

CYCLIC VOLTAMMETRIC STUDIES ON REDUCTION OF SILVER FROM SYNTHETIC COLOUR BLEACH FIX SOLUTIONS

N SATHAIYAN, P ADAIKKALAM, A VARADARAJ and J A M ABDUL KADER

Central Electrochemical Research Institute, Karaikudi-623 006, INDIA

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Cyclic voltammetric studies were carried out to understand the electrochemical aspects of the reduction of silver ion from synthetic colour bleach fix solutions (SCBF solution). The results obtained have helped in throwing light on the mechanism of the above process and for optimising the various parameters with a view to increase the current efficiency. Based on the cyclic voltammetric informations, controlled potential electrolysis experiments were also carried out to find out the silver deposition efficiency.

Key words: Synthetic colour bleach fix solutions, reduction of silver, ferric EDTA complex, cyclic voltammetry

INTRODUCTION

The recovery of silver from photographic fixer solutions and colour bleach fix solutions are considered to be worthwhile because of the increased consumption of silver and its demand. The silver concentration in the photographic fixer solution is about 2-4 g. dm⁻³, where as its concentration in colour bleach fix solution is about 6-8 g. dm⁻³. The recovery of silver from these sources is carried out by chemical as well as electrochemical methods [1-4]. The recovery by chemical methods from colour bleach fix solution involves costly chemicals and so recovery by electrochemical method is adopted. The advantage of this method is the regeneration of bleach-fix solution, which could be reused for further processing.

The photographic colour bleach fix solution contains in addition to sodium thiosulphate, ferric-EDTA complex and the current efficiency improves when the electrolysis is done using two compartment cell. It is attributed that the low efficiency is due to the dissolution of deposited silver by ferric ion since silver deposition is a preceding reaction [5].

The aim of this work is to study the reduction of silver ion from synthetically prepared colour bleach-fix solution and to optimise the experimental parameters with a view to increase the current efficiency. The techniques of cyclic voltammetry (CV) and potentiostatic polarisation are adopted to get information on the above aspects.

EXPERIMENTAL

The CV experiments were carried out using a conventional all-glass electrolysis cell with provision for inlet and outlet for deaerating the solution with pure and dry nitrogen gas. A three electrode set up consisting of a teflon covered platinum disc (6 mm dia) working electrode, a platinum foil counter electrode and a saturated calomel reference electrode (SCE), was used. Before carrying out the experiments, the working electrode was polished with emery papers down to 4/0 grade, degreased with acetone and finally washed with twice distilled water. The solutions were prepared from

analar grade reagents and double distilled water. The desired solution, after deaeration with pure nitrogen, was introduced into the cell. The CV were then run on the system chosen for the study at 298 ± 1K. The range of potential covered was +0.100 to -0.550V vs SCE, with the starting potential for all the experiments at + 0.100V. The potential was reversed to obtain the anodic branch of the cyclic voltammogram. A potentiostat coupled with a scan generator was used for controlling the potential and the i-E curves were recorded on an X-ray recorder

The potentiostatic experiments were carried out using a two compartment cell with Nafion-427 cation exchange membrane as diaphragm at 305 ± 1K. A rotating cylindrical stainless steel (area 20 cm²) acted as cathode and lead-silver alloy as anode. The anolyte was sodium sulphate (50 g. dm⁻³ silver, 150 g. dm⁻³ sodium thiosulphate, 5-15 g. dm⁻³ iron in ferric-EDTA complex and 25 g. dm⁻³ potassium metabisulphite was used as catholyte. A potentiostat was employed in potentiostatic experiments while in galvanostatic experiments power source of capacity 15V, 10A was used.

RESULTS AND DISCUSSION

CV experiments for the system synthetically prepared colour bleach fix solutions (SCBFS) on platinum disc electrode have been carried out using silver concentrations in the range from 1 to 10 g. dm⁻³ as well as varying the ferric ion concentration in the ferric-EDTA complex in the range from 5 to 15 g. dm⁻³. These experiments gave reproducible and well-defined current-potential curves.

The response of a SCBF solution having 15 g. dm⁻³ of ferric ion in ferric-EDTA complex without silver is given in Fig. 1 for identifying the single stage reduction and oxidation of ferric-EDTA complex. The cathodic peak potential value E_p is not shifting with scan rate (i.e. ν -170 ± 5 mV), while the anodic peak potential value is shifted to more anodic potential. The typical CV response of a SCBF solution containing 2 g. dm⁻³ of silver without ferric-EDTA complex in sodium thiosulphate solution is shown in Fig. 2.

