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The oscillation of concentration field at the membrane-solution interface and transport mechanisms under overlimiting current density

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ABSTRACT

Application of laser interferometry allowed visualization the process of formation and development of the concentration field at the boundary with cation-exchange membrane in a wide range of current densities. Using a cell with horizontally mounted membranes, Mach-Zehnder interferograms were obtained for the interface region of membrane -10^{-2} M NaCl system at constant current intensities and continuous feed of solutions. With an increase of the current density the area of the solution involved in convection intermixing grows, and there appears a non-steady vibrational concentration profile. Video clips demonstrate auto-oscillation of interference band near the surface of ion-exchange membrane, which is proportional to the change of concentration. Digital analysis of video-images showed that with an increase of the current density a stationary state and the inherent order disappear which are changed by non-symmetrical oscillations of the concentration field in a solution.

Keywords: Ion-exchange membrane; Overlimiting current density; Concentration field; Convection instability

1. Introduction

Solution of the problem of mass transfer intensification in the electromembrane systems is impossible without the investigations of the regularities of the ions transfer through membranes at the high and superhigh values of the current density and searching for the new mechanisms of their supply to the interphase boundary of membrane-surface. Therefore, much attention is drawn towards making of the theoretical and experimental investigations of the over-limited state of a membrane [1–17]. It should be noted that the elaboration of the general theory of over-limited state in the electromembrane system is restrained by the gap in the experimental investigations at the currents exceeding the limiting value. One of the reasons for these difficulties is a complex measuring technique for the thickness of diffusion layer and concentration field near the surface of membrane.

Application of laser interferometry allowed visualization the process of formation and development of the diffusion layers in a solution near the surface of a cation-exchange membrane in a wide range of current densities.

2. Experimental

The experiments were made in the seven-compartment electrodialysis cell where compartments were separated by cation-exchange and anion-exchange

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membranes. Central investigated compartment consisted of single-type heterogeneous cation-exchange membranes MK-40, that allowed to consider a membrane relative to cathode as an individual one. The cation-exchange membrane MK-40 consists of highly acidic cation-exchanger CU-2 with 65% sulpho-ionogenic groups and polyethylene as a filler material, which increases the mechanical strength of the membrane.

The length and intermembrane distance for this compartment were $4.2 \cdot 10^{-2}$ m and $2.0 \cdot 10^{-3}$ m respectively. The coordinate in the direction of solution feed was $2.7 \cdot 10^{-2}$ m. Sodium chloride solution of 10^{-2} M was supplied to the flow passage with the linear velocity $1.3 \cdot 10^{-2}$ m/s thus corresponding to the laminar flow mode (Re = 2). The experiment was performed at constant current intensities and the continuous feed of solutions.

Rotating compartment it was possible to assign any angle between the investigated membrane and the direction of the Earth gravity field. In the work membrane was in two horizontal positions. The density of solution thus varied with height (medium stratification). In the first case the current was directed in such a way that counterions moved upwards and the depleted diffusion layer was under membrane (less dense layers of solution were above the denser ones) In this case the vector product $\triangle\rho \cdot g = 0$ and hence, the electromembrane system proved to be in the state of a stable concentration-temperature stratification, i.e. convective flows due to the gradients of concentration and/or temperature did not appear. In case of unstable stratification desalination of the solution proceeded above the horizontally situated membrane (denser layers were above the less dense ones) and thereby spontaneous conjugated convective flows could appear in the system under certain conditions.

In the present work we used a Zender-Mach interferometer which has certain advantages over other types of interferometers. Providing high contrast, it enables to study large objects and to localize the bands of equal thickness in an arbitrary plane [18]. The use of laser with the wavelength of 480 nm as a monochromatic light source greatly increases greatly the degree of coherence which provides conditions for an accurate focusing of beams and increases the power of light flux necessary for the study of quick processes demanding quick exposures in photographing. In order to register rapidly varying concentration field video filming was applied (Fig. 1).

Interferograms represent the concentration profiles of solutions and their scale should be determined by the calibration procedure.

In order to calibrate an interferometer several standard solutions of the investigated substance were successively passed through optic cell which did not contain a membrane and then the shift of some arbitrary interference band has been measured (band-tag).

