

Electrochemical reduction of polyaromatic compounds

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The electrochemical hydrogenation of several polycyclic aromatic compounds was investigated in aqueous tetrabutylammonium hydroxide electrolytes at different concentrations. Appropriate electrochemical conditions were determined on the basis of polarization curves, and electrolyses were thereafter carried out at different cathodes, Hg, Pb, Zn and graphite. It was found that anthracene as a model compound can be reduced in a divided cell into 9,10-dihydroanthracene, not only on Hg, but also on other electrodes. At low current density more than 90% conversion can be reached. Octahydroanthracene was produced only at the mercury electrode. The possibility of electrochemical reduction of phenanthrene, fluoranthene and fluorene was also investigated.

1. Introduction

Over the last few years there has been increased interest in appraising the feasibility of coal reduction by direct electrochemical treatment. This field requires a systematic investigation of the electroreduction of polycyclic aromatic hydrocarbons.

It was assumed by most researchers that the mechanism of the electroreduction of polyaromatic compounds was similar to that of the Birch reaction, since it is generally carried out in homogeneous solution in organic solvents mixed with hydrogen donors such as alcohols, acetic acid or water, using tetraalkylammonium or perchlorate salts as electrolytes [1–5]. Studies on the cathodic reduction of model aromatic compounds show that hydrogenation can also be carried out in aqueous media which are preferable from an economic point of view [6–9].

Two procedures are known. In one the active hydrogen is generated from water in the presence of nickel powder and a suitable electron mediator [10]. In the other, tetrabutylammonium cation–water electrolytes are used with a mercury cathode. Although high electrolyte concentration and high temperature are needed for the electrolysis in an aqueous tetrabutylammonium hydroxide [TBAOH] solution, some encouraging results have been reported [6–8, 11].

In Monsanto's work in 1981 [6], reduction occurs on a mercury cathode, the hydrocarbons being dispersed in aqueous solutions of quarternary ammonium hydroxides. Under optimum conditions, benzene was converted to 1,4-cyclohexadiene with a 90% selectivity. In Kariv-Miller's experiments [8], the reduction of anthracene and phenanthrene on a

mercury cathode performed in concentrated aqueous solutions of tetrabutylammonium salts leads to decahydroanthracene and decahydrophenanthrene.

The aim of the present work was to find a suitable solid electrode system instead of mercury, in a dilute TBAOH-water electrolyte. The importance of the dilute TBAOH electrolyte is that using a 40% or less concentrated solution means an aqueous electrolyte, although in [11] water is no longer the actual solvent, but rather the proton donor. In the present work anthracene was chosen as a model compound for the electrochemical reduction.

2. Experimental procedure

Tetrabutylammonium hydroxide (TBAOH) 40 wt % (Aldrich) was either diluted or evaporated under vacuum to the required concentration (0.8 to 2.6 M). Anthracene 99% and 9,10-dihydroanthracene 97% from Aldrich were used as supplied.

A Princeton Applied Research (PAR) model 362 scanning potentiostat was used to either record the polarization curves on a Goerz Metrawatt SE 790 X–Y recorder or run, in the potentiostatic mode, the preparative electrolyses. The product of the electrolysis were analyzed by gas chromatography on a Varian-3700 machine.

Experiments were carried out at 80°C in a thermostated cylindrical glass cell (inner diameter 5 cm, height 12 cm). The cell configuration was of the three-electrode type. It was equipped with outlets for the electrodes, nitrogen and condenser. A G4 fritted glass cup dipped into the cell served as the anode compartment to make the cell a divided one. A platinum wire placed in a glass tube plugged with G4 fritted glass and filled with TBAOH solution, served as the

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comparison electrode. During electrolysis the catholyte was stirred by means of a magnetic bar. A water cooled condenser prevents the loss of water, which keeps the electrolyte concentration constant during the electrolysis.

In some cases, the electrolyses were performed using the constant current mode. The cathode potential and the cell potential were recorded during electrolysis.

