Transfer of charges and substances in a gas-discharge plasma from the liquid electrolyte cathode containing salts of alkali metal

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Abstract. A gas discharge in the air between the flowing liquid cathode and a solid anode was studied experimentally. Aqueous solution of sodium chloride was used as the liquid cathode electrolyte. Mass loss due to evaporating and sputtering was compensated by adding distilled water in a continuous mode. It was found that the specific electric conductivity of the aqueous solution is almost unchanged. The regularities of changes in the composition of an anionic solution were discovered.

1. Introduction
The work is devoted to the study of a gas discharge, which is excited between a liquid cathode and a metallic anode at atmospheric pressure. The advantage of such discharges is that they make it possible to obtain a nonequilibrium plasma at atmospheric pressure by relatively simple methods. Therefore, interest in them is growing steadily every year. In this case, the plasma produced in a gas discharge has broad practical applications [1-6].

2. Experiment
The experiments were carried out on an installation described in [7]. Electric power was supplied from sources based on an inverter converter. Power supplies of this type have the advantage that they allow maintaining current with high accuracy. According to the technical characteristics of the sources, the errors of current stabilization do not exceed 1%.

A solution of sodium chloride in distilled water as a liquid cathode, was used. The volume of the aqueous solution of the Vs in the hydraulic system of the experimental setup was kept constant. In experiments, the constancy of the Vs volume was ensured by compensating of the loss of the solution by adding distilled water. It was happening in a continuous mode. The physicochemical parameters of the aqueous solution (pH, specific electric conductivity and content of NaCl) were measured by the laboratory instrument ANION 4150.

3. The experimental results and their analysis
In the experiments it was found that after the action of the gas discharge the pH of the aqueous solution is increases. The alkalization of the aqueous solution was occurred. This process can be explained as
follows. During the combustion of the discharge, some of the Cl\(^-\) anions are re-moved from the solution. They are replaced by hydroxyl ions OH\(^-\). Since the solution contains Na\(^+\) cations, it can be considered that the action of a gas discharge leads to the formation of sodium hydroxide in a dissociated state.

Adding hydrochloric acid to the solution, it can be neutralized. In this case, a reaction will occur with the formation of sodium chloride

\[
\text{NaOH} + \text{HCl} = \text{NaCl} + \text{H}_2\text{O},
\]

This process was performed by titration. After exposure of gas discharge, a sample was taken and an acid (titrant) was added in, such an amount that completely restored the original pH value. It was found that the content of NaCl was also restored. The specific electrical conductivity of the aqueous solution remained practically unchanged. The deviation from the initial value was insignificant.

The processes of charges transfer and substance can be described as follows. Under the influence of the discharge, the solution is sprayed and the droplets are transformed into vapour. It must be assumed that under conditions of the discharge, the liquid – gas phase transition, proceeds rapidly and has an explosive character. In this case, the anions and cations that are carried out as a part of the drops from the aqueous solution is spread away. In the electric field of a gas discharge Cl\(^-\) ions are drifting toward the anode, and thus they are removed. The amount of chlorine in aqueous solution is reduced. Na\(^+\) ions are drifting to the cathode and returned to the aqueous solution. On the surface of the graphite plate which is mounted inside of the aqueous solution for supplying thereto negative potential, Na\(^+\) ions are restored. The metallic sodium is reacts instantly with water, forming a hydroxide of NaOH, which in turn dissociates into Na\(^+\) and OH\(^-\) ions. Thus, Cl\(^-\) anions that retired from the aqueous solution are replaced by the same amount of hydroxyl OH\(^-\) ions. When the pH is restored, an excessive amount of hydroxyl OH\(^-\) ions is neutralized and Cl\(^-\) ions are returned into aqueous solution. In this case, the NaCl content in the solution is restored, i.e. the initial variant of the aqueous solution is obtained. Hence it can be concluded that the amount of sodium in the aqueous solution does not change. Na\(^+\), ions, released from the aqueous solution as a part of drops, practically all return.

Negative chlorine ions will not be return back, unlike sodium ions. Let us consider how changing their content in the aqueous solution. In the volume of the sample \(v\) there is Cl\(^-\) in the amount of \(c \cdot v\). Here \(c\) – is the unknown molar concentration. In a freshly prepared solution with a volume equal to the volume of the sample \(v\), the amount of Cl\(^-\) ions is \(c_0 \cdot v\). During the combustion of the gas discharge, part of NaCl was converted into NaOH in a ratio of 1:1. In the same ratio, chloride ions Cl\(^-\) were replaced on hydroxyl ions OH\(^-\). The loss of chloride ions Cl\(^-\) in the sample is \(c_0 \cdot v - c \cdot v\).

