

**DIFFERENTIAL PULSE AND CYCLIC VOLTAMMETRY STUDY OF THE
Cd(II)/Cd(Hg) COUPLE IN THE PRESENCE OF TETRABUTYLAMMONIUM CATION
AND THE CHLORIDE ANION**

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Abstract

The influence of the tetrabutylammonium cation (TBA⁺) on the redox behaviour of the Cd(Hg)/Cd(II) couple in 1M chloride media was examined using differential pulse and cyclic voltammetry techniques. It was found that at low scan rates (tens to hundreds of mV/s) and with an increase in tetrabutylammonium cation concentration, some results from both techniques are consistent with observations made in classic polarographic studies (*e.g.* the increase in tetrabutylammonium ion concentration in a solution containing the cadmium(II) ion, in chloride media, promotes a similar decrease in the cathodic current intensity of the metallic cation). At higher scan rates, the results of cyclic voltammetry experiments are surprisingly different. Among various effects observed, the presence of the tetrabutylammonium cation, below a certain concentration, seems to have no effect on the electroreduction of cadmium(II) ions.

Keywords: cadmium(II) electroreduction, tetrabutylammonium cation, adsorption, differential pulse voltammetry, cyclic voltammetry.

Introduction

Work has been published [1] on attempts to find out and understand how the tetrabutylammonium cation (TBA⁺), a very common surface active agent, affects electrodic processes involving metallic cations in complexing media at mercury/solution interfaces, namely the cadmium(II) ion in chloride media (where cadmium(II) chlorocomplexes are predominant [2]). Most of this work deals merely with polarographic and/or electrocapillary curve data. With other voltammetric techniques such reports derive from few studies [3,4], some of them adopting a very restrictive point of view (*e.g.* TBA⁺ as an interference in electroanalytical determinations of metal cations). From classic polarography, as was seen before [1], the presence of TBA⁺ and the chloride ion, produces two significant modifications on cadmium polarograms: firstly a decrease in

limiting current intensity, and secondly the development of a second wave, at greater negative potentials. Accordingly, both effects were found to be more pronounced as TBuA⁺ concentration increases. It is generally accepted that both effects are due to the increasing adsorbability of these cations on the mercury surface. How these phenomena are affected by temporal effects on varying potential, like scan form or rate, and how this reflects on the kinetics of the electroreduction of metal cations is not known.

The aim of this paper is therefore to determine whether a TBuA⁺ influence of a similar or different nature exists on electrodic processes of the cadmium(II) ion in chloride media, when the electric (applied potential) perturbation is imposed in different ways at increasing rates. Two technics have been selected for this purpose: differential pulse voltammetry and cyclic voltammetry.

In this study, it was found that at low scan rates (tens to hundreds of mV/s) and with an increase in tetrabutylammonium cation concentration, some results using both techniques are consistent with the observations made in classic polarographic studies. At higher scan rates and with an increase in tetrabutylammonium cation concentration below a certain value, the results are different. The effect on the electroreduction of cadmium(II) ions seems to be negligible.

Experimental

Chemicals and Solutions

Stock solutions 0.01mol·dm⁻³ in CdCl₂ and TBuACl were prepared by dissolving CdCl₂ and TBuACl (*p.a.* from Fluka and Sigma, respectively) in distilled and deionized water.

The supporting electrolyte used was NaCl 1mol·dm⁻³.

Apparatus and Conditions

Differential pulse and cyclic voltammetry (staircase) experiments were performed with a potentiostat/galvanostat AUTOLAB/PGSTAT20 from Eco Chemie coupled to a Metrohm Stand 663 VA. This was equipped with a hanging mercury drop electrode, a silver/silver chloride/3M potassium chloride reference electrode and a glassy carbon auxiliary electrode. The following conditions were used in differential pulse experiments: initial potential 0V, final potential -1.8V, pulse amplitude 30mV, pulse duration 50ms, step potential 1.95mV and time between application of pulses 250ms (conditions corresponding to a scan rate of 7.8mV/s).

The following conditions were used in cyclic voltammetry (staircase) experiments: start potential 0V, first vertex potential -1.8V, second vertex potential 0V, step potential 2.44mV and scan rate of 1V/s (scan rates of 0.5V/s and 0.1V/s were also used).

The whole system runs on a GPES software program (version 4.5 from Eco Chemie, which enables the measurement of data and its subsequent analysis) on a personal computer.