After each run, the electrolyte recovered from the cell (100 cm³) was added to 200 cm³ of pure water and was extracted with diethyl-ether (2 × 120 cm³). The ether fraction was washed twice with water (2 × 120 cm³) and 10% hydrochloric acid (120 cm³) and again with water three times. The hydrocarbons recovery through the extraction procedure was better than 95%. The ether fraction was analysed by GC with internal standard.

The yield for each hydrogenated product was determined by the amount formed with respect to the starting amount of anthracene and the current efficiency was calculated from the ratio between hydrogen pick-up and the total electrical charge (coulombs) passed.

3. Results and discussion

3.1. Polarization curves

3.1.1. Influence of cathode material on hydrogen overvoltage. The aim of the investigation of electrode

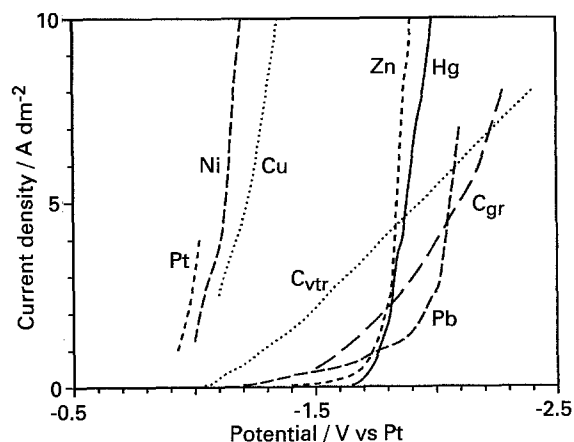


Fig. 1. Cathodic polarization curves at various cathode material. (Scanning rate: 50 mV s⁻¹; 80°C; 2.2 M TBAOH).

behaviour was to find a suitable electrode material other than mercury for hydrogenation of polyaromatic compounds. The model compound was anthracene. The polarization measurements were made on Hg, Pb, Zn, graphite, Ni, Cu, Pt (Fig. 1).

The comparison of the different electrodes has shown that in the case of Pt, Ni and Cu the hydrogen overvoltage is much smaller than with Hg. Since selective hydrogenation should be performed on electrodes with high hydrogen overvoltage, these electrodes are not suitable.

The polarization curve of Zn is closer to that of Hg but it is not possible to reach sufficiently reducing conditions without hydrogen evolution. A

