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Active Transport of Sodium Ions through Interpolymer Carboxylic Membranes

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Abstract

The active transport of sodium ions in the system NaOH/membrane/NaCl-HCl has been investigated. The membranes used were carboxylic membranes of the interpolymer type polyethylene/poly(methacrylic acid-*co*-divinylbenzene), PE/poly(MA-*co*-DVB), containing ~32 wt% of poly(MA-*co*-DVB) and 1.8–9.6 wt% of DVB. The best transport characteristics were achieved for membranes with 1.8–3.0 DVB wt% and 0.1 *M* HCl. However, the observed Na^+ fluxes and selectivities were rather small. To explain the observed effects, a three-layer laminate model of the carboxylic membrane has been postulated where the working membrane can be viewed as consisting of three parallel layers. The first layer, contacting alkaline solution, is regarded as an ideal carboxylic ion-exchange membrane. The second layer, contacting acidic solution, is regarded as a nonionic gel. The third layer is the intermediate part localized between the above-defined layers. It has the properties of an ion-exchange membrane to some extent but it is relatively nonselective and contains coions. It has been stated that for the most effective action of the interpolymer membrane, the thickness of the second membrane layer should be as small as possible during the whole process. This can be achieved at low HCl concentration. On the other hand, low HCl concentration cannot secure the required driving force. Moreover, the net effect of a DVB content increase in the membrane was a flux decline. Therefore, the carboxylic membranes are not effective for the active transport of Na^+ ions in the system studied.

INTRODUCTION

Any mass transport process can be generally viewed as passive or active. Passive transport takes place when the species under investigation (e.g., ions) move in the direction of the negative gradient of electrochemical potential. Active transport takes place when the species move into a direction opposite to that of the negative gradient of electrochemical potential. The process is usually coupled with a chemical reaction or another transport process which provides that the overall dissipation will be positive (*1*). To simplify the investigation, only systems with no pressure or temperature gradients will be dealt with in the following discussion. Additionally, concentrations will be used instead of activities. If the species under investigation move along the concentration descent or against it the process is called passive or active transport, respectively.

Carboxylic ion-exchange membranes have been used in separation processes where active transport of ions is operative (*2–5*). In a typical realization of such a process, the membrane is placed between aqueous solutions of a base at one side and a mixture of a salt and an acid at the other. The concentrations of the common cation are equal on both sides at the beginning. There appears to be transport of the common cation from the basic side to the acidic side, i.e., against the concentration descent. Therefore, the process is active transport. Uragami et al. (*3*) proposed a tentative model of the transport. They assume two mechanisms to be operative. The first one is the "chemical active transport" resulting from the exchange reaction between carboxylate groups and the competing cations: the common cation and the hydrogen ion. The hydrogen ions are transferred by a proton-jump mechanism, forcing the countertransport of the common cation. The second mechanism is the "physical active transport," related to swelling–contraction cycles within the membrane.

In fact, the whole process can be treated as several Donnan equilibria at both sides of the membrane. Additionally, two chemical reactions take place. The first one is the reaction at the acidic side:

$$\text{Ⓟ—COO}^-\text{Me}^+ + \text{H}^+ \rightarrow \text{Ⓟ—COOH} + \text{Me}^+ \qquad (1)$$

and the second one is the neutralization reaction:

$$\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O} \qquad (2)$$

at the alkaline side. Finally, all the ions are transported along the concentration descents within the membrane. From this point of view, there is no active transport within the membrane although in terms of the whole membrane system the Me^+ ions are actively transported from the basic side to the acidic side.

The present paper deals with studies on the active transport of sodium ions in the system NaOH/membrane/NaCl-HCl. The membranes used were of the carboxylic interpolymer type: PE/poly(MA-*co*-DVB). The membranes have been shown to be of microheterogeneous morphology (*6*). The poly(MA-*co*-DVB) component occurs as spherical domains of dimensions 10–30 nm dispersed within the PE matrix. The purpose of the studies was to find relationships between the DVB content in the membrane, the HCl concentration, and the active transport characteristics.

EXPERIMENTAL

Membrane Preparation and Properties

The interpolymer carboxylic membranes were prepared by swelling a PE in the foil form in a mixture of MA, DVB, and benzoyl peroxide (BP) with subsequent heating of the gel to interpolymerize the monomers. The DVB content in the membranes, determined by IR spectroscopy, was controlled by changing the DVB concentration in the swelling mixture. The carboxylic groups of the membranes were transformed into their sodium salt form by treating them with 0.1 *M* NaOH solution.

