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## ON THE ADSORPTION OF CADMIUM(II) IONS ON A HMDE FROM KF + THIOUREA AQUEOUS SOLUTIONS

### A CHRONOCOULOMETRIC STUDY

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#### ABSTRACT

The adsorption of cadmium(II) ions from thiourea aqueous solutions has been studied by double potential step chronocoulometry (DPSSC). The adsorption is strong on mercury electrodes and it has been studied as a function of thiourea concentration, cadmium(II) concentration and potential. A discrepancy between the double-layer charge values from either blank solutions or solutions containing reactant obtained by this technique has been found.

#### INTRODUCTION

Studies of heterogeneous processes have shown that their rates are largely dependent on the structure of the double layer since all electrode processes involve an electronic interaction between the reactants and the electrode surface, which can be affected drastically by phenomena such as the presence of adsorbed species.

In the present stage of the study of the factors that influence electrode processes, an interesting system is provided by thiourea (TU). This neutral molecule has been studied widely and its adsorptive behaviour on mercury–aqueous solution interfaces has been clearly established [1–3]. It adsorbs strongly in the region towards positive potentials and the adsorption decreases at more negative potentials, showing negligible adsorption at  $-1100$  mV (vs. SCE). This behaviour has been attributed to the short-range interactions of the sulphur atom with the mercury surface [4].

In addition, the influence of thiourea molecules on several electrode processes has been reported (see, for example, refs. 5–7). In particular, the catalytic effect of this molecule on the electrochemical reduction of cadmium(II) ions from  $1\text{ M}$  KF aqueous solutions has recently been reported [8].

Further information on the coordination complexes of thiourea with cadmium(II) ions is also available [9]. Therefore, we considered it worthwhile to study the effect

of this organic molecule on the inductive adsorption of cadmium(II) ions on mercury.

In this paper we report the results of a double potential step chronocoulometric study of cadmium(II)–thiourea complexes at a HMDE from 1 *M* KF solution, with thiourea added in concentrations between 0 and 50 mM.

## EXPERIMENTAL

### *Cell design and solutions*

The measurements were performed using a three-electrode cell. The working electrode was either a hanging mercury drop electrode (HMDE; Metrohm, model EA 290) or a dropping mercury electrode (DME). A mercury pool was used as the counter-electrode, while a saturated calomel electrode (SCE) served as the reference electrode. Measurement of the zero charge potential,  $E_z$ , was carried out with a streaming mercury electrode [10]. The cell and reference electrode were thermostated at  $25 \pm 0.1^\circ\text{C}$ .

Solutions were prepared from analytical grade chemicals (Merck) and doubly distilled water (first distillation from alkaline  $\text{KMnO}_4$ ). Solutions containing thiourea were freshly prepared prior to use. The ionic strength of the solutions was maintained at 1 *M* with potassium fluoride. Measurements were carried out in oxygen-free solutions by bubbling prepurified argon.

### *Measurement procedures*

Chronocoulometry was done with equipment built around a digital oscilloscope (Nicolet Explorer III) and a potential generator (EG & G PAR, model 175). A homemade potentiostat in conjunction with an integrator completed the experimental set-up. After the data had been collected, they were analysed and fitted by a computer to the theoretical equations of double potential step chronocoulometry (DPSCC) for the case of an adsorbed reactant and a non-adsorbed product [11]. An EG & G PAR model 173 potentiostat was added to this set-up for recording the cyclic voltammetric curves.

Measurements of the differential capacity of the double layer of the DME in contact with solutions of thiourea in the absence of reactant were recorded with a potentiostatic impedance bridge designed by Sluyters et al. [12]. Data were obtained at three frequencies between 420 and 2000 Hz, and at several drop lives in the interval from 3 to 12 s.

