Specifics of studying electrochlorination in a student chemistry practical

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Abstract. The suitability of the process of obtaining sodium hypochlorite by electrolytic chlorination of sodium chloride solution for the purposes in a chemical laboratory is shown. The process was carried out in a 1 l non-flowing cell with four bipolar titanium electrodes 6x10 cm with oxide-ruthenium anodes. The distance between the electrodes is 1 mm, the temperature of the initial solution is 7-8ºC. The concentration of sodium chloride 25 g/l is convenient for acquaintance with the basic electrochemical laws of the process since the dependence of the concentration of "active chlorine" on the electrolysis time is linear up to 9 g/l at a current density of 0.1 A/cm². The study of the effect of side processes on the output of the target product is carried out at a current density of 0.125 and 0.15 A/cm² (the dependence is nonlinear). The dependence at a concentration of 35 g/l, 0.1 A/cm² is similar to the dependence at 25 g/l and 0.125 A/cm². To determine the concentration of "active chlorine" the aliquot was taken from the reaction mixture at equal intervals, diluted by 25 times. The solution was acidified and titrated with methyl orange.

1. Introduction
The section "chemical and electrochemical processes in solutions" of the laboratory workshop on the course of chemistry for bachelors of technical specialties can be supplemented with work on the study of the electrochlorination process. It contains elements of scientific research - a research case, focused on the inclusion of a student in research activity. Such work is advisable to carry out at the end of the workshop on electrochemistry after mastering the lecture material and performing the corresponding homework. The electrolysis of sodium chloride solution was carried out in a non-saffron cell; a low-concentration sodium hypochlorite solution was obtained and the concentration of "active chlorine" was determined. Sodium hypochlorite solution is widely used as a disinfectant and bleaching agent. It is important that at a concentration of less than 1%, it is a non-hazardous reagent, so its use in laboratory practice does not require additional safety measures. To obtain electrolytic sodium hypochlorite, a well-developed process is used, based on the simultaneous production of chlorine and sodium hydroxide and their interaction in a non-saffron electrolyzer. The relative rates of chlorine and oxygen release at the anode and hydrogen at the cathode depending on the electrode material, electrolyte pH, sodium chloride concentration, current density and process temperature. Since the aim of the experiment was to obtain a low-concentrated solution of hypochlorite, sodium chloride solutions of low concentration were used. At the same time, during the transition to highly diluted solutions, together with chlorine released at the anode, an increasingly noticeable amount of oxygen begins to form. This is dictated by the use of
solutions with a concentration of 25 and 35 g/l. With the accumulation in the solution sodium hypochlorite, electrochemical and chemical decomposition of hypochlorite to chlorate is becoming more noticeable. It is known that the current yield decreases due to losses on cathodic reduction and electrochemical anodic oxidation of hypochlorite is proportional to its concentration increase, inversely proportional to the current density and falls by about 2% with an increase in temperature by 1°. Therefore, for obtaining the main process with a minimum of adverse reactions, it is optimal to electrolyze neutral solutions of sodium chloride at the lowest possible temperature and be limited to low concentrations of the product — sodium hypochlorite. Let us consider in more detail the effect of hypochlorite current density on the output: at very small values oxygen is released on the anode, then, when the equilibrium potential is reached, the joint release of oxygen and chlorine begins. With the increase in current density, the yield of chlorine rises rapidly and at 0.1 A/cm², the share of electricity that went to the release of oxygen is only a few percents. According to [1], the dependence of the current output of "active chlorine" on the current density has a maximum in the range from 0.1 to 0.2 A/cm². Thus, the optimal value is 0.1 a / cm². The optimal duration of the process in terms of power consumption should not exceed 15-17 minutes [1].

2. Materials and methods of research

During the work, one electrochlorination unit per group was used, located in the exhaust hood and consisting of a glass electrolytic cell with a volume of 1 l, a Teflon cover connected to a glass cylinder forming a hydraulic gate, and devices for conducting an electrochemical process and monitoring its parameters (Figure 1). Four titanium electrodes 6X10 cm with oxide-ruthenium anodes were placed at a distance of 1 mm and the process was carried out at a current density of 0.1 A/cm² [2]. The reaction mixture was stirred with a magnetic stirrer located at the bottom of the cell. Potentiostat-galvanostat Elins P-150X was used as a current source. Sodium chloride solution was prepared distilled water and sodium chloride of qualification "H. C.". The concentration of active chlorine was determined by titration with methyl orange (para-dimethylaminoazobenzesulfonic sodium).

The electrolysis solution was pre-cooled to 7°C. Electrochlorination was carried out in a non-flowing mode with a periodic sampling of the reaction mixture of 10 ml at equal intervals. The total electrolysis time did not exceed 20 minutes so that the final concentration of "active chlorine" did not exceed 1%. To plot the experimental dependence, four 10 ml samples of the reaction solution were taken at regular intervals, placed in 250 ml volumetric flasks; an excess of 5 n solution of hydrochloric acid was added, and distilled water was added to the mark. Then, from each volumetric flask, 20 ml was taken into three conical flasks for titration and the concentration of "active chlorine" was determined.