Ion-exchange capacity was measured in the following way. The membrane sample in COOH form was immersed in a known volume of 0.05 *M* NaOH solution for 48 h at room temperature. The amount of COOH groups (in millimoles) was determined by backtitration with a 0.05 *M* HCl solution. Then the sample was washed with distilled water, dried under vacuum, and weighed. Ion-exchange capacity was calculated at the ratio of the amount of COOH groups to the weight of the dried membrane sample.

Equilibrium swelling of the membrane was measured gravimetrically as a weight increase per weight of the swollen membrane after 100 h immersion in a given solution. Equilibrium swelling was measured in 0.1 *M* NaOH and in 0.01, 0.1, and 1.0 *M* HCl.

Equilibrium concentration of the carboxylate groups in the swollen membrane, c_i, was calculated as the ratio of the ion-exchange capacity to the volume of solution sorbed by the membrane swollen in 0.1 *M* NaOH. For an ideal membrane, c_i should be equal to the concentration of sodium ions of the internal membrane electrolyte.

Samples for transmission electron microscopy investigation were stained with uranyl acetate. The microscope used was a Philips EM-301.

Transport Experiments

The active transport of sodium ions was observed in a typical two-compartment Plexiglas cell at 25°C. The first compartment was filled with 35 cm^3 of 0.1 *M* NaOH solution. The second compartment was filled with the same volume of a mixture of 0.1 *M* NaCl and 0.01 (0.1 or 1.0) *M* HCl. The solutions were intensively stirred via magnetic stirrers. The two compartments were separated by the membrane being tested. The active area of the membrane was 4.91 cm^2, and its thickness was 0.2–0.3 mm. At 1-h intervals the pH in both compartments was recorded, and 30-μL solution samples were taken in order to measure the Na concentration by flame photometry. After termination of the experiment (8 h), solutions from both compartments were neutralized (to pH 6.5–7.5) with NaOH or H_2SO_4 and the concentration of Cl^- ions was determined with a chloride-sensitive electrode.

The following quantities were used to characterize the active transport.

The normalized flux, J_n [mol/cm·s], defined as the Na^+ ions flux multiplied by the membrane thickness at the end of the experiment.

The active transport efficiency, *EF*, defined by

$$EF = \frac{(c_t^{\mathrm{Na}})_a - (c_0^{\mathrm{Na}})_a}{(c_0^{\mathrm{Na}})_a} \tag{3}$$

where $(c_0^{\mathrm{Na}})_a$ and $(c_t^{\mathrm{Na}})_a$ are the concentrations of sodium ions in the acidic compartment at the beginning and at the end of the experiment, respectively. For an ideal process, *EF* should approach unity.

The relative selectivity of the active transport, *SE*, is defined as

$$SE = \frac{(c_0^{\mathrm{Na}})_b - (c_t^{\mathrm{Na}})_b}{(c_t^{\mathrm{Cl}})_b} \tag{4}$$

where $(c_0^{\mathrm{Na}})_b$ and $(c_t^{\mathrm{Na}})_b$ are the concentrations of sodium ions in the alkaline compartment at the beginning and at the end of the experiment, respectively. $(c_t^{\mathrm{Cl}})_b$ is the concentration of chloride ions in the alkaline compartment at the end of the experiment. For an ideal membrane, *SE* should reach infinity.

RESULTS AND DISCUSSION

For the purpose of the experiment, four carboxylic membranes were synthesized. Their characteristics are listed in Table 1. It can be seen that poly(MA-*co*-DVB) content is ~32 wt% for all the membranes, and the DVB content changes from 1.8 to 9.6 wt%. The ion-exchange capacities of the membranes are very close to each other and equal to ~2.9 mmol/g. This means that, within the limits tested, the DVB content has no influence on the accessibility of carboxylic groups for ion exchange. It is, however, seen from Table 1 that DVB influences membrane swelling which decreases from 0.50 to 0.39 and from 0.20 to 0.18, respectively, in 0.1 *M* NaOH and 0.01 *M* HCl when the DVB content is increased from 1.8 to 9.6 wt%. Similarly, the concentration of the fixed ions (carboxylate

TABLE 1
Basic Characteristics of Carboxylic Interpolymer Membranes

Membrane	Poly(MA-*co*-DVB) content (wt%)	DVB content (wt%)	Ion-exchange capacity (mmol/g)	Swelling (g/g) 0.1 *M* NaOH	Swelling (g/g) 0.01 *M* HCl	Swelling (g/g) 1.0 *M* HCl	c_i (mol/dm^3)
1	32.0	1.8	3.0	0.50	0.20	0.17	3.0
2	31.1	3.0	2.8	0.48	0.19	0.16	3.0
3	32.3	4.7	2.9	0.43	0.18	0.16	3.9
4	32.1	9.6	2.9	0.39	0.18	0.16	4.4

ions), c_i, increases from 3.0 to 4.4 *M*. This concentration determines the internal membrane electrolyte concentration—the higher the c_i value, the better should be the semipermeability of the membrane.