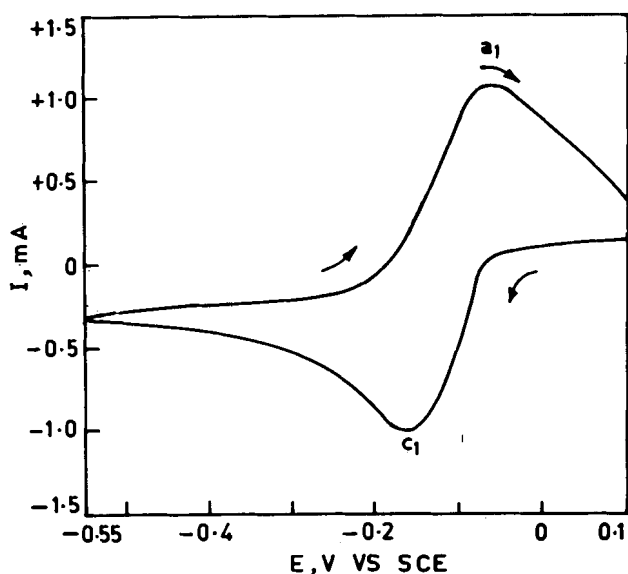


Fig 1: Cyclic voltammogram of SCBF solution without silver on platinum electrode.
 Fe concentration in ferric-EDTA complex : 15 g.dm^{-3} ; sweep rate : 10 mV s^{-1} ; Range of potential sweep : $+ 0.1$ to -0.55V

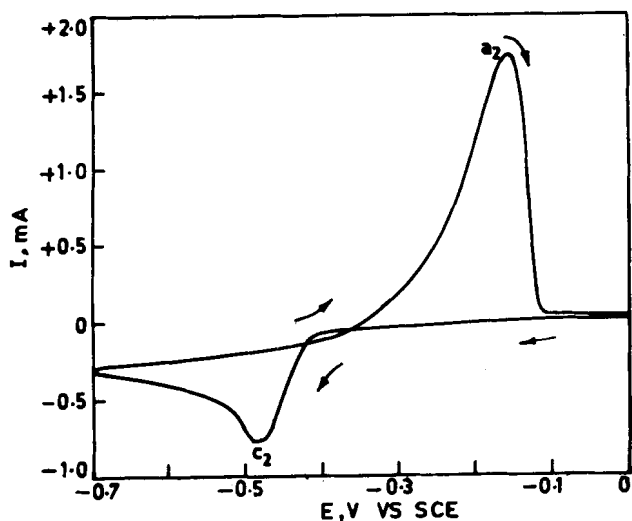


Fig.2: Cyclic voltammogram of SCBF solution without ferric-EDTA complex on platinum electrode.
 Silver: 4 g.dm^{-3} ; Sweep rate: 50mV s^{-1} ; Range of sweep: 0 to -0.7V

The C V response of the deposition and dissolution of silver shows the involvement of single step reduction and oxidation on platinum as evidenced by one cathodic (C2) and one anodic peak (a2). The cathodic peak potential value $E_p(C2)$ is about -0.480 mV whereas for the anodic peak, $E_p(a2)$ it is about -0.160V . The large peak potential difference between $E_p(a2)$ and $E_p(C2)$ is found to

increase with sweep rate, suggesting that the dissolution and deposition of silver on platinum are irreversible.

The typical C V response of a SCBF solution containing silver and ferric-EDTA complex in sodium thiosulphate solution is shown in Fig. 3. The two cathodic (C1 & C2) and anodic (a1 and a2)