The term "active chlorine" refers to the entire volume of chlorine produced when the reaction mixture is exposed to excess hydrochloric acid:

\[
\text{NaClO} + \text{HCl} \rightarrow \text{Cl}_2 \uparrow + \text{NaCl},
\]

\[
\text{HClO} + \text{HCl} \rightarrow \text{Cl}_2 \uparrow + \text{H}_2\text{O}.
\]
To determine it, we used the fact that the oxidizing potential of chlorine is sufficient to destroy methyl orange, as a result of which the methyl orange is discolored when the chlorine solution is titrated. A solution of 0.005% methyl orange in distilled water (25 mg per 1 liter of distilled water) was placed in a 5 ml microburet and titrated with 20 ml of the analyzed solution until a non-vanishing pink color appeared. The content of free residual chlorine was calculated by the formula

\[ X = \left(0.04 + 217a\right)/V, \]

where \( a \) is the volume of the methyl orange solution that went to titration, ml; \( V \) is the volume of the reaction mixture taken, in our case 10 ml; 0.04 is the empirical coefficient; 0.0214 is the methyl orange titer. Next, we plotted the concentration of "active chlorine" in coordinates - the time of electrochlorination and explained the type of dependence.

3. Results and discussion

The type of dependence of the concentration of "active chlorine" on time is affected by the concentration of the initial solution of sodium chloride and the current density value (Figure 2).

![Figure 2](image_url)  
Figure 2. Dependence of \( pH \) (right scale, dashed curves) and concentration of active chlorine in g/l (left scale, solid) on electrochlorination time for current densities of 0.15; 0.125; 0.1 A/cm\(^2\) and concentration of sodium chloride solution of 25 g/l (upper figure) and current density of 0.1 A/cm\(^2\) and concentration of 35 g/l (lower figure).
At a concentration of 25 g/l and a current density of 0.1 А/cm², the side processes are and the dependence is almost linear. Chlorine is mainly formed on the anode, water molecules decompose to form hydrogen and hydroxyl ions on the cathode.

\[ 2\text{Cl}^--2e^- \rightarrow \text{Cl}_2, \]
\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- . \]

The released chlorine dissolves and disproportionates to form hypochlorous and hydrochloric acids:

\[ \text{Cl}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{HClO} + \text{HCl}. \]

Due to the intensive mixing of the electrolyte in the interelectrode space hydroxyl ions formed on the cathode during the restoration of water neutralize these acids to form hypochlorite and sodium chloride.

The total equation of electrolysis:

\[ \text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{ClO}^- . \]

At a current density of 0.125 and 0.15 A/cm², there is a deviation of the dependence of the concentration of "active chlorine" on the time of electrolysis from the linear one and there is a site where the concentration increases more slowly due to the side processes of electrochemical reduction of sodium hypochlorite, which is directly dependent on the intensity of mixing:

\[ \text{ClO}^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{Cl}^- + 2\text{OH}^- , \]

and the side process of electrochemical oxidation of hypochlorite, amplified due to local overheating:

\[ 6\text{ClO}^- + 3\text{H}_2\text{O} - 6e^- \rightarrow 2\text{ClO}_3^- + 4\text{Cl}^- + 1,5\text{O}_2 + 6\text{H}^+ \]

as well as the process of chemical formation of chlorate:

\[ 2\text{HClO} + \text{ClO}^- \rightarrow \text{ClO}_3^- + 2\text{Cl}^- + 2\text{H}^+ . \]

Also, in Figure 2 three sites are visible: an almost linear pH increase in the first, the inflection region, and almost linear third section of constant values of the hydrogen index. The second section corresponds to the area of nonlinearity in the graph of the concentration of "active chlorine" on time.

The choice of current density depends on the purpose of laboratory work. If the study is subject to the basic chemistry of the process, the optimal current density is 0.1 A/cm² at which the effect of side processes is small, but if it is supposed to study the effect of side processes on the output of hypochlorite, higher current density values should be used. The type of dependence at a concentration of 35 g/l and a current density of 0.125 A/cm² is similar to the type of curve corresponding to the concentration of 25 g/l and 0.15 A/cm².

4. Summary

The electrochlorination process for studying the main regularities of the process of electrolysis in the laboratory course in chemistry for students was tested. It is shown that at the concentration of 25 g/l of the initial solution of sodium chloride and its current density 0.1 A/cm², the process proceeds with small side reactions, and the final dependence of "active chlorine" concentration on the time of electrochlorination is almost linear. At a higher current density or at a concentration of 35 g/l, side effects become noticeable. It allows us to work in two ways. In the first, at a current density of 0.1 A/cm², the chemistry of the main process of synthesis of sodium hypochlorite by electrolysis of chloride in a nonsaffron cell and the main reactions occurring on the electrodes are studied. At a higher current density, the effect of side processes leading to a decrease in the current output of the target product and to a nonlinear form of the dependence of the concentration of "active chlorine" on time is further studied.

To build the dependence, a method for determining the content of "active chlorine" by methyl orange titration was used. Inexpensive reagents available in each laboratory workshop are used in the work: sodium chloride, hydrochloric acid, methyl orange. The electrochlorination process is accompanied by the formation of chlorine gas, most of which is absorbed by the reaction solution and turns into hypochlorite, and the rest is released through a gas pipe, so the installation should be located in the exhaust hood. For safety reasons, samples from the reaction volume were taken with a remote-controlled crane located at the bottom of the cell. This allows you to keep the traction closed and avoid exhaust
gases in the air of the laboratory. The concentration of sodium hypochlorite in the reaction mixture did not exceed 0.8%, which makes it possible to classify it as a non-hazardous reagent. In addition, the solution was diluted by 25 times. The work done helps us to form the ability and willingness to carry out the technological process in accordance with the regulations and to use technical means to measure the main parameters of the technological process and products; to develop skills of using the theory of electrochemical processes for optimization of its basic parameters.

References
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