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SHORT COMMUNICATIONS

Effects of Circulation and Facilitated Electromigration of Amino Acids in Electrodialysis with Ion-Exchange Membranes

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Abstract—Dependences of fluxes of the mass of amino acids and mineral ions on the density of a direct electrical current in an electrodialysis process are obtained experimentally. Mutual influence of components on transport at low strengths of the electric field in membranes is discussed. Effects of circulation and facilitated electromigration of amino acids are considered. At a small excess of the limiting current density, the effects lead to a decrease in fluxes of amino acids through membranes. At a large excess of the limiting current, the effects result in an intensive conjugated transport of bipolar ions with the medium ions through membranes.

INTRODUCTION

An important feature of the transport of amino acids through ion-exchange membranes in an electrodialysis is the presence of a maximum of fluxes of mass as a function of the current density. The maximum occurs at a limiting diffusion current density [1]. It was established that, during an electrodialysis of a one-component solution of glycine (Gly), fluxes of its mass through ion-exchange membranes increase with increasing the current density to a limiting value (linear concentration polarization of ion-exchange membranes) and then decrease in the region of nonlinear concentration polarization. The decrease in the fluxes of an amino acid in the region of nonlinear concentration polarization is called the barrier effect [1, 2]. In this work, we study the way fluxes of mass depend on the density of an electrical current or strength in the course of electrodialysis of two-component solutions of glycine or phenylalanine (Phe) and sodium chloride. Such solutions model mixtures of amino acids and mineral components in the stage of purification of amino acids in biotechnology processes.

EXPERIMENTAL

The experimental work was performed in an electrodialyzing cell whose seven sections were separated by alternating cation-exchange and anion-exchange membranes of brands MK-40 and MA-40, respectively, in the order shown in Fig. 1. The anode was prepared from platinum, and the cathode was made of stainless steel. The direction of lines of a direct electrical current was orthogonal to that of the solution supply. The size of each section was 0.3 cm (intermembrane separation) by 1 cm by 20 cm (distance in the direction of the solution supply). The solution supplied into section 4 was a studied mixture of solutions of 0.1 M glycine (or, in some experiments, phenylalanine) and 0.01 M sodium chloride. The solution supplied into sections 1, 3, 5, and 7 was a 0.01 M sodium chloride solution. Sections 2 and 6 were supplied with a 0.05 M sodium chloride solution. The experiments were conducted in a galvanostatic mode, monitoring the current in the apparatus, or by imposing a constant strength on one of the membranes (potentiostatic mode). When conducting experiments in the potentiostatic mode, glass capillaries were positioned next to a membrane; the capillaries were connected with silver–silver chloride electrodes through salt bridges. The difference between electrical potentials of the capillaries was measured using a high-resistance voltmeter; it was maintained constant by varying the voltage across the terminals of the electrodialyzing cell.

Glycine and chlorides in solutions issuing from sections 3, 4, and 5 were assayed titrimetrically; phenylalanine was assayed by the method of direct spectrophotometry at a wave length of 257 nm; the content of sodium ions was measured by the method of flame photometry; and solution pH was determined by the method of direct potentiometry with the aid of a glass electrode. From the pH values measured in sections 3 and 5, we judged the attainment of a limiting state on membranes. To this end, we employed the procedure of an asymmetrical polarization of ion-exchange membranes [3]. In particular, to determine the limiting current density at the cation-exchange membrane separating sections 4 and 5, the sodium chloride solution supplied into desalination section 6 was more concentrated than that supplied into desalination section 4. Therefore, upon increasing the current density, the limiting current density was reached first at the cation-exchange membrane separating sections 4 and 5, but not reached at the anion-exchange membrane separating sections 5 and 6. At current densities exceeding limiting values, the excess current is transferred predominantly by ions of the medium that form in the course of irreversible catalytic dissociation of water molecules at interfaces

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between an ion-exchange membrane and solution in the desalination sections [4]. In the case under consideration, once the limiting current density at the cation-exchange membrane separating sections 4 and 5 was exceeded, the current in excess of the limiting value was transferred predominantly by the hydrogen ions. At the anion-exchange membrane separating sections 5 and 6, on the other hand, the limiting current density was not reached, and no neutralizing flow of hydroxyl ions of the medium existed. As a result, a variation in pH of the solution inside the concentration section 5 indicated that the limiting current density was reached at the cation-exchange membrane separating sections 4 and 5.

