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MEDIATED ELECTROCHEMICAL REDUCTION OF OXYGEN TO HYDROGEN PEROXIDE WITH NAPHTHOQUINONE REAGENT**

Strong adsorption properties of 8-hydroxy-1,2-naphthoquinone-3,6-disulfonic acid on mercury electrode, which have been found previously, are now used up practically. These properties give rise to changes in the reduction of oxygen on that electrode. This fact allowed to develop an electrochemical mediatory preparation of $\text{H}_2\text{O}_2$ using redox pair HNQ/HNQH$_2$ of the reagent under investigation.

8-hydroxy-1,2-naphthoquinone-3,6-disulfonic acid (HNQ) prepared by us previously [1] was examined by us many methods in order to establish utilization of its properties. Thus, its acid-base characteristic ($pK_a = 5.6$) and distinct colour change from yellow to red make it possible to use as an acid-base indicator. This reagent forms also stable complexes with Zr(IV) and Hf(IV) ions which allowed us to use HNQ for quantitative determination of those ions according to proposed method [2]. Using DC polarography, condition for polarographic reduction of the o-naphthoquinone system to the naphthohydroquinone form of this compound were found. A strong ion adsorption of HNQ on DMF was shown using the square-wave polarography [3]. These results have shown us the next field of application of this compound.

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**EXPERIMENTAL**

The aqueous stock solutions of HNQ were prepared from a weighted portions of solid reagent: disodium salt of 8-hydroxy-1,2-naphthoquinone-3,6-disulfonic acid which we described in paper [1]. All additional solutions were prepared from p.a. reagents and twice distilled water.

Two compartment cell was applied for preparative scale reduction of HNQ to HNQH₂. The electrolite consisted of 0.5 M Na₂SO₄ and 0.05 M H₂SO₄. The potential of -0.3 V vs. SCE of large Hg cathode was maintained and passing charge was measured by coulometric analyser OH-404 (Radelkis, Hungary). Polarograms were registered using OH-104 (Radelkis) and PA 3 (Laboratorni Pristroje, Praha) polarographs.

**RESULTS AND DISCUSSION**

An adsorption peak of HNQ is observed by SW polarography already at concentrations lower than 0.5 \(10^{-5}\) mole/l (Fig. 1). Changes in the peak value with the increase in HNQ concentration point to the increase of adsorption up to a full electrode coverage at a concentration of about 30 \(10^{-5}\) mole/l. Further increase in the concentration lowers the current values of the observed peaks (Fig. 2) due to reorientation of HNQ being adsorbed.

It is known that naphthoquinone compounds are use as mediators in potentiometric and voltamperometric studies on biological redox system [4]. Often the model reaction of oxygen is used to examine the mediatory properties of these compounds on electrodes modified with them [5-7].

In this paper the effect of HNQ strongly adsorbed on a mercury electrode on the oxygen reduction process has been examined. The results of voltamperometric measurements of HMDE in buffer solutions according to Britton-Robinson are shown in Fig. 3. The straight line with a slope of 60 mV/decade shows the changes in peak potentials of the reagent (di-electron, di-proton reduction). Peak potentials of oxygen reduction in the presence of HNQ shift towards
Fig. 1. Examples of SW polarograms of HNQ solutions with concentrations:
1 - $0.5 \cdot 10^{-5}$ mole/1, 2 - $4 \cdot 10^{-5}$ mole/1, 3 - $32 \cdot 10^{-5}$ mole/1

Fig. 2. Changes in the adsorption peak current vs. HNQ concentration

Mediated electrochemical reduction
Fig. 3. Dependence of the peak potential of oxygen reduction on HMDE on pH: 1 - without HNQ addition, 2 - in the presence of $0.8 \times 10^{-4}$ mole/l HNQ, 3 - deoxidized $0.8 \times 10^{-4}$ mole/l HNQ solution.

Fig. 4. Dependence of peak current of oxygen reduction on HMDE on pH: 1 - without HNQ, 2 - in the presence of $0.8 \times 10^{-4}$ mole/l HNQ.

the cathode direction. This shift is in excess of 200 mV at pH about 2 and decreases gradually with increasing pH. Some slight catalytic effect of the adsorbed HNQ on the peak current of oxygen reduction is also observed (Fig. 4). These effects have been used up by us in the synthesis of $\text{H}_2\text{O}_2$ according to the following scheme:
The adsorbed HNQ is a mediator in the electron transfer to oxygen in reduction to $H_2O_2$.