When titrating the loss is restored by ions contained in the titrant: \(c_1 \cdot \Delta v\). Here \(\Delta v\) is the volume of the titrant. In this way: \(c_0 \cdot v - c \cdot v = c_1 \cdot \Delta v\). From here

\[
\frac{c}{c_0} = 1 - \frac{c_1}{c_0} \cdot \frac{\Delta v}{v}, \tag{1}
\]

Provided that small portions (droplets) are removed from the aqueous solution without changing the composition, it is possible to obtain the formula

\[
\frac{C}{C_0} = \exp(-\Delta V/V_s). \tag{2}
\]

Here \(\Delta V\) – volume of distilled water, which is needed to compensate for loss of the aqueous solution. This condition is realized in the absence of a gas discharge \((I = 0)\), when the aqueous solution flows out of the hydraulic system and at the same time distilled water is added to it. As can be seen from figure 1, the results of such "idle" experiments (marked by squares) are in complete agreement with the calculation according to formula (2). At the same figure shows the experimental data (marked with circles) which processed using formula (1). They are significantly different from "idle". Thus, when the combustion of gas discharge, content of chlorine in the aqueous solution is decreases much more slowly than in the "idle" experiments. This is a very important experimental fact that deserves attention.
Suppose that in the near-boundary region "aqueous solution-plasma" the current is completely ionic. Positive Na\(^{+}\) ions are going to the cathode (into the aqueous solution), and the negative Cl\(^{-}\) and ОН\(^{-}\) ions leave from it. Let the concentration of Na\(^{+}\) ions in the drops is the same as in the aqueous solution, i.e. \(C_{+} = C\). Under this condition, the positive ion current can be calculated by using the rate of decrease \(m\) of the aqueous solution.

\[
I^{+} = \frac{q^{+}}{t} = \frac{N^{+} \cdot e}{t} = C^{+} \cdot \Delta V \cdot N_{A} \cdot e = \frac{C^{+} \cdot \Delta V \cdot N_{A} \cdot e}{\rho} = \frac{C^{+} \cdot N_{A} \cdot G}{\rho}.
\]  

Here \(q^{+}\), \(N^{+}\) and \(v^{+}\) – the total charge, the total number and the number of moles of positive ions. \(G\) and \(\rho\) – mass flow and density of the aqueous solution. For an approximate estimation of \(\rho\) can be taken as that of water, because the solution is weakly concentrated.

The concentration of sodium in the aqueous solution is practically unchanged. Therefore, in the first approximation, we can assume that \(C^{+} = C_0\).

Let us consider an example of calculation for the case \(I = 11.00\) А and \(C_0 = 0.1\) mol/l. In this case, the calculation gives \(I^{+} = 6.84\) А, which is slightly more than half of the total current \(I = 11.00\) А. Let us analyze the result obtained. To begin with, in general, the aqueous solution is electrically neutral. The molar concentrations of positive and negative ions in it are the same \(C^{+} = C^{-}\). The aqueous solution maintains electroneutrality in the process of gas discharge exposure. Consequently, the drops do not carry out ions of any sign in an excessive amount. They are also electrically neutral. The condition \(C^{+} = C^{-}\) also is being implemented in the drops. In this case, as follows from formula (3), the ion current \(I^{+}\) is proportional to \(C^{+}\). Similarly, \(I^{-}\) is proportional to \(C^{-}\). Therefore, the condition \(I^{+} = I^{-} = I/2\) must be fulfilled. Thus, the calculations of \(I^{+}\) give an overestimated result.

Let us accept \(I^{+} = 5.5\) А. Using formula (3), it is possible to find the corresponding value of the molar concentration \(C^{+} = 0.08\) mol/l. Thus, \(C^{+} < C_0\). It turns out that the part of the aqueous solution which is carried away by the drops as if diluting by water. The essence of this seeming effect is quite understandable. In fact, along with the drops ablation is decreased the loss of aqueous solution through an evaporation process. The volume of additional pure water enters in \(\Delta V\) as the volume of the droplets phase. Therefore, calculation by formula (3) gives an underestimate value of \(C^{+}\).

The picture of transport phenomena in a simplified form can be represented, as shown in figure 2. Distilled water with volume \(\Delta V\) is enters the hydraulic system. Under the influence of a gas discharge, the aqueous solution decreases in the same volume. The loss occurs in the form of drops and water vapor. The droplets phase is 4/5 parts, and the water vapor is 1/5 part.
Figure 2. A simplified picture of transport phenomena. 1 – graphite plate; 2 – aqueous solution of sodium chloride; 3 – droplets phase carried away from the cathode of solution; 4 – water vapour. $I = 11.0 \, \text{A}$, $V_s = 15.0 \, \text{l}$. $\Delta V/V_s = 2/3$.

The circular diagrams in this figure reflect the molar content of ions in the aqueous solution (5) and in the drops (6). The figures indicate the proportions of cations and anions in the total numbers of ions.

4. Conclusions
The substance comes from the water-solution cathode into the gas-discharge plasma in the form of drops and vapour, the droplets phase predominates substantially. Cations and anions contained in the aqueous solution are transferred in the drops. The cations of the alkali metal, in this case sodium, are almost completely returned to the water-solution cathode. The proportions of different anions in drops depend on their mobility. In a larger number in drops fall anions with higher mobility.

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