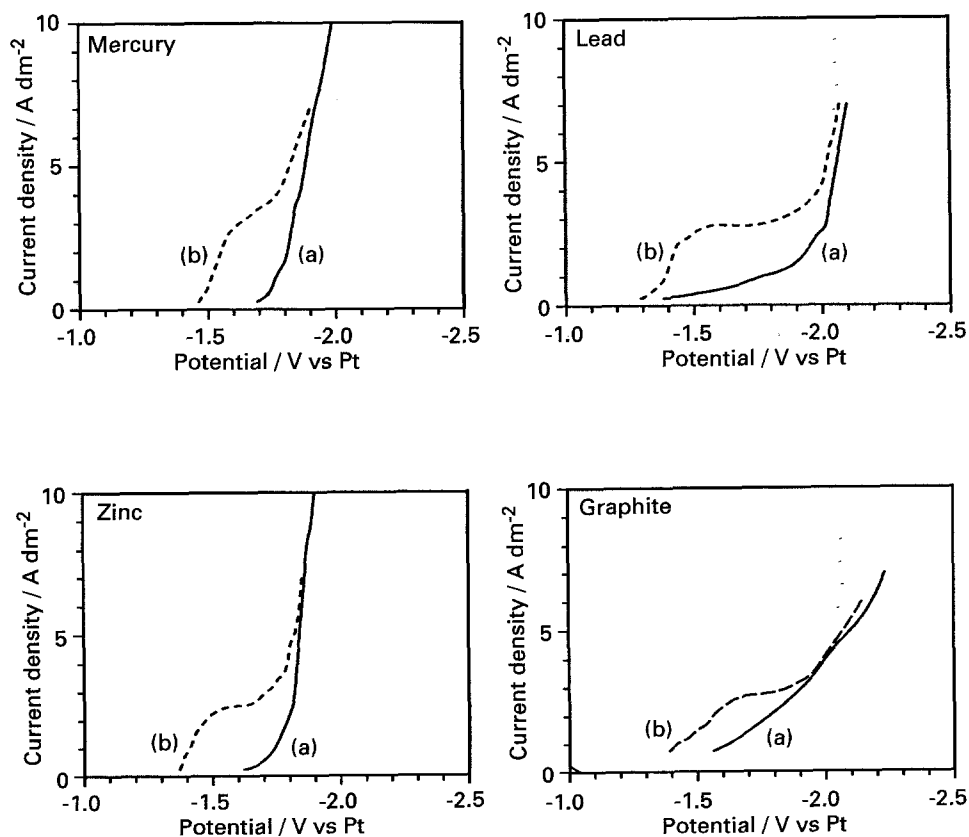


Fig. 2. Cathodic polarization curves at mercury, lead, zinc and graphite. (Scanning rate: 50 mV s⁻¹; 80°C) (a) 2.2 M TBAOH; (b) 2.2 M TBAOH, 0.03 M anthracene.

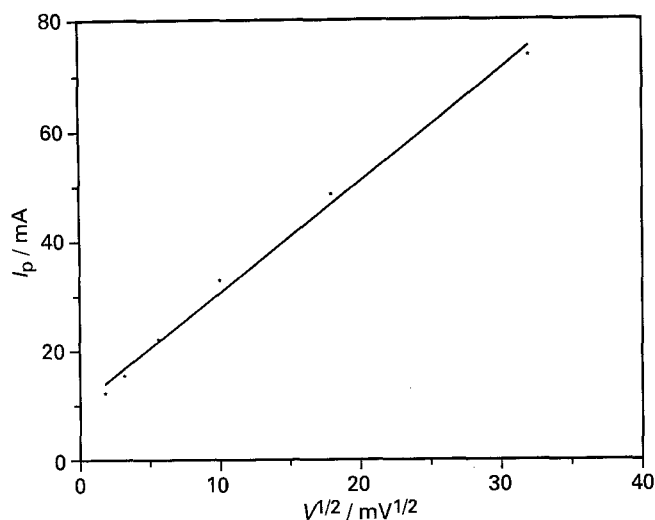


Fig. 3. Limiting current density against the square root of potential scan rate, lead cathode, 80°C, 2.2 M TBAOH, 2.4×10^{-4} M anthracene.

higher overvoltage has been observed with lead and graphite.

3.1.2. Anthracene reduction. The polarization curves obtained in the presence of anthracene exhibited a new cathodic wave at about -1.3 V vs Pt, which is less negative than required for hydrogen evolution (Fig. 2).

These curves are characterized by a limiting current density increasing from 0 to 3.5 A dm^{-2} as a function of the concentration of anthracene (0 to 0.03 M) at 80°C in 2.2 M TBAOH solution. A similar phenomenon was observed, not only in the case of mercury, but also with lead, zinc and graphite electrodes. The results show that these materials are also suitable for electrochemical hydrogenation of anthracene.

On decreasing the TBAOH concentration, the limiting current also decreased since the solubility of anthracene is modified by the TBAOH concentration. It was observed that reducing the stirring rate resulted in a decreased limiting current density. A plot of the limiting current density versus the square root of the potential scan rate clearly shows that a mass transfer limiting current operates (Fig. 3).

3.1.3. Reduction of other polyaromatic compounds. Polarization curves were recorded with a lead cathode, in the same electrolyte and in the presence of phenanthrene, fluoranthene or fluorene and finally with a mixture of these three compounds with anthracene (Figs 4–7). The reduction of phenanthrene is characterized by a small reduction wave at about -1.4 V vs Pt. Fluoranthene is characterized by two reduction waves preceding the hydrogen evolution at -1.15 and -1.55 V vs Pt.

