

Amplitude of the Electrical Potential Oscillations in the Salt-Water Oscillator

Lubica Adamčíková*

Department of Physical Chemistry, Comenius University, 842 15 Bratislava, Slovak Republic

and

Vladimir Adamčík

Department of Physical Chemistry, Faculty of Chemical Technology, Slovak Technical University, 812 37 Bratislava, Slovak Republic

Received May 6, 1994; revised July 12, 1994; accepted July 14, 1994

The amplitude of the electrical potential oscillations of the salt water oscillator depends on the character of an electrical double layer formed in the glass capillary or at the interface between the dilute and concentrated salt solutions. When a stationary mercury electrode was used, a new type of periodic behavior, compound oscillation, was observed.

INTRODUCTION

In 1970, the geophysicist Martin¹ discovered a curious phenomenon: rhythmic oscillations of water flow are generated when a vertically oriented hypodermic syringe, with the plunger removed, is filled with salt water and partially submerged in a beaker of pure water. The oscillations appear as a downward jet of salt water, followed by an upward jet of pure water, and so on for many cycles. Yoshikawa and coworkers² found that periodic up and down flow could be easily monitored by the measurement of the electrical potential between the salt water and pure water with a pair of Ag/AgCl electrodes. The periods with high and low electrical potentials correspond to the downward and upward flows. Noyes³ has remarked that it suggests an interesting electrochemical problem. Oscillations are followed by the difference in potential of two electrodes, each of which is specific to chloride concentration. The local environments at these electrodes probably change only slowly when solution

* Autor to whom correspondence should be addressed

flows between the inner and outer vessels, but the potential undergoes dramatic shifts of 10's of millivolts. Noyes supposed that shifts in electrical potential differences could be due to changes in the junction potential generated at the interface between the dilute and concentrated salt solutions. Recently, Upadhyay *et al.*⁴ postulated that the observed oscillating electrical potentials were due to streaming potentials. Amplitudes of the electrical potential oscillations showed a decrease with the decrease in the concentration of the salt solution in the inner tube and were found to be in the order aluminum chloride > barium chloride > sodium chloride.

This communication is devoted to the amplitude of the electrical potential oscillations in the salt-water oscillator.

EXPERIMENTAL

The electrical potential oscillations were measured in a system (Figure 1) consisting of a reservoir A filled with distilled water, a small glass vessel B containing a solution with a higher density and limiting the connection C between the two liquids; this connection is formed by a capillary or only by a small opening in the bottom of vessel B. The volumes of the solutions in compartments A and B were always 250 and 3 cm³, respectively. The inner vessel B was dipped into a glass vessel A so that, at the beginning, the level of the liquids in the inner vessel and in the outer vessel was the same. The electrical potential difference across the electrodes in the inner and in the outer vessels was recorded with time using a *x-t* recorder (OH-105 polarograph, Radelkis, Hungary).

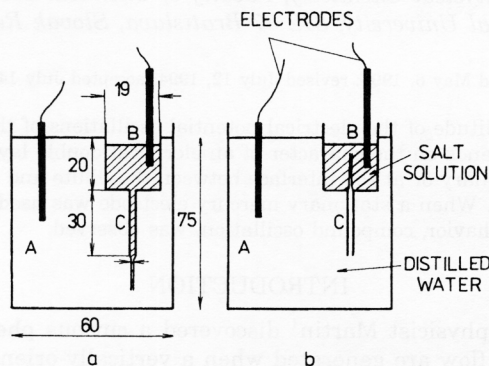


Figure 1. Hydrodynamic oscillator. a. Downward jet. b. Upward jet. The numbers are in millimeters.

RESULTS AND DISCUSSION

The essential feature of the hydrodynamic oscillator is that a fluid of higher density lies above one of lower density with a very restricted access between the two fluids. Due to the imbalance of the hydrostatic pressures, a rhythmic change is observed between the down-flow of the solution of higher density and the up-flow of the solution of lower density. The frequency of the hydrodynamic oscillation remains constant during several tens of cycles of the flow.

The periodic up and down flow was monitored by the measurement of the electrical potential between the salt water and pure water with a couple of arbitrary

electrodes regardless of the measured salt. The differences in the potential between the salt water and pure water could be measured with a pair of Ag/AgCl electrodes, calomel electrodes, with a pair of Pt electrodes, but also using a Pt electrode and a mercurous sulfate electrode (MSE). It is obvious that the differences in the potential of the two Ag/AgCl electrodes or the two Pt electrodes are not due to the change in chloride ion concentration or the change in redox system concentration. If, for example, an iodide-selective electrode was inserted in the inner vessel, which was filled with 1M KCl and MSE was inserted in the outer vessel (Figure 1), large oscillations were observed, with amplitude ≈ 60 mV (Figure 2d).

