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ACTIVE TRANSPORT OF SODIUM IONS THROUGH INTERPOLYMER CATION-EXCHANGE MEMBRANES PREPARED IN THE PRESENCE OF SOLVENTS

Active transport of sodium ions through strongly acid membranes prepared from PE/poly(St-co-DVB) interpolymers has been investigated. The interpolymers have been obtained in the presence of 5 or 40 wt. % of toluene (sol type solvent) or isooctane (non-sol type solvent) or without them. The active transport was examined in the system: 0.1 M NaCl+1 M HCl/membrane//0.1 M NaOH. The most effective and selective transport of sodium ions from the alkaline side to the acidic side has been observed when the membrane obtained from interpolymer with 5 wt. % of toluene has been used.

1. INTRODUCTION

In the last years, there are many reports on the ion transport against their concentration gradient [1]–[9]. This kind of transport has been called *the active transport* or *the uphill transport*. Cation-exchange membranes, both with strongly or weakly acid groups, have been used for those purposes [10]–[19].

URAGAMI [12] and NONAKA [19] proposed a tentative mechanism of alkaline metal ions transport through membranes with sulfonic groups (fig. 1). At the beginning of the process, the concentrations of the common cation are equal on both sides. The metal ion diffuses from the alkaline to acidic side through the membrane and takes part in the ion-exchange reaction. The hydrogen ion is transferred through the membrane in opposite direction by a proton-jump mechanism [20] forcing the counter transport of common cation. The additional factor enhancing the metal ion transport is the formation of weakly dissociated water molecules at the alkaline side of the membrane.

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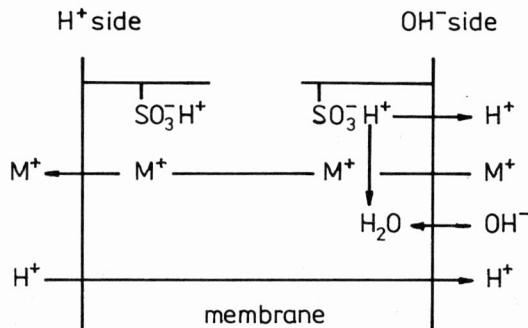


Fig. 1. Tentative mechanism of the active transport of metal ions through strongly acid cation-exchange membrane [12]–[19]

In our previous work [21], we presented the active transport of sodium ions through interpolymer membranes bearing sulfonic groups. The membranes were obtained from polyethylene/poly(styrene-co-divinylbenzene) [PE/poly(St-co-DVB)] interpolymers varying in the crosslinking agent content. It was observed that the transport effectiveness was dependent on the crosslinking degree of the interpolymer and on the initial hydrogen ion concentration on the acidic side.

However, properties of the interpolymer material based on styrene and divinylbenzene copolymer can be modified not only by the change of crosslinking degree [22]–[25] but also by carrying out the copolymerization in the presence of inert solvents [26], [27]. The influence of kind and amount of solvent on the dialytic properties of weakly alkaline interpolymer membranes with respect to various inorganic acids was demonstrated elsewhere [28], [29].

In this work, we have attempted to explore some influences of solvents during membrane material preparation on active transport of sodium ions through strongly acid interpolymer membranes.

2. EXPERIMENTAL

2.1. MEMBRANE PREPARATION AND CHARACTERIZATION

The membranes have been prepared according to the procedure described elsewhere [21], [24]. Interpolymerization of styrene (St) and DVB in the low density polyethylene (LDPE) has been carried out in the presence of 1 wt.% benzoyl peroxide. The two-phase reaction mixture contained 70 wt.% of LDPE and 30% of St and DVB (the DVB content in the monomer mixture was 2 wt.%). The interpolymerization has been carried out with no solvent (ESD-gel system) or in the presence of toluene (ESD/x-T-sol system) or isooctane (ESD/x-0-non-sol system),

where x is the solvent concentration with respect to St content in the monomer mixture, namely 5 or 40 wt.%. The membranes have been obtained by sulfonation of the interpolymers formed in sheets with chlorosulfonic acid followed by hydrolysis [24].

The total ion-exchange capacity and water content have been determined using standard methods [30].

Samples for transmission electron microscopy examinations were coloured with uranyl acetate. The Philips EM-301 microscope was used.

2.2. TRANSPORT EXPERIMENTS

Water permeability has been measured at transmembrane pressure of 0.15 MPa by the method similar to that described by SCATTERGOOD and LIGHTFOOT [31]. The active area of membrane in the hydrogen form was 12.5 cm².