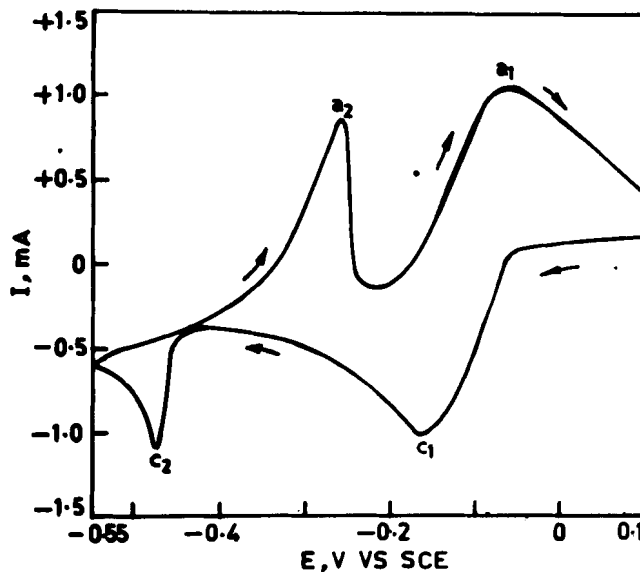


Fig.3: Cyclic voltammogram of SCBF solution on platinum electrode : Silver: 4 g.dm^{-3} ; Fe concentration in ferric-EDTA complex: 15 g. dm^{-3} ; Sweep rate : 10 mV s^{-1} ; Range of potential sweep + 0.1 to -0.55V

peaks appeared in the C V show the involvement of reduction and oxidation of ferric-EDTA complex and silver under the experimental conditions used. The peak potential values of $E_p(C1)$ and $E_p(a1)$ correspond to the reduction and oxidation of ferric-EDTA complex whereas the values of $E_p(C2)$ and $E_p(a2)$ correspond to the reduction and oxidation of silver. It is observed that the anodic peak, $E_p(a2)$ shown in Fig. 3 is shifted to more negative potential (about -100mV) which is due to the presence of ferric-EDTA complex.

The typical influence of silver and ferric ion concentration in SCBF solution is demonstrated in Figs.4 & 5 respectively. The typical C V response of the effect of silver ion concentration on the cathodic and anodic peaks for a fixed concentration of other constituents in SCBF solution is given in Fig. 4. The silver ion concentration is varied from 1.0 to 10 g.d^{-3} . It is clear that the magnitude of both the cathodic and anodic peaks are increased with silver concentration in the solution. The values of $E_p(C2)$ shift anodically with increasing silver concentration, whereas the values of $E_p(a2)$ also shift anodically. The peak current values of cathodic and anodic peaks i.e $i_p(C2)$ and $i_p(a2)$ are also increasing with silver ion concentration and the ratio of $i_p(a2)/i_p(C2)$ also increases. These observations suggest that increasing silver ion concentration in solution shifts the reduction potential to more anodic, resulting in greater amount of silver accumulation which is also reflected on the silver dissolution. It may also be attributed to the fact that

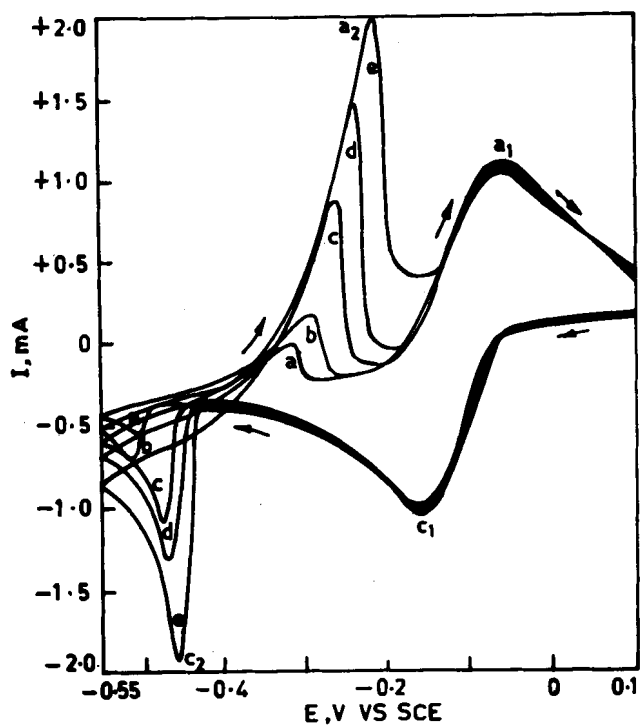


Fig. 4: Cyclic voltammograms of SCBF solution on platinum electrode with varying concentrations of silver. Fe concentration in ferric-EDTA complex : 15 g. dm^{-3} ; Sweep rate: 10 mV s^{-1} ; Range of potential sweep : $+0.1$ to -0.55V ; Concentration of silver: (a) 1; (b) 2; (c) 4; (d) 6 and (e) 10 g. dm^{-3}