The reduction of the fluorene-containing solution shows a wave around -1.2 V vs Pt, but appears to correspond to the reduction of oxidized fluorene (*vide infra*).

When mixing together the four aromatic compounds, their respective reduction waves are observed before the occurrence of hydrogen evolution.

These results show that the electrochemical reduction of these polyaromatic compounds is possible on lead cathodes in concentrated aqueous TBAOH solutions, without significant hydrogen evolution.

3.2. Electrochemical reduction of anthracene in the undivided cell

The electrolyses were performed at different temperatures (40, 60 and 80°C) and for different TBAOH concentrations between 0.8 and 2.6 M, using lead cathodes (1 to 12.5 cm^2) and a current range of 2.4 to 100 A dm^{-2} . The anthracene concentration was 4×10^{-2} M. The charge passed through the cell varied from 10 to 30 F mol^{-1} . In varying the current density and the TBAOH concentration systematically, it was observed that the reaction never exceeded the stage of dihydroanthracene.

At high TBAOH concentration, the best yield ever (93.6% of dihydroanthracene) was obtained on lead at 80°C and 2.4 A dm^{-2} with 2.2 M TBAOH. At the same low current density, no dihydroanthracene was detected, either at higher TBAOH concentration

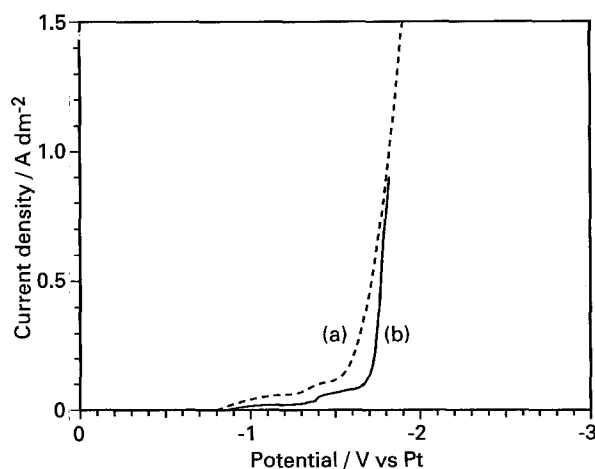


Fig. 4. Cathodic polarization curves at a lead cathode. (Scanning rate: 50 mV s^{-1} ; 80°C; 2.2 M TBAOH). (a) Without aromatic; (b) 0.03 M phenanthrene.

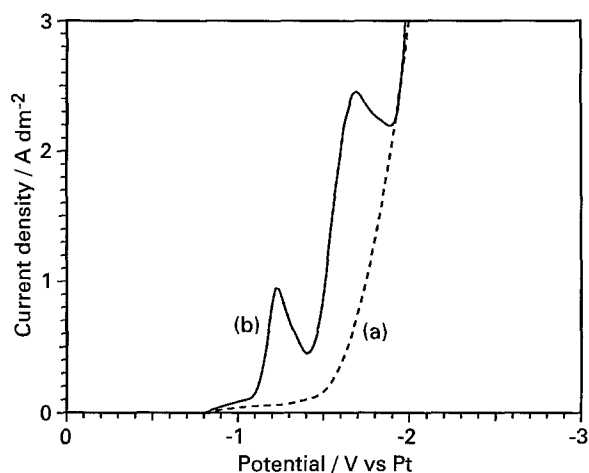


Fig. 5. Cathodic polarization curves at a lead cathode. (Scanning rate: 50 mV s^{-1} ; 80°C ; 2.2 M TBAOH). (a) Without aromatic; (b) 0.03 M fluoranthene.

