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Short communication

The effect of sonication on glass electrodes

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Abstract

This communication describes observations made on the disturbing effect of ultrasound on the functioning of glass electrodes. It was observed that the signal of glass electrodes drops significantly, with as much as several pH units, if sonication is applied to the sample solution. The effect was studied for a variety of electrolyte solutions and for several glass electrode makes, and was always found to be reversible and reproducible. The quality and the concentration of the electrolyte, as well as the ultrasonic power applied were seen to strongly influence the magnitude of the effect. These findings suggests that (i) if a glass electrode is being used to follow chemical reactions in sonicated solutions, irradiation should be intermitted for the time of measurements, and (ii) the phenomenon may provide an alternative method for sensing ultrasound or mapping ultrasound energy distribution.
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Keywords: Glass electrode; Ultrasound; pH change

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1. Introduction

Ultrasonic irradiation is now a widely applied technique in research, industry and medicine to promote and control chemical or physical processes. When chemical reactions in the liquid phase are to be influenced by sonication, the use of optical methods for monitoring the reactions is hampered by cavity, degassing and other disturbing effects well known to be present in sonically agitated solutions. One may think that conventional electrochemical methods are less affected by ultrasound and therefore should be better suited to the task. Reality is however, that more and more recent studies describe sonication-induced phenomena at liquid/solid interfaces in, among other fields, electrosynthesis [1,2], voltammetry [3–5] and potentiometry [5]. These sonoelectrochemical phenomena have been recently reviewed by Compton et al. [6]. Studies were also published which scrutinized the effect of sonication on the functioning of platinum [7,8], carbon [2], diamond [8] and mercury pool [9] electrodes. At the same time, glass electrodes have not yet been studied for such effects.

The present communication describes observations made on the disturbed functioning of glass electrodes in sonicated solutions. The aim of this work is to provide data for the characterization of the observed effects.

2. Experimental

The experiments were carried out using a Sonics and Material VC54 type ultrasonic generator. This instrument generates ultrasound with a frequency of 40 kHz and a maximum of 50 W power. The titanium alloy tip of the transducer ("horn") has a diameter of 3 mm. This instrument also provides a continuous control and readout for the ultrasonic power coupled into the agitated solution. During the experiments, the tip of the transducer was immersed into 100 mL of the sample solutions placed in a glass reaction vessel to the same depth and in parallel with the combined glass electrode, at a distance of 2.5 cm. This arrangement was kept as fixed as possible throughout all experiments. Stirring of the sample solutions

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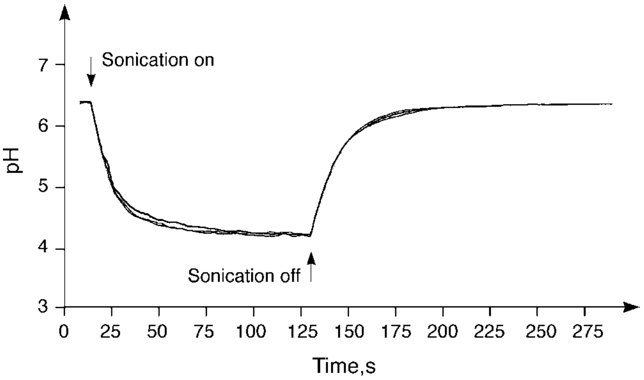

Fig. 1. Time resolved effect of sonication on the pH measured by a combined glass electrode in a 0.001 mol/L KCl solution (three repeated measurements are shown).

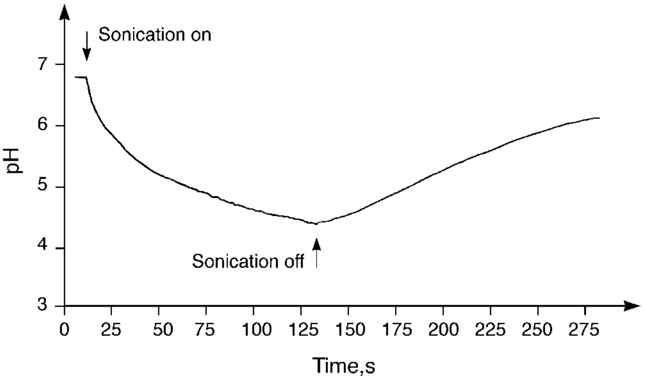

Fig. 2. Time resolved effect of sonication on the pH measured by a combined glass electrode in a 0.1 mol/L boric acid solution.

was not applied considering the well documented fact that linear velocities in sonicated solutions are much higher than those generated by stirring [10,11].

In experiments which aimed at studying the effect of ultrasonic frequency, an Undatim UL 03/1 type ultrasonic generator (517 kHz and 25 W), and two bath type generators, a Branson 2200 (47 kHz and 60 W) and a Ney 3006QT (40 kHz and 160 W), were also applied.

