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Influence of Solution Mineralization on Decomposition of Its Components under Discharge Electroradiolysis Conditions

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Abstract

Based on the measured yields of the hydrogen peroxide formation and capture of radicals by OH acceptor (isopropanol, phenol), dependences of the current efficiency of water decomposition as well as of an efficiency of an electron capture by an acceptor (nitrobenzene) on the electrolyte concentration (sodium and ammonium tetraborate) in water solutions being exposed to anodic microdischarges have been determined. Non-monotone dependences with maxima have been obtained at concentrations 0.03 mol/l for water decomposition and 0.1–0.15 mol/l for electron capture. This effect is attributable to an increase in a proportion of the anionic current through the discharge plasma–liquid cathode interphase boundary with an increase in electrolyte concentration that lowers the current and power efficiency of the water decomposition and treatment under conditions of a high mineralization of the solution.

INTRODUCTION

In the previous works [1, 2], we have demonstrated that discharges with the electrolyte cathode, including anodic microdischarges, can be used efficiently for purification of household and commercial sewage from the dissolved highly toxic substances that are present in minor quantities much exceeding MPC, though. Literature [3–5] gives evidence that water solutions that are exposed to the discharges exhibit a strong (occasionally extreme) dependence of a gas formation and current efficiencies for transformation of solution components on the electrolyte concentration (electric conductivity). So, it is necessary to consider a mineralization degree of the processed waters in an estimation of a prospective efficiency of decontamination and in selection of the conditions of the action.

As it has been noted in [3], during the process of an intensive mass transfer on the plasma–liquid boundary, a dissolved substance can appear inside the plasma and thus it can be exposed to irreversible thermal decomposition. However, as we have illustrated by the example of phenol solutions, liquid-phase reactions of decomposition [6] obviously dominate at low concentrations of an impurity (<1 mmol/l). Their proportion comprises at least 75–80 % of a total yield of the decomposition of the dissolved impurity, and moreover, the contribution of a plasma pyrolysis in the range of concentrations right up to 0.1 mol/l is significantly less or, at least, it does not exceed a half of the gross yield of phenol decomposition under the effect of microdischarges. In these conditions, the decomposition of an impurity in the solution is initiated for the most part by radical and ion-radical products of so-called electroradiolysis of water (OH radicals, hydrated electrons). The more is the yield of these products under conditions of the discharge influence, the more is the respective energy efficiency of the decontamination method for a given composition of the solution. If a toxic impurity acts as a acceptor of oxidizing radicals (as is, for example, the case with phenol), it will be destructed more effectively under the conditions whereby a greater amount of water molecules is decomposed through the mechanism of electroradiolysis [5, 7] by the ions accelerated within the discharge and, accordingly, more OH radicals are formed. Alternatively if the reactivity of a toxicant is higher in relation to the processes of an electronic capture (for example, organochlorine derivatives), then the efficiency of the destruction of these impurities must be to a greater extent related to the formation of hydrated electrons in the system.

Although hydrated electrons along with OH radicals also represent the products of water ionization decomposition during electroradiolysis, the emergence of their additional quantity due to the formation of a radical-electronic pair is not ruled out during the transfer of energy onto the anion of an electrolyte dissolved in water [5]. Hence, it can be assumed that the destruction efficiency of the toxicants that undergo disintegration by the electron-capture must rise with the increased concentration of the electrolyte in the water solution. However, the regularities of a change in the yields of water decomposition to form radicals and of the formation of electrons have not been studied yet in a wide range of electrolyte concentrations.

The purpose of this work is the study of a dependence of the yields of water decomposition to form radical products and of the capture of excess electrons by acceptors in the liquid phase of an electrolyte cathode on the factors that are determined by the concentration of water solution of the electrolyte.