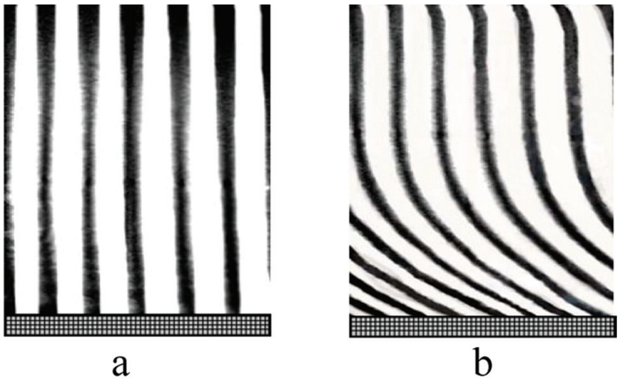


Fig.1. Interferograms at the interface of cation-exchange membrane – 10^{-2} M NaCl solution in the horizontal position at the current density of 0 A/m^2 (a) and 14 A/m^2 (b).

The ratio of the shift for band-tag to the distance between maximum optical density of the interference bands was considered as the relative shift of the band S. Passing successively several standard solutions through the optic cell we obtained linear dependencies of the relative shift on concentrations up to the concentrations of 10^{-2} M.

$$S = \gamma b c_i, \qquad (1)$$

where b is the thickness of a solution layer which is passed by the beam in the optic cell and γ is the partial molar sensitivity.

The study of hydrodynamic state of the diffusion boundary layers is complicated by the presence of the concentration and temperature field. Furthermore, a specific feature of the investigated flows assumes the possible presence of the pulse components of rates in the unstable state of the boundary layer. Visualization of hydrodynamic pattern of the flow in this work was made as follows. Solutions of the investigated substances containing the particles of the aluminium powder or colophony in the suspension state were supplied into the cell compartment. The flow pattern was recorded using video camera with comparison beam of interferometer being shut. The flow rate in a certain local point was determined by the measurement the pass time of the particle for a certain pathway taking into account the preliminarily determined scale measure.

3. Results

Fig. 2 represents interferograms allowing to observe the changes in the interference pattern near the surface

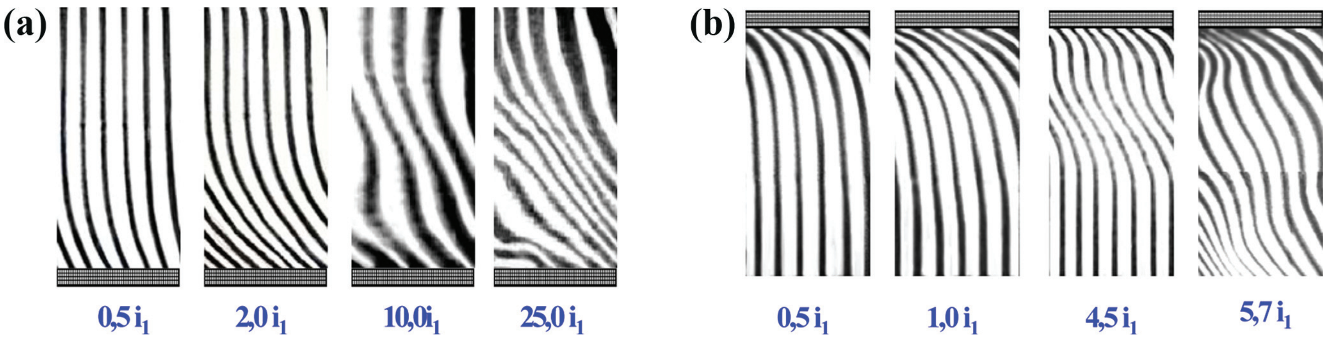


Fig.2. Effect of current density on the fringe pattern at the interface of cation-exchange membrane – 10^{-2} M NaCl solution in the horizontal positions: the depleted diffusion layer is at the bottom (a) and on the top (b) of solution layer.

of MK-40 membrane for the stable (a) and unstable (b) stratification. Normalization was made by the value of limiting current i_1 corresponding to the first inflection point at I–V curve.

With an increase of the current density the shift of the interference fringes in the diffusion boundary layer was observed proportional to the change of concentration in a solution. Concentration distribution was stationary one within the current limits up to 1.5 i_1 at the unstable stratification. Arrangement of membrane system in the Earth gravity filed for the stable stratification did not assume the development of convective instability at the interphase boundary, however, at the one and a half exceeding of the limiting current density an oscillatory character of the interference bands was detected. Irregular and undulating changes in the position and width of the interference bands were observed and oscillatory concentration profile appeared instead of the stationary concentration distribution.