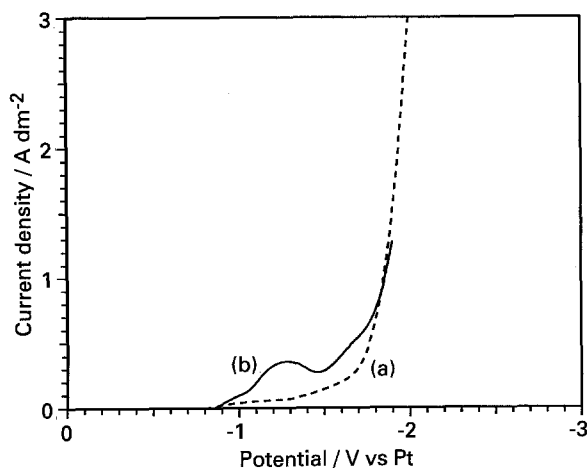


Fig. 6. Cathodic polarization curves at a lead cathode. (Scanning rate: 50 mV s^{-1} ; 80°C ; 2.2 M TBAOH). (a) Without aromatic; (b) 0.03 M fluorene.

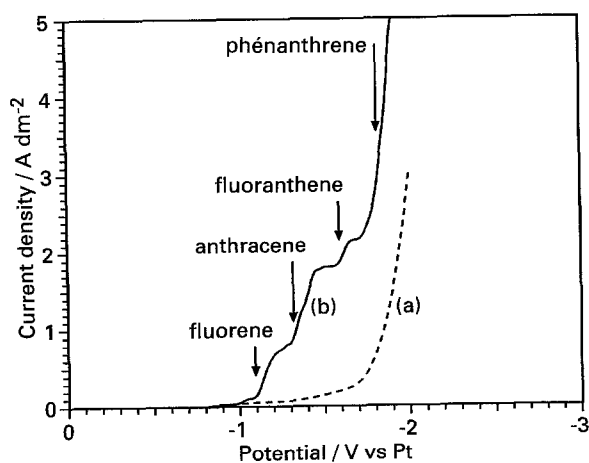
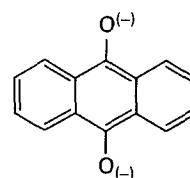


Fig. 7. Cathodic polarization curves at a lead cathode. (Scanning rate: 50 mV s^{-1} ; 80°C ; 2.2 M TBAOH). (a) Without aromatic; (b) equimolar mixture of fluorene, anthracene, fluoranthene and phenanthrene, total 0.03 M .

(2.6 M) or in less concentrated electrolytes. A temperature decrease also decreased the yield.

At lower *TBAOH* concentrations, it was preferable to use higher current densities in order to minimize side reactions, but in dilute solutions of *TBAOH*, even at high current densities, the contribution of anodic oxidation cannot be neglected. A red coloured oxidation product derived from dihydroanthracene in basic media was observed and at the same time, the precipitation of yellow crystals of anthraquinone took place during the extraction step. The product of oxidation was analysed by infrared spectrometry and identified as the salt of 9,10-dihydroxyanthracene I.



The hydrogenation reaction of anthracene into 9,10-dihydroanthracene is known to be reversible [12]. Similarly, the electroreduction of anthracene is also reversible. The reduction of anthracene is hindered by three competitive reactions:

(i) electrochemical oxidation of the dihydroanthracene to anthracene, which can be avoided in a divided cell;

(ii) electrochemical oxidation of dihydroanthracene to the red oxidation product, which can also be avoided in a divided cell;

(iii) chemical oxidation of the dihydroanthracene to the same red species, which is favoured by high *TBAOH* concentrations. This chemical oxidation is particularly enhanced in the presence of copper metal.

The electrochemical oxidation of the dihydroanthracene was confirmed by the electrochemical reduction starting from 9,10-dihydroanthracene instead of anthracene in the same undivided cell, where 40 to 50% of the starting material was oxidized anodically to anthraquinone.