The active transport has been carried out in a laboratory dialyser consisting of two compartments. The first compartment was filled with 35 cm³ of mixture: 0.1 M NaCl and 1 M HCl. The second one was filled with the same volume of 0.1 M NaOH. The solutions were vigorously stirred via magnetic stirrers. The active area of membrane separating the compartments was 4.9 cm² and its thickness was 0.02–0.03 cm.

At one-hour intervals, sodium ion concentration was determined on both sides of the membrane using atomic absorption photometry. The pH values were monitored in the alkaline compartment. Chloride ion concentration was measured on the alkaline side by the Volhard method after termination of experiment.

The active transport was characterized by the following parameters:

1. Active transport effectiveness EF

$$EF = \frac{(c_{\max}^{\text{Na}})_a - (c_0^{\text{Na}})_a}{(c_0^{\text{Na}})_a} \quad (1)$$

2. Mean rate of sodium ion transport MTR

$$MTR = \frac{(c_{\max}^{\text{Na}})_a - (c_0^{\text{Na}})_a}{At_{\max}} \text{ (mol/dm}^3\text{m}^2\text{h)}. \quad (2)$$

3. Relative selectivity of the active transport SE

$$SE = \frac{(c_0^{\text{Na}})_b - (c_t^{\text{Na}})_b}{(c_t^{\text{Cl}})_b} \quad (3)$$

where $(c_0^{\text{Na}})_a$ and $(c_{\max}^{\text{Na}})_a$ are the initial and maximum sodium ion concentrations in the acidic compartment, respectively; A is the active surface of the membrane; t_{\max} is the time for $(c_{\max}^{\text{Na}})_a$; $(c_0^{\text{Na}})_b$ and $(c_t^{\text{Na}})_b$ are the initial and final concentrations of sodium ions in the alkaline compartment, respectively; $(c_t^{\text{Cl}})_b$ is the concentration of chloride ions in the alkaline compartment at the end of experiment.

3. RESULTS AND DISCUSSION

The interpolymer cation-exchange membrane obtained from the PE/poly(St-co-DVB) system should be regarded as a microheterogeneous material [25], [32] consisting of:

- (i) poly(St-co-DVB)-SO₃⁻ microdomains forming membrane polyelectrolyte,
- (ii) inert polyethylene matrix.

It is assumed that poly(St-co-DVB) in this interpolymer system behaves similarly to the copolymer of St and DVB obtained by suspension copolymerization [32]. It is well known that properties of such a copolymer can be varied either by change of a crosslinking agent content [22] or by dilution of the monomers with inert solvents [26]–[29].

The interpolymerization of St and DVB in PE has been carried out under conditions where the following parameters have been kept constant:

- (i) monomer content with respect to PE (ensuring good ion-exchange properties of membrane) [24],
- (ii) DVB content in the monomer mixture (for which active transport of sodium ions was the most effective) [21],
- (iii) concentration of polymerization initiator,
- (iv) time and temperature [24].

In the experiments, the amount and kind of solvent subject to interpolymerization have been changed according to our requirements. In our previous studies [28],[29], the following solvents have been chosen:

- (i) toluene – sol type solvent (solvating the copolymer of St and DVB) [26],[27],
- (ii) iso-octane – non-sol type solvent [26],[27].

The gel type interpolymer obtained without the presence of solvents has been taken as a reference system. Ion-exchange groups have been introduced into all the

Table 1

Characteristics of cation-exchange membranes

Membrane	Exchange capacity Z_c mmol/g dry membrane	Water content P_w g/g dry membrane	Molarity of ion groups* C_m mmol/cm ³	Water permeability $10^7 J_h$ mol/cm ² sMPa
ESD	1.98	0.444	4.46	1.47
ESD/5-T	1.95	0.477	3.98	1.83
ESD/40-T	1.97	0.437	4.51	1.44
ESD/5-0	1.92	0.419	4.58	2.34
ESD/40-0	1.90	0.533	3.56	3.31

* The molarity of ion-exchange groups was calculated as $C_m = (Z_c/P_w)\rho_w$, where ρ_w (g/cm³) is density of water.

types of interpolymers under the same conditions [24]. The characteristics of the membranes are presented in table 1.

The membranes have similar ion-exchange capacity, while their equilibrium swelling in water depends on interpolymers conditions. Small toluene content (5 wt.%) increases the membrane swelling (ESD/5-T) when one refers to gel type membrane (ESD). According to MILLAR [26], during the polymerization in the sol system, the copolymer formed is in the swollen state. As a consequence, the microdomains contain less coiled copolymer chains in comparison to those generated in the gel system (with the same crosslinking degree). This can be seen on the electron micrographs (figs. 2 and 3). Examinations under transmission electron microscope were carried out at magnification of $36,000\times$.

