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Direct evidence for the electroconvective mechanism of neutral amino acid transport during electrodialysis

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1 Experimental Section

1.1 Chemicals

The transport characteristics of sulfonated cation-exchange membranes with different mass fractions of the ion exchanger were studied by electrodialysis separation of model mixed solutions of the aromatic amino acid phenylalanine (0.05 M) and sodium chloride (0.01 M). Model solutions of amino acid (Sigma-Aldrich, USA, 99.77%) and mineral salt (VEKTON, Russia) were prepared from chemically pure reagents of 'puriss.' grade. All additional reagents were qualified as 'puriss.' or 'p.a.' and were used without further purification.

1.2 Physicochemical and structural characteristics of membranes

The physicochemical properties of the experimental ion-exchange membranes and structural characteristics of their surface are presented in Table S1.

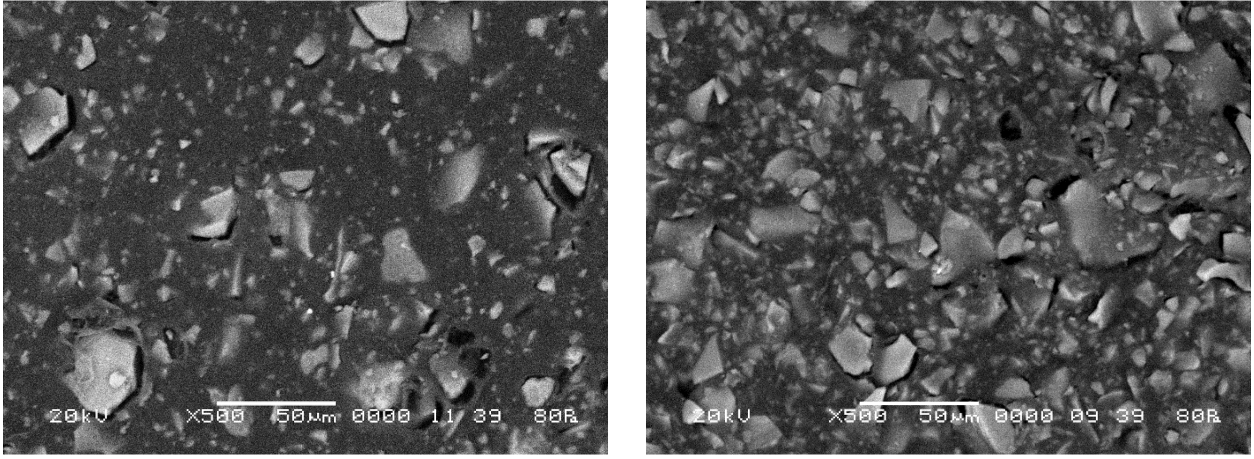
Table S1 Physicochemical and structural characteristics of experimental cation-exchange membranes.

Ion-exchange resin content (wt%)	IEC[a]/ mmol g^{-1}	W[b] (%)	d[c]/µm	S[d] (%)	P[e] (%)	$\bar{R}$[f]/µm	$\bar{r}$[g]/µm
45	1.88±0.07	29±2	540±20	21±1	1.9±0.1	2.2±0.1	1.9±0.1
50	1.90±0.02	33±1	550±10	23±1	2.0±0.1	2.2±0.2	1.8±0.1
55	1.93±0.05	36±2	585±5	25±2	2.2±0.3	2.2±0.1	1.9±0.2
60	2.07±0.04	39±1	610±5	29±1	2.4±0.2	2.1±0.2	1.8±0.2
65	2.16±0.06	42±1	655±5	34±2	3.1±0.5	2.2±0.1	1.8±0.2
70	2.34±0.05	45±2	715±15	38±2	3.2±0.4	2.3±0.1	1.9±0.1

[a] Total ion-exchange capacity of the swollen membrane. [b] Water content. [c] Thickness of the swollen membrane. [d] Fraction of ion-exchange resin on the surface. [e] Surface porosity. [f] Weighted average radius of ion-exchange particles. [g] Weighted average macropore radius.

1.3 Scanning electron microscopy

The membrane surface was visualized (Figure S1) using scanning electron microscopy (SEM) on a JSM-6380 LV microscope (Japan).



(*a*) (*b*)

Figure S1 SEM images of the surface of samples of swollen membranes with a mass fraction of sulfonated cation-exchange resin of (*a*) 45 and (*b*) 70 wt%.

1.4 Electrodialysis

Electrodialysis of solutions was performed in the galvanostatic mode using a seven-compartment electrodialysis apparatus with a horizontal orientation. The demineralization channel was formed from the sulfonated cation-exchange membrane under study and a highly basic anion-exchange membrane with a mass fraction of ion-exchange resin of 65 wt%. The fixed groups were quaternary amino groups $–N(CH_3)_3^+$. The intermembrane distance of section *4* was 2 mm. The schematic configuration of the electrodialysis cell is shown in Figure S2. A solution of phenylalanine (0.05 M) and sodium chloride (0.01 M) was pumped through section *4* at a flow rate of 3.5×10^{-4} m s^{-1}.

The voltage across the test membrane was measured between two Ag/AgCl electrodes using an APPA Technology Corporation model APPA 207 digital multimeter. The tips of the Ag/AgCl electrodes were located on both sides of the membrane under study at a distance of 1 mm.

