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Recovery and concentration of basic amino acids by electrodialysis with bipolar membranes

T.V. Eliseeva*, E.V. Krisilova, V.A. Shaposhnik, A.E. Bukhovets

Voronezh State University, Universitetskaya pl., 1, Voronezh 394006, Russia
Tel.: +7 4732 208932; Fax: +7 4732 208755; email: tatyanaeliseeva@yandex.ru

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ABSTRACT

Recovery and concentration of basic amino acids by electrodialysis with bipolar membranes are studied. The utilization of bipolar membranes leads to an increase of amino acids fluxes through monopolar membranes. No-flow concentration compartments give the possibility to concentrate amino acid solutions. Concentration factors have been obtained in a wide range of current density for basic amino acids with various side chains (lysine, arginine, histidine). The feed solution concentration influence on concentration factor is discussed. The correlation between the hydration of monopolar membranes in amino acids forms and concentration efficiency during the electrodialysis with bipolar membranes is found.

Keywords: Electrodialysis with bipolar membranes; Basic amino acids; Recovery and concentration

1. Introduction

Amino acids are typical ampholytes. They exist preferably in the form of bipolar ions in individual solution and even in solid state. Bipolar ions do not migrate in the electric field. However, during the interaction with hydrogen and hydroxyl ions they form cations and anions, accordingly, which are able to transfer under the influence of electric current.

Bipolar membranes generate hydronium and hydroxyl ions in the course of water splitting:

$$2H_2O \Leftrightarrow H_3O^+ + OH^- \quad (1)$$

This process leads to the recharging of amino acids and to the increase of their fluxes through the following monopolar membranes.

$$\underset{\text{bipolar ion}}{{}^+H_3N - RCH - COO^-} + H_3O^+ \Leftrightarrow {}^+H_3N - \underset{\text{cation}}{RCH - COOH} + H_2O \quad (2)$$

$$\underset{\text{bipolar ion}}{{}^+H_3N - RCH - COO^-} + OH^- \Leftrightarrow NH_2 - \underset{\text{anion}}{RCH - COO^-} + H_2O \quad (3)$$

Amphoteric nature of amino acids one can consider a basis for their recovery and concentration in the system with bipolar and cation-exchange membrane using reaction (2) and in the system with bipolar and anion-exchange membrane using reaction (3).

However, for basic amino acids extraction it is preferable to use the system containing cation-exchange membranes.

Some aspects of amino acids separation by electrodialysis with bipolar membranes have been discussed

*Corresponding author

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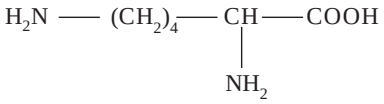
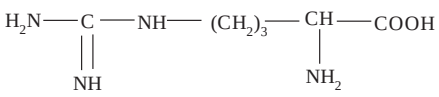
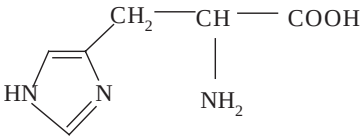
Table 1
Characteristics of basic amino acids used

Amino acid	Formula	M (g/mol)	pI	pK_1 (COOH)	pK_2 (α-NH_2)	pK_3 (R)
Lysine		146.19	9.74	2.18	8.95	10.53
Arginine		174.21	10.76	2.18	9.09	13.20
Histidine		155.16	7.60	1.77	9.00	6.00

in literature [1–4]. The aim of this work is the study of basic amino acid concentration peculiarities in the electromembrane system with bipolar and cation-exchange membranes.

2. Experimental

The amino acids used in the experiments are listed in Table 1. Their isoelectric points are in the basic range of pH values.

Distribution diagram for basic amino acid ionic forms (example of arginine) is shown in Fig. 1.

This diagram allows to determine what forms of amino acid exist at a given pH value and to predict their transport through the membranes.

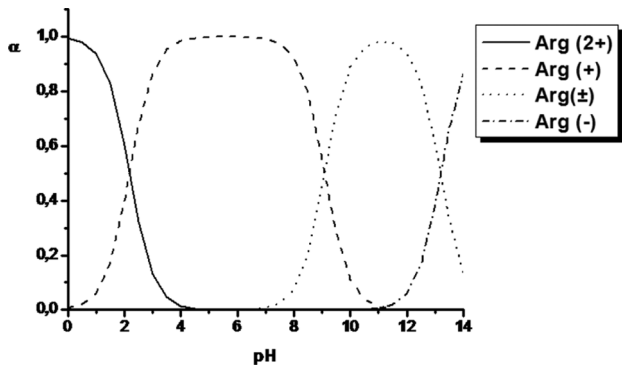


Fig. 1. Amount fraction of various arginine ions as pH function.

