

GRAPHITE PASTE CYCLIC VOLTAMETRIC STUDIES OF SOME URANYL COMPOUNDS

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Results of graphite paste cyclic voltametry on some uranyl compounds like uranyl nitrate (I), uranyl zinc acetate [2] and uranyl nickel acetate [3] in aqueous KCl, HCl, and CH₃COOH system are reported. The over all electrochemical behaviour of these compounds was found to be a two step process involving an irreversible chemical reaction preceding with aquasi-reversible charge transfer process, in KCl and HCl system, while in CH₃COOH system the reduction step was found to be an irreversible electron transfer followed by an irreversible regeneration of starting material. The species generated electrochemically (during CV) were stable with respect to time in some of these cases.

Key words: Carbon paste, Graphite electrode, Uranyl compounds, Cyclic voltametry.

INTRODUCTION

Cyclic voltametry has become the most versatile technique for the last two decades [1-3]. The extensive use of cyclic voltametry is due to rapid determination of redox behaviour over a wide potential range. Similarly, information about reversible irreversible nature [4,5] of electron transfer processes [6] including formal reduction potential, formation constant, rate constant [4] and sometimes number of electron transferred per reactant molecule of electroactive species are found more conveniently by this method. Many text books dealing with the theoretical as well as experimental aspects give a very brief over view of this method [2,3,7,8].

Further advancement in electrochemistry is the introduction of graphite paste voltametry by Adams [9b], where he replaced usual test electrode by graphite paste electrode impregnated with some chemically inert liquid like silicon oil etc. [9a, 10]. Graphite paste voltametry was conveniently used in many electrochemical systems due to its relative ease [11, 13], improved sensitivity [12] and reproducibility of the electrode surface. Cathodic or anodic peak heights (I_p) and sometimes $E_{1/2}$ have been found more significant due to extended (oxidation) potential range, better residual current magnitude and less interference by dissolved oxygen [14,15].

Considering the above advantages in mind, Kissinger and Heineman [15], Van Bensichoten [16] and others used graphite paste cyclic voltametry to analyse various electrochemical systems. However, little work has been reported so far on graphite paste cyclic voltametry. Recently, some quantitative studies have been made to analyse some uranyl compounds with graphite paste voltametry [15],

but no work has been reported on the study, of the cyclic voltametry on these compounds at graphite paste electrode. Therefore, the present studies were carried out to determine the properties concerning cyclic voltametry.

EXPERIMENTAL

(a) *Paste electrode.* 3 g graphite powder (E. Merck B-3 grade) was impregnated with 2 ml. of silicone oil (BDH). The resulting paste was filled in a laboratory made paste electrode as reported earlier [17, 18].

(b) *Material.* Uranyl compounds (all from BDH) like uranyl nitrate [1], uranyl zinc acetate [2] and uranyl nickel acetate [3], each of 10^{-3} M were prepared in 0.1 M KCl (E. Merck), 1.0 M HCl (E. Merck) and 1.0 M CH₃COOH (E. Merck). A polarographic analyser (model 174-A; PARC) in conjunction with an X-Y recorder (model R.E. 0074; PARC) were used for recording cyclic voltammograms.

(c) *Method.* Three electrode assemblies i.e. graphite paste test electrode, Pt wire auxiliary (counter) electrode and a saturated calomel electrode (SCE) were arranged accordingly, while solutions of pure supporting electrolytes (KCl, HCl and CH₃COOH) followed by the electroactive systems were taken in the cell. After bubbling nitrogen for 3 min. for generating an inert atmosphere, cyclic voltammograms of these uranyl compounds were recorded keeping a scan rate 100 or 50 mV/sec. with a current magnitude 0.2 mA at $25 \pm 1^\circ$. The switching potentials of these compounds were selected depending upon their reduction potentials. Each time a fresh solution of uranyl compound was taken. To avoid adsorption of electroactive material on graphite paste electrode [19], the electrode surface was also renewed by extruding graphite paste (2 mm.) and

rubbing the inner surface of the electrode on a fine filter paper. All reagents used were of reagent grade and the solutions were prepared in doubly distilled water.

RESULTS AND DISCUSSION

Cyclic voltammograms of all these supporting electrolytes at silicon oil impregnated graphite paste electrode vs. saturated calomel electrode showed straight, well extended and oxygen interference free line similar to the reported work [16].

Graphite paste cyclic voltammograms of uranyl compounds I, II and III in KCl, HCl and CH₃COOH system. are shown in Fig 1, 2 and 3. Information based on these cyclic voltammograms is collectively given in Table 1.