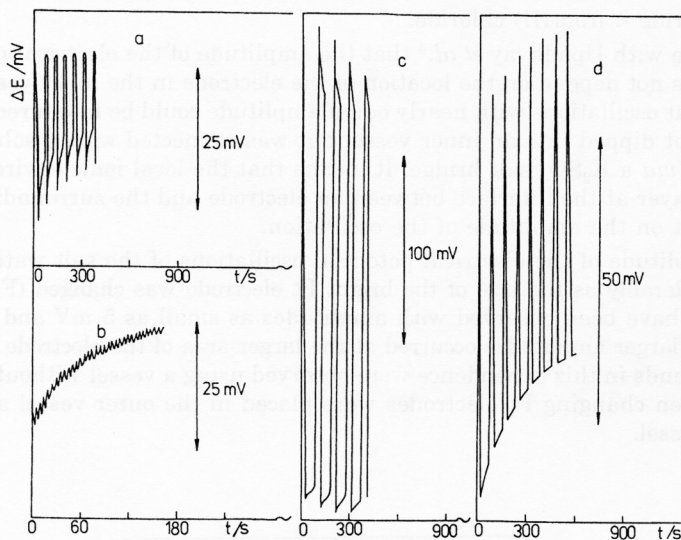


Figure 2. Traces of the oscillations of the electrical potential differences. Outer vessel A: 250 ml of distilled water and saturated mercurous sulfate electrode (MSE), a. Inner vessel B: 2M LiCl (3 ml) and Pt electrode with the area $S = 42.5 \text{ mm}^2$; b. Inner vessel without a capillary: 2M LiCl (3 ml) and Pt electrode with the area $S = 42.5 \text{ mm}^2$, other conditions as in (a); c. Inner vessel B: 2M LiCl (3 ml) and Pt electrode with the area $S = 80 \text{ mm}^2$; d. Inner vessel B: 1M KCl (3 ml) and an iodide-sensitive electrode.

Upadhyay *et al.*⁴ postulated that oscillating electrical potentials are due to streaming potentials. When liquids flow up and down, the mobile phase of the double layer, which is formed in the capillary, is also carried along causing charge separation. The direction of the charge separation when the liquid moves upward would be opposite to that when the liquid moves downward. The streaming potential $\Delta\phi$, derived on the basis of a simple Helmholtz double layer,^{5,6} in a simple capillary is given by equation

$$\Delta\phi = \frac{\epsilon \varphi_2 \Delta p}{\eta \kappa}$$

where Δp is the pressure difference, φ_2 is the electric potential at the outer Helmholtz plane, and ε , η and κ are the permittivity, coefficient of viscosity and the electrical conductivity of the medium, respectively. Our experiments were performed in a vessel with a capillary but also in a vessel without a capillary. The capillary C in our Figure 1 was replaced by a pinhole (diameter 1 mm and length 1 mm) in the bottom of vessel B. Amplitude of the electrical potential oscillations was decreased if the vessels with a shorter capillary⁷ or without a capillary were used (Figure 2a, b). This trend can be understood in terms of displacement of the mobile phase of the double layer. The amplitudes of the electrical potential oscillations showed an increase with the increase in the concentration of the KI solution placed in the inner vessel and were found to be in the order $\text{KCl} \doteq \text{KBr} < \text{KI}$ and sodium chloride < copper (II) chloride < iron(III) chloride.

We agree with Upadhyay *et al.*⁴ that the amplitude of the electrical potential oscillation does not depend on the location of the electrode in the inner vessel because we found that oscillations with nearly equal amplitude could be measured if the electrode was not dipped into an inner vessel but was connected with a solution in the inner vessel *via* a K_2SO_4 salt bridge. It means that the local ionic environment and the double layer at the interface between an electrode and the surrounding solution had no effect on the amplitude of the oscillation.

The amplitude of the electrical potential oscillations of the salt water oscillator varied considerably as the size of the bright Pt electrode was changed (Figure 2a, c). Oscillations have been observed with amplitudes as small as 5 mV and as large as 240 mV; the larger amplitudes occurred at the larger area of the electrode (Figure 3a). The same trends in this dependence were observed using a vessel without a capillary and also when changing Pt electrodes were placed in the outer vessel and MSE in the inner vessel.

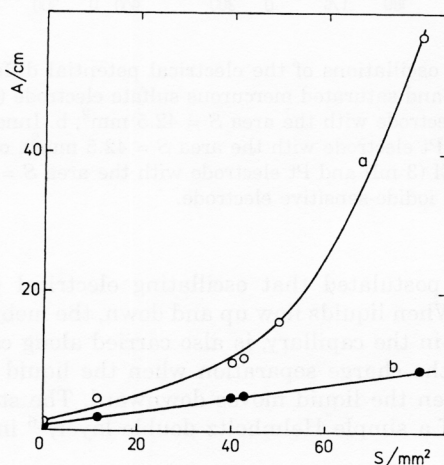


Figure 3. Amplitude of the oscillations vs. the area of Pt electrode. a. Inner vessel B: Salt (3 ml) and Pt electrode, outer vessel A: 250 ml of distilled water and MSE electrode. b. Inner vessel B: 3 ml of distilled water and Pt electrode, outer vessel A: 250 ml of methanol and MSE electrode.