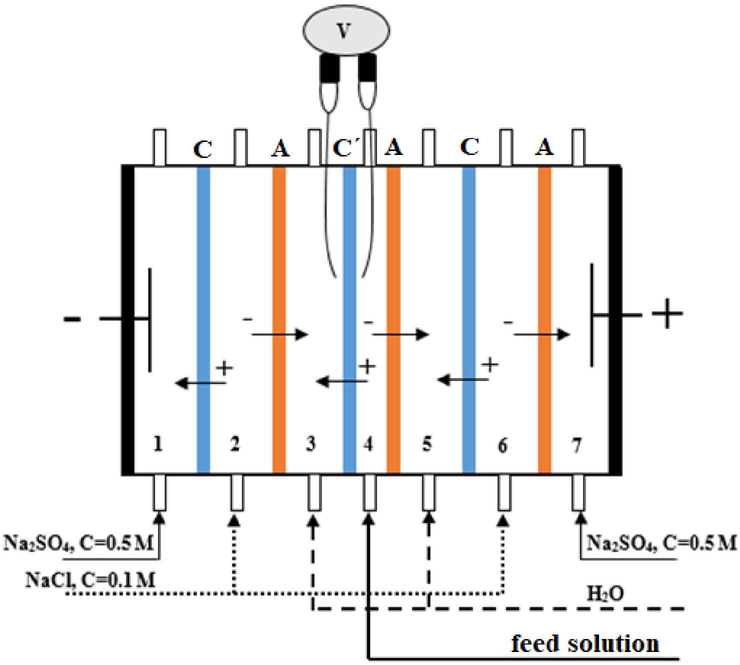


Figure S2 Schematic representation of an electrodialyzer with alternating (C) cation-exchange membranes and (A) anion-exchange membranes forming seven sections numbered *1*–*7*. C′ denotes the investigated cation-exchange membrane, V is a digital multimeter.

1.5 Laser interferometry

To visualize the interference pattern characterizing the emergence and development of electroconvective instability at the membrane–solution interface, we used laser interferometry according to the Mach–Zehnder scheme. The light source was a helium–neon laser (λ = 632.8 nm). The local change in the concentration ΔC associated with the change in the refractive index Δn of the solution was expressed in terms of the shift of the interference fringes $S = \gamma \times \Delta C \times l$, where l is the thickness of the electrodialyzer section towards light transmission, and γ is the detection sensitivity factor. The size of the region of electroconvective instability was defined as the distance from the membrane surface to the point in solution at which the interference fringe (concentration profile) was unstable and oscillatory.

1.6 Flicker noise spectroscopy

The Fourier power spectrum was used to estimate the energy contribution of different frequency components. For signals of a flicker-noise nature with a continuous spectrum and containing a wide set of frequency components, the noise power spectrum consists of sections of the form $P \sim f^{\,n}$, which are linear functions in double logarithmic coordinates with a slope equal to the factor $n = \Delta[\lg P_i(f)]/\Delta \lg f$, where f (Hz) is the frequency and P (Hz^{-1}) is the density of the fluctuation spectrum.

2 Calculations

The concentrations of various ionic forms of phenylalanine in aqueous solutions with different pH were calculated using the material balance equations and the corresponding amino acid dissociation constants:

$$C_{\mathrm{Phe}^+} = C_{\mathrm{Phe,0}}/\left(K_1K_2/C_{\mathrm{H}^+}^2 + K_1/C_{\mathrm{H}^+} + 1\right), \quad (1)$$

$$C_{\mathrm{Phe}^-} = K_1K_2C_{\mathrm{Phe}^+}/C_{\mathrm{H}^+}^2, \quad (2)$$

$$C_{\mathrm{Phe}^\pm} = K_1C_{\mathrm{Phe}^+}/C_{\mathrm{H}^+}, \quad (3)$$

where $C_{\mathrm{Phe,0}} = C_{\mathrm{Phe}^\pm} + C_{\mathrm{Phe}^+} + C_{\mathrm{Phe}^-}$ is the total concentration of all phenylalanine species in the solution.

An increase in the current density during electrodialysis was accompanied by a change in the pH of the solution, and, accordingly, the concentrations of Phe^+ cations, Phe^- anions and bipolar $\mathrm{Phe}^\pm$ ions of phenylalanine in the solution of the demineralization section changed. The dependence of the calculated values of bipolar ions and cations of phenylalanine in a demineralized solution on the dimensionless current density during electrodialysis of a mixed solution of sodium chloride and phenylalanine is shown in Figure S3.

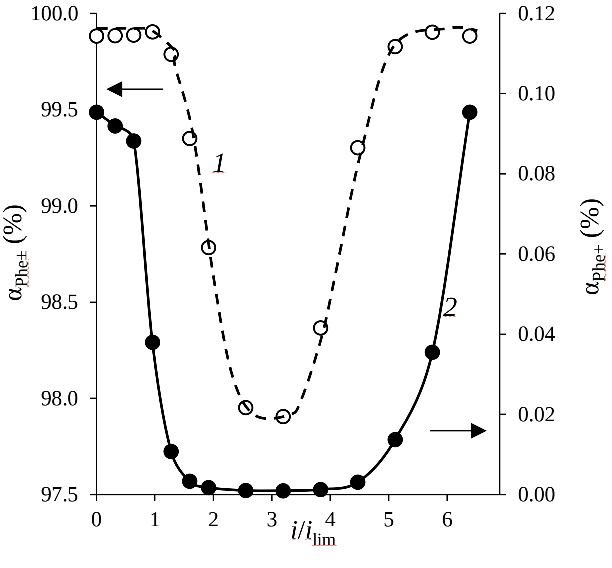


Figure S3 Dependence of the calculated values α of (*1*) bipolar ions and (*2*) cations of phenylalanine in a demineralized solution on the dimensionless current density during electrodialysis of a mixed solution of sodium chloride and phenylalanine. The mass fraction of sulfonated cation-exchange resin is 45 wt%.