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Electrochemical reduction of rubber seed oil to stearic acid

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The reduction of rubber seed oil to stearic acid was investigated under potentiostatic conditions in a medium of isopropanol and hydrochloric acid at a pH of 2.0–2.2. The efficiency of reduction was studied on various cathode materials. No reduction was observed on low-hydrogen-overvoltage materials such as platinum and nickel. However, rubber seed oil underwent successful reduction to stearic acid at a monel gauze cathode, which showed high hydrogen overvoltage. The yield was in the region of 70% at a current efficiency of 65%. The final crystalline product showed the presence of 81.5% stearic and oleic acids in contrast to the original oil which contained only 39.3% of these two acids, thus showing the almost complete reduction of linolenic and linoleic acids to stearic acid. The cathode material, the porosity of the ceramic diaphragm, the cathode potential and the pH of the medium were found to be the most critical parameters controlling this reduction process. Studies are now in progress to look into the industrial and economic viability of this conversion.

1. Introduction

Stearic acid is one of the most important fatty acids used in industrial applications [1]. It is normally produced (a) from fat by the Twitchell process, (b) by fat-splitting under high pressure and (c) from fatty oils by hydrogenation. The former two methods usually yield about 50% stearic and oleic acids, whereas the third method yields stearic acid with a minimum of by-products. Hydrogenation of fish and vegetable oils by method (c) has been found to result in much higher stearic acid content (≈90%) than obtained by methods (a) and (b). However, hydrogenation of such oils is normally carried out chemically in an autoclave, under high pressure [1] and in the presence of active catalysts such as raney nickel. This is rather costly from an economic point of view and we have therefore attempted this hydrogenation process electrochemically at a metal cathode, begining from rubber seed oil, an abundant by-product of the rubber industry in Sri Lanka. Gas–liquid chromatographic analysis of the methyl esters of the mixture of fatty acids, obtained by the base hydrolysis of rubber seed oil, confirmed the presence of mainly unsaturated fatty acids in the original oil, which had the composition indicated in Table 1. This analysis further confirmed that the complete hydrogenation of this fatty acid mixture should theoretically yield 83.5% stearic acid and 12.6% palmitic acid.

Table 1. Unsaturated fatty acids in the original rubber seed oil

Acid	*Amount (%)*	*Number of carbon atoms*
Linolenic	10.5	18
Linoleic	33.7	18
Oleic Stearic	39.3	18
Palmitic	12.6	16

Electrochemical reductions of many simple unsaturated organic compounds have been previously carried out on electrode materials such as platinum, nickel, palladium-coated platinum and mercury [2–8]. The advantage of electrochemical methods in these reduction processes is the avoidance of both elevated pressures and expensive catalysts such as raney nickel.

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2. Experimental

2.1. *Potentiostatic measurements*

Electrochemical reduction of the mixture of unsaturated fatty acids was attempted by the potentiostatic method. A detailed description of the practical aspects of such organo-electrochemical reductions is reported elsewhere [9]. Experiments were performed with a 5% solution of the fatty acid mixture, obtained by the base hydrolysis of rubber seed oil, in a solvent–supporting-electrolyte system containing 80 vol% isopropanol and 20 vol% 5 N HCl. The pH of the solution was between 2.0 and 2.2.

The cell used was a typical two-compartment cell. The separation of the anodic and cathodic compartments was achieved by means of a cylindrical ceramic diaphragm of controlled porosity. The porosity of the diaphragm was controlled by firing the raw cylindrical ceramic cast to 1000° C in a furnace with a slow heating rate. The porosity was selected so as to minimize, as far as possible, the mixing of anolyte and catholyte and also to prevent the diffusion of chlorine formed at the anode to the cathode compartment without increasing excessively the cell resistance.