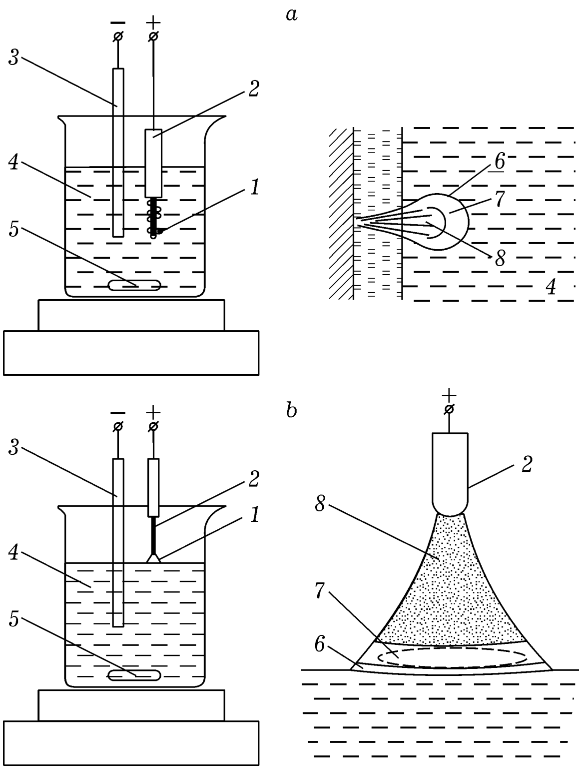

Fig. 1. Diagram of experimental setups and the discharge systems: *a* − anodic microdischarges, *b* − steady state discharge above electrolyte; *1* − gas discharge, *2* − anode, *3* − counter electrode, *4* − aqueous electrolyte, *5* − magnetic stirrer, *6* − field of cathodic drop, *7* − field of negative luminescence, *8* − positive column.

EXPERIMENTAL

Experimental research of the treatment processes of the model water solutions of electrolyte by anodic microdischarges and by a steady state glow discharge were conducted in the setups that are schematically represented in Fig. 1, and in a setup of a flow-through type [1]. The solution of sodium tetraborate in a range of concentrations up to 10^{-1} mol/l was for the most parts used as an electrolyte, and to provide higher concentrations of an anion (up to 0.5 mol/l) at an elevated electric conductivity, a solution of ammonium tetraborate was used. A specific electrical conductivity of the solutions was measured by the OK-102/1 conductivity apparatus directly in a cell. The full range of a variation in the concentration of an electrolyte comprised $(0.2-500) \cdot 10^{-3}$ mol/l.

Selection of electrolyte has been determined by its properties. On the one hand, the characteristics of the anodic oxide and microdischarges in this electrolyte are constant during the experiment. On the other hand, the anion of this electrolyte does not possess the acceptor properties in relation to OH radicals and to excess electrons, and in addition, it is typified by a sufficiently high value of vertical potential of the intraliquid ionization, this value being close to that for water. The selection of acceptors was restricted to those of them that have no effect on the electrical conduction of the solution. Selectivity of the acceptors and of the channels for their transformation in the course of the reactions with various types of radicals was taken into account, as well as potential for reliable distinguishing the characteristic bands during spectrophotometric registration of the products of their reactions with radicals against the background sinal of alternative components of the solution. Isopropanol was applied as an OH radical acceptor (registration of the product of OH capture, specifically, acetone). Nitrobenzene was used as an electron sink (registration based on the product of a selective reaction with the electron, specifically, nitrosobenzene).

Experiments with anodic microdischarges at the reduced concentrations of the electrolyte (see Fig. 1, *a*) as well as comparative experiments with a steady state glow discharge between a wolframic anode and the surface of the electrolyte (see Fig. 1, *b*) were conducted in a water-cooled pyrex glass beaker under stirring with a magnetic stirrer. In a flow-through setup, a water solution of an electrolyte from a receiver of capacity 0.5 l was cyclically pumped at a rate of ~1 l/min through a titanium flow-through reactor of capacity ~10 ml, inside of which an anode was arranged that was made from tantalum or aluminium. The walls of the reactor served as a negative counter electrode of the cell. To attain a steady regime of the microdischarge burning, a layer of anodic oxide was previously moulded in the electrolyte solution, the composition of which was the same as the examined one. A process was considered to be completed when the voltage of the cell flattened out with a steady state level, and the moulding quality was considered to be satisfactory unless the fraction of leakage currents through the shaped oxide layer was over 3 % with reference to the total discharge current. A volume of the processed solution comprised 0.5 l.

