ACTA UNIVERSITATIS LODZIENSIS
FOLIA CHIMICA 9, 1991

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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 develope an electrochemical mediatory preparation of H_2O_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 = 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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[**] This work was supported by the program CPBP 01.15.

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 destilled water.

Two compartment cell was applied for preparative scale reduction of HNQ to $HNQH_2$. The electrolite consisted of 0.5 M Na_2SO_4 and 0.05 M H_2SO_4. The potential of -0.3 V vs. SCE of large Hg cathode was maintened 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 $30 \cdot 10^{-5}$ 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

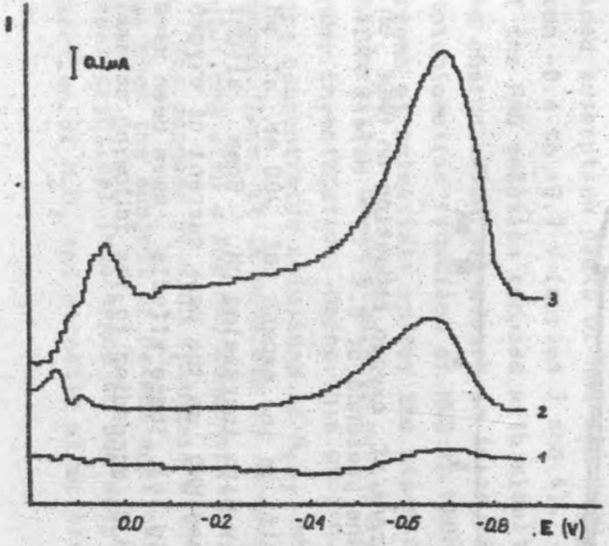


Fig. 1. Examples of SW polarograms of HNQ solutions with concentrations:
1 - $0.5 \cdot 10^{-5}$ mole/l, 2 - $4 \cdot 10^{-5}$ mole/l, 3 - $32 \cdot 10^{-5}$ mole/l

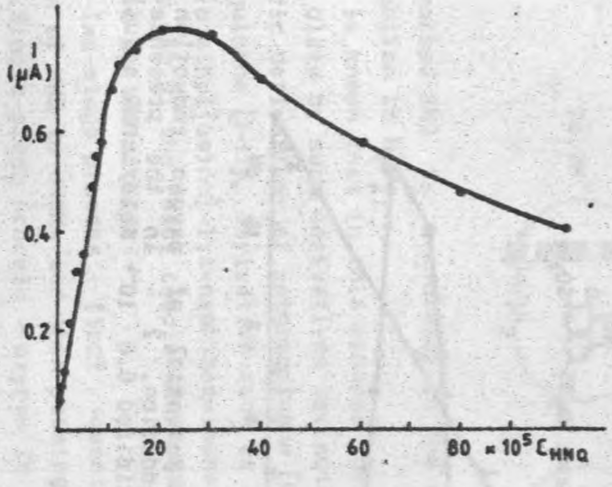


Fig. 2. Changes in the adsorption peak current vs. HNQ concentration

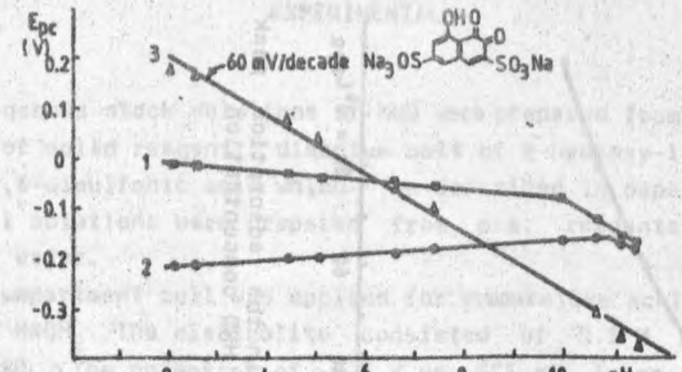


Fig. 3. Dependence of the peak potential of oxygen reduction on HMDE on pH: 1- without HNQ addition, 2 - in the presence of $0.8 \cdot 10^{-4}$ mole/l HNQ, 3 - deoxidized $0.8 \cdot 10^{-4}$ mole/l HNQ solution