RESULTS AND DISCUSSION

Is there any difference between mass transfers of an amino acid from a one-component solution and from a mixed solution with a strong electrolyte? To answer this question, we conducted a series of experiments at a constant strength at the cation-exchange membrane MK-40 separating sections 4 and 5 while supplying one-component solutions of sodium chloride or phenylalanine ($c_0 = 0.01$ M) or their two-component solution. For the experiments, we selected the linear portion in the dependence of fluxes on the strength of the field. The results of these experiments are shown in Fig. 2. Fluxes of sodium ions through the cation-exchange membrane from one-component solutions are larger than those of phenylalanine. This is explained, in the first place, by the fact that sodium chloride is almost completely dissociated, whereas the concentration of the phenylalanine cations is equal to a mere 6×10^{-6} M, and the greater fraction is present in the form of bipolar ions. The low concentration of the phenylalanine cations is responsible for the small phenylalanine flux through the cation-exchange membrane.

As follows from the data presented in Fig. 2, fluxes of sodium ions through the cation-exchange membrane from the two-component solution containing phenylalanine are lower than the fluxes in the electrodialysis of the one-component solution. The reason for the decrease in the fluxes observed during the electrodialysis of the mixed solution is conjugated transport of sodium ions and bipolar ions of phenylalanine. The radius of a sodium ion, whose solvation sheath contains bipolar ions of the amino acid in addition to water molecules, is larger than the radius of hydrated sodium ions. This leads to a decrease in the migration rate of sodium ions. Simultaneously, as seen in Fig. 2, the phenylalanine transport increases at the expense of the partial transport of bipolar ions in a conjugated transport with sodium ions. The obtained results suggest that the amino acid transport from mixtures containing strong electrolytes is considerably higher than that from their one-component solutions.

Consider the amino acid transport through ion-exchange membranes during an electrodialysis con-

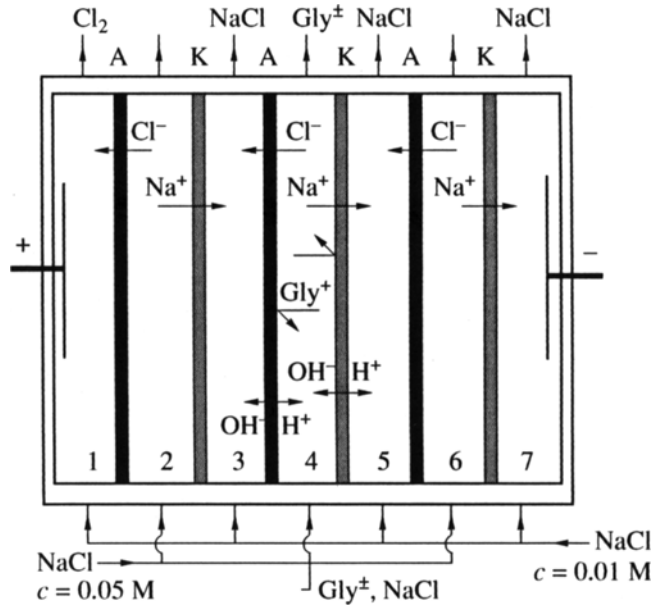

Fig. 1. Schematics of the electrodialyzing cell: (A) anion-exchange membrane, (K) cation-exchange membrane, and (1–7) section numbers.