The solutions of amino acids (Ajinomoto) were analyzed by the method of photometry based on cooper complexes formation [5].

The experiments were carried out in a laboratory multi-compartment cell with alternating bipolar membranes MB-3 (Shchekino, Russia) and cation-exchange membranes: heterogeneous MK-40 (Shchekino, Russia) or homogeneous MF-4SK (St-Petersburg, Russia).

The scheme of the multi-compartment cell fragment is shown in Fig. 2. The experiments were carried out in the constant current regime.

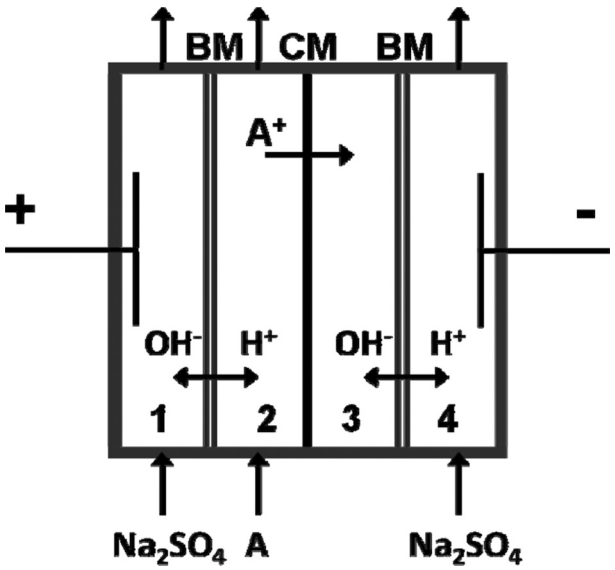


Fig. 2. The fragment of the cell with bipolar and cation-exchange membranes for amino acid concentration.

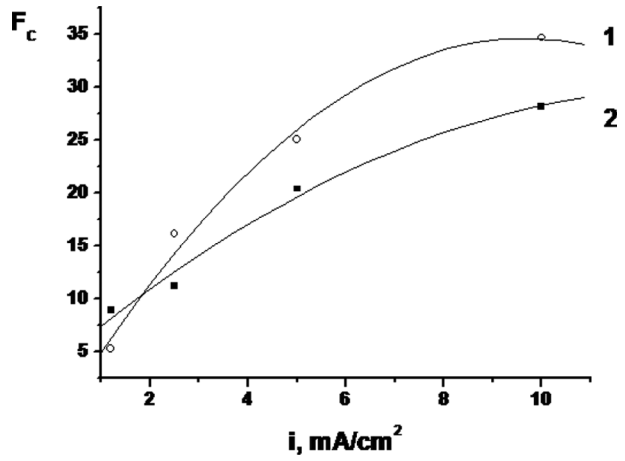


Fig. 3. The dependence of arginine concentration factor on the current density in the system with bipolar membranes MB-3 and heterogeneous membranes MK-40 (1) or with bipolar membranes MB-3 and homogeneous membranes MF-4SK (2; $C_0 = 0.01$ M).

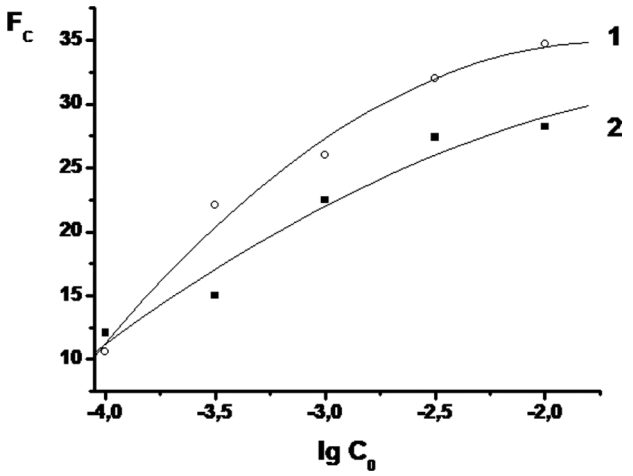


Fig. 4. The dependence of concentration factor on feed solution concentration: 1—MK-40, 2—MF-4SK.