In all experiments a graphite anode was used while the cathode material was varied in order to identify the best electrode material for this electrochemical hydrogenation. Cathode materials used were: graphite, palladium-plated graphite, platinum, copper, stainless steel, lead, nickel and monel (65Ni, 35Cu). Palladium plating of graphite was carried out according to a method reported elsewhere [10]. All potentials were measured and are quoted versus the SCE.

Potentiostatic cathodic polarization was carried out by means of a Wenking LB 75M potentiostat and the current was recorded with a Servoscribe strip chart recorder. In these studies, a step by step potentiostatic polarization was performed with 50 mV steps at two minute intervals. Polarization curves were obtained with each of the above-mentioned cathode materials in order to identify the potential region corresponding to hydrogen evolution in the presence of the fatty acid mixture. Experiments were performed with both stationary and rotating electrodes.

2.2. *Long-term electrolysis*

After identifying the potential region representing the hydrogen evolution reaction in the presence of the fatty acid mixture, long-term electrolysis was performed with each electrode material to ascertain the efficiency of hydrogenation. The cell used was identical to the one described in Section 2.1, but had a much larger electrolyte capacity. A conventional stabilized power supply was used which was able to deliver a maximum current of 3 A at a voltage of 15 V. Copper, platinum and monel electrodes were used in gauze form with a geometric area of 1.5 dm^2 (considering both sides), whereas other electrodes were in rod form of differing area.

The duration of electrolysis was 21 hours, and the iodine value was determined at the beginning of an experiment and thereafter at seven-hour intervals in order to estimate the efficiency of hydrogenation. At the end of 21 hours, the pale yellow crystalline product formed was recrystallized and identified by gas–liquid chromatography and melting-point determination.

3. Results

3.1. *Potentiostatic measurements*

The polarization curves for all cathode materials (except monel metal) exhibited similar behaviour in the absence and presence of the fatty acid mixture. Hydrogen evolution on platinum and palladium-plated graphite electrodes occurred at considerably more positive potentials than for monel. The hydrogen evolution current for the palladium-plated graphite electrode was one order of magnitude greater than those for nickel and monel electrodes, while the corresponding current with a graphite electrode was one order of magnitude lower. Other electrodes showed currents comparable with those of both nickel and monel.

The current–potential curve for hydrogen evolution on a monel electrode in the absence and presence of the fatty acid mixture is shown in Fig. 1. Clearly, the *i–E* curves exhibit similar variation up to -1075 mV (SCE), beyond which a considerable deviation occurs leading to lower currents in the presence of the fatty acid mixture. This type of behaviour was observed only with monel metal and is attributed to the hydrogen-

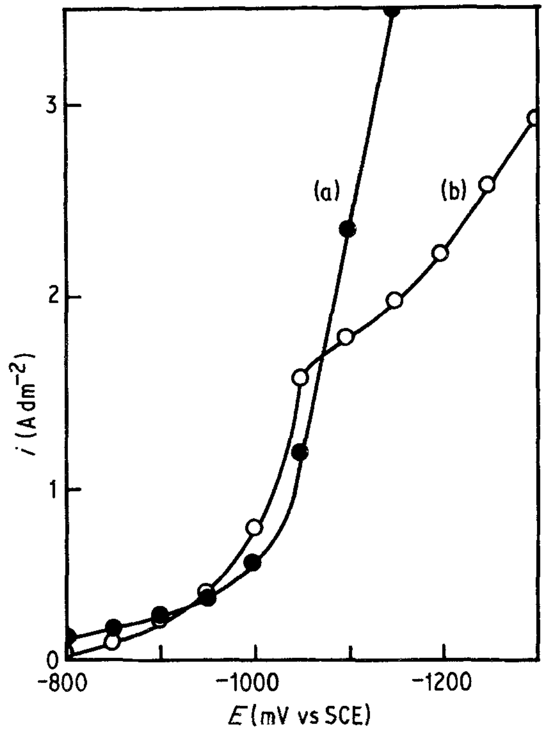


Fig. 1. The cathodic current density versus potential for the monel electrode in (a) isopropanol + HCl medium and (b) isopropanol + HCl + 5% fatty acid mixture.