Source of the rectified voltage with current stabilization was made up of a mains supply transformer, an autotransformer, and a diode bridge (with the additional parallel equalizing capacity that was equal to 50 μF, at the output in the experiments with the steady state discharge). In the latter case, the discharge cell was connected additionally to the output of the source via a ballast series-connected resistor of the 2 kЩ resistance. A soft current stabilization was provided by a connection in series with a primary winding of the transformer of 12 μF capacity; therefore, a downward-sloping volt-ampere characteristic of the source with an idling voltage U_{idl} = 2 kV and a short circuit current $I_{s.c.}$= 180 mA was shaped. The working parameters of the process were as follows: mean stabilised current intensity 0.1 A, potential drop in the cell 500–1500 V (depending on the solution electroconductivity). A temperature of the electrolyte solution didn't exceed 25 °C.

In the experiments with a steady state discharge, a length of the discharge gap was set constant and equal to (1 ± 0.05) mm. Igniting of the "oversurface" discharge was made at $U = U_{idl}$ of the power supply by approaching the anode to the surface of the solution by means of the fine adjustment screw. To make an estimate of the dependence of the current density at the electrolyte cathode on the mineralization of the solution, an intensity of the discharge current was preset in the range of 20–150 mA with the step of 10 mA. A time-averaged diameter of the cathodic spot was measured, the spot being under these conditions in the form of an evenly shone circle on the surface of the electrolyte. Measurements were made by means of a MBS-2 microscope with the scale that was built in the eyepiece, the scale being divided into 100 points. The scale interval at two magnification degrees we have used was 0.067 and 0.033 mm. An integrated current density on the cathodic spot of the discharge was determined as a ratio of the preset current intensity to the measured spot area. In the studied ranges of concentrations, the measured current density on the spot varied within the limits of 0.3–3 A/cm^2. Current density experimental values dispersion was as high as 20 %.

Analysis of a sample was performed from the absorption spectra in the region of 200–800 nm by means of an UV-2201 Shimadzu two-beam spectrophotometer. H_2O_2 concentration was determined from an integral intensity of the band of a titanium-peroxide complex with an absorption maximum in the region of 406 nm with a calibration from the results of the iodometric titration. The nitrosobenzene concentration was determined from the intensity of a band with λ_{max} = 745 nm (ε = 45 l/(mol · cm)), and that of acetone, from a band with λ_{max} = 270 nm (ε = 17.6 l/(mol · cm)).

Accumulation curves of all the specified products had a linear form up to the values of an integrated current doze (normalized to the reactor volume) of about 0.1 A · s/cm^3. Faradaic efficiency (current efficiency) of the products was determined from a slope of the initial linear sites in the accumulation curves. The yields y_{-H_2O} of water decomposition (in moles per Faraday of the total discharge current) were determined by the procedures set forth in [7]: from the sum of the yield $2y(H_2O_2)$ recombination and the yield y_R of capture product of OH radicals by an acceptor [S], and also from a slope of the experimental curve in $y_R[S]$ − [S] coordinates.