Every compartment had individual input and output for a solution. The height of the compartments was 20 cm. The membrane effective area was 20 cm^2. Concentrate compartments had no flow through. In order to prevent amino acids transformations in the electrode compartments they were fed by sodium sulphate.

3. Results and discussion

The recovery and concentration of arginine—the most basic amino acid (pI = 10.76) has been studied in the electromembrane system with bipolar and various cation-exchange membranes – heterogeneous MK-40 and homogeneous MF-4SK. Bipolar membrane generates hydrogen ions from the side of dilute compartments. This process leads to decrease of pH value in these compartments and to formation of arginine cations that are capable to migrate through a cation-exchange membrane. The distribution diagram (Fig. 1) indicates that acidic and even neutral media permit to increase the amount fraction of arginine cations. Cations flux provides the possibility to concentrate amino acids in the adjacent compartments which have no flow through.

For the estimation of process efficiency concentration factor $F_c = C/C_0$ was used (C—concentration in concentrate solution, C_0—concentration in feed solution). The dependence of F_c on the current density (i) is shown in the Fig. 3.

As it follows from the Fig. 3 concentration factor increases with current and reaches $F_c = 27$–35 at values of current density $i \approx 8$–10 mA/cm^2. The further growth of current density leads to increase of electrical resistance in the system and warming up of the solution because of Joule heat release. The comparison of two studied membranes shows that in intensive current regime use of heterogeneous membrane MK-40 allows to reach deeper concentration of amino acid solution, than use of homogeneous membrane MF-4SK.

The dependence of concentration factor F_c on feed arginine solution concentration is presented in Fig. 4. Process was carried out at the current density corresponding to the maximum obtained value of F_c for the definite concentration.

Use of heterogeneous membrane MK-40 is preferable in comparison with homogeneous MF-4SK. However, at low values of initial concentrations ($\lg C_0 = -4$) concentration factor (F_c) decreases and one can not observe any difference between membranes. According to [6], electrodialysis concentration of electrolytes is limited basically by electroosmotic transport of water with migrating ions, so hydration characteristics of cation-exchange membranes used are important.

Water content values for studied swollen membranes are presented in the Table 2.

Table 2
Water content for various cation-exchange membranes

Membrane (form)	Water content (% mass)	Specific water capacity (mol H_2O/eq)
MK-40 H-form	40.0	8.9
Arg-form	28.8	6.4
MF-4SK H-form	19.6	14.4
Arg-form	11.2	8.2

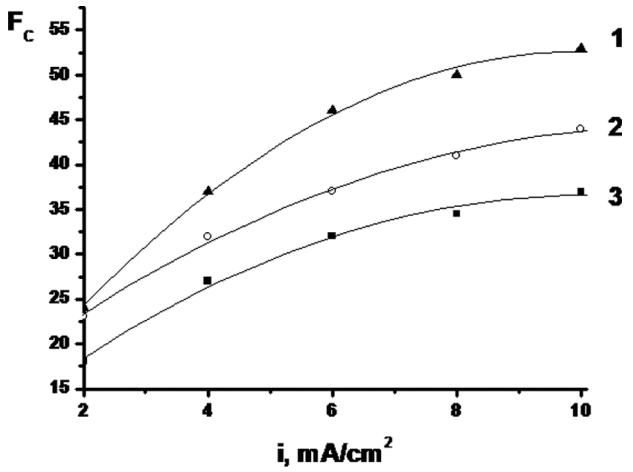


Fig. 5. The dependence of concentration factor on the current density during the electrodialysis of basic amino acids tartrates solutions: 1—histidine, 2—arginine, 3—lysine.

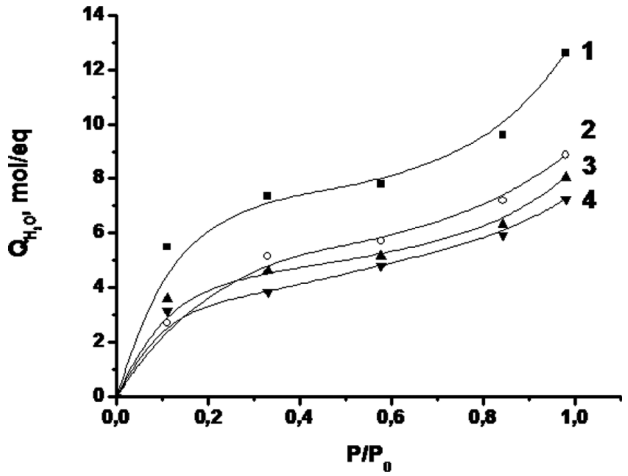


Fig. 6. Water sorption isotherms for the membrane MK-40 in various forms: 1—H-form, 2—lysine form, 3—arginine form, 4—histidine form.