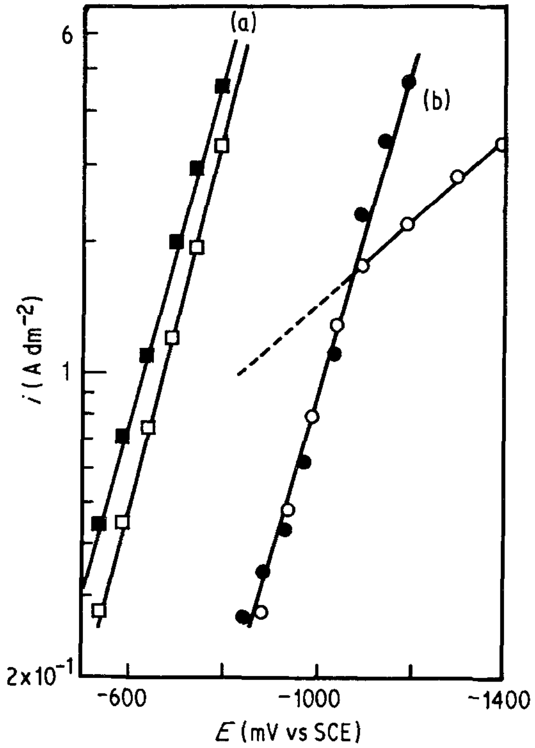


Fig. 2. The cathodic Tafel lines for (a) nickel in the absence (■) and presence (□) of the fatty acid mixture, and (b) monel in the absence (●) and presence (○) of the fatty acid mixture.

ation of the unsaturated fatty acids in the electrolyte.

Cathodic polarization curves for both nickel and monel electrodes in the absence and presence of the fatty acid mixture are depicted in Fig. 2. The Tafel region of the polarization curves with platinum, copper, stainless steel and lead exhibited a behaviour similar to that of nickel, showing no indication of hydrogenation of the fatty acid mixture, as further confirmed by long-term electrolysis experiments. Graphite and palladium-plated graphite electrodes showed rather complex, curved Tafel lines, probably due to the porosity of the graphite electrodes. The Tafel slopes obtained with nickel and monel electrodes were 235 mV and 245 mV respectively (Fig. 2). Clearly, the Tafel slopes are only slightly affected by the presence of the unsaturated fatty acid mixture with both these metals. However, the monel showed a considerably larger Tafel slope at potentials more negative than — 1075 mV (SCE). An interesting feature was the large potential shift ($\approx$350 mV) of the Tafel slopes between nickel and monel electrodes; the Tafel slope for monel appearing at more negative potentials (Fig. 2).

The current–potential behaviour of all the electrodes investigated remained unaffected by the rate of rotation of the electrodes.

3.2. *Long-term electrolysis*

Iodine value estimations during potentiostatic electrolysis indicated that the unsaturated fatty acids present in the hydrolyzed rubber seed oil underwent hydrogenation only when the reduction was performed with monel metal. This is clearly seen in Fig. 3, where the iodine value drops from an initial value of 132 before electrolysis to 21.1 after 21 hours of electrolysis. The drop in iodine value during electrolysis indicates the extensive hydrogenation of the fatty acid mixture. Curve (a) shows the variation of iodine value with time of electrolysis for hydrolyzed rubber seed oil, while curve (b) depicts the variation for unhydrolyzed rubber seed oil. The iodine value of