RESULTS AND DISCUSSION

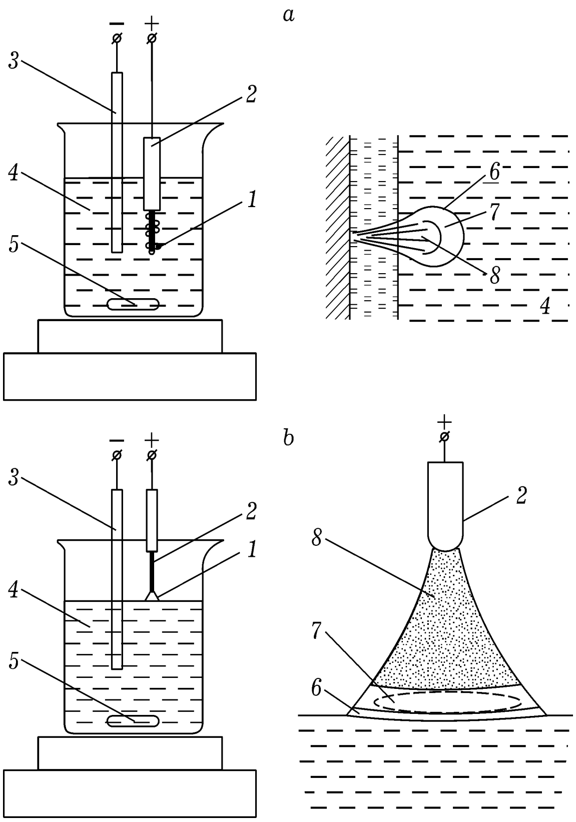

Fig. 2. Dependences of cathodic density of discharge current j_c (*a*) and current efficiencies of OH radical capture by acceptor (isopropanol, phenol) (*b*), of water decomposition (c), of an electron capture by the acceptor (nitrobenzene) (*d*) on the electrolyte concentration. Yields are normalized to their intrinsic maxima.

Figure 2 represents the dependences of characteristic parameters *vs.* electrolyte concentration (anion − tetraborate) for the process of influence of the discharges under investigation upon the water solution. The current density j_c (see Fig. 2, *a*) on the electrolyte cathode was determined during the experiments into an optical measurement of the area of a shone spot. We succeeded in experimental measuring of this density only for a steady state glow discharge over the surface of the electrolyte cathode. Nevertheless, given that chemical effects of influence of the steady state and quasistationary discharges are close in their quantitative characteristics [5], makes it possible to use these data for qualitative comparisons in the case of anodic microdischarges also. It is evident that the j_c magnitude grows with an increase in the concentrations of the electrolyte up to 0.02–0.03 mol/l, and further remains practically constant. Experimental dependence of the yield y_{S+OH} of a capture of the OH radical by an acceptor S (see Fig. 2, *b*) has been constructed on the basis of determination of the yield of phenol decomposition and of the yield of acetone as a reaction product of the OH radical with isopropanol. It can be seen that the maximum of the yield y_{S+OH} is observed in the range of the values of the electrolyte concentration in the vicinity of 0.01 mol/l. Dependence of the y_{-H_2O} yield of water decomposition (see Fig. 2, c) on the concentration of tetraborate anion in the solution is also characterized by the availability of a maximum, but it is displaced in the region of great concentration values (0.03 mol/l). The yield y_{S+e} of nitrosobenzene, the product of a capture e_{aq} by nitrobenzene (see Fig. 2, *d*), appears differently: a long site of monotonous increase up to a maximum at the tetraborate concentration about 0.1–0.15 mol/l gives way to a drop that is as great (with allowance made for variability of the data) as approximately 15–20 % of the maximum value of the yield of electron-capture.

It should be remarked specially that the position of the maximum y_{-H_2O} (see Fig. 2, *c*) belongs to the region of a maximum gas-making that has been observed in [3] for concentrated aqueous-alcoholic solutions. This coincidence can be suggestive of an appreciable contribution to the gas-making process at high concentrations of a low-boiling organic component [S], the contribution being made not only by the reactions of plasma pyrolysis that are recognized as those prevailing in the work [3], but also by the liquid-phase reactions of oxidizing radicals.