Based on the experiments performed with the undivided cell, it was concluded that, in every case, a large amount of the 9,10-dihydroanthracene cathodically produced in an initial step is later oxidized, so that it is advisable to use a divided cell and to avoid very high *TBAOH* concentrations.

3.3. Electrochemical reduction of anthracene in the divided cell

The reduction of anthracene in *TBAOH* [2.2 M] aqueous solution using mercury, lead, zinc and graphite electrodes was investigated and further experiments were done in the concentration range 0.8 to 2.2 M of *TBAOH*.

The results of the electrolysis of anthracene on mercury at 2.4 A dm^{-2} , with 2.2 M aqueous *TBAOH* and for a 0.03 M anthracene concentration support the results of Kariv-Miller (Fig. 8). Nevertheless,

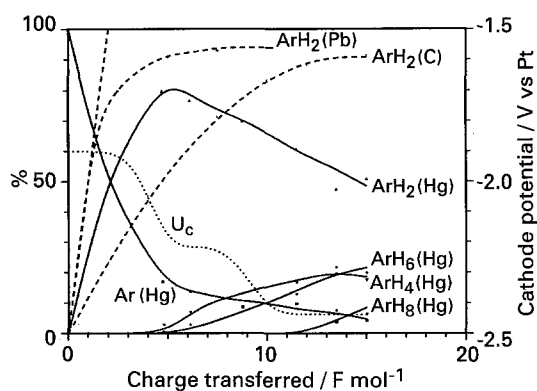


Fig. 8. Electrochemical reduction of anthracene as a function of the charge transferred; mercury, lead and graphite cathodes. (Divided cell; 80°C; 2.2 M TBAOH; 2.4 A dm⁻²; 0.03 M anthracene).

with the mercury cathode, the curve displays two distinctly different domains, depending on the charge Q transferred. The first step is characterized by the formation of 9,10-dihydroanthracene; at a charge of 2 F mol⁻¹, 50 to 100% current efficiency can be observed, with 50 to 100% conversion. Further increasing the amount of charge, the potential of the cathode remains at the same level and there is no more reduction of the dihydroanthracene. When the potential is decreased by about 0.4 V, the reduction of 9,10-dihydroanthracene to produce tetrahydroanthracene starts with a lower current efficiency and is followed by reduction to hexa- and octahydroanthracene.

The reduction of 9,10-dihydroanthracene as the starting material was investigated under the same conditions: it produced 1,4,5,8,9,10-hexahydroanthracene and some other hydrogenated compounds, a result similar to that obtained when starting from anthracene. The product yield was about 40% and the current efficiency was 50%.

In Fig. 8, the results of electrolysis, using lead and graphite electrodes at 2.4 A dm⁻² in a 2.2 M TBAOH solution, are presented. In the case of lead, only the first step of the hydrogenation, i.e. formation of dihydroanthracene, takes place. The current efficiency was about 100% up to 1 F mol⁻¹ and then progressively decreased to reach 30% at 5 F mol⁻¹; the final product yield was then 91%. The reaction stopped at that stage and there was no change in the value of the cathodic potential. Using a graphite electrode the current efficiency was 25% at 2 F mol⁻¹ and a 90% product yield was reached only after transfer of 15 F mol⁻¹.

Experiments carried out under similar conditions with dihydroanthracene as a starting material revealed that the dihydro derivative cannot be reduced further on the lead cathode.

It was assumed that formation of tetrahydroanthracene requires a more negative cathode potential. To adjust the cathodic potential to an appropriate value for reduction to take place, the electrolysis was performed at higher current density.

