EFFECT OF ULTRASOUND ON VOLTAMMETRIC MEASUREMENTS ON A MINIATURIZED MERCURY ELECTRODE; SONOVOLTAMMETRY AND SONOPOLAROGRAPHY

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The influence of ultrasound on voltammetric measurements at a mechanically stable renewed mercury electrode was described. The measurements were carried out in a solution of 4,4′-bipyridyl in 0.1 M KCl + 0.01 M NaOH, in $1 . 10^{-4}$ M $CdSO_4$ + $5 . 10^{-6}$ M tribenzylamine in 0.1 M H_2SO_4 and in $3 . 10^{-3}$ M $CdSO_4$ + $1 . 10^{-4}$ M tribenzylamine hydrochloride. Possible development and applications of related electroanalytical techniques by using mercury and solid electrodes were discussed. A pronounced influence of ultrasound was observed mainly in cases where the kinetics and irreversibility of the electrochemical and related processes played an important role.

Key words: Ultrasound; Voltammetric measurements; Mercury electrode.

One of the disciplines that have encountered an increasing interest in last years is sonochemistry[1,2], which deals with the study of the influence of ultrasound on chemical systems. One of its branches is sonoelectrochemistry. The relevant publication are mostly related to technologically important problems, such as electrolysis of aqueous solutions of NaCl and HCl, organic electrosyntheses[1], sonochemical processes in biochemistry, or arrangements for electrochemical studies[1,3,4–6]. The publications concerning the field of sonoelectroanalytical chemistry[4,5,11], especially using renewed miniaturized electrodes[4,5,7,8], are rather rare.

The aim of the present work was to find the principal effects of ultrasound on selected electroanalytical systems and to indicate further possibilities of their electroanalytical exploitation, as a continuation of the preliminary results obtained earlier[4].

EXPERIMENTAL

The measurements were carried out with the use of an ultrasound bath (Tesla Trutnov), a polarographic analyzer PA 3 (Laboratorni pristroje, Prague), a home made, programmable control unit, and a home made pen-type mercury electrode[7]. Two ultrasound generators enabled working at frequencies of 32 kHz and 46 kHz. The pen-type mercury electrode involved a spindle-type capillary[7,8] with an inner diameter of the central part 35 μm and inner diameter of the orifice 55 μm. The radius of the working miniaturized hanging mercury drop electrode (HMDE) was 50 μm. A saturated calomel electrode (SCE) was the reference electrode, the salt bridge connected with the SCE was filled with 0.5 M Na_2SO_4, a Pt wire was respectively used as auxiliary electrode. The work was carried out at constant temperature of 293.15 K.

All solutions were prepared from reagent grade chemicals; twice distilled water was used throughout. The measurements were carried out in a solution of 4,4′-bipyridyl (BP) in 0.1 M KCl + 0.01 M NaOH, in $1 . 10^{-4}$ M $CdSO_4$ + $5 . 10^{-6}$ M tribenzylamine (TriBA) in 0.1 M H_2SO_4 and in $3 . 10^{-3}$ M $CdSO_4$ + $1 . 10^{-4}$ M tribenzylamine hydrochloride.

The experimental arrangement is shown schematically in Fig. 1. The cell 1 with the measured solution 2 was dipped into the bath 3 of the ultrasound generator 4. The pen-type mercury electrode 5 with a minitapper 6, a stirrer 7, the reference 8 and auxiliary 9 electrodes were dipped into the measured solution 2 as well. The control 10 of the pen-type mercury electrode 5, the minitapper 6 and the stirrer 7 were connected with the programmable control unit 11. The current leads from the mercury indicator electrode 12, reference 8, and, respectively, also auxiliary 9 electrode were connected to the voltammetric analyzer 13 with the evaluation and recording unit 14. The analyzer 13 and the ultrasound generator 4 were also connected, in parallel, with the programmable control unit 11. During measurements in micro amounts of solution or in capillary systems, the tip of the capillary 15 was either inserted into the capillary of the flow-through system 16, or (together with the reference electrode) into a drop of solution 17 placed on a dish or on the bottom of the cell.

The parameters of the spindle-type[8] capillary were, together with the working regime of the programmable control unit, chosen so that, by using the pen-type mercury electrode[4,7], a renewed, miniaturized, stationary mercury electrode of various size could be realized at selected intervals at the capillary orifice. In this way, it was easily possible to find such a size of the stationary drop that was sufficiently stable and reproducible even during intense ultrasound vibrations. In the same experimental arrangement solid indicator electrodes could be used.