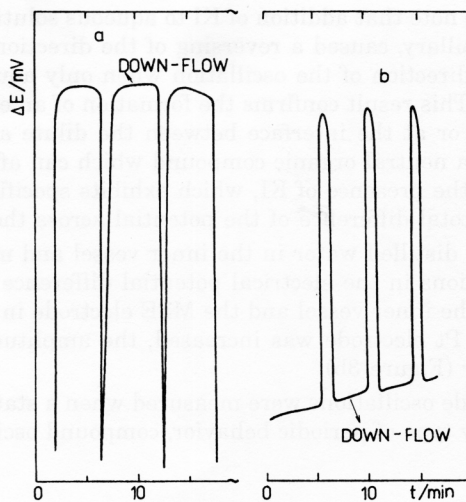


Figure 4. The reversal of the oscillation direction. a. Inner vessel B: glycerol – water system (1:1), (3 ml) and Pt electrode, outer vessel A: 250 ml of distilled water and MSE electrode. b. Inner vessel B: 0.16 M KI was added to glycerol – water system (3 ml), other conditions as in (a).

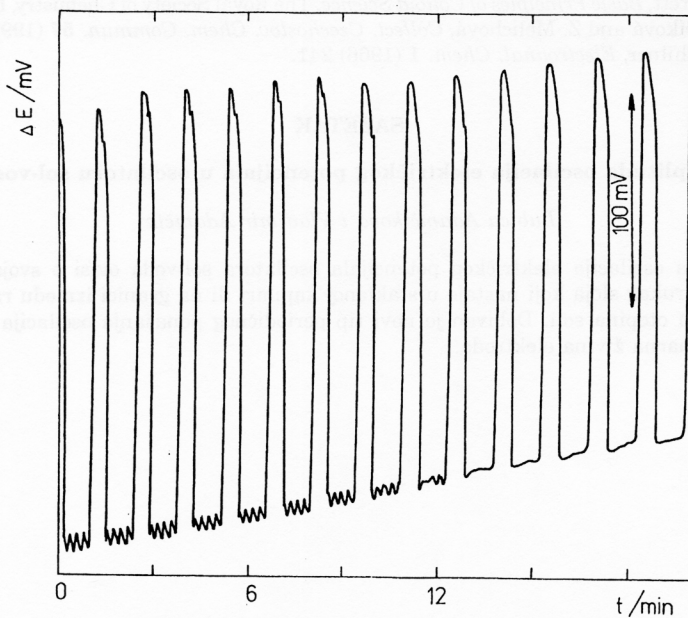


Figure 5. Traces of the oscillations of the electrical potential differences. Inner vessel B: 1M KBr (3 ml) and a stationary mercury electrode, outer vessel A: 250 ml of distilled water and Hg/Hg₂SO₄/Na₂SO₄ electrode.

It is interesting to note that addition of KI to aqueous solution of glycerol, placed in a vessel with a capillary, caused a reversing of the direction of the oscillation in comparison with the direction of the oscillation when only aqueous glycerol was in the vessel (Figure 4). This result confirms the formation of an electrical double layer in the glass capillary or at the interface between the dilute and concentrated salt solutions. Glycerol is a neutral organic compound which can affect the properties of the double layer, but the presence of KI, which exhibits specific anionic adsorption, affects markedly the total difference of the potential across the diffuse layer φ_2 .⁸

Experiments with distilled water in the inner vessel and methanol in the outer vessel showed oscillations in the electrical potential difference across the bright Pt electrode inserted in the inner vessel and the MSE electrode in the outer vessel but, when the area of the Pt electrode was increased, the amplitude of the oscillations became slightly larger (Figure 3b).

The large-amplitude oscillations were measured when a stationary mercury electrode was used. A new type of periodic behavior, compound oscillation, appeared, as shown in Figure 5.

REFERENCES

1. S. Martin, *Geophys. Fluid. Dyn.* **1** (1970) 143.
2. K. Yoshikawa, S. Nakata, M. Yamanaka, and T. Waki, *J. Chem. Educ.* **66** (1989) 205.
3. R. M. Noyes, *ibid.* **66** (1989) 207.
4. S. Upadhyay, A. K. Das, V. Agarwala, and R. C. Srivastava, *Langmuir* **8** (1992) 2567.
5. S. Glasstone, *An Introduction to Electrochemistry*, D. Van Nostrand, New York, 1965.
6. D. H. Everett, *Basic Principles of Colloid Science*, The Royal Society of Chemistry, London, 1988.
7. L. Adamčíková and Z. Melichová, *Collect. Czechoslov. Chem. Commun.* **57** (1992) 1621.
8. D. M. Mohilner, *Electroanal. Chem.* **1** (1966) 241.

SAŽETAK

Amplituda oscilacija električkog potencijala u oscilatoru sol-voda

Lubica Adamčíková i Vladimír Adamčík

Amplituda oscilacija električkog potencijala oscilatora sol-voda ovisi o svojstvima električkoga dvostrukog sloja koji nastaje u staklenoj kapilari ili na granici između razrijeđenih i koncentriranih otopina soli. Dobiven je novi tip periodičnog ponašanja oscilacija spoja, kada se rabi stacionarna živina elektroda.