It is interesting to note that the influence of DVB on membrane swelling is not as strong as in the case of free poly(MA-*co*-DVB) gel (7). This is because of PE matrix elasticity which reduces the swelling of the poly(MA-*co*-DVB) domain system. Therefore, the membranes behave as if the DVB content were much larger.

Sample micrographs of Membranes 2 and 4 are shown in Fig. 1. The very pronounced effect of DVB on membrane morphology is evident. At low DVB content, only microdomains (10–30 nm) evenly distributed within PE are present. At higher DVB content, large aggregates (100–300 nm) of microdomains are formed. The situation is similar to the case of suspension copolymerization when a nonsolvating diluent is used (*8*).

The courses of the active transport experiments are presented in Fig. 2. It is important to notice the different scenarios of pH change in the compartments. For Membrane 1 and 1 *M* HCl, the initial pH difference of solutions in both compartments (which is the driving force for the active transport) decreases to ~1 unit after 3 h. For Membrane 4 and 0.01 *M* HCl, the difference remains practically unchanged during the whole experiment.

The detailed description of all the runs is shown in Table 2. From the first column it is evident that J_n increases with decreasing DVB content in the membrane and with increasing HCl concentration. This behavior is obvious because low DVB content allows for higher swelling (Table 1) and thus makes the membrane structure more open and more permeable. Analysis of the second column of Table 2 leads to a similar conclusion for *EF* as for J_n. Here, one should notice that *EF* is time-dependent, and higher values of *EF* could be expected after longer times. However, for sulfonic interpolymer membranes working in a similar system, *EF* higher than 0.9

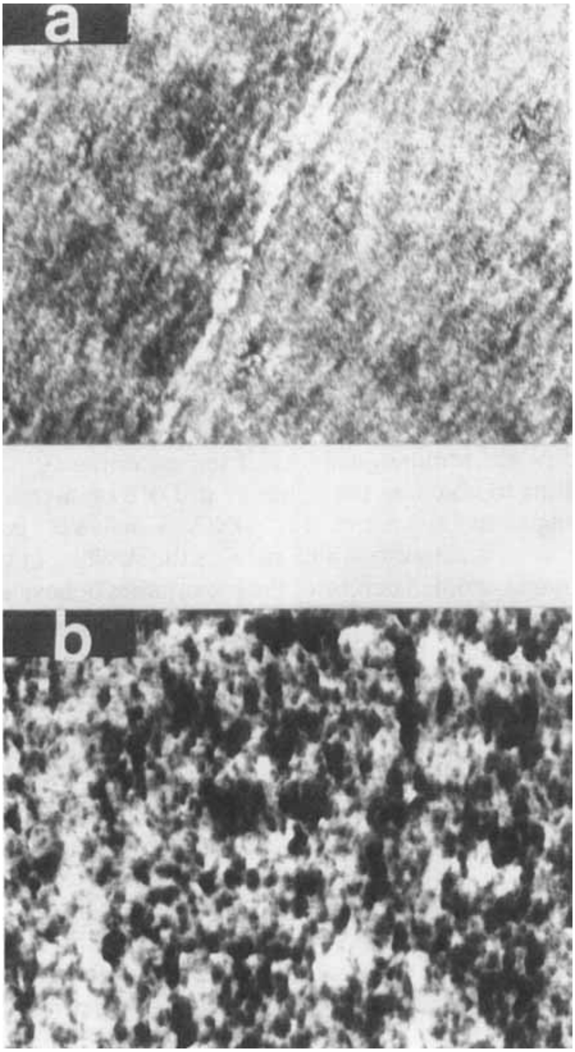

FIG. 1. TEM micrographs of thin sections of the carboxylic interpolymer membranes stained with uranyl acetate. (a) Membrane 2; (b) Membrane 4. Magnification 5900×.