Procedure

Differential pulse and cyclic voltammetry (staircase) experiments were carried out in 20cm³ of NaCl 1mol·dm⁻³ varying the analytical concentrations of cadmium(II) and tetrabutylammonium cations and the molar ratios between them. The following experiments were performed: (i) addition of 200×10⁻⁶ dm³ of TBuACl 0.01mol·dm⁻³ to the cell followed by further additions of same quantity of TBuACl; (ii) addition of 200×10⁻⁶ dm³ of CdCl₂ 0.01mol·dm⁻³ to the cell followed by further additions of same quantity of CdCl₂; (iii) addition of 200×10⁻⁶ dm³ of CdCl₂ 0.01mol·dm⁻³ to the cell followed by further additions of 200×10⁻⁶ dm³ of TBuACl 0.01mol·dm⁻³; and (iv) addition of 200×10⁻⁶ dm³ of TBuACl 0.01mol·dm⁻³ to the cell followed by further additions of 200×10⁻⁶ dm³ of CdCl₂ 0.01mol·dm⁻³.

The supporting electrolyte solution (NaCl 1mol·dm⁻³) was deaerated with nitrogen for 15 minutes. The time used after each addition was just 2-3minutes. All measurements were carried out three times and at 19.0 ± 0.1 °C.

Results and Discussion

Differential Pulse Voltammetry

Fig.1, shows the differential pulse voltammograms of cadmium(II) (0.1mmol·dm⁻³) obtained in NaCl 1mol·dm⁻³ in the presence of different concentrations of TBuA⁺. It can be seen that the presence of TBuA⁺ has no significative influence on the peak potential of Cd(II) species but its peak height decreases (Table 1). In the post-negative region of these peaks two other small consecutive peaks can also be observed. The height of these two peaks seems to be dependent only on Cd(II) concentration (see below Fig.2).

Table 1. Characteristics of Cd(II) electroreduction peak with and without tetrabutylammonium cation in NaCl 1mol·dm⁻³ (corresponding to Fig. 1).

Composition of NaCl 1mol·dm ⁻³ solution	Peak potential	Peak height	Peak width
	E _p /mV	I _p /nA	W _{1/2} /mV
Cd(II) 0.100mmol·dm ⁻³	- 585	- 309	54
	1/1	- 591	- 88
	1/3	- 593	- 71
Cd(II)/TBuA ⁺ molar ratio	1/5	- 595	- 56
			69

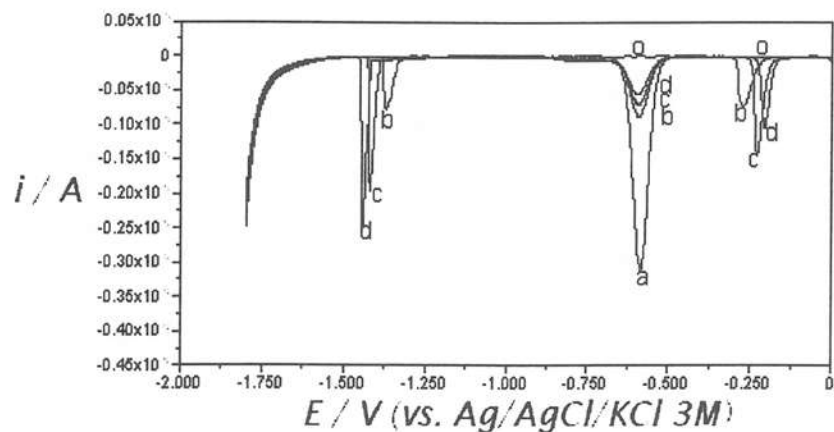


Fig 1. Differential pulse voltammograms of cadmium(II) with and without tetrabutylammonium cation $0.100\text{mmol}\cdot\text{dm}^{-3}$ in $\text{NaCl } 1\text{mol}\cdot\text{dm}^{-3}$. Blank solution ($\text{NaCl } 1\text{mol}\cdot\text{dm}^{-3}$) (o); Cd(II) $0.100\text{mmol}\cdot\text{dm}^{-3}$ (a); Cd(II)/TBuA⁺ molar ratios: 1/1 (b), 1/3 (c) and 1/5 (d).