## RESULTS

### *Cyclic voltammetry*

The objective of the cyclic voltammetric experiment was to demonstrate qualitatively the effects of adsorption. Figure 1 shows typical curves for a wide range of

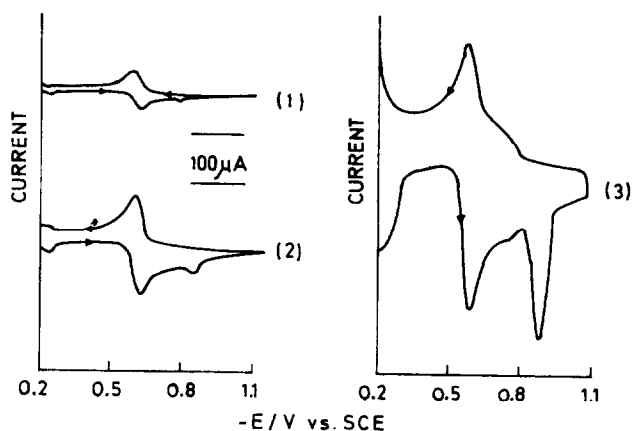


Fig. 1. Cyclic voltammograms for 0.5 mM Cd(II) in 40 mM TU. Scan rate/ $\text{V s}^{-1}$ : (1) 0.1, (2) 1, (3) 10. Electrode area =  $0.032 \text{ cm}^2$ .

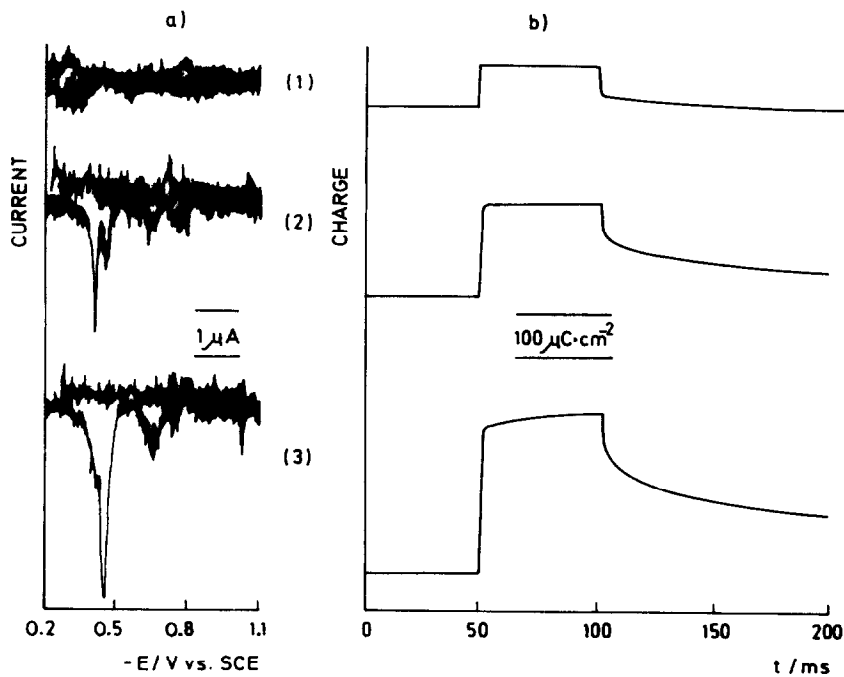


Fig. 2. Dependence of the electrical response of a 50 mM TU solution on the equilibration time. (a) Cyclic voltammograms with a scan rate of  $0.1 \text{ V s}^{-1}$ ; (b) DPSCC with  $E_i = -200$  and  $E_f = -1100 \text{ mV}$ . Equilibration time: (1) 5 s, (2) 1 min, (3) 5 min.

scan rate. There is a post-peak which can be attributed to strong reactant adsorption [13]. At a scan rate of  $0.1 \text{ V s}^{-1}$  it is hardly noticeable. With increasing scan rate, the ratio of the height of the adsorption peak to the main peak increases, the adsorption peak moves towards slightly more negative potentials and a corresponding anodic adsorption peak appears.

On the other hand, the cyclic voltammograms of blank solutions showed the appearance of a reduction peak in the negative sweep as the mercury drop was exposed to the solution for a longer time (see Fig. 2). Therefore, decomposition of thiourea on the surface of mercury leading to the formation of  $\text{HgS}$  has to be considered. But this effect was not observed in the time scale of our study from solutions containing cadmium(II) as well.

