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Current–voltage curves of ion-exchange membranes in electrodialysis of solutions containing alkyl aromatic amino acids and various mineral salts

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ABSTRACT

The work is aimed at studying electrochemical behavior of ion-exchange membranes in order to optimize the electrodialysis desalination of amino acid solution. The current–voltage and transport characteristics of ion-exchange membranes MA-40, MA-41, and MC-40 in electrodialysis demineralization of tyrosine or phenylalanine solutions containing also one of the mineral salts such as NaCl, NaBr, and KCl have been researched. The influence of the mineral salt ion nature (ion radius and mobility, hydration shell kind) and membrane functional groups on the amino acid and mineral ion fluxes through the membrane at the overlimiting currents has been revealed.

Keywords: Electrodialysis; Alkyl aromatic amino acid; Demineralization; Ion-exchange membrane; Current–voltage characteristic; Transport

1. Introduction

Nowadays, numerous research results are dedicated to various applications of electrodialysis (ED) with ion-exchange membranes [1,2]. However, there are limited examples of studies dealing with the bases of ED utilization in amino acids extraction from technological solutions [3–8]. At the same time amino acids production, especially, by the microbiological synthesis is being rapidly developed. It demands the subsequent development of separation, concentration and purification membrane-based downstream stages in the manufacturing processes.

ED is a perspective green technology for amino acids and mineral salts separation [9,10]. To provide the industry with efficient procedures for such separation, it is necessary to reveal the conditions and factors having influence on the performance [1]. Electrochemical behavior of membranes is of great importance. The current–voltage curves (CVCs) of ion-exchange membranes and also their transport characteristics have been studied, in this work, for the ED of solutions containing alkyl aromatic amino acid and various mineral salts to predict the features of electromembrane demineralization.

2. Experiments

Experiments have been carried out in a seven-compartment ED stack with alternating heterogeneous

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cation-exchange membranes (CEM) MC-40 and anion-exchange membranes (AEM) MA-40 or MA-41 (Fig. 1). The AEM MA-41 is composed of styrene–divinylbenzene co-polymer with functional quaternary ammonium groups and AEM MA-40 is based on polyethylenimine with secondary, tertiary as well as quaternary ammonium groups.

The ED stack has AgCl electrodes placed on each side of the studied membrane surface at the distance of 0.2 mm to obtain CVC.

Phenylalanine (Phe) and tyrosine (Tyr) in mixed solutions with sodium chloride, potassium chloride, or sodium bromide have been used throughout this study. Some characteristics of amino acids are shown in Table 1.

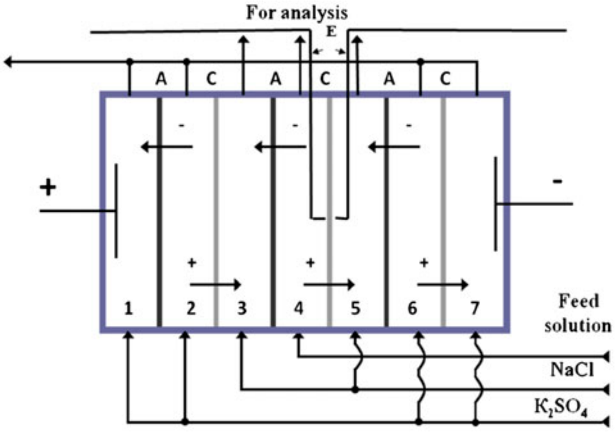
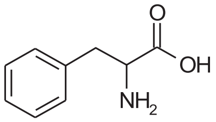
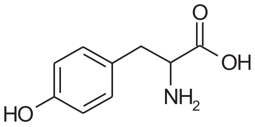


Fig. 1. Seven-compartment ED stack with alternating cation (C)—and anion (A)—exchange membranes, “+”—cation, “−”—anion, E—electrodes (AgCl | Ag, Cl^-).

