

ELECTROCHEMICAL PREPARATION OF ERYTHROSIN AND EOSIN

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The paper highlights the preparation of erythrosin (tetra iodofluorescein) and eosin (tetra bromofluorescein) by electrolytic method at a graphite anode using a solution of sodium carbonate containing iodine and fluorescein for erythrosin and sodium bromide and fluorescein for eosin at a divided cell. The yield is compared with that of chemical method.

Key Words: Erythrosin, eosin, electrochemical oxidation

INTRODUCTION

Erythrosin is a disodium salt of 2:4:5:7 tetra iodofluorescein and eosin a disodium salt of 2:4:5:7 tetrabromofluorescein. Erythrosin stands as one of the seven permitted food colours, as a sensitizer of photographic plates, and is used to distinguish live and dead yeast cells as the latter adsorbs the dye much more quickly. Erythrosin is employed in the cotton and paper industries. It is used as a sensitizer in photoelectric experiments and in the irradiation of ergosterol. It is an indicator in analysis. Eosin is used commercially in the manufacture of red inks to a small extent, as a dye for silks and paper, for dyeing cellulose esters and in cosmetics [1].

Three methods are described for the preparation of erythrosin: (a) the electrolysis of an alkaline solution of fluorescein containing a little excess iodine [2] (b) the treatment of a comparatively cool alkaline solution of fluorescein and sodium iodide with ammonium or potassium persulphate [3] and (c) direct halogenation in hot dilute acetic acid with an excess of iodine [4]. Eosin is prepared by brominating fluorescein either directly or in glacial acetic acid solution or on a large scale, by acidifying an alkaline solution of fluorescein containing bromide and bromate, then dissolving the precipitated dye in aqueous carbonate and evaporating to crystallise [1].

It was observed that chemical methods gave di-iodo compounds in addition to tetraiodo compound [4]. Since the tetraiodofluorescein is a food dye, the regulations are very strict for producing pure compound. Hence it was thought of trying electrochemical method as the existing method is covered by a patent [3] and much details are not available. The same was the reason for the electrochemical method of producing eosin also. Moreover, the handling of liquid bromine can be avoided by this method.

EXPERIMENTAL

The cell consists of a beaker of one litre capacity with a graphite anode (either stationary or rotating) or RuO₂ coated titanium anode and steel cathode kept in a ceramic porous pot which acts as a diaphragm. Anolyte solution consists of powdered iodine and sodium salt of fluorescein in equivalent proportion dissolved in 500 ml 10% sodium carbonate solution. The catholyte consists of 100 ml 10% sodium carbonate solution. The cell assembly may be suitably covered with a PVC cover with necessary provision for anode, porous pot, thermometer and stirrer. The area of the anode was measured before experiment, and the temperature was adjusted to 25°C by cooling the vessel from outside. Since one molecule of fluorescein takes 8F for tetraiodination or bromination, the equivalent current was passed accordingly. After the experiment the solution was filtered and the solution was carefully neutralised by dilute sulphuric acid. The solid at acidic pH was collected and dried till constant weight is obtained. The iodine content of erythrosin and bromine content of eosin were determined by Carius method [5]. In both the cases, the halogen content was as per the theoretical value. The results of experiment on erythrosin are given in Table I and that of eosin in Table II.

The purity of the tetra iodofluorescein was further confirmed by converting the compound to diacetate, recrystallised and the melting point determined, which was 293°C thereby corresponding to literature value.

To compare the electrochemical method with chemical method tetraiodofluorescein was prepared by ammonium persulphate method [1]. The yield obtained was 34%. Tetraiodofluorescein was prepared chemically by direct halogenation method [1]. The yield obtained was 35%.

Since dibromofluorescein is soluble in alcohol, pure tetrabromofluorescein can be separated from dibromocompound [6]. Yield reported in literature is 73.4% [7].

TABLE I: Results of the experiment on erythrosin (F: Fluorescein; Temp: 25°C)

No.	Anode and area	Anolyte	Current (A)	Voltage (V)	C.D. (A.dm ⁻²)	Yield (%)	C.E. (%)
1.	RuO ₂ Ti 0.2 dm ²	500 ml 10% Na ₂ CO ₃ + 10g F + 15g I ₂	2	5.5-7.0	10	51.2	48.6
2.	Graphite 0.3 dm ²	-do-	3	5.5-6.0	10	42.8	40.6
3.	Graphite 0.6 dm ²	1000 ml 10% Na ₂ CO ₃ + 10g F + 15 g I ₂	6	5.5-6.0	10	47.8	45.3
4.	Graphite 1.2 dm ²	1000 ml 10% Na ₂ CO ₃ + 10g F + 15g I ₂	6	7-9	5	42.3	39.3
5.	Rotating graphite 0.5 dm ²	500 ml 10% Na ₂ CO ₃ + 10g F + 15g I ₂	5	8-10	10	54.0	46.0
6.	Rotating graphite 0.5 dm ²	500 ml 10% Na ₂ CO ₃ + 20g F + 30g I ₂	5	8-10	10	37.0	33.4 (without diaphragm)
7.	Rotating graphite 0.5 dm ²	500 ml 10% Na ₂ CO ₃ + 10 g F + 15g I ₂	10	13	20	15.0	18.0

Table II: Results of the experiments on eosin

F: Fluorescein; Temp: 25°C

Conditions: Anode: Rotating graphite (0.5 dm²); Current : 2.5 A;
C.D: 5 A.dm⁻²; Anolyte 500 ml of 10% Na₂CO₃ + 10g F + 20g NaBr.

No.	Voltage (V)	Yield %	C.E.	Remarks
1	7-9	53.5	48.7	No diaphragm
2	7-9	72.5	66.2	With diaphragm
3	6-7	49.4	45.0	No. of A.hr was doubled to that of (2)
4	6-7	42.9	39.0	

RESULTS AND DISCUSSION

From Table I it is evident that stationary RuO₂/Ti electrode gives better yield than stationary graphite electrode. Rotating graphite with diaphragm gives better yield than rotating graphite without diaphragm. The yield and purity of the compound (m.p. of acetyl derivative was 294°C) prepared by electrolytic method were better than the yield and purity (m.p. 175°C) obtained by chemical method. It is clear from literature that

diiodo-compound is very difficult to remove from tetraiodofluorescein as the solubilities of both the compounds are the same in almost all solvents.

In the case of tetrabromofluorescein rotating graphite with diaphragm gives better yield than without diaphragm as observed from Table II. The yield reported in literature for chemical method of preparation of tetrabromofluorescein is 73.4% and the yield achieved by electrochemical method as seen from Table II is 72.5%. In chemical method liquid bromine is used, the handling of which is hazardous whereas in electrochemical method sodium bromide is used which is safe and cheaper. It is also observed from Table II that by doubling the quantity of theoretical current the yield decreased from 72.5% to 49.4%. This may be due to the further oxidation of the finished product.

As per ISI standard (IS: 1697-1974) the material erythrosin must conform to the requirements as per tests mentioned.

CONCLUSION

For optimum yield of erythrosin and eosin the electrochemical parameters are almost the same with slight difference in the anolyte composition.

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