Compounds, I, II and III showed cathodic as well as anodic peaks in KCl and HCl system. However, in the systems II(KCl), II (HCl) and III(HCl) two cathodic waves or peaks were observed reflecting the two-electron transfer process in these systems. But the 2nd wave was not found in the reverse scan and only the first wave was found in the oxidation process. However, these uranyl compounds showed only a cathodic peak in the CH₃COOH system. These cathodic peaks in the II(KCl), II(HCl) and III(HCl) systems consisted of two peaks showing that the first reduction step in each of these systems was found to be quasi-reversible rather than reversible, because in a reversible

system, the reaction is quite fast so that the concentrations of oxidised and reduced species are in equilibrium at the electrode surface [20]. This produces a peak to peak difference (Or $E_{p_c} - E_{p_a}$) = 60 mV, for one electron transfer process [16]. Here, this difference was found to be

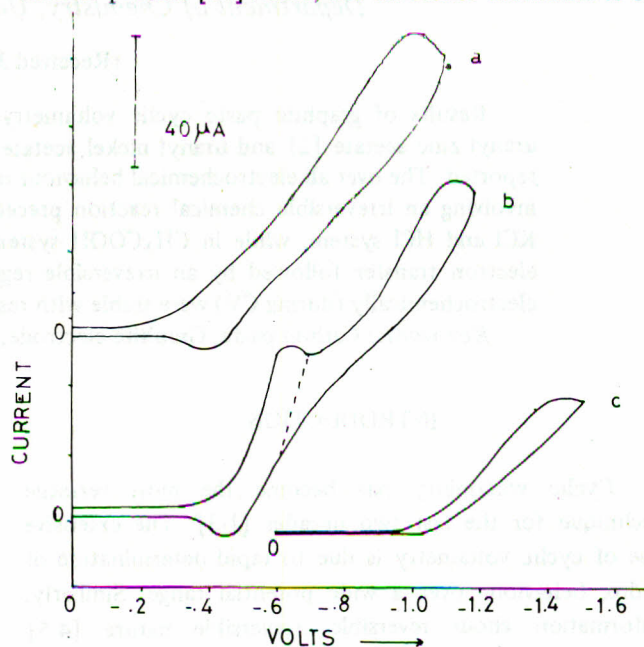


Fig. 1. Graphite paste cyclic voltammograms of uranyl nitrate (1) in (a) 0.1 M KCl, (b) 1.0 M HCl and (c) 1.0 M CH₃COOH vs. SCE., keeping scan rate at 50mv/sec. and current magnitude at 0.2 mA.

Table 1. Electrochemical data on uranyl compounds

Compound	$E_{1/2}$ Volts	E_p Volts	$(E_{p_c} - E_{p_a})$ mv.	I_{p_a} / I_{p_c}	Reversible or irreversible
Uranyl nitrate (I)	- 0.66 ^a	- 1.00 ^a	120	1.00	quasi-rev.
	- 0.90 ^b	- 1.20 ^b	850	-	irreversible
	- 0.76 ^c	- 1.10 ^c	-	-	irreversible
Uranyl zinc acetate (II)	- 0.40 ^a (1)	- 0.55 ^a (1)	300	1.00	quasi-rev.
	- 0.79 ^a (2)	- 1.02 ^a (2)	-	-	irreversible
	- 0.59 ^b (1)	- 0.70 ^b (1)	240	1.00	quasi-rev.
	- 0.96 ^b (2)	- 1.12 ^b (2)	-	-	irreversible
	- 0.74 ^c	- 1.10 ^c	-	-	irreversible
Uranyl nickel acetate (III)	- 0.67 ^a	- 0.86 ^a	430	1.00	quasi-rev.
	- 0.61 ^b (1)	- 0.76 ^b (1)	280	1.00	quasi-rev.
	- 0.98 ^b (2)	- 1.16 ^b (2)	-	-	irreversible
	- 0.61 ^c	- 0.90 ^c	-	-	irreversible

Where a, b and c are the values taken in KCl, HCl and CH₃COOH respectively.

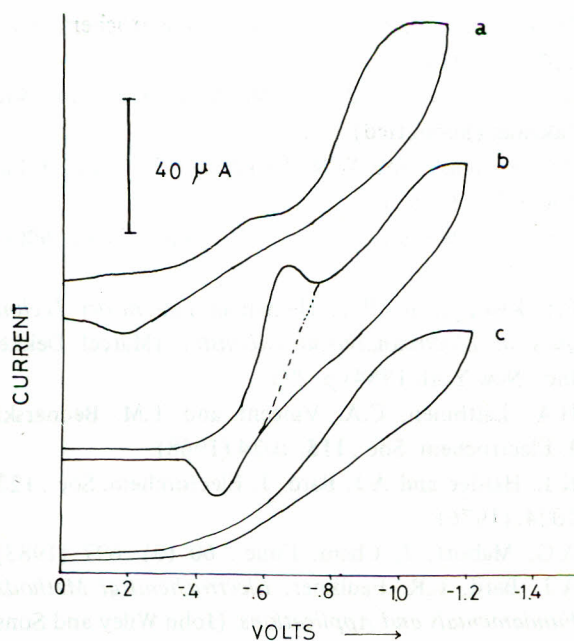


Fig. 2. Graphite paste cyclic voltammograms of uranyl zinc acetate (ii) in (a) 0.1 M KCl, (b) 1 M HCl and (c) 1.0 M CH₃COOH vs. SCE, keeping scan rate at 50 mV/sec. and current magnitude, at 0.2 mA.