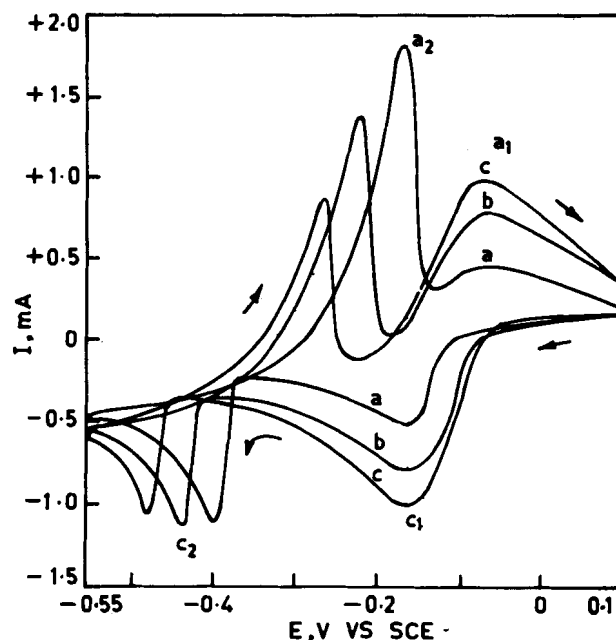


Fig. 5: Cyclic voltammogram of SCBF solution on platinum electrode with varying concentrations of iron. Silver: 4 g. dm^{-3} ; Sweep rate: 10 mV s^{-1} ; Range of potential sweep: $+0.1$ to -0.55V ; Fe concentration in ferric-EDTA complex: (a) 5; (b) 10 and (c) 15 g. dm^{-3}

increasing silver concentration retards the chemical dissolution arising out of ferric ion concentration. These observations are in good agreement with the earlier work [5].

Fig. 5 depicts the effect of concentration of ferric ion in ferric-EDTA complex in SCBF solution on the reduction and oxidation of silver. The concentration of ferric ion in ferric-EDTA complex is varied from 5.0 to 15 g. dm^{-3} . The values of $E_p(C1)$ and $E_p(a1)$ do not shift with increasing ferric ion concentration whereas the values of $E_p(C2)$ and $E_p(a2)$ shift cathodically. The values of $i_p(C1)$ and $i_p(a1)$ are found to increase with ferric-EDTA complex concentration. In case of silver, the values of $i_p(C2)$ and $i_p(a2)$ are decreased with increasing ferric ion concentration. This may be attributed to the fact that the cathodic shift of the $E_p(C2)$ as well as the chemical dissolution of the silver arising out of increasing ferric-EDTA complex concentration retard the deposition of silver.

These observations are in good agreement with the results reported earlier using galvanostatic technique [6]. The galvanostatic experiments carried out with the SCBF solution reveal that beyond the current density of 100 A. m^{-2} , a black deposit is obtained. This is because of the formation of silver sulphide. The same observation is confirmed when the potential is reversed at -0.700V in C V and a black coating is seen on the electrode surface. The formation of silver sulphide is taking place at about -0.650 V .

Based on the above results, controlled potential electrolysis experiments are carried out with a view to increase the silver deposition efficiency. But these results show that the current efficiency is low. It is noted that the reduction and oxidation of ferric-EDTA complex is taking place at more positive potential. If the ferrous-EDTA is not protected, it is readily oxidised to the ferric state. Thus the ferric ion concentration is maintained almost constant which is responsible for the low current efficiency. It has been confirmed by carrying out the experiments using paraffin oil over the surface of the electrolyte to prevent the atmospheric oxidation of ferrous ion. The results of the experiments with and without the paraffin oil layer is given in Table-I.

TABLE-I: Effect of paraffin oil on current efficiency of silver deposit

No.	Electrolyte	Time (hrs)	Current efficiency (%)	Weight of silver deposit (gm)
1	SCBF solution	10	11	0.13
2	SCBF solution + paraffin oil	10	40	0.40
3.	SCBF solution with ferrous-EDTA complex + paraffin oil	1	98	0.48

The noninterference of the ferrous-EDTA complex on silver reduction is also proved where the current efficiency for silver deposition is about 98%.

CONCLUSION

The current efficiency of silver deposition from SCBF solution depends on the ferric ion concentration because of the fact that ferric ion reduction is expected to take place in preference to silver under cyclic voltammetric conditions. It is found that the current efficiency is increased if the electrolysis is carried out in a divided cell and the catholyte is covered with paraffin oil to prevent the air-oxidation of ferrous ion.

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