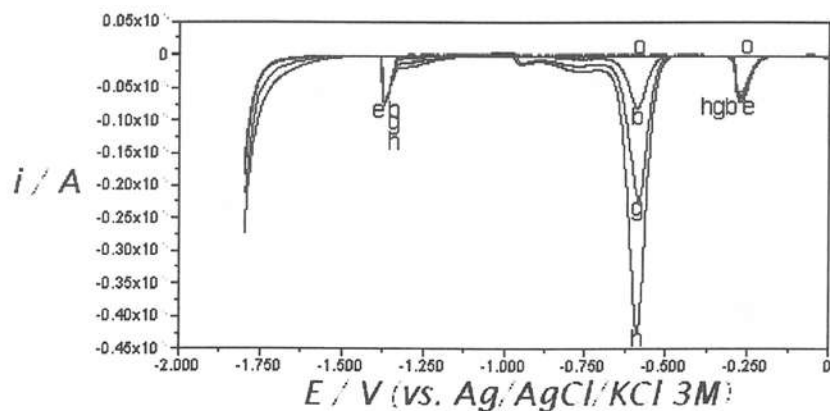


Fig 2. Differential pulse voltammograms of cadmium(II) with tetrabutylammonium cation $0.100\text{mmol}\cdot\text{dm}^{-3}$ in $\text{NaCl } 1\text{mol}\cdot\text{dm}^{-3}$. Blank solution ($\text{NaCl } 1\text{mol}\cdot\text{dm}^{-3}$) (o); TBuA⁺ $0.100\text{mmol}\cdot\text{dm}^{-3}$ (e); Cd(II)/TBuA⁺ molar ratios: 1/1 (b), 3/1 (g) and 5/1 (h).

At greater anodic and cathodic potentials than the Cd(II) reduction peak there are also significant modifications to the voltammograms. At these potentials single peaks develop, whose presence is due only to TBuA⁺ (see below Fig.3).

As the concentration of TBuA⁺ is increased (up to five times the Cd(II) concentration) (Fig.1), the peak that is observed at greater anodic potentials shifts to greater positive potentials and their height passes through a maximum. For the more cathodic peak, the shift is in the opposite direction and the height always increases. For both peaks these characteristics (peak potential and height variation) seem to be dependent only on TBuA⁺ (see below Fig.3). However, there exists a curious effect with the more cathodic peak (*i.e.* an increase in the previous baseline) when Cd(II) and TBuA⁺ are in the same solution, which seems to be independent of TBuA⁺ concentration but dependent on Cd(II) concentration (compare Fig.1 with Fig.2).

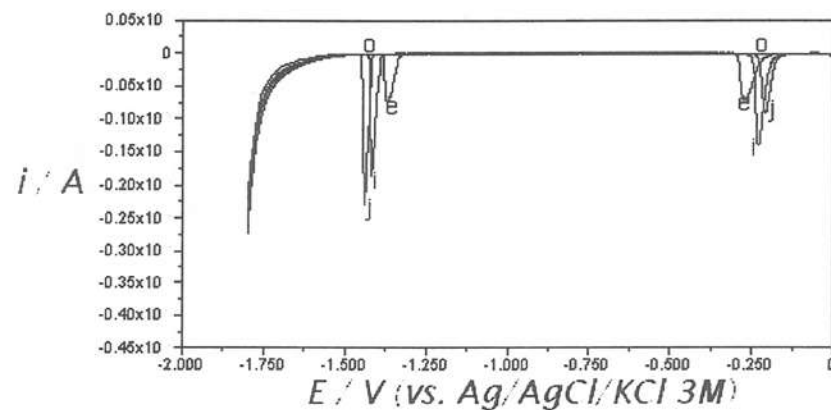


Fig 3. Differential pulse voltammograms of TBuA⁺ in $\text{NaCl } 1\text{mol}\cdot\text{dm}^{-3}$. Blank solution ($\text{NaCl } 1\text{mol}\cdot\text{dm}^{-3}$) (o); TBuA⁺ $0.100\text{mmol}\cdot\text{dm}^{-3}$ (e); TBuA⁺ $0.300\text{mmol}\cdot\text{dm}^{-3}$ (i); TBuA⁺ $0.500\text{mmol}\cdot\text{dm}^{-3}$ (j).

For solutions of TBuA⁺ and Cd(II) ions with molar ratios of Cd(II)/TBuA⁺ > 1, besides the effects already observed in Fig.2, the height of more anodic peaks can be seen to decrease with increasing molar ratio Cd(II)/TBuA⁺ and the height of more cathodic peaks seems to be independent of this ratio.

Cyclic Voltammetry

Fig.4, shows the cyclic voltammograms (first scan; sweep rate = 1000mV/s) of cadmium(II) (0.1mmol·dm⁻³) obtained in NaCl 1mol·dm⁻³ and in the presence of different concentrations of TBuA⁺.