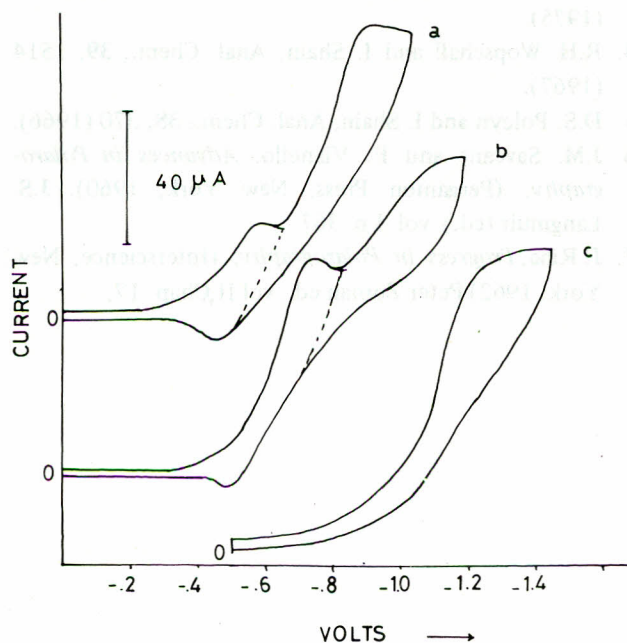
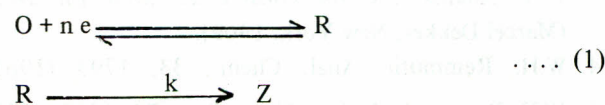


Fig. 3. Graphite paste cyclic voltammograms of uranyl nickel acetate (III) in (a) 0.1 M KCl, (b) 1 M HCl and (c) 1.0 CH₃COOH vs. SCE., keeping scan rate at 50 mV/sec. and current magnitude at 0.2 mA.

greater than 60 mV. (see Table 1). This shows that the system is quasi-reversible where the greater splitting of cathodic and anodic peaks showed a sluggish (slow) electron transfer process [20] due to large activation over potentials required for charge transfer to occur [21]. Another aspect

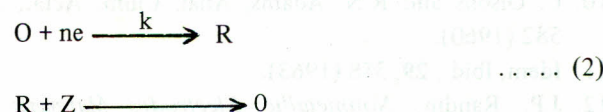
which categorises this reaction as quasi reversible is the cathodic shift of the redox couple which increases as the scan rate is increased [20].

The absence of the anodic peak corresponding to the second cathodic peak in the reverse scan could not be observed even at higher scan rate (100 mV/sec.). Therefore, the reaction scheme on the basis of above facts reflect that it is a chemical reaction preceding with a irreversible or quasi-reversible charge transfer process [22], i.e.,



The irreversible behaviour of the second cathodic peak may also be characterised by the adsorption phenomenon [23,24] occurring at this potential, because the adsorption of electroactive species has been reported in most of the graphite paste voltametry work.

While considering the behaviour of these compounds in CH₃COOH, it was noticed that the absence of anodic peak even at higher scan rate and the nature of the curve which was found to be lower and more spread out on potential axis indicates that it is either due to catalytic reaction with irreversible charge transfer process [22], i.e.,



or an irreversible electron transfer followed by an irreversible regeneration of the starting material [21]. Because both schemes follow the above mentioned process (i.e. eq. 2), here products were not found to be recycled electrochemically due to (i) an extensive bond breaking and (ii) loss of substituents to solution [20] (e.g. those chemically irreversible reactions which may yield no return peak at all). The second possibility i.e. (ii) is more favourable in the CH₃COOH system in which all these uranyl compounds showed irreversible behaviour, because the reduced product of uranyl compounds associates more strongly with the acetate ion. This sort of association may be responsible for the loss of substituents to solution [20] (as discussed above) giving no peak in the reverse scan which was not found in the other systems like KCl and HCl.

The values of I_{p_a} / I_{p_c} ratio [25] of some of these uranyl compounds are listed in Table 1. These values indicate the chemical stability of these reduced forms. The degree of deviation from unity is correlated with the kinetics of the electrode process [26], where the effect of the chemical reaction on the cathodic portion of the cyclic wave led to increase in the value of the peak current [27].

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