All experimental data shown in this paper were measured using a Radelkis OP-0808P combined glass electrode connected to a Metrohm E336 type potentiograph/pH meter. The potentiograph also allowed the electrode potential or pH be recorded as a function of time. Confirming test experiments were done using more than a dozen glass electrode–pH meter combinations manufactured by various companies (e.g. Radelkis, Metrohm, Hanna Instruments, Radiometer, Orion, Jenway, etc.).

Electrolyte solutions used were freshly prepared from analytical grade chemicals with Millipore MilliQ quality deionized water.

3. Results and discussion

The starting point was the observation that pH measurements in electrolyte solutions performed using a combined glass electrode gave rise to significantly lower values if sonication was applied to the solution. The dynamic of the effect, as is illustrated in Fig. 1 for a KCl solution, was seen to be such that the electrode signal started to decrease when sonication was turned on, and it continued to decrease until after 15–120 s later when it settled at a value 0.2–6 pH unit lower than that measurable without sonication. The settling time and the apparent pH drop was seen to vary with experimental conditions as described later. When the sonication was turned off, the signal started to increase slowly and asymptotically approached its initial value. The signal always fully recovered, however, the recovery usually took a longer time than the deflection process. The phenomenon was found to be well repeatable, as is also illustrated in Fig. 1. The reproducibility was also tested by using a variety of glass electrode–pH meter combinations, also with enhanced electromagnetic shielding of the instruments in order to exclude the possibility that the effect is a result of some electromagnetic interference or peculiar instrumental condition only. The phenomenon was always found to be reproducible and reversible for any given electrolyte solution and instrumentation used.

The effect of the quality of the electrolyte solution on the observable pH drop was also studied. Table 1 lists the pH drop measured for various electrolyte solutions, as well as for pH buffer solutions, under similar experimental conditions. All ΔpH values given here and later in this study are the difference found between the initial (unsonicated) and the sonicated electrode signals, the latter measured after allowing the electrode signal to settle fully. For the sake of comparison with Fig. 1, the signal versus time trace for a boric acid solution is shown in Fig. 2. As it is evidenced by these results, the phenomenon was observable for all electrolytes and buffers, however, the magnitude of the effect and the shape of the electrode signal versus time traces was different for different chemicals. It can also be immediately seen that there is no obvious correlation between the magnitude of the effect and the initial (actual) pH of the solutions.

Acid–base indicator dyes were also added to two sample solutions to decide if the observed pH drop is real or only apparent. The choice of indicator dyes in these experiments were based on their colour change pH interval and the initial pH of the sample solution. Phenolpthalein (colour change range: pH = 8.2–10.0) was used in a saturated MgO solution and a bromocresol green/methyl red mixture (colour change range: pH = 5.0–5.2) was used in a 0.001 mol/L KCl solution. These solutions gave rise to ΔpH values of several units (Table 1 and Fig. 1), but the colour of the indicators did not change nor faded. It was therefore concluded that the sonication only affects the electrode potential and not the actual pH of the solutions.

Experiments were also carried out to elucidate whether the observed phenomenon can be attributed only to the glass

Table 1
Effect of sonication on the measurable pH by a combined glass electrode in various electrolyte and buffer solutions

Compound dissolved	pH measured without sonication	Apparent pH drop (ΔpH) if sonication is applied
$NaHCO_3$	9.00	1.70
MgO (saturated)	10.80	6.26
$FeCl_3$	3.60	0.18
KBr	6.90	1.36
$Na_2B_4O_7$	9.30	1.24
CH_3COONa	6.98	1.12
H_3BO_3	6.70	5.99
KCl	6.80	1.29
Na_2S	11.70	1.06
Na_2HPO_4	8.73	1.01
KI	6.95	1.15
KH_2PO_4	5.10	1.09
Na_2SO_4	7.31	0.56
Na_3PO_4	11.60	0.84
$C_4H_4O_7KSb$	5.07	1.12
$MgCl_2$	6.80	0.95
$CuSO_4$ (0.002 mol/L)	6.50	0.28
Sigma B-4770 buffer, undiluted	7.00	0.09
Sigma B-4770 buffer, 1:10 diluted	7.00	0.44
Fluka 82559 buffer, undiluted	9.18	0.53
Fluka 82559 buffer, 1:10 diluted	9.18	2.06
Radelkis RB-4-F1 buffer, undiluted	4.00	0.18
Radelkis RB-4-F1 buffer, 1:10 diluted	4.00	0.48

Concentration was 0.01 mol/L, if not indicated otherwise.

electrode or also to the reference electrode present in a combined glass electrode. For this purpose, electrode potential difference measurements in sonicated solutions were done using two references (a calomel type Radelkis OP-0830P and a AgCl type Radelkis OP-0820P) and also using two glass (Radelkis OP-0931P and Radelkis OP-0718P) electrodes. It was found that the potential difference (expressed on the pH scale) between two reference electrodes only accounts for not more than about 10–20% of that measurable using combined glass electrodes. At the same time, the use of two glass electrodes resulted in significantly larger, sometimes twice as large, ΔpH values than that measurable using a combined glass electrode. Our opinion therefore is that the apparent pH drop observable with combined glass electrodes in sonicated solutions is mainly due to reversible changes at or near the glass electrode surface.