Comparison of the obtained dependences makes it possible to come to the following conclusions. The region of electrolyte concentrations that is ≤0.02 mol/l is characterized by a monotonous increase in the current density as the electrolyte concentration increases. On the one hand, the more is j_c, the more is the intensity of an accelerating field in the cathodic region of the glow discharge [8] and, accordingly, the more is the mean kinetic energy of the incident ions and the number of H_2O^+ electron geminal pairs that are generated per one accelerated ion. On the other hand, with an increase in j_c, the local density of tracks in a near-discharge layer of a solution increases and thus the yield y_{OH+OH} of the quadratic OH recombination rises because of a convergence of the adjacent tracks. Therefore, with an increase in j_c, the yield y_{S+OH} of the products of OH capture competitively declines. The mere fact that the yield y_{S+OH} continues to drop with an increase in the concentration upon a termination of the growth in the observed density of the total discharge current is indicative of the influence of another factor (in addition to the competitive recombination channel) that depends on the electrolyte concentration.

At higher concentrations of the electrolyte (>0.03 mol/l), the current density j_c is practically constant, the yield y_{S+e} of a capture e_{aq} continues to increase, while y_{-H_2O} (the sum of y_{S+OH} and y_{OH+OH}) drops, which is caused probably by the competition of H_2O_{aq} and the dissolved anion to gain an energy of the ionization excitation that is transferred by an accelerated ion. The contribution of such kind of competition at small (unlike the classical radiolysis) kinetic energies of the accelerated particles can become significant in spite of a lower concentration of anions as compared to water molecules. There are, at least, two reasons for such behaviour. The first one lies in the fact that a formation cross-section of the electron–anion radical geminal pair is more than that for an electron – so-called H_2O^+ water hole pair, because the potential of an electron separation from anion is less as compared to water molecules [9]. The second reason is a smaller probability of recombination reaction of the radical – electron pair that is formed from anion in view of the lacking Coulomb attraction of the recombining partners. Therefore, even though the comparable cross-sections of competitive processes of the formation of radical – electron and water hole – electron geminal pairs from anion and from a water molecule, the probability of the formation e_{aq} from an anion is more. A decrease in y_{-H_2O}, upon a maximum is attained in this region of concentrations, is explainable quite logically by the reverse reactions of cross recombination of an electron, which has arisen upon disintegration of an anion, and a water hole or by the reactions between OH and an electron.

In the range of values of the electrolyte concentration that is > 0.1 mol/l, both y_{-H_2O} and y_{S+e} decrease (see Fig. 2, *c*, *d*), although $j_c \approx$ const. Accordingly, the intensity of the accelerating field, and consequently, the capability of the particles accelerated in plasma to decompose water have to be invariant. Most likely, the secondary ion-electronic emission takes leading role at these concentrations or, owing to concentrating of an excessive anionic charge near to the plasma–solution interface, an appreciable component of the current appears by way of delivery of anions into plasma of the discharge. By virtue of the fact that the yield of the products in the experiment is normalized to the total measured current intensity, and the real action is determined by a current of the accelerated positive ions, then the measured current efficiency decreases. An assumption can also be made that the drop in a comparative fraction of the current of positive ions occurs at the penalty of an increase in the coefficient of the secondary ion-electronic emission. However, a drop in the yield of the excess electrons in a liquid will inevitably cause the fraction of the electronic current through the liquid–plasma interphase boundary to lower and thus the fraction of the current of positive ions to increase. Therefore, the effect of the ion-electronic emission can manifest, in an extreme case, as tendency of y_{S+e} to a certain asymptotical value and not to its decrease in the process of an increase in the electrolyte concentration.