Table 1
Characteristics of amino acids used

				pK		
Amino acids	Structural formula	Molecular weight	pI	pK_1	pK_2	pK_R
Phe		165.19	5.91	2.58	9.24	–
Tyr		181.19	5.63	2.20	10.07	9.40

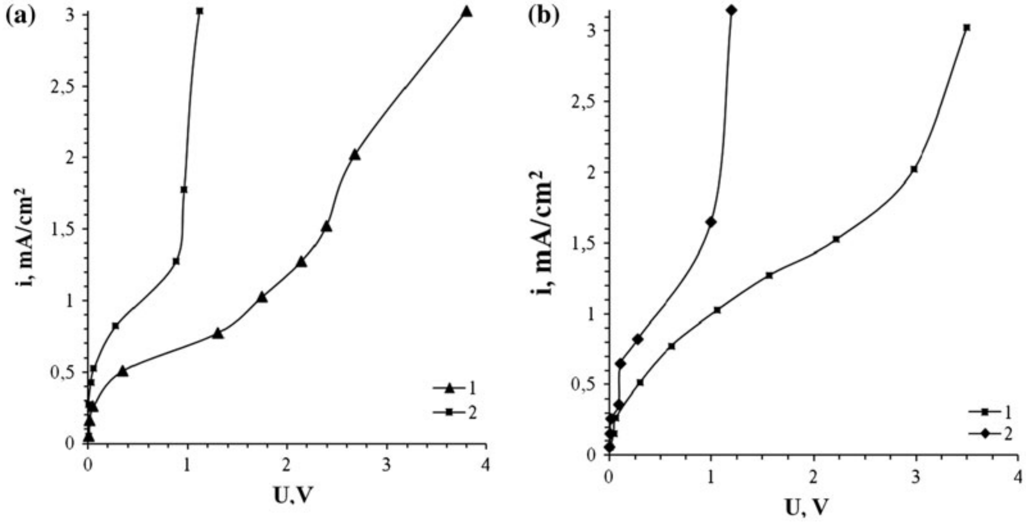


Fig. 2. CVCs of anion-exchange membranes: (a) 1—MA-40 in solution Tyr (0.0025 M) + NaCl (0.01 M) and 2—MA-41 in solution Tyr (0.0025 M) + NaCl (0.01 M); (b) 1—MA-40 in solution Phe (0.02 M) + NaCl (0.01 M) and 2—MA-41 in solution Phe (0.02 M) + NaCl (0.01 M).

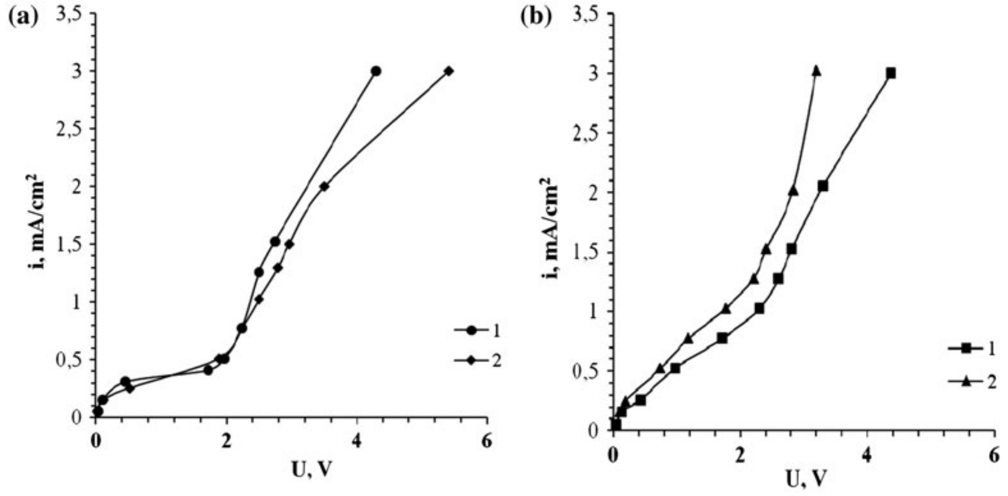


Fig. 3. CVCs of the membrane MC-40 in solutions: (a) 1—Tyr + KCl, 2—Tyr + NaCl; (b) 1—Phe + NaCl, 2—Phe + KCl.