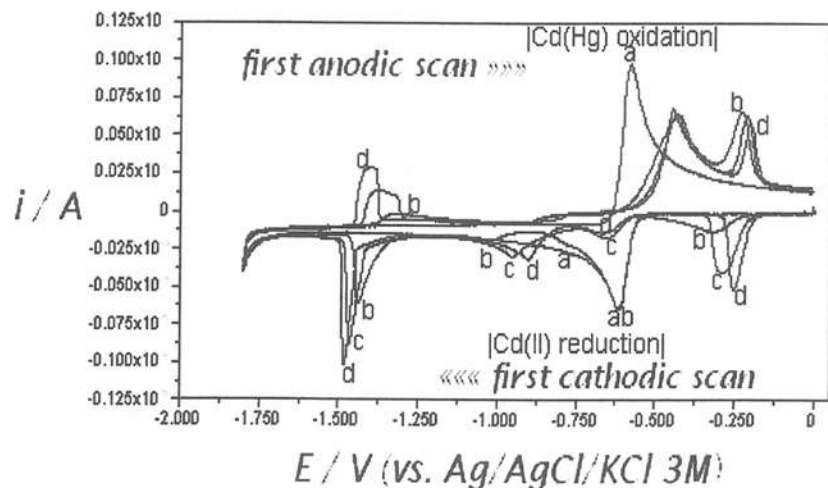


Fig 4. Cyclic voltammograms (1st scan; sweep rate = 1000mV/s) of cadmium(II) with and without tetrabutylammonium cation in NaCl 1mol·dm⁻³. Cd(II) 0.100mmol·dm⁻³ (a); Cd(II)/TBuA⁺ molar ratios: 1/1 (b), 1/3 (c) and 1/5 (d).

Looking at the cathodic branch of the cyclic voltammograms, it can be seen that when the concentration of TBuA⁺ is the same as Cd(II) (*i.e.* Cd(II)/TBuA⁺ = 1) the peak potential and the peak height of Cd(II) reduction is unaffected by TBuA⁺ presence; the only modification observed to these peaks occurs on their negative side, with a more pronounced decrease in current, a small shoulder and a well-defined post-peak. As the concentration of TBuA⁺ is increased (up to five times the Cd(II) concentration, *i.e.* Cd(II)/TBuA⁺ < 1), the peak potential of Cd(II) seems to shift in a negative direction and its height decreases; for the well-defined post-peak the shift occurs in the opposite direction and its height increases.

Besides these effects on the Cd(II) reduction area single peaks can also be observed in anodic and cathodic regions. As TBuA⁺ concentration is increased in the solution containing the Cd(II) species the peak that is observed in the anodic area shifts to less negative potentials and the peak

that is observed in the cathodic area shifts to greater negative potentials; for both peaks height always increases. These characteristics (peak potential and height variation) seem to be dependent only on TBuA⁺ (see Fig.5 below).

Looking at the anodic branch of the cyclic voltammograms, it can be seen that the presence of TBuA⁺ modifies the peak potential and peak height of Cd(Hg) oxidation (the peaks shift to more anodic values and their height decreases). Besides these modifications to these peaks an increase in the previous baseline can be observed. This increase and the modifications to peak potential and peak height seem to be identical whatever the-TBuA⁺ concentration.

In regions which are more anodic and cathodic than the Cd(Hg) oxidation area single peaks can also be observed whose presence and characteristics seems to be dependent on TBuA⁺ (Fig.5). As TBuA⁺ concentration is increased in the solution containing cadmium(II) the peak that is observed in the anodic area shifts to less negative potentials and its height decreases; the peak that is observed in the cathodic area shifts to more negative potentials and its height increases.

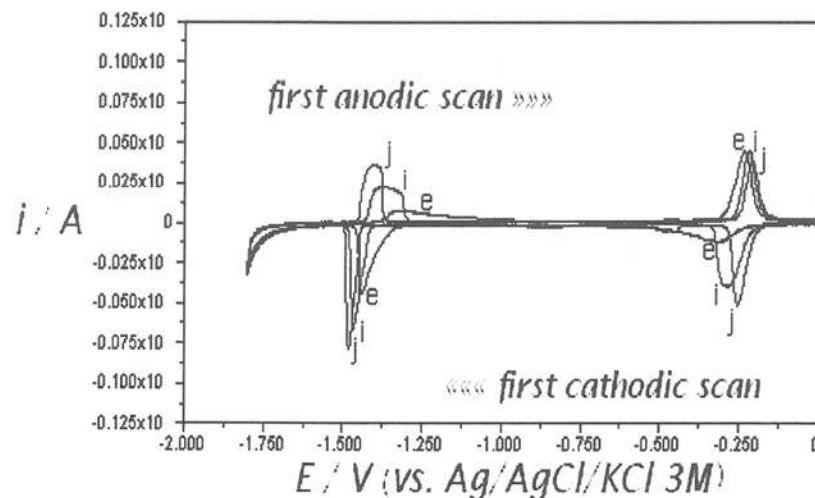


Fig 5. Cyclic voltammograms (1st scan; sweep rate = 1000mV/s) of TBuA⁺ in NaCl 1mol·dm⁻³. TBuA⁺ 0.100mmol·dm⁻³ (e); TBuA⁺ 0.300mmol·dm⁻³ (i); TBuA⁺ 0.500mmol·dm⁻³ (j).

