B. Electrochem 3(5) September-October 1987, pp 451-453

ELECTROCHEMICALS

CATALYTIC OXIDATION OF LACTOSE USING ELECTROGENERATED Br^-/OBr^- REDOX MEDIATOR

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Electrolytic oxidation of lactose to calcium lactobionate has been studied using electrogenerated Br/OBr redox mediator. Process conditions such as electrolyte concentration, current density, temperature of electrolysis etc, have been optimised for maximising product yield and minimising bromide loss. An electrochemical method for the production of calcium lactobionate has been established with the use of rotating graphite anodes and stationary graphite cathodes and sodium bromide solution as electrolyte.

Key words: Catalytic oxidation, lactose, calcium lactobionate

INTRODUCTION

Electrolysis of dilute solutions of sodium bromide has been successfully utilised earlier for the generation of Br^-/OBr^- redox couple for oxidising glucose to calcium gluconate [1-4] and the process has been successfully commercialised using rotating graphite anodes [5-6]. Calcium lactobionate (CLB) is a very important pharmaceutical intermediate [7] and can be produced by the electro-oxidation of lactose in bromide medium. However compared to the calcium gluconate process, this process has received less detailed investigations [8-10]. Most of these works have employed $CaBr_2$ medium and have generally dealt with the isolation problems in the process. When $CaBr_2$ is used as the electrolyte, the isolation of calcium lactobionate from the electrolyte involves a number of unit operations such as the precipitation of calcium bromide lactobionate, removal of $CaBr_2$ by addition of lime to the calcium bromide lactobionate, passing CO_2 to precipitate out lime as calcium carbonate and finally concentration and isolation of calcium lactobionate itself. In the present studies, sodium bromide solution has been used as the electrolyte and the process involves the removal of sodium bromide by repeated washings of the calcium lactobionate - sodium bromide solid mass obtained by concentrating the electrolyte and isolation of the pure product by filtration and drying. A detailed investigation on the preparative aspects of calcium lactobionate using NaBr medium is reported in the present work.

EXPERIMENTAL

A 1-litre beaker with perspex cover having provisions to introduce the rotating graphite electrode and two counter electrodes of graphite, was used as the electrolytic cell. The immersion area of the rotating electrode was 1 dm^2. The temperature of electrolysis was controlled with the help of a water bath. Theoretical quantity of electricity corresponding to two electron oxidation of the sugar was passed during electrolysis. The electrolyte composition was varied during the experimental studies and has been indicated in Tables I and IV.

After electrolysis, excess clacium carbonate was filtered off and the amount of lactose in solution was estimated by Bertrands method [11] and the amount of calcium lactobionate in solution was estimated by complexometric titration of calcium [12]. The Br^- ion in the electrolyte was estimated by titration against $AgNO_3$ solution by the Volhard's method. Based on these estimations, the yield, current efficiency and Br^- loss were calculated.

Calcium lactobionate was isolated from solution by concentrating the electrolyte over a water bath and isolating the product using alcohol. The solid mass was then washed free from bromide. The filtrate after recovering the product could be reused in this method after recovering the alcohol from the filtrate by distillation.

RESULTS

The effect of sodium bromide concentration on current efficiency and bromide loss was investigated (Table I). Under otherwise identical conditions, increase in sodium bromide concentration improves the current efficiency upto 2% NaBr solution. No improvement is noticed when 3% NaBr solution was employed. With further increase in NaBr concentration, it is noted that there is a fall in current efficiency. It is also noticed that bromide loss is directly associated with decrease in current efficiency at concentration ranges greater than 3%.

TABLE I: Effect of NaBr concentration on current efficiency for the electro-oxidation of lactose

Volume of electrolyte: 750 ml; Lactose: 150g and $CaCO_3$: 30 g; Temperature: 30-35°C; Current: 10 Amps; Current density: 10 A.dm.$^{-2}$

No.	Concentration NaBr (g/l)	CLB formed (g)	Current efficiency (%)	Loss of NaBr (%)
1	10	95.5	60.8	12.5
2	20	122.8	78.2	14.0
3	30	120.7	76.8	26.0
4	50	82.3	52.3	37.5

Table II presents the effect of temperature of electrolysis on the overall current efficiency and bromide loss in the electrochemical preparation of calcium lactobionate. It is noticed that optimum

TABLE II: Effect of temperature on current efficiency and NaBr loss for the electro-oxidation of lactose

NaBr concentration: 20 g/l; other conditions as in Table I

No.	Temperature (°C)	CLB formed (g)	NaBr at the end of electrolysis (g)	Current efficiency (%)	Loss of NaBr (%)
1	20 - 25	108.3	2.1	68.9	14
2	35 - 40	118.7	1.8	75.6	12
3	50 - 55	93.2	4.2	59.3	28

current efficiency and minimum bromide loss values are obtained at 35-40°C. At higher temperatures of electrolysis, current efficiency decreases and bromide loss increases.