#### *Differential capacity of the double layer*

Measurements of the differential capacity of the DME in contact with solutions of thiourea (in the absence of reactant) were performed. The differential capacity-potential curves obtained were in close agreement with those reported previously for other supporting electrolytes:  $0.1 \text{ M NaF}$  [1], and  $0.1 \text{ M KNO}_3$  [3]. The characteristic hump on these plots can be observed from inspection of Fig. 3,

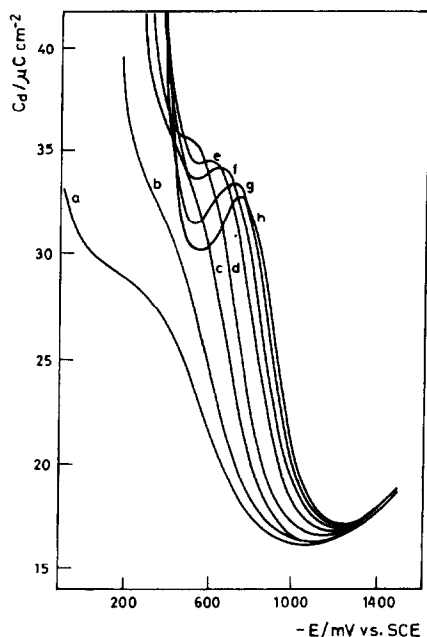


Fig. 3. Differential capacities of the electrical double layer for a DME in aqueous TU + KF mixtures.  $[\text{TU}]/\text{mM}$ : (a) 0, (b) 1, (c) 5, (d) 10, (e) 20, (f) 30, (g) 40, (h) 50. Frequency = 1000 Hz; drop life = 3 s.

TABLE 1

Experimental values of  $\Delta\sigma^m$ , determined by different techniques, from 30 mM TU + 1 M KF solution

$E_i/\text{mV}$	$\Delta\sigma^m/\mu\text{C cm}^{-2}$			
	Ac bridge	DPSCC <sup>dir</sup> <sub>blank</sub>	DPSCC <sup>rev</sup> <sub>blank</sub>	DPSCC ([Cd(II)] = 0.5 mM)
-200	32.8	87.9	30.5	28.5
-250	29.2	77.8	27.2	26.0
-300	26.0	65.1	25.1	24.2
-350	23.0	57.4	23.1	21.8
-400	20.4	38.3	21.0	19.6
-450	18.4	32.7	19.3	17.6
-500	16.7	30.3	17.7	16.0
-550	15.0	28.2	15.1	14.1

which is especially noticeable at  $c_{\text{TU}} \geq 10 \text{ mM}$ , and moves to more negative potentials as the concentration of thiourea increases.

The frequency dependence of the capacity was investigated, and was found to be rather small. Thus, it could be analysed in a similar way to that described by Parsons and Symons for thiourea adsorption in aqueous  $\text{KNO}_3$  [3]. The dependence on the drop life was also found in the potential region in which the hump occurs, although it did not lead to changes in the shape of the curves, and its magnitude was similar to that exhibited with the variation of the frequency of the ac signal.

By integration of these experimental plots, the charge of the electrode,  $\sigma^m$ , was obtained. As the integration constant, the value of the potential of zero charge,  $E_z$ , determined with a streaming mercury electrode, was introduced. Later,  $\Delta\sigma^m$ , the change in the charge on the electrode required to change the electrode-electrolyte double-layer capacitance from the initial to the final electrode potential corresponding to a chronocoulometric experiment, was calculated directly. This calculation involved subtraction of the charge value at the desired initial potential. Table 1 shows some of the values of  $\Delta\sigma^m$  calculated for a solution 30 mM in thiourea.