It is known that in this process the part of redox pairs $Q/QH_2$ can be plaid by such derivatives as: metal macrocycle complexes [8], polymeric derivatives of anthraquinone [6], sulfonic derivatives of anthraquinone [9-11], derivative such as 2-chloro-3(2-dimethylpropylammonio ethyl)amino]-1,4-naphthoquinone bromide [5, 12].

The use of the redox couple HNQ/HNQH$_2$ to synthesize $H_2O_2$ was realized by two methods:

1. Two-stage process - first quantitative electrochemical reduction of HNQ to HNQH$_2$ and then passing $O_2$ through the solution.

2. Single-stage process - oxygen is continuously passed through the HNQ solution which is reduced.

The formation of $H_2O_2$ was observed by the differential pulse polarography (dpp). Polarograms of standard solution of $H_2O_2$, HNQ and those of reduced solutions are shown in Fig. 5. The above mentioned adsorption peaks of HNQ and HNQH$_2$ appear within the range from -0.6 to -0.7 V (curves 3 and 4). Curve 6 shows the polarogram of the HNQ solution reduced with simultaneous passing of oxygen. The charge which has passed is twice as high as that needed for the stoichiometric reduction of HNQ to HNQH$_2$. The distinct current increase at potentials as for the standard $H_2O_2$ solutions points to the formation of considerable quantities of $H_2O_2$ in the solution under investigation. Using this procedure, it is possible to obtain more concentrated solutions of $H_2O_2$ when the reaction time is prolonged. Thus, it is possible to prepare hydrogen peroxide using solutions with a low HNQ concentration.

The process of $H_2O_2$ synthesis with the use of HNQ as a mediator has been the subject of patent application [13]. It would be of great practical importance to use dilute $H_2O_2$ solutions without separation of $H_2O_2$ and directly after preparation as in the described
Fig. 5. Polarograms of differential pulse polarography (dpp) of the solution: 1 - $0.5 \cdot 10^{-4}$ mole/l $H_2O_2$, 2 - $2.0 \cdot 10^{-4}$ mole/l $H_2O_2$, 3 - $0.5 \cdot 10^{-4}$ mole/l HNQ, 4 - $0.5 \cdot 10^{-4}$ mole/l HNQH, 5 - solution after reduction of HNQ and partial oxidation of HNQH with oxygen (dilution in relation to the initial solution subjected to reduction as in sample 4), 6 - solution after continuous reduction and oxygen passig (as described in the text) (dilution in relation to the initial solution 5x higher than that of sample 5). Electrolyte: $0.05$ mole/l $Na_2SO_4$, $H_2SO_4$ (pH = 2).

electrochemical process. Such possibilities exist in technological processes carried out on commercial scale. One of the examples is the processing of wood pulps. Additions of $H_2O_2$ improve the delignification of wood fiber [14] and the yield of pulp. At the same time the degree of brightness is increased and the process toxicity is decreased, which lowers the environment hazard [15, 16]. Owing to the $H_2O_2$ treatment, the properties of pulp are improved in the paper forming process as well as the mechanical and dielectric properties of capacitor paper [17]. Addition of $H_2O_2$ are also used in electrochemical manufacturing of copper (to remove scale [18]) or in processing of sugar beet juice (to eliminate melanoidine compounds [19]).

The given examples, of course, do not use up all the possible
applications of $\text{H}_2\text{O}_2$ and only show some directions of the utilization of relatively-diluted $\text{H}_2\text{O}_2$ solutions as prepared by the described, energy-saving, process of electrochemical reduction of oxygen.

REFERENCES

Wykorzystano, stwierdzone wcześniej, silne własności adsorpcyjne kwasu 8-hydroksy-1,2-naftochinono-3,6-disulfonowego (HNQ) na elektrodzie rtęciowej. Zbadano wpływ tego odczynnika na polarograficzną redukcję tlenu. Umożliwiło to opracowanie elektrochemicznego, mediacyjnego otrzymywania $\text{H}_2\text{O}_2$ z wykorzystaniem pary redox HNQ/HNQH$_2$ badanego odczynnika.