has been reached (*9*). The very important parameter characterizing the active transport process is the relative selectivity, *SE*. It gives the relative rate of sodium ion transfer with respect to chloride ions. It must be stressed here that an ideal cation-exchange membrane should not be permeable to chloride ions and should give high *SE* values. From the third column of

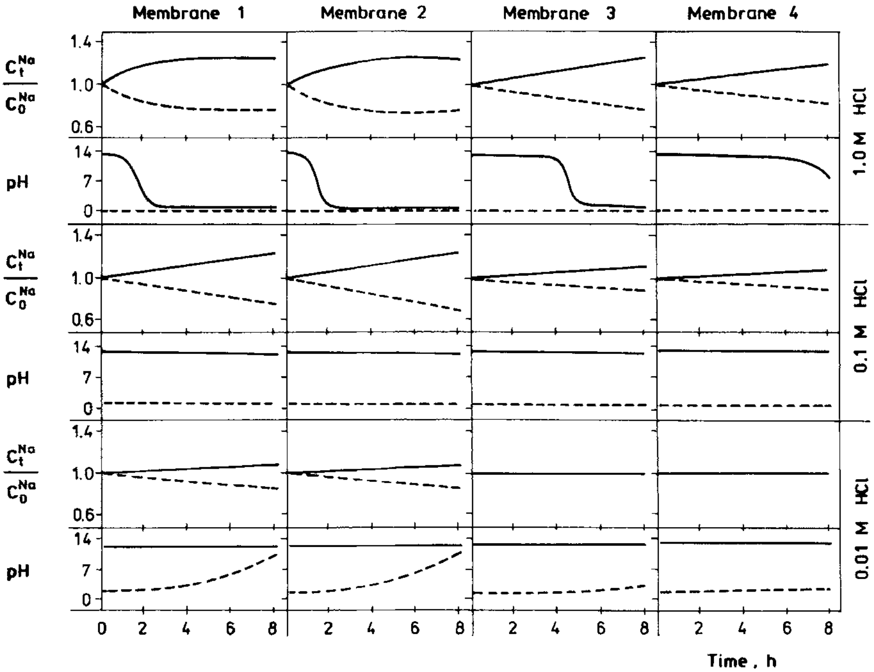

FIG. 2. The active transport of Na$^+$ ions through carboxylic membranes and pH changes in both compartments. c_0^{Na} and c_t^{Na} stand for Na$^+$ concentrations at times 0 and t, respectively. (——) The acidic compartment; (- -) the alkaline compartment.

TABLE 2
Results of the Active Transport Experiments

Membrane	HCl concentration (mol/dm^3)	$J_n \times 10^{10}$ mol/cm·s	*EF*	*SE*
1	0.01	0.9	0.10	4.20
	0.1	1.5	0.25	0.96
	1.0	3.9[a]	0.25	0.08
2	0.01	0.7	0.10	4.40
	0.1	1.4	0.25	0.99
	1.0	3.2[a]	0.25	0.09
3	0.01	0	0	—
	0.1	0.9	0.12	0.99
	1.0	1.5	0.25	0.12
4	0.01	0	0	—
	0.1	0.2	0.08	1.04
	1.0	1.0	0.20	0.17

[a] Initial flux.

Table 2 it is seen that *SE* increases with increasing DVB content in the membrane and with decreasing HCl concentration. The highest *SE* values (4.20) have been obtained for Membranes 1 and 2, and 0.01 *M* HCl. In this case the selective removal of 1 mol Na^+ ions has to be compensated for by the nonselective introduction of 0.24 mol Cl^- ions at the same time.

In order to explain the observed low selectivity, a three-layer laminate model of the membrane has been postulated. According to this model, the working membrane can be viewed as consisting of three parallel layers (Fig. 3). The first layer, contacting alkaline solution, is regarded as an ideal carboxylic ion-exchange membrane. It contains the fixed COO^- groups and Na^+ counterions. This layer contains no coions (except for a small amount of OH^- ions to maintain the dissociation of carboxylic groups). This layer is responsible for the selectivity of the whole membrane. The second layer, contacting acidic solution, is regarded as a nonionic gel. It contains undissociated COOH groups and is regarded to be nonselective. Therefore this layer contains both cations and anions at concentrations similar to that of the contacting acidic solution. Moreover, this layer is very compact because of its low water content (see Table 1, swelling in HCl) and it is responsible for the dynamic properties of the whole membrane (the highest flux reduction). Finally, the third layer of the membrane is the intermediate part localized between the above defined layers. It has the properties of an ion-exchange membrane to some extent but it is relatively nonselective and contains coions.