Let us consider the second variation, entering of an excessive quantity of anions into the plasma of the discharge upon an evaporation of the near-discharge layer of the solution. It also constitutes an electric current through the interphase boundary and makes a contribution to the total current intensity that is measurable in the experiment. It is easy to demonstrate that in a shallow layer near to the plasma-solution interphase boundary, a superfluous density of the negative charge z is created in the liquid, the density defined by the Poisson equation with allowance for the Debye shielding [5]: $\rho_{ex} = 2FcE_0L_D(zF/RT)$, where c is the electrolyte concentration (mol/cm^3); E_0 is the intensity of the electric field on the interface from a liquid side that is equal to $E_c/\varepsilon_{H_2O} \approx E_c/80$ (E_c is the near-cathode intensity in the discharge, ε_{H_2O} is a relative dielectric constant of water), L_D is the Debye length of shielding in the electrolyte [10] that is approximately equal to $c^{-1/2}10^{-9}$ cm; F is Faraday constant. If we accept that a temperature of the near-boundary solution layer is close to the boiling point of water, then the local “mole fraction” of an excess negative charge in this shallow layer $x_Z \approx 2.16 \cdot 10^{-6}c^{1/2}E_0$.

The solute, for example A, can get inside the plasma in the following manner. At first, diffusive-convective and electromigratory transfer occurs from a depth of the solution to the boundary of a steam-plasma bubble. Further, there are several ways: in the first place, this is a layer-by-layer evaporation of the volume of the solution, which immediately adjoins to the plasma, as a whole, *i.e.* with the composition preserved; second, a cathode sputtering of the liquid phase in the form of clusters or fine drops with their subsequent full or partial evaporation within the plasma; third, a selective evaporation with one or other selectivity degree. The third variant can lead to the gas phase that is enriched by a more volatile substance A relative to the x_A/x_{H_2O} mole fraction ratio in the solution. In practice, the combination of all the listed mechanisms, most likely, occurs.

For the impurity that is less volatile than water, for example for an inorganic salt (of a strong electrolyte), it has been found experimentally that the substance transferred into plasma and the initial solution show the identical composition, *i.e.* no enrichment or depletion occurs upon the transfer [11]. Therefore, having accepted that the concentration [A] at the interphase boundary is equal to the concentration in the depth of the solution, and knowing the current efficiency $y_{vap}(H_2O)$ of water evaporation, we can easily estimate the faradaic efficiency (current efficiency) y_T of transfer of the solute A through the interphase boundary: $y_T(A) = y_{vap}(H_2O)x_A/x_{H_2O}$. In so doing, it will suffice to make the allowance only for evaporation of the boundary layer of the liquid (together with the solute) or its droplet sputtering with the preserved composition.

Only electric power that is passed on to a near-discharge boundary layer from the near-solution region of the discharge can be expended in delivering a substance into plasma due to an evaporation of this layer of the solution. In the case of evaporation of droplets, the power that is generated in the other regions of the discharge is expended as well. It is evident that only the substance inherent in the evaporated portion of the droplets enters into plasma and takes part in the transfer of current. Therefore, the yield $y_T(A)$ of those fed into plasma for not so concentrated solution ($[A] << [H_2O]$) in both cases is determined by product of a mole fraction $x_A \approx [A]/[H_2O]$ by the faradaic efficiency of water evaporation

$y_{vap}(H_2O) = F\Delta U/(\Delta H_{vap} + C_p\Delta T)$

Here ΔH_{vap} and C_p are the molar evaporation heat of water and heat capacity respectively; ΔT is the temperature difference in the depth of a solution and on the interphase boundary, ΔU is the drop of potential that determines electric power for heating and evaporation into plasma at a given discharge current; F is Faraday constant. If temperature in the bulk solution is assumed to be ambient, then $(\Delta H_{vap} + C_p\Delta T)/F \approx 0.5$ V and a power yield of water evaporation $G_{vap}(H_2O) \approx 200$ molecules/100 eV, faradaic efficiency $y_{vap}(H_2O)$ of evaporation equals numerically to $2\Delta U$ (U is expressed in V). Hence for the faradaic efficiency of a transfer of the dissolved component through the interphase boundary into plasma may be written as $y_T(A) \approx 2x_A\Delta U$. This is true only for a case when

$[A] << [H_2O]$, when a heat capacity and an evaporation heat of the mixture are practically the same as for the pure solvent. To make the top estimate of $y_T(A)$, it is logical that the ΔU parameter is set equal to the total drop of potential at the discharge gap.