The results of electrolysis using high current density

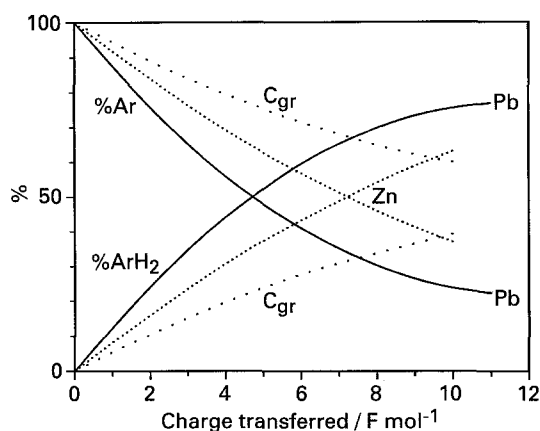


Fig. 9. Electrochemical reduction of anthracene as a function of the charge transferred at high current density. (Divided cell; 80°C; 50 A dm⁻²; 2.2 M TBAOH; 0.03 M anthracene).

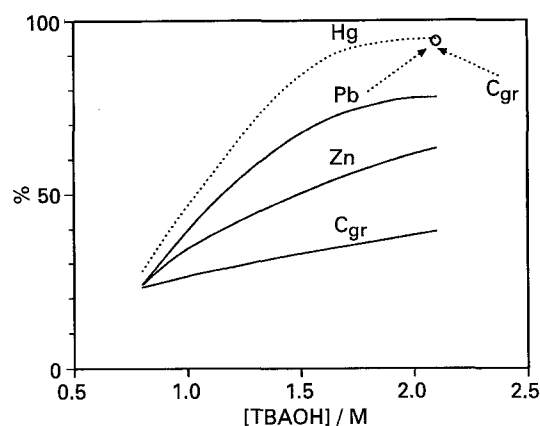


Fig. 10. Electrochemical reduction of anthracene as a function of TBAOH concentration at two current densities (divided cell, 80°C). (.....) 2.4 A dm⁻²; (—) 40–50 A dm⁻².

(50 A dm⁻²) with zinc, lead and graphite electrodes are summarized in Fig. 9. During the first stage of the reduction, the formation of dihydroanthracene was also found, but the current efficiency was only 24% at lead, 15% at zinc and 13% at graphite after

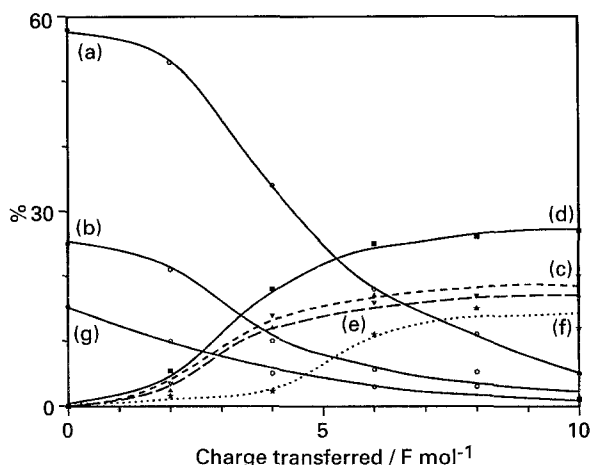
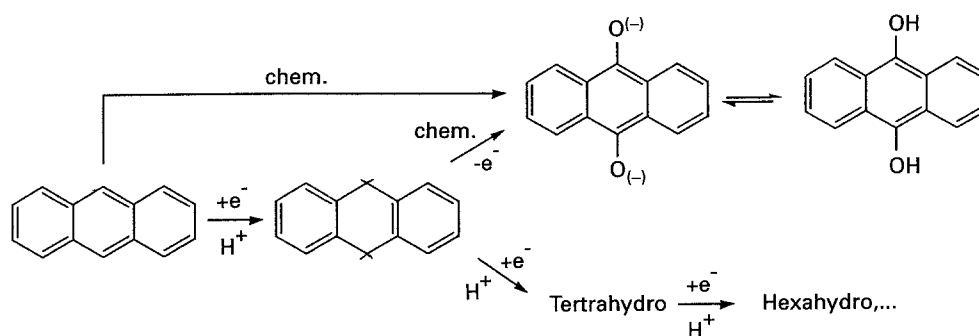


Fig. 11. Electrochemical reduction of a model mixture as a function of the charge transferred. (Divided cell; 80°C; 10 A dm⁻²; 2.2 M TBAOH; Pb cathode). (a) Anthracene and phenanthrene together, (b) fluoranthene, (c) fluorene, (d) 9,10-dihydroanthracene, (e) 9,10-dihydrophenanthrene, (f) 3,10b-dihydrofluoranthene, and (g) reaction product of fluorene with TBAOH.



