the apparent value of the logarithmic stability constant is $\log K_{ox} = 4.90$.

In the present work, one 1 : 1 complex is formed which is in agreement with the findings in potentiometric [19] and direct current polarographic studies. Our results are very close to that reported by Mahgoub et al. [20] using a spectrophotometric method. The polarographic characteristics for UO $_2$ (II)-*OTC* system are given in Table 5.

Table 6. Voltammetric characteristics of $1 \cdot 10^{-5} \text{ mol dm}^{-3}$ metal ions in absence and in presence of oxytetracycline

Metal ion	[OTC] 10^5 mol dm^{-3}	$-E_{pc}$, V	$-E_{pa}$, V	$-(E_{pc} - E_{pa})$, V	i_{pc} , nA	i_{pa} , nA
Cu(II)	—	0.01	+0.025	0.035	110	100
Cu(II)	1	0.192	0.135	0.057	500	200
UO ₂ (II)	—	0.198	0.135	0.065	190	190
UO ₂ (II)	5	0.242	—	—	230	—
Cd(II)	—	0.605	0.575	0.03	125	125
Cd(II)	4	0.705	0.588	0.117	220	120
Pb(II)	—	0.430	0.462	0.032	130	130
Pb(II)	4	0.520	0.37	0.15	275	50

**Fig. 4.** Cyclic voltammograms for $1 \cdot 10^{-5} \text{ mol dm}^{-3}$ Cd(II) in 0.05 mol dm^{-3} NaClO₄ + $4 \cdot 10^{-5} \text{ mol dm}^{-3}$ OTC, scan rate = 100 mV/s, equilibrium time = 15 s, 1 first cyclic voltammogram, 2 second cyclic voltammogram

Cyclic Voltammetric Investigations of the Cu(II), Cd(II), UO₂(II) and Pb(II)-OTC Systems

In order to examine the irregularities in both peak potential and peak heights during the polarographic investigation of metal-OTC interactions, the CV of Cu(II), Cd(II), UO₂(II), and Pb(II) at constant concentration of each ($1 \cdot 10^{-5} \text{ mol dm}^{-3}$) were recorded using the HMDE in non complexing media and in presence of OTC.

For the free metal ions, Cu(II), Cd(II), Pb(II), and UO₂(II), normal diffusion controlled and reversible cyclic voltammograms were obtained as is shown in Table 6. On addition of OTC to Cu(II) ions in a ratio 1:1, the peak becomes symmetrical with enhancement in the current indicating the adsorption of Cu(II)-OTC complex at the mercury surface. In the case of UO₂(II)-OTC in 1:5 ratio,

the anodic peak completely disappeared from the first cycle and the cathodic current is completely vitiated after few cycles. This indicates the formation of non-oxidizable strongly adsorbed products which prevent further reduction of $UO_2(II)$. However, upon addition of *OTC* to $Cd(II)$ in the ratio 4:1 a deformation of the cathodic peak and the adsorption phenomenon becomes clear from the first cycle (Fig. 4). The same adsorptive character is observed in the $Pb(II)$ -*OTC* system. It is concluded that there is an interaction between metal-*OTC* and mercury surface via adsorption.

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