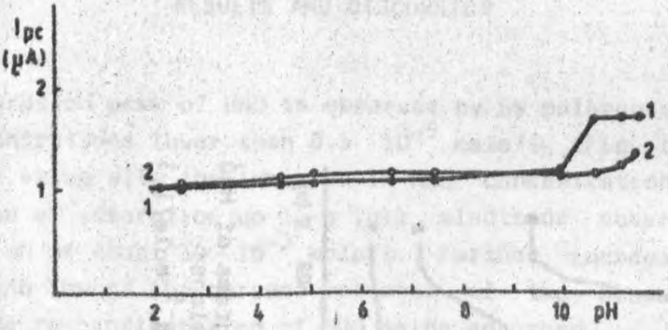
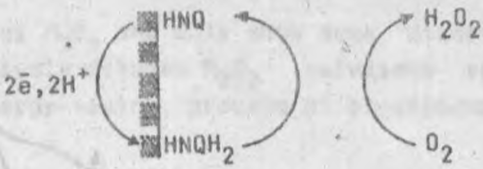


Fig. 4. Dependence of peak current of oxygen reduction on HMDE on pH: 1 - without HNQ, 2 - in the presence of $0.8 \cdot 10^{-4}$ mole/l HNQ

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 H_2O_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 mentined 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

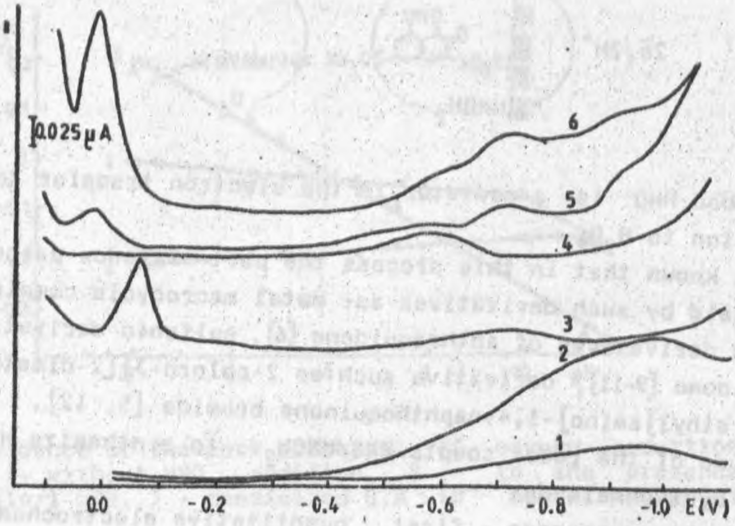


Fig. 5. Polarograms of differential pulse polarography (dpp) of the solution: 1 - $0.5 \cdot 10^{-4}$ mole/l H_2O_2 2 - $2.0 \cdot 10^{-4}$ mole/l H_2O_2, 3 - $0.5 \cdot 10^{-4}$ mole/l HNQ, 4 - $0.5 \cdot 10^{-4}$ mole/l HNQH, 5 - solution after reduction of HNQ and partial oxidation of $HNQH_2$ with 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 H_2O_2 and only show some directions of the utilization of relatively·diluted H_2O_2 solutions as prepared by the described, energy-saving, process of electrochemical reduction of oxygen.

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ELEKTROCHEMICZNA REDUKCJA TLENU DO NADTLENKU WODORU Z MEDIACYJNYM UDZIAŁEM POCHODNEJ NAFTOCHINONOWEJ

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 H_2O_2 z wykorzystaniem pary redox HNQ/$HNQH_2$ badanego odczynnika.