#### *Double potential step chronocoulometry*

To measure the surface excess of the cadmium(II)-thiourea complex we employed double potential step chronocoulometry. These experiments were performed by stepping the potential of the mercury drop from selected initial potentials, where Cd(II) is not reduced, to  $-1100 \text{ mV}$ , the potential at which diffusion-controlled reduction of cadmium(II) occurs, and then back again to the initial potential  $E_i$ . The parameter measured is the total charge passed as a function of time. To ensure that adsorption equilibrium was attained at the beginning of the experiment, each newly extruded mercury drop was exposed to the stirred solution for 30 s before the first potential step. No change in the measured parameter was found when the waiting time was varied between 15 and 50 s. The resulting  $Q$  vs.  $t$  curves were analysed following the procedure outlined by Anson and co-workers [11,14] to yield

TABLE 2

Thiourea induced adsorption of cadmium(II)

$E_i/\text{mV}$	$2F\Gamma_{\text{Cd(II)}}/\mu\text{C cm}^{-2}$						
	$c_{\text{TU}} = 1$ mM	$c_{\text{TU}} = 5$ mM	$c_{\text{TU}} = 10$ mM	$c_{\text{TU}} = 20$ mM	$c_{\text{TU}} = 30$ mM	$c_{\text{TU}} = 40$ mM	$c_{\text{TU}} = 50$ mM
<i>Cadmium(II) concentration = 0.5 mM</i>							
-250		4.4	5.9	11.2	15.1	22.8	24.4
-300		4.6	7.9	13.0	17.9	25.2	29.4
-350		5.1	10.0	16.4	19.6	25.7	30.2
-400		5.8	11.8	17.5	21.3	26.9	31.4
-450		7.2	12.9	20.4	23.3	27.1	32.2
-500		7.7	13.3	20.9	24.9	30.2	34.8
-550		8.1	14.6	21.4	27.4	30.4	35.0
<i>Cadmium(II) concentration = 1 mM</i>							
-250	1.2	3.7	6.3	10.1	13.4	16.1	18.2
-300	1.3	4.8	8.3	12.8	16.4	19.4	21.5
-350	1.4	5.6	9.6	14.7	18.4	21.5	23.8
-400	1.5	6.1	10.8	16.7	20.4	23.1	25.8
-450	1.6	6.5	11.8	17.8	21.7	24.3	26.5
-500	1.8	7.0	12.5	19.3	23.2	26.3	27.8
-550	2.2	8.3	14.3	21.2	25.5	28.4	30.6
<i>Cadmium(II) concentration = 2 mM</i>							
-250	3.3	7.5	10.9	12.8	14.7	16.5	18.2
-300	3.7	7.8	11.5	16.1	17.2	18.6	19.4
-350	6.4	9.6	13.3	18.6	18.7	19.8	20.5
-400	6.9	9.9	15.6	20.0	21.8	23.7	26.1
-450	7.6	11.5	16.3	22.2	24.5	25.6	27.7
-500	9.6	13.1	17.2	23.7	26.7	27.5	28.2
-550	10.2	16.2	19.9	26.6	28.8	29.3	29.8

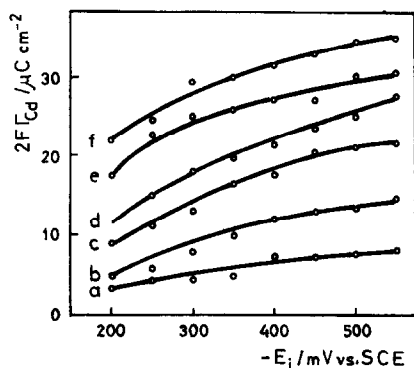


Fig. 4. Potential dependence of Cd(II) adsorption induced by thiourea.  $[\text{Cd(II)}] = 0.5 \text{ mM}$ .  $[\text{TU}]/\text{mM}$ : (a) 5, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50.

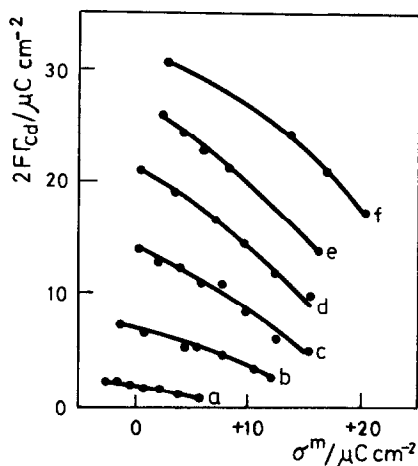


Fig. 5. Charge dependence of Cd(II) adsorption.  $[Cd(II)] = 1 \text{ mM}$ .  $[TU]/\text{mM}$ : (a) 1, (b) 5, (c) 10, (d) 20, (e) 30, (f) 50.  $[TU] = 40 \text{ mM}$  was deleted for clarity.

the adsorbed amounts,  $\Gamma_{Cd(II)}$ , at  $E_i$ . The experimental data could be fitted satisfactorily for solutions with thiourea concentrations up to  $50 \text{ mM}$ .