ducted in a galvanostatic mode in a wide range of current densities. Figure 3 shows how fluxes of sodium, chloride, and glycine depend on the current density. Fluxes of chloride ions through the anion-exchange membrane (curve *1*) and fluxes of sodium ions through the cation-exchange membrane (curve *2*) are much higher than those of glycine through both the anion-exchange (curve *3*) and the cation-exchange (curve *4*) membranes—exactly as in the experiments conducted at low electrical field strengths in the course of the phenylalanine electrodialysis (Fig. 2). The dependence of the glycine flux on the current density exhibits two extremums. The maximum corresponds to the attainment of a limiting current density on the membranes, determined from changes in the solution pH in sections 3 and 5. At high current densities, we observed a sharp increase in the fluxes of hydrogen ions through the cation-exchange membrane and hydroxyl ions through the anion-exchange membrane, which formed during an irreversible dissociation of water molecules at interfaces. Remaining after their electromigration through membranes, the hydroxyl ions in the diffusion boundary layer near the cation-exchange membrane and the hydrogen ions in the diffusion boundary layer near the anion-exchange membrane in section 4 form barrier layers hampering electromigration of glycine (Fig. 4). When electromigrating to the anode, glycine anions find themselves in the diffusion boundary layer near the anion-exchange membrane and, being in the acid medium, recharge to cations in accordance with the reaction

$$NH_2\text{–}CH_2\text{–}COO^- + 2H^+ \longleftrightarrow \overset{+}{N}H_3\text{–}CH_2\text{–}COOH \quad (1)$$

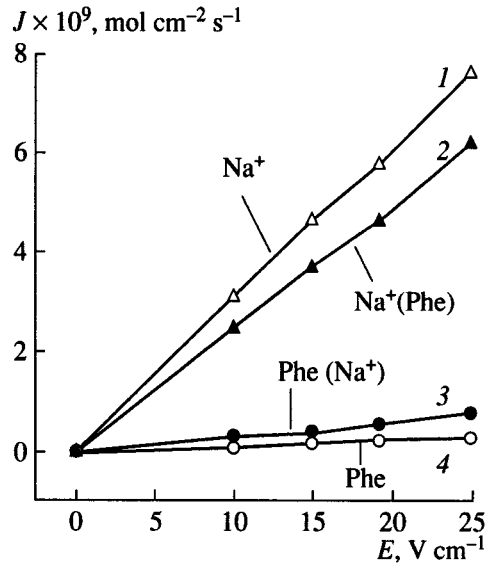

Fig. 2. Dependences of fluxes (J) of (*1*, *2*) sodium ions and (*3*, *4*) phenylalanine through cation-exchange membrane MK-40 on the electrical field strength (E) in (*1*, *4*) individual solutions of components and (*2*, *3*) mixed solutions.

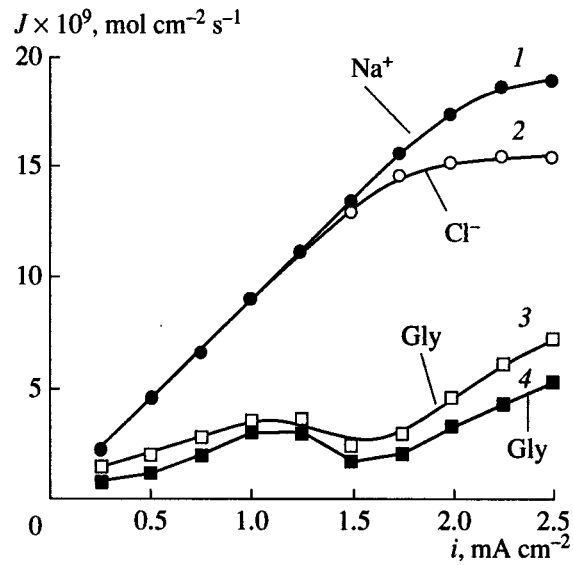

Fig. 3. Dependences of fluxes (J) of (*1*) sodium ions and (*3*) glycine through cation-exchange membrane MK-40 and fluxes of (*2*) chloride ions and (*4*) glycine through anion-exchange membrane MA-40 on the current density (i).

Then the glycine anions start to migrate in the opposite direction, that is, to the cathode. The amino acid cations, when finding themselves in the diffusion boundary layer near the cation-exchange membrane (the layer has an alkali reaction of the medium), recharge to anions in accordance with the reaction

$$\overset{+}{N}H_3\text{–}CH_2\text{–}COOH + 2OH^- \longrightarrow NH_2\text{–}CH_2\text{–}COO^- + 2H_2O \quad (2)$$

and then migrate in the opposite direction. These cycles occur repeatedly, leading to a decrease in the fluxes of amino acids, after the limiting current density is exceeded. In this process, each diffusion boundary layer near the membranes represents, in the course of a nonlinear concentration polarization, a barrier for electromigrating amino acid ions. The combined action of two barrier layers results in the circulation of amino acids in the solution of the desalination section.