The effect of current density on the overall current efficiency and bromide loss in the electrochemical oxidation of lactose is presented in Table III. It is seen from the results that decrease

TABEL III: Effect of current density on the current efficiency and bromide loss for the electro-oxidation of lactose

Temperature : 35-40°C; Other conditions as in Table II

No.	Current density ($A.dm^{-2}$)	CLB formed (g)	NaBr at the end of electrolysis (g)	Current efficiency (%)	Loss of NaBr (%)
1	5	131.1	12.8	83.4	14.6
2	10	122.5	13.1	77.9	12.7
3	15	104.7	11.1	66.7	26.0
4	20	81.1	8.2	51.6	45.3

in current efficiency is associated with high bromide loss at higher current densities. It is also seen that the maximum current density at which current efficiency is high and bromide loss is low is 10 Amp/dm^2.

Calcium lactobionate is highly soluble in water and hence the product can be recovered from the solution only by concentration. It is thus desirable to build up as concentrated a solution as possible during electrolysis. Experiments were carried out to investigate the effect of lactose concentration on the overall current efficiency of the process. The results are presented in Table IV and it is seen that the current efficiency decreases above 200 g/l of lactose concentration.

TABLE IV: Effect of lactose concentration on current efficiency

NaBr: 15 g (Other conditions same as in Table III)

No.	Lactose concentration (g/l)	CLB formed (g)	Current efficiency (%)
1	150	88.1	74.8
2	200	122.8	78.2
3	250	161.2	68.4
4	300	135.7	57.6

The variation of current efficiency with duration of electrolysis (vide Fig. 1) will indicate the viability of the process and will be useful during the scale up of the process. It is observed that the

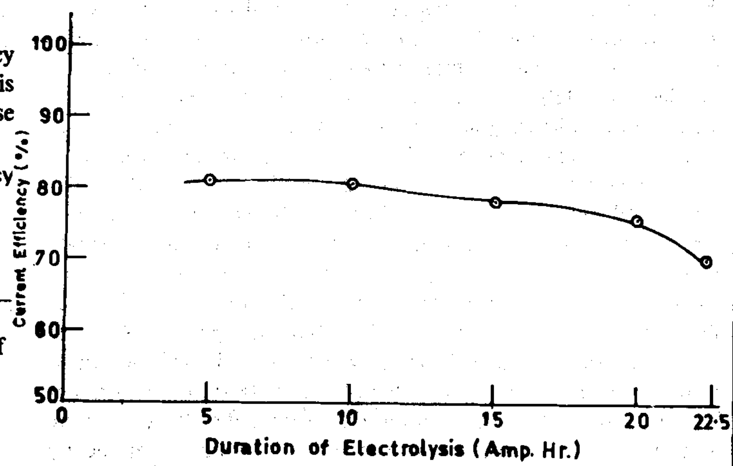

Fig. 1: Variation of current efficiency with duration of electrolysis during the oxidation of lactose

current efficiency falls after 80% conversion of lactose to calcium lactobionate. It is further noticed that the current efficiency is around 80% and is nearly constant from the start of electrolysis upto 20 A.hrs in the total duration of 22 A.hrs.

DISCUSSION

It has been reported from voltammetric studies [13] that lactose is not directly oxidized under the present experimental conditions. Bromide oxidation is the only process that takes place on the electrode surface and lactose is oxidized by the hypobromite formed in the electrochemical step. It has also been established that the chemical reaction between the hypobromite and sugars is rather slow in the time scale of the voltammetric studies and the present work substantiates these findings, by the observation that higher temperatures are required for the preparative work. However, at higher temperatures (>40°C), the current efficiency decreases due to Br_2 loss through evaporation. The finding that increase in

NaBr concentration beyond 2% does not increase the current efficiency is also explained by the fact that the chemical reaction between OBr^- and lactose is rather slow and the overall reaction rate cannot be pushed to higher levels by simply generating hypobromite faster. The decrease in current efficiency towards the end of electrolysis (Fig. 1) is due to the higher rate of generation of OBr^- and its lower rate of consumption with the depleted concentration of lactose towards the end of electrolysis. This may also result in the formation of bromate which can oxidize the sugar further.

CONCLUSION

The present work on the oxidation of lactose in presence of sodium bromide solution as electrolyte establishes a route for the electro-oxidation of lactose to calcium lactobionate at current efficiencies of the order of 80%. Optimum conditions of electrolysis have been established for high current efficiencies and low bromide losses.

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