The values obtained for the amount of adsorbed cadmium(II) as a function of  $E_i$ , thiourea concentration and cadmium(II) concentration are summarized in Table 2. The limits of  $E_i$  which could be employed were set on the positive side by the oxidation of mercury and on the negative side by the onset of cadmium(II) reduction. Thus, the inductive effect of thiourea on the adsorption of cadmium(II) species could be observed from the dependence of the amount of adsorption on the concentration of thiourea applying to all the potentials under study.

It is more interesting to analyse the dependence of the adsorption on the electrical parameters of the system. Figures 4 and 5 show the dependence of  $2F\Gamma_{Cd(II)}$  on  $E_i$  and  $\sigma^m$ , respectively, for one concentration of cadmium(II), and various thiourea concentrations. Both plots are consistent with the behaviour expected for an adsorbate with positive charge; i.e. with a shift of the potential to more negative values, the positive charge on the electrode decreases resulting in a lower repulsion between the electrode and the adsorbate, and it allows an increase in the amount of adsorption. At a given charge on the metal there is more adsorbed thiourea on the electrode the higher the thiourea concentration, so this behaviour suggests that the amount of adsorbed thiourea influences the adsorption of cadmium(II) species.

#### *Charge of the double layer*

The fit of the  $Q-t$  curves to the theoretical equations of DPSCC leads to values of  $\Delta\sigma^m$  [11]. In the last column of Table 1, the values of this parameter determined



from a solution 0.5 mM in cadmium(II) and 30 mM in thiourea are listed. Special attention should be paid to the fact that these values are of the same order as those obtained from the differential capacity measurements in the absence of reactant (blank solutions).

Chronocoulometric measurements of blank solutions were also performed, although in this case the intercept points  $^{\circ}Q$  of the forward step presented very high values and depend greatly on the time the drop was exposed to the solution (see Fig. 2b). Nevertheless, the values of  $\Delta\sigma^m$  were of the same order when the initial potential of the step was set at  $-1100$  mV, and the considered potential was  $E_f$  ("reverse pulse"), as can be observed on inspection of Table 1.

Therefore, the discrepancy found can be related to the above-cited experimental evidence of the decomposition of adsorbed thiourea on mercury surfaces with time. Reproducible values for  $\Delta\sigma^m$  from blank solutions by DPSCC can be obtained only by application of "reverse potential steps" to the electrode in this system.

Finally, the magnitude of the values obtained for the change in charge on the electrode,  $\Delta\sigma^m$ , brought about by the adsorption of the cadmium(II)–thiourea complex had a similar order to the amount of cadmium(II) which was adsorbed. This fact suggests that the adsorbing cadmium(II)–thiourea species are positively charged. Therefore, there is no evidence of coordination of fluoride anions to the metal complex, at least not to such an extent as to cancel its positive charge. The last feature introduces a different situation from that of the adsorption of metal complexes with anionic ligands in which the net charge of the adsorbing complex differs from that of the unadsorbed hydrated metal cation, and is usually zero [15].

## DISCUSSION

A strong inductive effect of thiourea on the adsorption of cadmium(II) ions on mercury electrodes has been found, since these metal ions show very little tendency to adsorb when they are present in solutions containing a non-adsorbing anion such as fluoride. This inductive behaviour of thiourea can be compared to that exhibited by anions such as  $I^-$ ,  $Br^-$ ,  $S_2O_3^{2-}$  and  $SCN^-$ , which adsorb strongly on mercury too. Anson [16] has attributed this behaviour to the result of two competitive factors: (a) the extent of the adsorption of the inductive species, and (b) the formation of coordinated species. Therefore, the inductive species must have the capacity to adsorb on the electrode, and to act as a ligand of the metal ion for the formation of an adsorbable complex.