2 F mol^{-1} charge. The product yields were 75% (Pb), 63% (Zn) and 39% (graphite) at 10 F mol^{-1} charge.

Fig. 10 summarizes the results obtained at different current densities and cathode materials as a function of the concentration of TBAOH.

At low current density (2.5 A dm^{-2}) and high TBAOH concentration, the conversion achieved rose to more than 90% but hexahydroanthracene and octahydroanthracene were produced only at the mercury cathode.

Increasing the current density and diluting the TBAOH electrolyte resulted in decreased conversion and current efficiency. As shown in Fig. 10, the product yield decreased slowly on decreasing the TBAOH from 2.2 to 1.8 M (from 95% to 91% on Hg), and then from 90% to less than 30% when TBAOH fell to 0.8 M. The current efficiency followed the same pattern.

3.4. Electroreduction of a model-mixture in the divided cell

The electrolysis of a model-mixture of different polyaromatic compounds was carried out at 80° C and 10 A dm^{-2} using a lead cathode and a 2.2 M TBAOH electrolyte solution. The cathode potential was held at -2.02 V vs Pt . The model-mixture contained anthracene, phenanthrene, fluoranthene and fluorene. The total concentration of the starting materials was $2 \times 10^{-3} \text{ M}$. The results of the electrolysis are shown in Fig. 11.

During the electrolysis of the model-mixture, the electrochemical reduction of all of the components but fluorene took place simultaneously. At the end of the electrolysis, after transfer of 10 F mol^{-1} , aside of unaffected fluorene, only 5–7% of the starting aromatics were detected. The product-mixture contained mainly dihydroaromatic derivatives.

4. Conclusions

The cathodic material has a big influence on the quantity of hydrogen atoms which can be added to the anthracene in these strongly basic water–TBAOH solutions. Kariv-Miller [8] has shown the possibility of reaching the reduction stage of hexahydroanthracene on a mercury cathode, and has shown that further hydrogenation requires an isomerisation step leading to a conjugated π system, but no indications

of the electrochemical conditions were given. In the present work for the described conditions, the potentiostatic hydrogenation of anthracene on mercury stops at the dihydro level if the potential is kept at about -1.9 V vs Pt , and further hydrogenation occurs only if the potential is lowered to a few hundred millivolts more negative value.

On lead, zinc and graphite, using the experimental conditions described herein, it has not been possible to drive the potential to values negative enough to proceed further than the dihydro species, whether for anthracene, for phenanthrene or fluoranthene.

It appears that mercury, present in these systems, plays a very important catalytic or mediator role [13]. Moreover, surprisingly, Kariv-Miller's experiments on mercury were successful even in undivided cells, in contrast with our results on solid cathodes, for which the anodic oxidation of the dihydro species produced in the first place was observed.

Furthermore, it has been shown that the dihydroanthracene produced at the cathode and the starting fluorene, which correspond to similar hydrogenation levels, are also chemically oxidized in these strong basic conditions. The same kind of oxidation of fluorene to fluorenone in concentrated water–TBAOH solutions has been observed previously [14].

If the electrochemical oxidation of dihydroanthracene can be avoided by the use of the divided cell, the scheme above can be proposed as a reasonable one, the reduction of anthracene to 9,10-dihydroanthracene being easy on lead and mercury cathodes. The dihydroanthracene is then subjected to two competitive reactions, namely further electrochemical reduction of the dihydroanthracene or chemical oxidation by the electrolyte.

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