Transmembrane potentials in systems containing 18-crown-6

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Electric potentials of MK-40 cation-exchange membrane, which is immersed in aqueous solutions of KCl, RbCl, and macrocyclic polyether 18-crown-6, have been measured. The possibility of preliminary calculations of biionic and multiionic potentials from equilibrium constants of ionic exchange and electrochemical mobilities of cations in the sulfo cationite is demonstrated.

Key words: cation-exchange membrane, equilibrium constant, electric potential, 18-crown-6.

Separation factors and ratios of counterion flows through cationite membranes under conditions of the quasi-stationary state have previously been determined[1] on the basis of data on the electric conductivity of cationites in the form of K^+ and Rb^+ cations coordinated by 18-crown-6.

In this work, transmembrane potentials of the following systems are measured and calculated:

Inner solution	Membrane	Outer solution	
K^+, Cl^-, H_2O	|MK-40|	Rb^+, Cl^-, H_2O,	(1)
K^+, Cl^-, H_2O	|MK-40|	K^+, $[KL]^+$, Cl^-, H_2O,	(2)
Rb^+, Cl^-, H_2O	|MK-40|	Rb^+, $[RbL]^+$, Cl^-, H_2O,	(3)
K^+, $[KL]^+$, Cl^-, H_2O	|MK-40|	Rb^+, $[RbL]^+$, Cl^-, H_2O,	(4)

where the MK-40 membrane is the heterogeneous membrane based on KU-2-8 sulfocationite, L is 18-crown-6.

It is known that transmembrane potentials in multiionic systems with equivalent charges can be calculated[2] by the equation

$$E_m = \frac{RT}{zF}\ln\left(\frac{\sum\limits_j \bar{D}_j a_j \bar{f}_i}{\sum\limits_i \bar{D}_i a_i \bar{f}_j}\right), \qquad (5)$$

where E_m is the transmembrane potential (the difference in electric potentials between outer and inner solutions); z is the charge of a cation; F is Faraday's number; $\bar{D}_i$ and $\bar{D}_j$ are the diffusion coefficients of ions i and j in the ionite phase (in the membrane); a_j is the activity of the ion j in the outer solution; a_i is the activity of the ion i in the inner solution; $\bar{f}_i$ and $\bar{f}_j$ are the activity coefficients of the ions i and j in the ionite phase.

It is known[3] that $\bar{f}_i / \bar{f}_j = k^a_{j/i}$. Here $k^a_{j/i}$ is the corrected coefficient of selectivity of ion exchange,[4] the index i is related to counterions of the inner solution (A, B, ...), and the index j is related to counterions of the outer solution (C, D, ...) for the multiionic system of the type

AY, BY, ... | Membrane | CY, DY, ... (6)

with the common ion Y. Systems (2), (3), and (4) considered in this work are referred to this type.

Equation (5) is valid for the gel kinetics, the absence of convection and the flow of concomitant ions in the membrane, and when the ratios of activity $\bar{f}_i / \bar{f}_j$ and diffusion $\bar{D}_i / \bar{D}_j$ coefficients in the membrane are constant.[2] The latter condition means that the transmembrane potential in the multiionic system can be calculated, if it consists of additive contributions of potentials of biionic systems of the type

AY | Membrane | DY. (7)

Experimental

KU-2-8 cationite based on the sulfonated copolymer of styrene and divinylbenzene, an MK-40 heterogeneous industrial membrane containing a KU-2-8 sulfo acidic cationite, and 18-crown-6 macrocyclic polyether prepared at the Novosibirsk Institute of Organic Chemistry (Siberian Branch of RAS) were used. Chemically pure grade reagents were used for conditioning ionites and preparing solutions. Hg, Hg_2Cl_2|inner solution|MK-40|outer solution|Hg_2Cl_2, Hg type cells and an OR-208/1 digital precision pH-meter were used for measuring transmembrane potentials. The potentials of calomel electrodes were controlled before each measurement.

Considerable diffusion flows must take place in the systems studied; therefore, the structure of the cell was the following: one solution was continuously renewed, and the volume of the

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Table 1. Transmembrane potentials

System		E_m/mV	
		Calculation by Eq. (5)	Direct measurements
K^+ | MK-40 | Rb^+	(1)	4.1	(3.1±1.2)
K^+ | MK-40 | K^+, $[KL]^+$	(2)	−16.4	−(16.1±1.7)
Rb^+ | MK-40 | Rb^+, $[RbL]^+$	(3)	−6.2	−(6.7±0.4)
K^+, $[KL]^+$ | MK-40 | Rb^+, $[RbL]^+$	(4)	14.8	(12.8±1.8)

Table 2. Selectivity coefficients of ion exchange and electrochemical mobilities of cations in KU-2-8 cationite

Cation	k^a_{j/K^+}	$\bar{U}_j \cdot 10^4/cm^2\ V^{-1}\ s^{-1}$
K^+	1	3.00±0.10
Rb^+	1.08±0.05	3.30±0.10
$[KL]^+$	0.50±0.10	0.52±0.02
$[RbL]^+$	1.09±0.15	0.64±0.03

other solution was sufficiently great (0.5 L) to avoid noticeable change in concentration. The analytical concentration of the potassium and rubidium chlorides and uncomplexed crown ether was 0.01 mol L^{-1}. Constants of complex formation[5] and the Debye—Hückel equation were used for calculating activities of free and complex cations. Transmembrane potentials for systems (1)—(4) were calculated by Eq. (5). The measured and calculated values of E_m are presented in Table 1. The values of electrochemical mobilities and coefficients of selectivity of ion exchange in KU-2-8 ionite, which were necessary for calculating E_m, were determined and calculated by the procedures described previously.[1,6,7] These values are presented in Table 2. Confidence intervals were calculated with a 0.95 probability.

Results and Discussion

The mass and charge transfers coincide in ionic conductors to which crown-containing cationites are referred.[8] In this connection, the ratio of the diffusion coefficients of ions in the polymer phase $\bar{D}_j / \bar{D}_i$ is equal to the ratio of their electrochemical mobilities $\bar{U}_j / \bar{U}_i$. We have shown[1] that electrochemical mobilities of charged particles are independent of the counterion composition of the polymer in the sulfo acidic cationite in the form of alkaline metal cations and their complexes with 18-crown-6. In addition, the energy equivalency of exchange sites are retained in the systems considered.[6,9] Systems (1)—(4) as a whole are a convenient subject for experimental checking Eq. (5).

It can be seen from Table 1 that the calculated and measured values of potentials coincide in systems (1)—(4). Thus, transmembrane potentials can be calculated from the results of studying the gel kinetics and equilibria of ion exchange using Eq. (5). On the other hand, this means that KU-2-8 sulfo cationite that is in equilibrium with an aqueous solution of potassium and rubidium chlorides and 18-crown-6 is a mixture of noninteracting polyelectrolytes. Parameters of such multicomponent systems, including transmembrane potentials, can be calculated from a set of data on the properties of biionic systems.

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