After comparing the results of differential pulse voltammetry (DPV) with the results of cyclic voltammetry (CV), regards the Cd(II) reduction (especially the decrease of peak height observed at 7.8mV/s (with DPV) versus the independence of peak height observed at 1000mV/s (with CV), when the molar ratio of Cd(II)/TBuA⁺ = 1), cyclic voltammetry was attempted at lower sweep rates (500mV/s and 100mV/s). The results from this study show that when the sweep rate decreases the influence of TBuA⁺ on Cd(II) potential and current reduction becomes important (Fig.6).

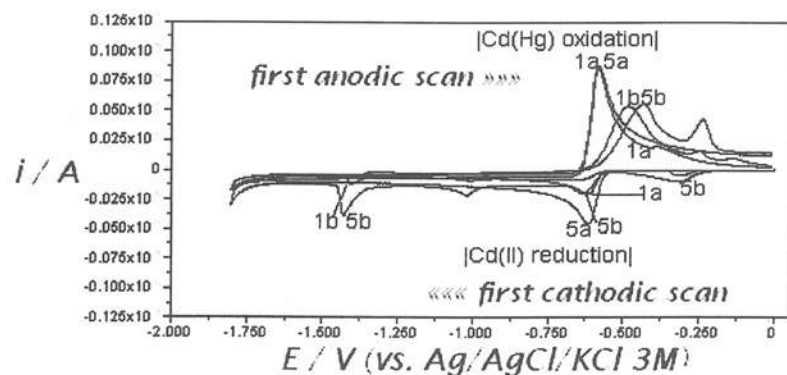


Fig 6. Cyclic voltammograms (1st scan) of cadmium(II) 0.100mmol·dm⁻³ (a) without and (b) with tetrabutylammonium cation 0.100mmol·dm⁻³ in NaCl 1mol·dm⁻³, at (1) 100mV/s and (5) 500mV/s.

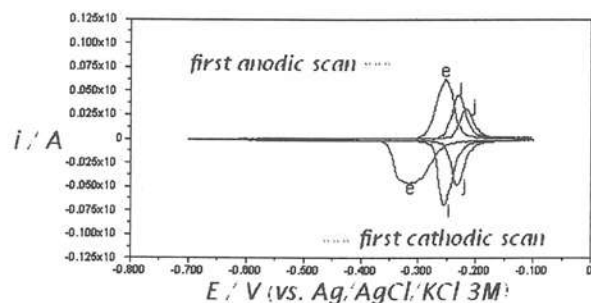


Fig 7. Cyclic voltammograms (1st scan between -0.1V and -0.7V; sweep rate = 100mV/s) of TBuA⁺ in NaCl 1mol·dm⁻³. TBuA⁺ 0.100mmol·dm⁻³ (e); TBuA⁺ 0.300mmol·dm⁻³ (i); TBuA⁺ 0.500mmol·dm⁻³ (j).

In complementary studies, as regards only the cathodic branch of the voltammogram, another important effect was observed: the dependence of peak height on the sweep rate of the anodic peak attributable to the presence of TBuA⁺. For sweep rates much lower than 1000mV/s the height of these peaks does not increase but passes through a maximum as the concentration of TBuA⁺ increase (Fig.7). This shows that TBuA⁺ adsorption is rate- and concentration-controlled.

A more fully discussion of the experimental data about TBuA⁺ “peaks” (namely, their origin, shape and shifts), is important and requires further and new investigations.

Conclusions

The results of this study show that the influence of TBuA⁺ on the redox behaviour of the Cd(II)/Cd(Hg) couple is not only concentration-dependent but also scan rate-dependent. If one assumes that the decrease in the reduction rate of cadmium(II), is due to TBuA⁺ adsorption on the mercury electrode, one is also tempted to conclude that the adsorption extension and its influence on faradaic processes are co-determined by time effects and TBuA⁺ concentration. It seems that at higher scan rates and with a limited concentration of TBuA⁺, the adsorption is not extensive, or its inhibitory effects, with regard to reduction processes of cadmium(II), are negligible.

References

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