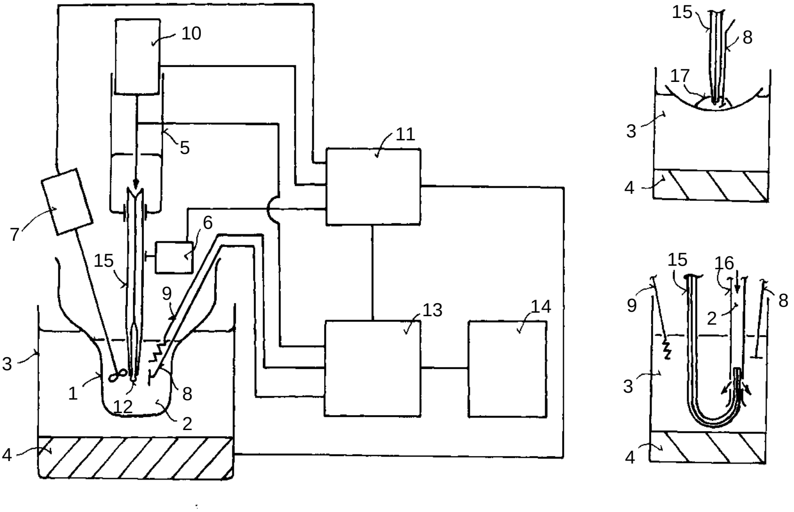

FIG. 1
Scheme of the experimental arrangement for sonovoltammetric measurements on a miniaturized mercury electrode

RESULTS AND DISCUSSION

First, the direct current (DC) voltammetric curves for 1 . 10^{-5} M BP in 0.1 M KCl in the presence of 0.01 M NaOH (Fig. 2a) without sonication were measured. The curves were always recorded immediately after renewal of the miniaturized HMDE at a potential E_{in} = –0.5 V vs SCE at a scan rate of 500 mV s^{-1}. After finishing the scan, the potential of the indicator electrode was set equal to E_{in}. The measurement was repeated (see sonovoltammetric curves in Fig. 2b) under the same conditions except that the ultrasound generator was switched on, and after finishing the sonovoltammetric scan at E_{fin} = –1.75 V it was switched off. The corresponding peak current–concentration (*i*–*c*) dependences of BP, both without and under sonication, are given in Fig. 2c. It is known[9] that BP is adsorbed under the given conditions in a broad potential range, especially between 0 V and –1.2 V, and that it is reduced at potentials around –1.4 V. The observed voltammetric signal of BP is, therefore, the result of a complicated electrochemical mechanism[9] connected with adsorption of BP on the mercury electrode. So, the depolarization process causes large changes of the BP surface concentration at the electrode, related to the transport and to other processes. These are strongly influenced by ultrasound, as follows from Fig. 2, causing a marked increase of the voltammetric signal of BP, as well as an increase in sensitivity of its voltammetric determination. Another example of sonovoltammetric effects, by using of the DC voltammetry, is a potential shift *E* (Fig. 3) of a hydrogen evolution in 3 . 10^{-3} M $CdSO_4$ + 1 . 10^{-4} M TriBA . HCl due to

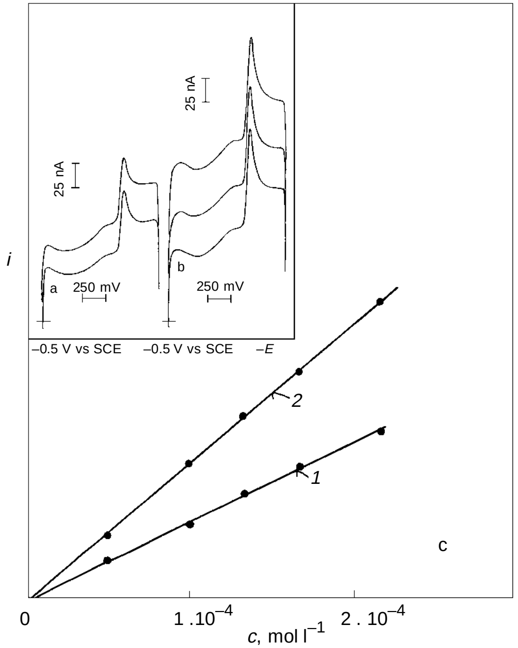

Fig. 2

Effects of ultrasound on voltammetric measurements in 1 . 10^{-5} M 4,4′-bipyridyl (BP) in 0.1 M KCl + 0.01 M NaOH; the miniaturized mercury electrode; voltammetry without the sonication (a), sonication during the voltammetric scan (b), *i*–*c* dependences of BP (c), both without (*1*) and under (*2*) sonications; DC voltammetry; 500 mV s^{-1}; *i* electric current; *E* electrode potential vs SCE (salt bridge 0.5 M Na_2SO_4)

the application of the ultrasound. Under the mentioned conditions, E was approximately 50 mV. A peak around –1.2 V (SCE) can be considered a desorption peak of TriBA, shifted to more negative potentials when the ultrasound is applied, probably due to the more rapid transport of TriBA to the electrode surface and, therefore, the more effective adsoptive accumulation of TriBA and change of its adsorption/desorption kinetics.