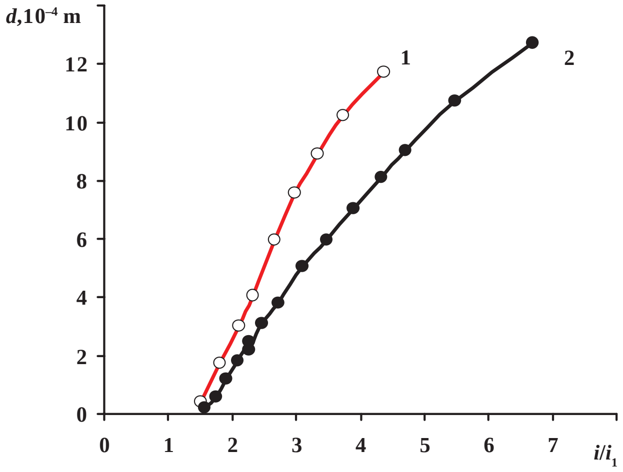


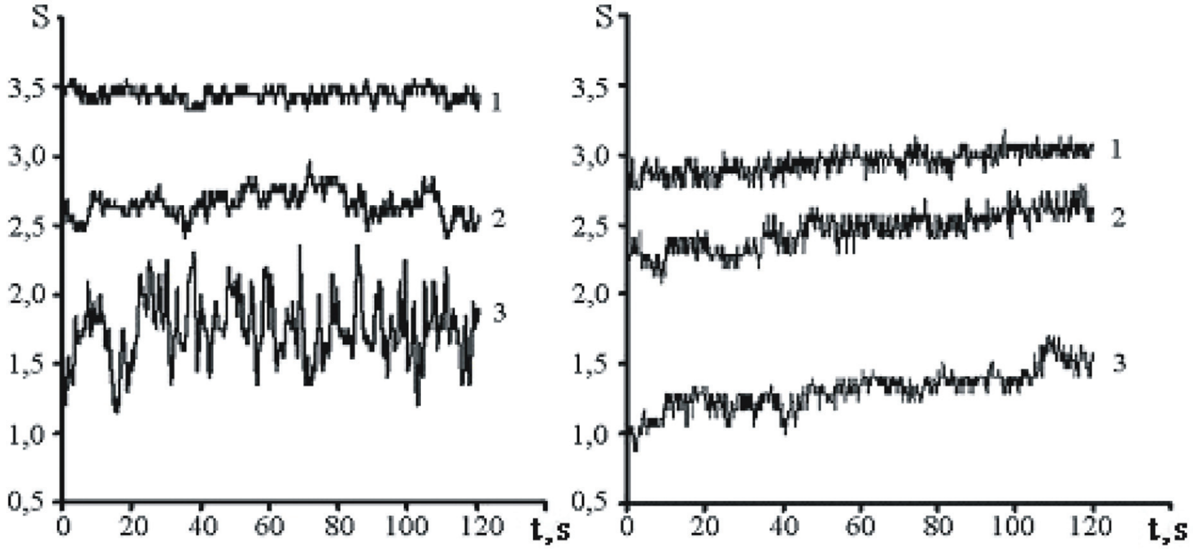
Fig. 3. The size of convective instability area in solution at the boundary with cation-exchange membrane MK-40 under stable (1) and unstable (2) stratification.

In the range of the current values up to fivefold excess of the limiting diffusion one a plateau was still observed meaning constant concentration and laminar flow mode. At the further increase of the current turbular pulsations of the flow passage towards the membrane surface were observed. For the current values of 5–7 i_1 stirring of solution proceeded practically over all the width of the flow passage that was revealed as the fringes broadening and plateau disappearance.

As a result of the performed investigations it was found that with an increase of the current density both the size of the convective instability area (Fig. 3) and oscillations amplitude of the interference fringe were enhanced (Fig. 4).

The character of the obtained dependence for the further increase of current meant the loss of oscillatory stability for the concentration profile. The frequency of oscillations in the investigated current range increased by 4 times for unstable stratification and by more than 2 times – for stable stratification of the system.

The study of hydrodynamic state in a solution at the interphase boundary was made by the flow visualization with the use of colophony suspension. The shaded flow pattern was registered with video camera and interferometer beam being shut. The flow rate in a certain local point was determined by the measurement the pass time of colophony particle for a certain pathway taking into account the preliminarily determined scale measure. Thus, longitude and normal components of the rate for hydrodynamic pulsations in a solution at the boundary with the membrane were estimated. Analysis of the obtained results (Fig. 5) demonstrated that in the high-intensive current modes the values of the normal component for the flow rate in case of hydrodynamic pulsations supplying a substance from the bulk of solution to the membrane surface and thus intensifying mass transfer were comparable with supply flow rate of solution to the membrane flow passage.



a

b

Fig.4. The oscillations of interferometry fringe at interface of cation-exchange membrane – 10^{-2} M NaCl solution in the horizontal position under unstable (a) and stable (b) stratification under current density i/i_1: (a) 3.5 (1), 4.7 (2), 12.2 (3), (b) 2.3 (1), 4.5 (2), 12.3 (3).