The amino acid fluxes decrease to a certain limit, which is characterized by a minimum in Fig. 3. After this, the circulation effect diminishes. Once the current density is increased further, amino acid fluxes increase. Hence, the most effective way to separate mineral ions and amino acids is to conduct the electrodialysis at a current density corresponding to a minimum flux of the amino acid. The ratio

$$\alpha = J_1/J_2 \quad (3)$$

between fluxes of chloride ions and glycine through the anion-exchange membrane equals 2.2, 2.5, and 5.7 at current densities of 0.5, 1.0, and 1.5 mA cm^{-2}, respectively. Upon a further increase in the current density, the ratio between these fluxes again decreases.

The increase in the amino acid flux at current densities exceeding 1.5 mA cm^{-2} is due to a conjugated transport of bipolar ions and hydroxyl ions in the cation-exchange and the anion-exchange membranes, respectively:

$$\begin{aligned} &\overset{+}{N}H_3\text{–}CH_2\text{–}COO^- + H^+ \longleftrightarrow NH_3\text{–}CH_2\text{–}COOH, \\ &\overset{+}{N}H_3\text{–}CH_2\text{–}COO^- + OH^- \longleftrightarrow NH_2\text{–}CH_2\text{–}COO^-. \end{aligned} \quad (4)$$

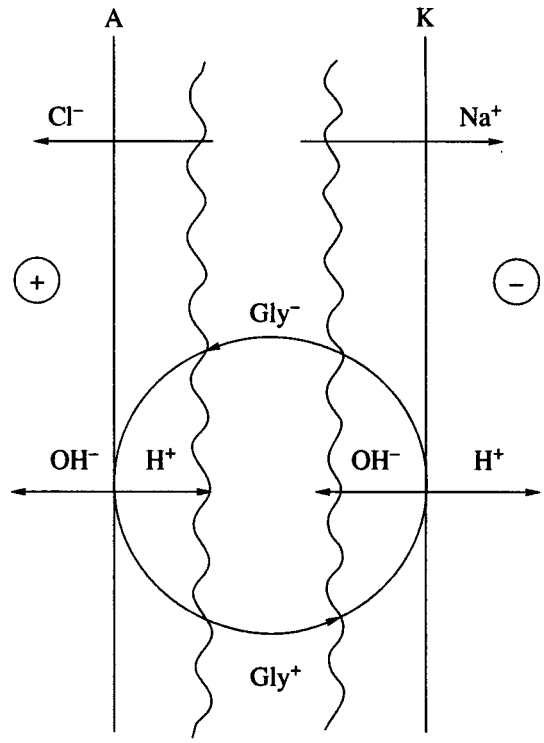

Fig. 4. Scheme illustrating the principle of the circulation effect during electromigration of glycine ions.

The ions carry a current that exceeds the limiting value under a nonlinear concentration polarization of membranes. The authors of [5] studied facilitated transport of borate-sugar complexes in which borate ions act as carriers in an electrodialysis. In our experiments, the carriers in the facilitated electromigration of bipolar ions were hydrogen ions or hydroxyl ions. The gradient of an electrical potential makes no direct impact on bipolar ions. Therefore, the formation of cations or anions via reactions (4) leads to a fundamental intensification of the amino acid transport through the membranes. The hydrogen and hydroxyl ions do not leave the membranes; instead, they pass over bipolar ions as in a relay race. In doing so, as opposed to the known processes, the carriers are not introduced into a solution or a membrane on purpose, rather they form spontaneously during a nonlinear concentration polarization of ion-exchange membranes.

At different polarization stages, glycine fluxes through the cation-exchange membrane were higher than those through the anion-exchange membrane. This was due to the fact that the secondary and tertiary amines, which are ionogenic groups in the anion-exchange membrane, catalytically accelerate the water dissociation reaction at the membrane–solution interface to a higher extent than do the sulfo groups in the cation-exchange reactions [6]. As a result, in all stages of polarization of the anion-exchange membranes, the barrier action was stronger and the fluxes were lower.

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