Figure 6 compares the adsorption of uncoordinated thiourea with that of the cadmium(II)–thiourea complexes. The similar shape of the two plots is noteworthy. This result led us to consider that initially adsorbed thiourea strongly induces the cadmium(II) adsorption. The adsorbed thiourea molecules act as a bridge for the adsorption of metal ions via the sulphur atom. This higher participation of the sulphur in the adsorption process could prevent, at least to some extent, the formation of  $HgS$  on the mercury surface, resulting in a new adsorbed layer that is more stable with time than in the absence of reactant.

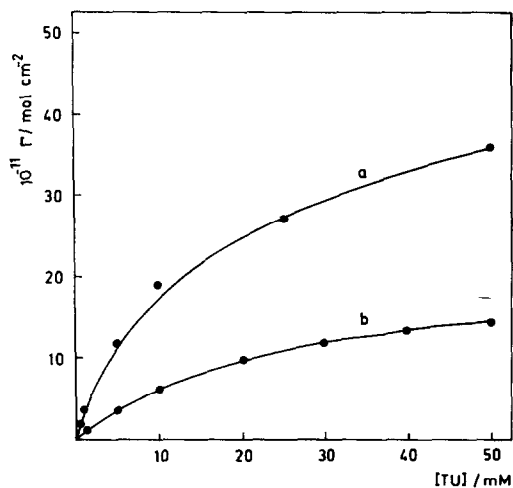


Fig. 6. Comparison of adsorption of thiourea and its Cd(II) complexes at  $-500$  mV. (a) Adsorption of TU (data from refs. 2 and 3); (b) adsorption of the Cd(II)-TU complex from  $1$  mM Cd(II) solutions.

A similar conclusion can be drawn when the dependence of the adsorption of cadmium(II) on the average coordination number is investigated. From inspection of Fig. 7 a strong dependence is clear, but the adsorption of the complexes is

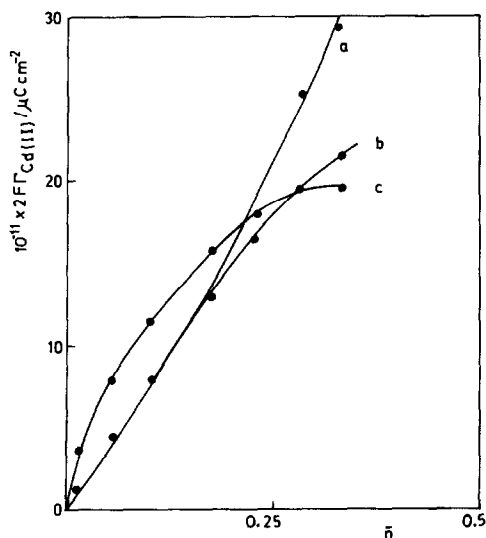


Fig. 7. Dependence of Cd(II) adsorption on the average coordination number. Initial potential =  $-300$  mV.  $[Cd(II)]/mM$ : (a) 0.5, (b) 1, (c) 2.

already strong at very low values of  $\bar{n}$ , close to zero, conditions at which most of the cadmium(II) is free. This observation suggests that adsorbed thiourea molecules play the main role in the induction of the adsorption. Then, it is possible that the cadmium(II)-thiourea complexes existing in the solution have to compete with the hydrated cadmium(II) ions, which are in such an excess that the adsorption process is performed with low coordination numbers.

On the other hand, the reported data do not offer enough information for the elucidation of the composition of the adsorbing complex and the number of thiourea ligands brought to the surface by each adsorbing cadmium(II) cation. The reported values were obtained at rather low coordination numbers ( $\bar{n} < 1$ ), although the adsorption was already high from 1 mM TU solutions ( $\bar{n} \sim 0.02$ ), which strongly suggests participation in the process of previously adsorbed thiourea.

Therefore, we think further studies should be performed in order to obtain more information on the process of adsorption and coordination, not only in the interval of potentials covered in the present study but in the region of cadmium(II) reduction, by the use of normal and substituted thiourea. They should throw more light on the elucidation of the adsorption mechanism of metal ions, and on the participation in this process of metal complex formation.

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