Transfer of a substance by convective flows of liquid from the bulk of solution to the surface of membrane in pulsation mode can be characterized by the coefficient of turbulent diffusion in the direction perpendicular to the interphase boundary. Coefficient of turbulent diffusion D_{turb} is connected with the values characterizing turbulent flow.

$$D_{\text{turb}}(x) = V_x \times l_x = V_x^2 T, \quad (2)$$

where V_x is the normal component of the rate of turbulent pulsations, l_x is a scale of pulsation motion towards the interphase boundary that can be estimated with the account of pulsation period of the rate T.

$$l_x = V_x \times T \quad (3)$$

This value exceeds the coefficient of molecular diffusion for sodium chloride ($1.5 \cdot 10^{-9}$ m^2/s) approximately by two orders of magnitude, meaning a high efficiency of mass transfer.

The convection intermixing which appears spontaneously at the membrane-solution interphase destroys the diffusion boundary layer near ion-exchange membrane. Fig. 6 presents experimentally obtained dependence of the total (δ), effective (δ_N) thickness of the diffusion boundary layer and the size of convection instability (d) on the non-dimensional current density under stable stratification.

In the figure the dimensions of the total diffusion boundary layers δ obtained by laser interferometry and linear Nernst approximations δ_N obtained as the intersection of a tangent to the concentration profile drawn from interphase surface to the straight line corresponding to the initial concentration are presented.

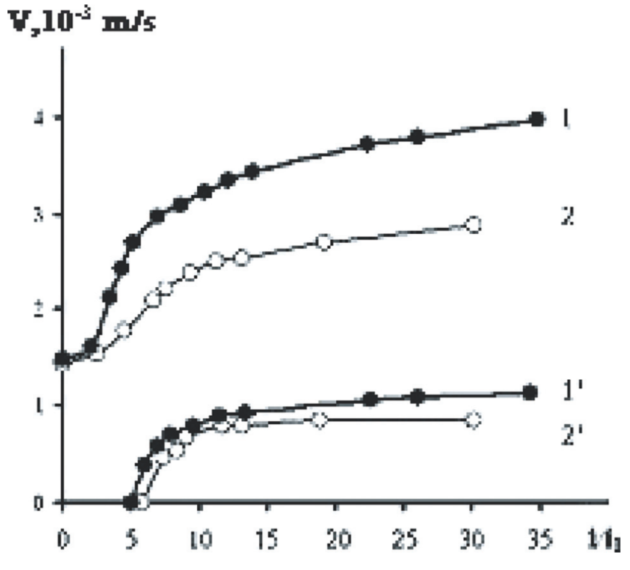


Fig. 5. Longitude (1,2) and normal (1′,2′) components of the hydrodynamic pulsations of flow rate in a solution at the boundary with MK-40 membrane for unstable (1,1′) and stable (2,2′) stratifications.

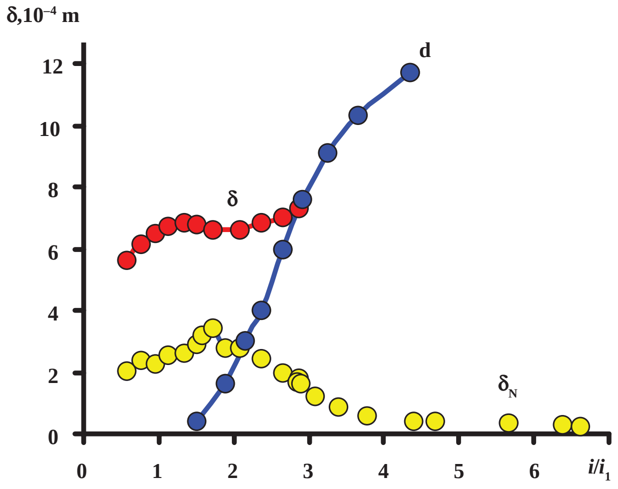


Fig. 6. Total (δ), effective (δ_N) thickness of the diffusion boundary layer and the size of convection instability (d) near cation-exchange membrane MK-40 in stable stratification, 10^{-2} M of sodium chloride solution under linear velocity $1.26 \cdot 10^{-3}$ m/s and the coordinate in the direction of solution feed $2.7 \cdot 10^{-2}$ m.

Linear Nernst profiles were characterized by fewer values than the total values of thickness of diffusion boundary layers. The thickness of a total diffusion boundary layer is equal to the distance from the membrane surface to the point at which the substance concentration reaches 0.99 C_o [19].