The concentration of the electrolyte solution being sonicated was seen to have a strong influence on the magnitude of the pH drop effect. More concentrated solutions, in general, gave rise to a smaller apparent pH drop. Fig. 3 displays the ΔpH results obtained for a series of KCl solutions. At the same time, the magnitude of the effect was found be readily affected by the electrode to transducer distance (the larger was the distance the smaller was the effect) which suggested a correlation with ultrasonic power. ΔpH values measured at different ultrasonic powers coupled into the same electrolyte solutions resulted in observations illustrated in Fig. 4 for KCl. These results indicate that the ΔpH is proportional to the ultrasonic power (or power density) coupled into the solution.

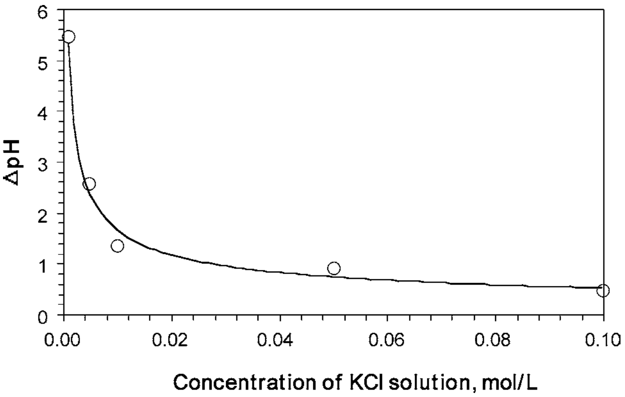

Fig. 3. Influence of electrolyte (KCl) concentration on the apparent pH drop at 14 W ultrasonic power applied.

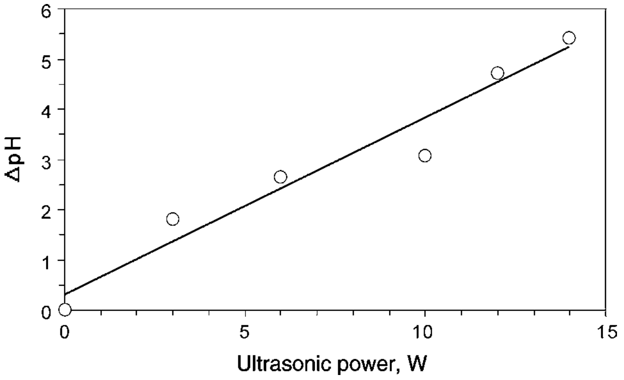

Fig. 4. Influence of ultrasonic power on the apparent pH drop in a 0.001 mol/L KCl solution.

The effect of the ultrasonic frequency on the ΔpH was also briefly studied. However, the ultrasonic generators at our hand did not cover a wide frequency range (40, 47 and 517 kHz) but showed large variation in transducer geometry (horn versus bath type), our preliminary experiments showed that a higher frequency results in a larger ΔpH.

4. Conclusions

In our view, the observed sonication-induced pH drop phenomenon is probably a combination of at least two effects caused by ultrasonic irradiation. One of the effects is clearly the significantly increased mass transport from the solution to the electrode surface [1,2,7], which efficiently increases the hidroxonium ion concentration in the close vicinity of the glass surface. The other effect can perhaps be attributed to a change at the glass surface layer which determines the electrode potential. Unfortunately, there are several competing theories, a critical review of which was given by Pungor [12,13] and more recently by Baucke [14–16], that aim at describing of glass electrode functioning, and this fact makes the finding of an exact explanation more difficult. Nevertheless, sonication is known to decrease the thickness of the electric double-layer at electrode surfaces [9,17], which should result in a change of the electrode signal. Further studies on the topic will hopefully be able to deliver a detailed explanation.

The first, practical conclusion that can be drawn is that the conventional method of pH measurement by a combined glass electrode, cannot be reliably used in sonicated solutions. The transducer needs to be temporarily turned off for the time of pH measurements. A sufficiently long (ca. 5 min) waiting period to allow the electrode processes to recover is also neccessary. The glass electrode needs not be taken out of the solution as it seems not to suffer any irreversible change from the irradiation. Still looking at the phenomenon from a practical point of view and also considering its dependence on the ultrasonic power, this effect suggests that it might as well provide a new and easy way of mapping the ultrasonic energy density inside an irradiated larger vessel. This method, which we described in detail elsewhere [18], could be an alternative to thermoenergetic detection [19].

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