The maximum yield of a transfer of an excess anionic material z (the mole fraction x_Z of which in the solution is small) through the interphase boundary into plasma is $y_Z = y_{vap}(H_2O)x_Z = 2\Delta U 2.16 \cdot 10^{-6} c^{1/2} E_0$. The cathode vicinity potential E_c in a discharge plasma with the electrolyte cathode, according to the estimates of [12], comprises ~10^6 V/cm, and an effective magnitude ΔU can be taken to be equal to 250–400 V [6]. With these assumptions, a fraction y_Z of the anionic current for the electrolyte solution strength of 0.5 mol/l will be equal to ≈0.15–0.24, what approximately matches a comparative magnitude of the observed drop in the yield of electron-capture (see Fig. 2, *d*).

CONCLUSION

Thus, under conditions of elevated (>0.1–0.15 mol/l) electrolyte concentrations, a perceptible contribution to the current passing through the plasma–solution interphase boundary during a discharge with the electrolyte cathode is made by the process of the evaporative interphase transfer of the electrolyte anions, the excess of which is accumulated in the near-discharge region of the solution. At a substantial fraction y_Z of the anionic current, the observed current efficiency of the formation or the decomposition of the substances, even in the case of a constant ionizing power of the ions that are accelerated in the discharge, drops with the increasing concentration of the electrolyte. Therefore, a further increase in the mineralization of the solution is inexpedient to reach a greater effect that is suggested in electroradiolytic cleansing of waters from electrophilic toxicants [2] (for example, organochlorine compounds) by the electroradiolysis method. In this case, a reasonable efficiency of water purification from electrophilic toxicants occurs in a range of electrolyte concentrations of ~10^{-2}–10^{-1} mol/l that is typical for the majority of waste and household waters.

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REFERENCES

1 A. M. Badalyan, O. V. Polyakov, L. F. Bakhturova, *Chem. Sust. Dev.*, 8, 3 (2000) 339.
2 O. V. Polyakov, A. M. Badalyan, L. F. Bakhturova, *Ibid.*, 8, 6 (2000) 855.
3 L. T. Bugaenko, E. G. Wolf, E. P. Kalyazin *et al.*, Plazmokhimiya-90, in L. S. Polak (Ed.), vol. 1, izd. INKHS AN SSSR, Moscow, 1990, p. 8.
4 A. Gyuntershultse, G. Betts, Elektroliticheskiye kondensatory, Oborongiz, Moscow–Leningrad, 1938.
5 O. V. Polyakov, A. M. Badalyan, L. F. Bakhturova, *Khim. Vys. Energiy*, 37, 5 (2003) 367.
6 O. V. Polyakov, A. M. Badalyan, L. F. Bakhturova, *Ibid.*, 38, 2 (2004) 158.
7 O. V. Polyakov, A. M. Badalyan, L. F. Bakhturova, *Ibid.*, 36, 4 (2002) 315.
8 Yu. P. Raizer, Osnovy fiziki gazorazryadnykh protsessov, Nauka, Moscow, 1980.
9 D. A. Babikov, E. E. Son, *Poverchnost`*, 9 (1997) 47.
10 G. Falkengagen, Elektrolity, ONTI-Khimteoret, Leningrad, 1935.
11 A. V. Khlyustova, A. I. Maksimov, V. A. Titov, in: 3 Mezhdunar. simp. po teoreticheskoy i prikladnoy plazmokhimii ISTAPC-2002, Ivanovo, 2002, vol. 1, p. 110.
12 Z. Sternberg, Int. Conf. Gas Discharges, 1970, Inst. Elec. Eng., London, 1970, p. 68.