It was found that the decrease of effective thickness δ_N was observed at the currents corresponding to beginning of the convection instability at the interphase boundary and (1.3–1.5) exceeded current value corresponding to the first inflection point at I–V curve. At the currents twice exceeded the limiting current hydrodynamic instability comprises the area of solution equal to the effective thickness of the diffusion boundary layer. The destruction of the concentration profile when convection area corresponds to the total thickness of the diffusion layer was observed at the current value 2.5–3.0 i_1. The obtained dependence proved to be unusual and makes the interpretation of the experimental results in accordance with common classical ideas when the thickness of diffusion layer is considered to be constant.

Application of laser interferometry allowed visualization the membrane-solution interface allowed to reveal two stages in the development of convective instability. 1 stage. If the current exceeds the limiting diffusion current density within the range from one and a half up to five times then the following facts are observed: laminar character of convective flows in the diffusion boundary layer, oscillation stability of the concentrations profiles; the main transfer mechanism is migration and diffusion. 2 stage: for 5–6 fold exceeding of the limiting current value the following is characteristic: turbulent pulsations of hydrodynamic flow rate towards the surface of membrane; concentration profiles loose their oscillation stability; transfer mechanism is convective one (i.e. transfer of a substance towards membrane is performed due to pulsations of hydrodynamic flow rate that are normal to the surface of membrane).

The main idea for explanation of the phenomenon of superlimiting currents in electromembrane systems is revealing of the mechanism resulting in destruction of diffusion boundary layers formed in a solution near the surface of membrane during the pass of the current flow. There are two mechanisms of convection providing additional, in comparison with forced convection, mixing of depleted solution. The fist type of convection is gravitational convection, which arises due to the nonuniform distribution of solution density (gradients of concentration and/or temperature). Pevnitskaya [7], Budnikov and Timashev [8], Shaposhnik [14] reported that convection instability is connected with thermo-convection phenomenon due to release of Joule heat in the desalinated solution being in contact with the surface of cation-exchange membrane. Hence, this phenomenon is more likely to occur in case when the lighter layer is at the bottom.

If the depleted diffusion layer is on the top of solution layer, then no gravitational convection arises. The most probable mechanism of intensive mixing is electroconvection occurring due to the action of the electric field on the electric space charge in the boundary depleted solution [9,12].

One of the main factors determining behavior of the ion-exchange membranes at the current density exceeding the limiting diffusion values are the properties of their surfaces. Materials used for producing of MK-40 membranes are known to be heterogeneous. They represent rather large regions of inert binding agent around the grains of conductive resin. From the analysis of the data [15–17] it follows that for this kind of membranes the size of conductive areas at the surface is of 10–30 mcm while the part of conductive surface is 0.22 of the total surface area for the membranes MK-40.

Unlike of homogeneous membranes heterogeneous ones are characterized by concentration of the current paths near the surface regions with rather high conductivity thus resulting in a higher local current density through these regions. Hence, a higher step in the potential and a greater value of water dissociation rate at the heterogeneous surface. Moreover, inhomogeneous membrane structure favours initiation of convection transfer mechanisms. The presence of electrical nonuniformity on the cation-exchange membrane surface should facilitate the rising of electroconvection.

Theoretical and experimental investigations devoted to the role of electroconvection as a possible mechanism for destruction of diffusion layer have demonstrated that this phenomenon is one of the main mechanisms for intensification of mass transfer during electrodialysis of diluted solutions [1,2,9–12,15–17].

4. Conclusion

Experimental investigations of the regularities in the appearance and development of the oscillatory instability for the concentration field in a solution near the surface of sulpho-cation-exchange membrane were performed in the work.

Appearance of hydrodynamic instability in the solution was observed at the currents exceeding the limiting value. Vibration character of concentration field was visually observed and the size of instability area of this field was also determined. The increase of the convection instability region of the solution in the vicinity of the membrane surface and the decrease of the effective thickness of the diffusion layer with the uprising of the current density in an overlimiting region has been revealed experimentally. There are two effects of convection destroying the diffusion boundary layer: gravitational free convection and electroconvection. The fact that development of oscillation does not depended on the membrane position in the gravity field approves that the most probable mechanism of oscillation is electroconvection.

The study of hydrodynamic state in solution at the interphase boundary demonstrated that in the high-intensive current modes the values of the normal components of the flow rate for hydrodynamic pulsations supplying substance from the bulk of solution to the surface of membrane and intensifying mass transfer were comparable with supply flow rate of solution into membrane passage flow.

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