3. Results and discussion

The influence of mineral ion type, its hydration shell kind, and membrane's functional groups on current–voltage characteristics of ion-exchange membranes, and on fluxes of the components in ED of solutions containing alkyl aromatic amino acid (Tyr or Phe) and one of the various mineral salts (NaCl, NaBr, and KCl) are of great interest.

The difference in the functional groups catalytic activity of AEM MA-41 and MA-40 leads to the decrease in the length of CVC "plateau" for MA-41 (in comparison with MA-40) in solution containing NaCl and amino acid (Tyr Fig. 2(a), Phe Fig. 2(b)).

The study of CEM i–U curves in the solutions containing K^+ or Na^+-salts as well as amino acid makes it possible to show smaller value of the membrane resistance in potassium salt solution (Fig. 3). This can be due to K^+-ions negative hydration resulting in higher mobility of H_2O molecules in the hydration shell.

However, the amino acid can be retained in the hydration shell of positive hydrated Na^+-ion and transported through the CEM after exceeding the limiting current density. Therefore, the difference between CEM CVC in KCl and NaCl solutions is negligible.

For cation-exchange membranes, limiting current density is less than that for AEM placed in mineral salt (Kooistra, 1967) [11,12] solution. This is due to the transport number of Na^+ ions to be less than that of Cl^- ions in a NaCl solution. The same phenomenon occurs in a mixed solution mineral salt—amino acid. The amino acid additive does not affect significantly the limiting current density value of the membrane measured in NaCl solution, because the solutions' pH value is close to the isoelectric point of the amino acid. This renders most of the amino acid ions to be in the bipolar form, so they do not take part in current transfer through the membrane [13].

The correlation between amino acid, mineral salt mass transfer through the ion-exchange membranes, and their CVC in ED of solutions containing alkyl aromatic amino acid and various mineral salts has been observed in this research.

The alkyl aromatic amino acid flux (Tyr and Phe) through AEM and CEM has a conventional shape for

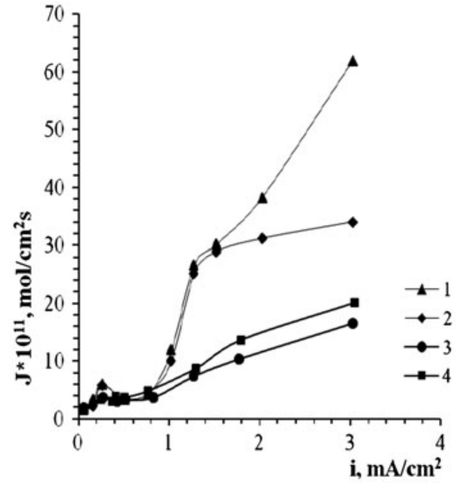


Fig. 4. The dependence of Tyr fluxes through the membrane MA-40 on the current density in the ED of solutions: 1—Tyr (0.0025 M) + NaCl (0.01 M), 2—Tyr (0.0025 M) + NaBr (0.01 M); and through the membrane MA-41, 3—Tyr (0.0025 M) + NaCl (0.01 M), 4—Tyr (0.0025 M) + NaBr (0.01 M).