In spite of the fact that total water content for membranes MK-40 is more, one sulfonic group in MF-4SK membrane holds more water molecules. The studied membranes have identical functional groups, however, distinction in the nature and structure of polymer matrix has an influence on the state and quantity of water in membrane and, as consequence, on electrodialysis concentration parameters. According to the literature data [7] water molecules in perfluorosulfonated ion-exchange membrane MF-4SK are weakly associated than in membranes based on polysterene (MK-40). That is accompanied by destruction of hydrogen bonds. Presence of water with the destroyed hydrogen bonds can lead to increase in its transport through a membrane and dilution of a concentrate. Similar conclusions are made for the explanation of regularities obtained during the electrodialysis concentration of NaCl solution [8].

However, electrodialysis concentration efficiency in the case of relatively large organic ion such as arginine, can be limited not only by electroosmotic water transport, but also by the steric factor. Migration of amino acids cations (the size without hydration shell ca. 1.6 nm [9]) through the membrane MK-40 containing nano- and micropores (1.5–100 nm) in the structure as well as channels with radius up to 1,000 nm [10] does not have steric hindrance. At the same time, homogeneous membranes MF-4SK have more dense structure, the size of transport channels for ions is 3.5–4.0 nm [7] that can lead to difficulties of amino acid cations transport and, hence, lower concentration efficiency.

Another task of this study is consideration of various basic amino acids concentration in the course of their salts conversion into free amino acids with simultaneous concentration. Such task appears at the last stage of amino acids chemical synthesis. Chemical synthesis allows to produce only racemate. So it is necessary to recover L-form. For example, high-purity L-lysine racemate is produced from cyclohexanone. Separation of racemate is carried out taking into account different solubility of D- and L-forms salts which are formed in the reaction of racemate with tartaric acids.

At the final stage of the process it is necessary to convert salts into basic amino acids. This task has been solved by the ion-exchange method that requires the solutions of acids and bases for regeneration. The suggested procedure using electrodialysis with bipolar membranes is non reagent, advisable from ecological point of view and it can be used for the recovery of basic amino acids obtained in the course of chemical synthesis.

Bipolar membranes generate hydrogen ions recharging basic amino acids into doubly charged and single-charged cations which transfer through the cation-exchange membrane being free of tartaric acid. Tartaric acid can be returned from even-numbered compartments to the stage of racemate separation. The solution of pure basic amino acid has been collected from all non-even numbered compartments which had no flow through in order to concentrate the product.

The influence of current density on the concentration factor is shown in the Fig. 5 for three basic amino acids.

Electrodialysis with bipolar membranes permits to increase concentration of basic amino acids 35–50 times at room temperature without any danger of destruction. Concentration process of model solution with lysine tartrate content 0.025 mol/L leads to the

concentration 0.88 mol/L. For arginine we can reach in this case concentration 1.25 mol/L.

The efficiency of concentration is restricted by water transport through the membrane to the ''stripping'' solution by osmotic and electroosmotic solvent flux [6]. Water flux to the concentrate compartment depends of membrane hydration in the following solution. It is obvious that concentration of histidine is the most effective process. We have found the correlation between membranes hydration in amino acids forms and efficiency of concentration. Fig. 6 shows the water sorption isotherms for various basic amino acid forms and H-form as well.

The length of amino acids side chain decreases from lysine to histidine. Lysine form of membrane is the most hydrated among other amino acids forms. The more hydration of the membrane leads to the decrease of concentration factor.

4. Conclusions

Electrodialysis with bipolar membranes is the efficient method of amino acids recovery on the basis of their amphoteric nature.

The comparison of heterogeneous membrane MK-40 and homogeneous membrane MF-4SK shows the better efficiency of heterogeneous membrane for the purpose of amino acid concentration from their dilute solutions.

The procedure of basic amino acids salts (tartrates) conversion into free amino acids followed by their concentration by electrodialysis with alternating cation-exchange and bipolar membranes is suggested as a final stage in the industrial chemical synthesis on the basis of cyclohexanon.

The correlation between the hydration properties of cation-exchange membranes with amino acids recovery and concentration efficiency is revealed.

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