Study of the factors that determine the transfer of water and organic compounds into the gas phase from aqueous solutions in a discharge with a liquid cathode

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Abstract. A study was performed to investigate the transfer of organic compounds and water from an aqueous solution to the gas phase under the action of a direct current discharge, in which an aqueous solution that contains organic compounds plays the role of a cathode. The effect of the area of the free surface of a liquid in various reactors, as well as the effect of the stirring mode of a solution near the surface of a liquid on the rate of transfer of water and organic compounds under the action of a discharge of this type, have been investigated. It is shown that a change in the area of the free surface of a liquid has no significant effect on the rate of transfer of water and organic compounds from solution to the gas phase under the action of a direct current discharge with a liquid cathode. It is shown that the stirring mode and the temperature of the solution, on the contrary, have a very significant effect on the rate of nonequilibrium transfer of both water and organic compounds from solution to the gas phase under the action of a discharge with a liquid cathode.

1. Introduction

In the last two decades, there has been a significant increase in interest in the study of the interaction of an electric-discharge plasma with a liquid surface [1-3]. To a large extent, this interest is associated with the prospects for the practical application of this type of electric-discharge plasma. In [4], it was proposed to call the discharge systems in which plasma interacts with the liquid surface as plasma-solution systems. A direct current discharge with a liquid electrode is the simplest option for organizing such a plasma-solution system [5].

If the plasma-solution system is organized in such a way that the liquid is the cathode in the gas discharge, then the radiation effects in the liquid are the strongest. This is due to the fact that in this case the surface of the liquid is bombarded with positive ions accelerated in the cathode layer. Since the magnitude of the cathode voltage drop in such discharge systems is quite large and depending on the composition of the liquid cathode varies from 400 to 800 V [4], then the ion energy can be very significant. Since the radiation effects in a liquid in a discharge with a liquid cathode significantly exceed the radiation effects in other types of discharges, the study of a discharge with a liquid cathode is of great interest from the point of view of plasma-chemical applications.
Discharges with a liquid cathode have prospects of application in new methods of water purification, modification of high-molecular compounds, sterilization of aqueous solutions, and analysis of solutions for the content of metals. An essential feature of this type of discharges is the nonequilibrium transfer of solution components into the gas phase under the action of ion bombardment of the solution surface. The transfer of the solutions components into the gas phase changes the composition of the plasma and affects its parameters. This, in turn, leads to a change in the kinetics of the active particles formation, both in the plasma itself and in the solution.

Thus, the study of the processes of transfer of solutions components into the gas phase in plasma-solution systems is important both for the creation of theoretical models of plasma-solution systems and for the development of new technologies based on them [6-8]. In this work, we investigated the factors affecting the transfer of water and organic compounds into the gas phase from aqueous solutions under the action of a discharge with a liquid cathode. This task can be of great practical importance from the point of view of water purification from organic impurities.

2. **Experimental setup and measurement methods**

In the course of the work, an experimental setup was used in which a direct current discharge was created between a rod metal electrode and the surface of a solution inside a glass discharge chamber in a flow-through discharge cell. To maintain a constant temperature of the solution in the discharge cell, its circulation was created through the discharge cell and a special heat exchanger using a membrane pump. The components of the solution, passing into the gas phase as a result of interaction with the discharge plasma, moved through the discharge chamber and then along a glass tube to a glass heat exchanger, in which their condensation took place. The condensate was collected in a special sample receiver and subsequently analyzed.

The discharge chamber was purging with atmospheric air. To do this, a reduced pressure was created in the sample receiver using a peristaltic pump, which led to the intake of atmospheric air into the discharge chamber through a special slit, its passage further through the refrigerator into the sample receiver and subsequent removal into the atmosphere using a peristaltic pump together with gaseous products formed in the discharge chamber (Figure 1).