Example of a marked acceleration of transport processes to the electrode surface by ultrasound is apparent from Fig. 4, showing a change of the voltammetric peak of Cd^{2+} ions caused by accelerated transport of the strongly adsorptive tribenzylamine (TriBA) to the electrode surface by the action of ultrasound. TriBA is a well-known inhibitor of electrode processes by its strong adsorption[10] at the electrode boundary. When the voltammogram was recorded immediately after formation of the HMDE, the peak of Cd^{2+} ions was almost uninfluenced by TriBA, whose concentration ($5 . 10^{-6}$ mol l^{-1}) was so

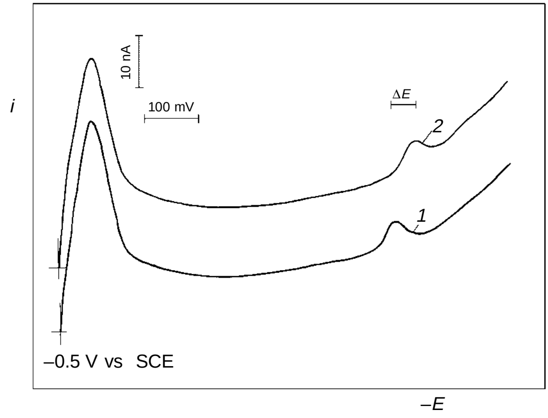

FIG. 3
Potential shift ΔE of the hydrogen evolution in $3 . 10^{-3}$ M $CdSO_4$ + $1 . 10^{-4}$ M TriBA . HCl due to the application of the ultrasound (*2*), compared with corresponding curve in the absence of the ultrasound (*1*); DC voltammetry; 500 mV s^{-1}; i electric current; E electrode potential vs SCE (salt bridge 0.5 M Na_2SO_4)

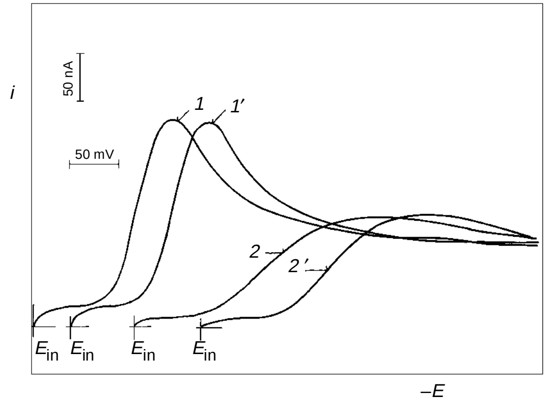

FIG. 4
Change in the voltammetric peak of Cd^{2+} as a result of adsorption of the strongly adsorptive TriBA, of which the transport to the electrode boundary is accelerated by ultrasound; $1 . 10^{-3}$ M $CdSO_4$ + $5 . 10^{-6}$ M TriBA in 0.1 M H_2SO_4; DC voltammetry; 500 mV s^{-1}; immediately after formation of the HMDE (*1*, *1′*), elapsed from and after forming 30 s of sonication of the system HMDE (*2*, *2′*); E_{in} = –0.5 V vs SCE; HMDE of the radius r = 50 μm

low that the amount of TriBA brought by diffusion to the electrode surface was negligible. If, however, the HMDE was renewed, exposed to ultrasound for a certain time, and the voltammetric record (without ultrasound) was repeated, the obtained signal of Cd^{2+} ions was markedly suppressed. A short-term convection of the solution had an effect similar to that of ultrasound. It is obvious that ultrasound accelerated the transport of TriBA to the electrode surface, thus enabling inhibition of the electrode process by TriBA. (This effect was not observed in the absence of TriBA.) The convective effect of ultrasound on the voltammetric measurements is probably related with cavitation[1–3] in the solution. This effect can be employed in electroanalysis, namely in stripping voltammetry with accumulation (anodic, cathodic, adsorptive, etc.). Its use may be especially attractive when treating microquantities of solution, in flow-through systems, or at the interface between nonmiscible liquids, where a magnetic stirrer cannot be used for controlled convective accumulation.

Analogous effects of ultrasound in the mentioned arrangement were observed by using the dropping mercury electrode with a controlled drop-time and with solid (carbon and gold) electrodes as well.

The effects of ultrasound on polarographic, voltammetric and related measurements are complex. Beside the phenomena mentioned above, its long term application during measurement may lead to a decrease of the concentration of dissolved oxygen from the air, warming up of the measured solution, influencing the state of microheterogeneous and micellar solutions, etc.

Application of ultrasound under constant or alternate intensities and frequencies to polarographic, voltammetric and related techniques opens the possible introduction of new group of related sonoelectrochemical techniques (direct and alternating current sonopolarography and sonovoltammetry; anodic, cathodic or adsorptive stripping sonovoltammetry; impedance sonotechniques; etc.) enabling new electroanalytical and electrochemical applications. The study of the mentioned and other phenomena, development of corresponding methods and instrumentation, as well as their analytical exploitation, will be the object of further work.

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