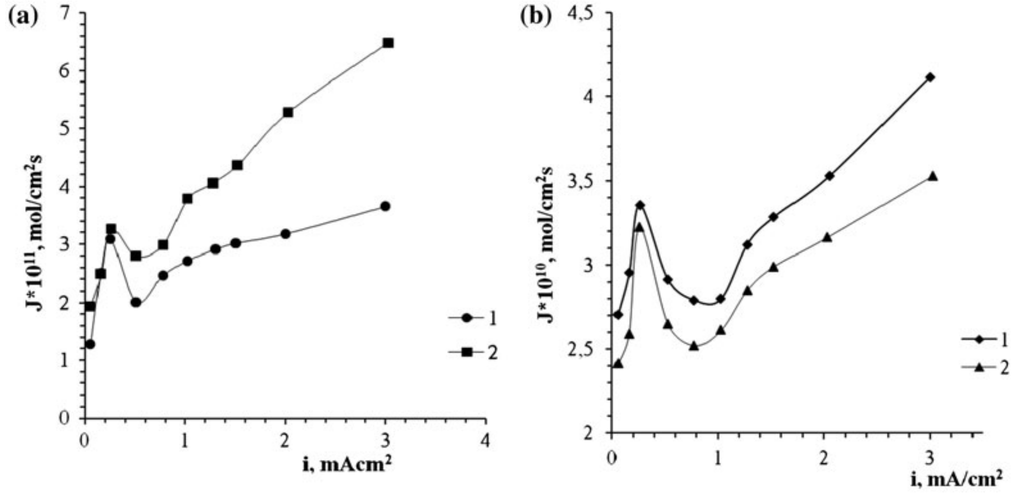


Fig. 5. The dependence of amino acid fluxes through the membrane MC-40 on the current density in the ED of solutions: (a) 1—Tyr (0.0025 M) + KCl (0.01 M), 2—Tyr (0.0025 M) + NaCl (0.01 M); and (b) 1—Phe (0.02 M) + NaCl (0.01 M), 2—Phe (0.02 M) + KCl (0.01 M).

ampholyte with a maximum at the limiting current density and further decrease in mass transfer due to the barrier effect [14] that corresponds to the limiting diffusion current density at the ion-exchange membrane CVC. Facilitated electromigration of amino acids is observed at the intensive overlimiting conditions [15].

The amino acid flux (Tyr (Fig. 4 curves 3 and 4) as well as Phe) through the AEM MA-41 from solution containing bromide anions is larger than the amino acid flux in the presence of chloride ions at the overlimiting conditions of ED. This can be caused by larger amino acid competitive transport with chloride anions than that with bromide anions.

The dependences of bromide and chloride anions fluxes through MA-41 are different at high current densities. Namely, the flux of bromide ions is lower than the chloride ions flux. It deals with Cl^--ion smaller radius, its larger hydration shell, and more steric hindrances in membrane MA-41 phase in comparison with Br^--ions.

However, amino acid flux through the AEM MA-40 in the presence of chloride ions is larger than that from solution containing bromide ions, because bromide ion fluxes through this membrane are larger than the flux of chloride ions at the overlimiting conditions of ED (Fig. 4 curves 1 and 2). The electrostatic interaction of Br^--ions with AEM functional groups is less than the interaction between Cl^--ions and AEM functional groups.

In this work, alkyl aromatic amino acids transport through the CEM MC-40 in the presence of potassium and sodium ions has been also studied (Fig. 5).

As it is clear from Fig. 5, the presence of Na^+-ions in the system promotes transport of amino acids through the CEM more than the presence of K^+-ions. The comparison of sodium cations flux with potassium cations flux through the CVC MC-40 reveals slightly smaller sodium ions flux than that of potassium ions.

4. Conclusion

The membranes transport and current–voltage characteristics comparison prognosticates larger losses of studied amino acids due to their conjugative transport with sodium ions through the CEM than that with potassium ions at the overlimiting conditions of ED.

As per anions different influence, one can predict the maximum losses of Tyr and Phe from solutions containing bromide ions due to their higher conjugative flux through the AEM MA-41 and from solutions containing chloride ions in the system with the membrane MA-40.

The revealed features of CVCs and mass transfer in the studied solutions show that it is very important to take into account the nature of amino acids and mineral ions as well as membrane type for the forecast of amino acid electromembrane demineralization results.

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