![Figure 1. Schematic of the experimental setup. 1 - flow-through discharge cell, 2- circulation pump, 3- heat exchanger for circulating liquid, 4- ammeter, 5- voltmeter, 6- voltage divider, 7- glass discharge chamber, 8- discharge, 9- cathode, 10- slit, for the intake of atmospheric air, 11- anode, 12- gas outlet tube, 13- heat exchanger for steam condensation, 14- sample receiver, 15- condensate, 16- tube leading to a peristaltic pump pumping out gas from the discharge chamber.](image-url)
In the course of the research, three different discharge chambers were used, differing in diameter and, as a consequence, in the area of the free surface of the liquid (Table 1).

**Table 1. Parameters of discharge chambers (reactors).**

| Reactor № | Inner diameter, mm | Free surface area of liquid, mm² |
|-----------|--------------------|---------------------------------|
| 1         | 8                  | 50                              |
| 2         | 15                 | 177                             |
| 3         | 22                 | 380                             |

A DC discharge was ignited in the discharge chamber between a tungsten rod electrode 2 mm in diameter and the surface of the solution, which served as the cathode. The distance between the electrode and the surface of the solution was set by a micrometric adjusting screw. The discharge current was set by an adjustable direct current source and was maintained throughout the experiment with an accuracy of no worse than ± 1%. The discharge took place at atmospheric pressure. The rate of air pumping through the discharge chamber was 280 ml/min.

The voltage across the discharge cell was measured with an AM-1118 multimeter connected to the discharge cell through a DNV high-voltage voltage divider. The current through the discharge cell was measured using a DT9208A multimeter. The determination of the amount of liquid formed in the sample receiver for a fixed period of time (20 minutes for the mode without stirring and 40 minutes for the mode with stirring) was carried out by the gravimetric method, for which a VIBRA AB623RCE balance with a scale value of 0.001 g was used. Determination of the concentration of organic components from the initial solution in the condensate was carried out by gas chromatography, using a gas chromatograph Chromos GC 1000 with a capillary column ZB-FFAP 50m*0.32mm*0.5μm. Based on the data on the concentration of the corresponding substance in the initial solution and in the condensate, as well as using the measured value of the current through the discharge system, the transfer coefficients were calculated for water and the corresponding organic substances (a value equal to the number of particles transferred from the solution to the gas phase in an unchanged form per one ion bombarding the liquid surface).

The calculations were carried out according to the following formula [9]:

\[ S = \frac{N_a C V}{I \epsilon}, \]

where \( N_a \) is the Avogadro number, \( C \) is the concentration of solvent molecules or solutes in the condensate obtained from the gas phase (mol/L), \( V \) is the volume of condensate (L), \( I \) is the discharge current (A), \( \epsilon \) is the discharge burning time (s), \( \epsilon \) - elementary charge (C).

Three types of alcohols were used as organic substances for the preparation of solutions: isopropanol, butanol-1 and benzyl alcohol (phenylcarbinol), as well as acetic acid. The concentration of organic substances in the prepared solutions was 1% from volume. The conductivity of the solutions was measured with an Ekspert-002 conductometer, the pH of solutions was measured with an Ekspert-001-3.0.4 liquid analyzer.

To prepare solutions of alcohols, deionized water was used, to which sodium hydroxide was added with a concentration of 3*10⁻³ mol/L (120 mg/L), which provided an initial specific conductivity of the solution of 660 μS/cm.

In experiments with acetic acid, sodium hydroxide was not added to deionized water. In this case, the initial conductivity of the solution was provided by the acetic acid itself. The 1% acetic acid solution used in our experiments had a specific conductivity of 650 μS/cm at pH = 3.3.