At the very beginning of the active transport process, the membrane consists of only two layers: Layer 1 contacting the alkaline solution and the very thin Layer 3 contacting the acidic solution. Layer 2 appears during

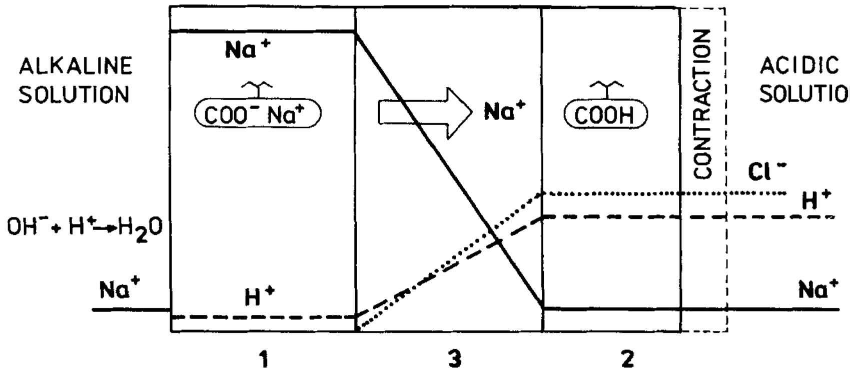

FIG. 3. The three-layer laminate model of the carboxylic membrane. The effect of contraction of Layer 2 has been marked.

the process, and the relative thicknesses of the three layers change. Depending on the initial HCl concentration and the DVB content in the membrane, the final situation may be different. When 0.01 *M* HCl is used together with Membrane 4, it may be assumed that during the experiment the thickness of Layer 2 will be small. Moreover, H^+ concentration will be relatively low, which results in a high Na^+ concentration in this layer and in a very small driving force for the active transport of Na^+. Additionally, low membrane swelling results in very small diffusion coefficients of ions in the membrane. All these factors cause the net flux of Na^+ ions to be undetectable. When Membrane 1 is used instead of Membrane 4, the normalized flux, J_n, increases (0.9×10^{-10} mol/cm·s). Here, however, another phenomenon appears: nonideality of Layer 1. This results in OH^- flux from the alkaline solution to the acidic solution. This is an unfavorable process because it effectively reduces the driving force. When 1 *M* HCl is used, the relative thicknesses of Membrane Layers 2 and 3 significantly increase during the process. After some time, depending on the DVB content in the membrane, only Layer 2 extends through the whole membrane thickness. The driving force for active transport ceases to exist, and the Na^+ flux is reversed (passive transport).

Analysis of Fig. 3 and Table 2 leads to the conclusion that the best transport characteristics have been achieved for Membranes 1 and 2, and 0.1 *M* HCl. Moreover, it is seen that increasing DVB content in the membrane causes some increase of c_i, which should result in an increased Donnan exclusion effect and better membrane selectivity. However, at the same time there is a significant decrease in the diffusion coefficients of ions in the membrane. The net effect is the Na^+ flux reduction, as is clearly seen from Table 2 data.

Finally, it can be stated that for the most effective action of the interpolymer membrane, the thickness of Membrane Layer 2 should be as small as possible during the whole process. This can be achieved at low HCl concentration. On the other hand, the low HCl concentration cannot secure the required driving force, so the carboxylic membranes are not effective in the active transport of Na^+ ions.

CONCLUSIONS

The best active transport characteristics have been achieved for membranes with 1.8–3.0 DVB wt% and 0.1 *M* HCl. However, the observed Na^+ fluxes and selectivities were rather small.

To explain the observed effects, a three-layer laminate model of the carboxylic membrane has been postulated where the working membrane can be viewed as consisting of three parallel layers. The first layer, contacting alkaline solution, is regarded as an ideal carboxylic ion-exchange membrane. The second layer, contacting acidic solution, is regarded as a nonionic gel. The third layer of the membrane is the intermediate part localized between the above-defined layers. It has properties of an ion-exchange membrane to some extent, but it is relatively nonselective and contains coions.

It has been stated that for the most effective action of the interpolymer membrane, the thickness of the second membrane layer should be as small as possible during the whole process. This can be achieved at low HCl concentration. On the other hand, the low HCl concentration cannot secure the required driving force. Moreover, the net effect of the DVB content increases in the membrane as the flux declines. Therefore, the carboxylic membranes are not effective for the active transport of Na^+ ions in the system studied.

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