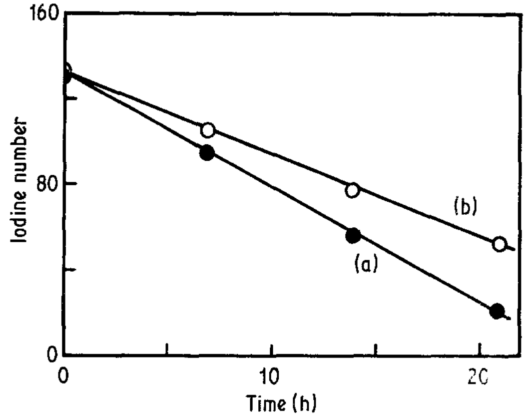


Fig. 3. Iodine number versus time of electrolysis. (a) For hydrolyzed rubber seed oil and (b) for unhydrolyzed rubber seed oil, with monel metal as the cathode material.

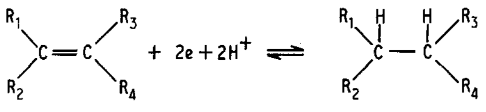
unhydrolyzed rubber seed oil dropped from 132 to 53.4 after 21 hours. Clearly, the efficiency of hydrogenation is better with the hydrolyzed rubber seed oil, as indicated by the iodine values.

After 21 hours of electrolysis the pale-yellow crystalline product was separated by filtration and re-crystallized. The gas–liquid chromatographic analysis of the methyl esters of this crystalline product showed the presence of 14.4% palmitic acid, 81.5% stearic and oleic acids, 0.6% linolenic acid and a trace amount of linoleic acid. This analysis confirmed the extensive hydrogenation of the fatty acid mixture. The melting point of the hydrogenated crystalline product was 65° C, whereas that of pure stearic acid is 69° C. The lowering of the melting point of this final product is attributed to the presence of palmitic acid in the mixture.

The yield of the final product was about 70% at a current efficiency of 65%. The cathode material and the porosity of the ceramic diaphragm were found to be two of the most critical parameters controlling this reduction process. The monel electrode used during long-term electrolysis experiments remained unattacked by the electrolytic medium.

4. Discussion

The change in Tafel slope with monel as the cathode material, at potentials more negative than -1075 mV (SCE) (Fig. 2b), is attributed to the hydrogenation of the fatty acids present in the oil by electrolytically generated hydrogen following the charge transfer reaction. Such electrochemical hydrogenation of olefinic and acetylinic double bonds has been previously studied [7, 11] for low-hydrogen-overvoltage metals such as platinum, where the reaction is believed to proceed through electrochemically generated active hydrogen, and for high-hydrogen-overvoltage metals where the reaction is expected to be initiated by electron transfer followed by a chemical reaction between the intermediate and the solvent. It is possible, that on metals having low hydrogen overvoltage, rapid catalytic recombination of chemisorbed atomic hydrogen occurs, producing molecular hydrogen instead of causing the reduction of olefinic groups. The catalytic nature of the recombination of chemisorbed atomic hydrogen is particularly evident from the very much higher currents (by an order of magnitude) obtained with palladium-plated graphite electrode as compared with nickel or graphite alone. Hence the use of palladium-plated graphite in order to establish whether chemisorbed hydrogen facilitates the hydrogenation of fatty acids gave negative results. On the other hand, it is most likely that on metals having high hydrogen overvoltage, such as monel, the coverage of the electrode surface by adsorbed hydrogen is low and hence direct electron transfer to a reducible substrate is facilitated. Considering the fact that in the present study electrochemical hydrogenation occurs on a metal having high hydrogen overvoltage, this implies that the rate-determining step for the hydrogenation of the fatty acid mixture is a charge transfer process at the electrode/solution interface, leading to a net reaction of the form



5. Conclusion

Our studies confirm that the fatty acid mixture obtained by the base hydrolysis of rubber seed oil can be hydrogenated electrochemically to yield stearic acid in crystalline form containing some palmitic acid. Pilot-plant studies are now being conducted with a cell in the form of a fractionating column to look into the industrial and economic viability of this hydrogenation process. The cell is intended to be a flow cell with facilities for continuous operation.

Acknowledgements

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