All experiments were carried out at a discharge current of 80 mA and a distance between the electrode and the surface of the solution of 6 mm. The solution was circulated through a 250 ml discharge cell using a KNF Flodos NF 30 KPE membrane pump at a rate of 0.25 L/min.
3. Results and discussion

Two series of experiments were carried out. In the first series of experiments, the dependence of the transfer coefficients of water and isopropanol on the type of reactors was investigated, the main difference of which was the different diameters of the discharge chambers and, as a consequence, different areas of the free surface of the liquid (Table 2). It was found that the water transfer coefficient when passing from a discharge chamber with a diameter of 8 mm to a discharge chamber with a diameter of 15 mm (an increase in the free surface area of the liquid by a factor of 3.5) decreases, and when passing from a discharge chamber with a diameter of 15 mm to a discharge chamber with a diameter of 22 mm (increase of the free surface area of the liquid by a factor of 2.15) does not change. That is, it was found that the water transfer coefficient does not increase with an increase of the free surface of the liquid. Thus, it can be concluded that the transfer of solution components into the gas phase occurs mainly in the discharge zone itself, and not from the free surface of the liquid under the action of hot air flows. The higher water transfer coefficient in the discharge chamber with a diameter of 8 mm can be explained by the significant heating of the chamber walls due to its small diameter and, as a consequence, the boiling of the liquid in contact with the wall. This can also explain the higher transfer coefficient of isopropyl alcohol in this discharge chamber. To avoid this effect, the following series of experiments were carried out with a discharge chamber 15 mm in diameter (discharge chamber No. 2).

Table 2. Transfer of the components of 1% isopropanol solution in different reactors with different free surface area of the liquid, the operating mode of the reactors is without stirring.

| Reactor   | Water transfer rate, g/min | Water transfer coefficient, molecules/ion | The ratio of the concentration of alcohol in the condensate and in the solution | Alcohol transfer coefficient, molecules/ion |
|-----------|---------------------------|------------------------------------------|--------------------------------------------------------------------------------|------------------------------------------|
| Reactor №1 | 1.5                       | 1680                                     | 0.46                                                                          | 1.8                                      |
| Reactor №2 | 1.12                      | 1250                                     | 0.29                                                                          | 0.86                                     |
| Reactor №3 | 1.12                      | 1250                                     | 0.20                                                                          | 0.59                                     |

In the second series of experiments for reactor No. 2 (discharge chamber 15 mm in diameter), the dependence of the transfer coefficients of water and various organic substances on the stirring mode of the solution in the reactor was investigated. In the experimental setup, to maintain a constant temperature of the solution, it was circulated through the discharge cell and a special heat exchanger using a membrane pump. This made it possible to maintain the temperature of the solution in the discharge cell outside the discharge chamber at a level of 20-30 °C. However, in the discharge chamber itself, near the surface (Figure 1), the solution temperature could differ significantly from this value. As shown by direct thermocouple measurements, the temperature of the solution at a distance of 2–3 mm from the surface in the discharge chamber significantly depended on the stirring mode of the liquid in the discharge chamber. The stirring mode of the liquid near the surface depended on the height of the part of the discharge chamber that is filled with the solution (X value in Figure 1).

Two modes have been investigated. In the mode, which we will conventionally call the "solution stirring mode", the discharge chamber only touched the solution surface, that is, the height of the part of the discharge chamber filled with the solution was practically zero. In this case, the solution was well mixed. Direct thermocouple measurements showed that the water temperature in the discharge chamber near the surface, as in the rest of the discharge cell, was equal to 20-30 °C.

In the mode, which we will conventionally call the “mode without the solution stirring” the height of the part of the discharge chamber filled with the solution was 5 mm. This five-millimeter layer of liquid was strongly heated and did not convectively mix with the rest of the solution due to the higher temperature and lower density. The boundary of the heated layer was clearly observed visually due to the difference in refractive indices. Direct thermocouple measurements showed that the water temperature in this layer reached 80-90 °C.
It was found that in the mode without stirring, the transfer coefficients of water and organic compounds are significantly higher than in the mode with stirring (Table 3, 4). So for water without organic compounds, the water transfer coefficient in the mode without stirring is 7.3 times higher than with stirring. For a 1% isopropanol solution, the transfer coefficient of water in the mode without stirring is 14 times higher than with stirring, and the transfer coefficient of isopropanol is 17.6 times higher. For a 1% solution of benzyl alcohol, the transfer coefficient of water in the mode without stirring is 8.8 times higher than with stirring, and the transfer coefficient of benzyl alcohol is 11 times higher.

Table 3. Transfer of the components of the solution, with different compositions of solutions, reactor No. 2 with stirring.

| Solution         | Rate of water transfer g/min | Water transfer coefficient, molecules/ion | The ratio of the concentration of alcohol in the condensate and in the solution | Alcohol transfer coefficient, molecules/ion |
|------------------|------------------------------|------------------------------------------|--------------------------------------------------------------------------------|---------------------------------------------|
| No organics      | 0.17                         | 190                                      | -                                                                           | -                                           |
| 1% isopropanol   | 0.08                         | 90                                       | 0.23                                                                       | 0.049                                       |
| 1% benzyl alcohol| 0.16                         | 180                                      | 0.14                                                                       | 0.044                                       |

Table 4. Transfer of the components of the solution, with different compositions of solutions, reactor No. 2 without stirring.

| Solution         | Rate of water transfer g/min | Water transfer coefficient, molecules/ion | The ratio of the concentration of organic matter in the condensate and in the solution | Transfer coefficient of organic matter, molecules/ion |
|------------------|------------------------------|------------------------------------------|--------------------------------------------------------------------------------|-----------------------------------------------------|
| No organics      | 1.24                         | 1390                                     | -                                                                           | -                                                   |
| 1% isopropanol   | 1.12                         | 1250                                     | 0.29                                                                       | 0.86                                               |
| 1% butanol-1     | 1.03                         | 1150                                     | 0.41                                                                       | 0.93                                               |
| 1% benzyl alcohol| 1.40                         | 1570                                     | 0.18                                                                       | 0.49                                               |
| 1% acetic acid   | 1.12                         | 1250                                     | 0.16                                                                       | 0.63                                               |

This means that the transfer coefficients of water and organic compounds from aqueous solutions in a discharge with a liquid cathode depend significantly on the temperature of the solution. But, if the transfer coefficients substantially depend on the temperature of the solution, is the transfer of the components of the solution into the gas phase nonequilibrium in this case? It is known that isopropanol, for example, is a lower-boiling component of a solution than water and can be effectively transferred into the gas phase simply by heating the surface of the solution; therefore, its study does not allow us to give an unambiguous answer to this question. In this regard, the study of high-boiling substances is of particular interest. Such, for example, butanol-1 (boiling point 117 °C), acetic acid (boiling point 118 °C) and benzyl alcohol (boiling point 205.8 °C). The transfer coefficients obtained by us for these substances are comparable with the transfer coefficient for isopropanol, which indicates the nonequilibrium character of the transfer (Table 4).

This means that the temperature of the solution, apparently, has a decisive effect on the nonequilibrium transfer of water and organic compounds from aqueous solutions to the gas phase under the action of a discharge with a liquid cathode.
4. Conclusion
It is shown that a change in the area of the free surface of a liquid in a plasma-chemical reactor has no significant effect on the rate of transfer of water and organic compounds from solution to the gas phase under the action of a direct current discharge with a liquid cathode.

It is shown that the stirring mode and the temperature of the solution have a decisive effect on the rate of nonequilibrium transfer of water and organic compounds from solution to the gas phase in a discharge with a liquid cathode. With an increase of the temperature of the solution, the rate of nonequilibrium transfer of water and organic compounds into the gas phase increases rapidly. It is also shown that a significant increase of the temperature of the solution near the surface of the liquid in the discharge chamber of the plasma-chemical reactor can be caused by heating from the action of the discharge in the presence of walls in a narrow layer of solution with a thickness of only a few millimeters.

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