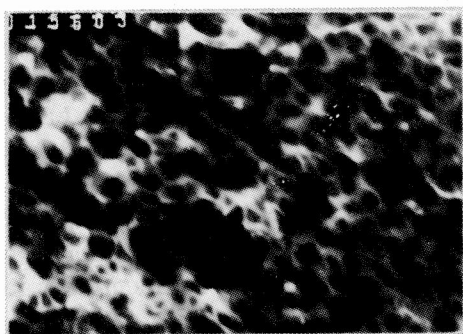


Fig. 2. Transmission electron micrograph of ESD membrane

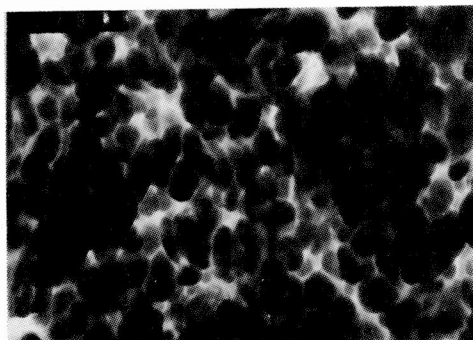


Fig. 3. Transmission electron micrograph of ESD/5-T membrane

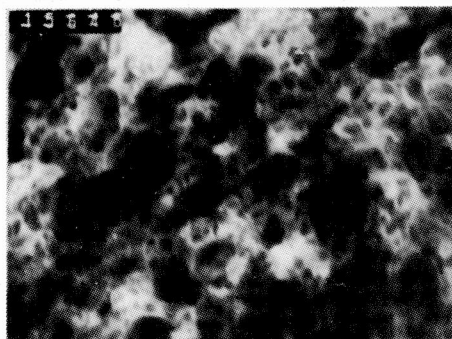


Fig. 4. Transmission electron micrograph of ESD/40-0 membrane

The sol type membrane does not swell so much when toluene content increases from 5 to 40 wt.% (ESD/40-T). Moreover, its swelling degree is comparable to that of gel type membrane (ESD). This behaviour was observed also for weakly basic

membranes [28]. It seems that elasticity of LDPE matrix reduces the swelling of the poly(St-co-DVB) microdomains when it is compared to the swelling of the suspension polymerized copolymer.

Presence of the non-sol solvent (isooctane) during interpolymerization accelerates phase separation which leads to a higher entanglement of copolymer chains inside weakly swollen microdomains. More porous structure is formed [33],[34]. At low isooctane content (ESD/5-0), the membrane swelling in water is smaller than that of the gel membrane (ESD). When isooctane content increases to 40 wt.%, the structure of ESD/40-0 membrane becomes more porous (fig. 4). The similar behaviour was observed when DVB content was higher [25].

According to TASAKA [35], the physical state of water is significantly affected by hydrogen bonding in gel and sol type membranes. In these cases the transport by site-to-site mechanism is performed, which means the transport through continuous polyelectrolyte network [36]. In non-sol type membranes, some amount of water is in free state and it fills pores among polyelectrolyte regions. Thus, volume diffusion plays a significant role in this case.

The electron microscope (figs. 2-4) allows observation of various structures of gel, sol and non-sol membranes. This observation confirms the above mentioned dependences. Moreover, the determination of water permeability through cation-exchange membranes supports our conclusions (table 1). Water permeability of ESD/5-0 membrane is higher than these of ESD membrane and membranes of both sol types (ESD/5-T and ESD/40-T), although the swelling of ESD/5-0 membrane in water is smaller.

The active transport of sodium ions through the membranes has been carried out in the system: 0.1 M NaCl+1 M HCl//membrane//0.1 M NaOH. The experimental results are shown in table 2 and in figures 5-9.

The active transport of sodium ions from the alkaline side to the acidic one through the gel type membrane (ESD) and the sol type membranes (ESD/5-T and

Table 2

Transport properties of cation-exchange membranes

Membrane	Efficiency of transport EF	Mean transport rate MTR mol/dm ³ m ² h	Relative selectivity SE	Time* t_{max} h
ESD	0.90	45.9	3.3	4
ESD/5-T	0.99	67.3	5.2	3
ESD/40-T	0.89	45.4	2.9	4
ESD/5-0	0.95	64.6	1.2	3
ESD/40-0	0.99	102.0	0.8	2

* t_{max} is the time at which the maximum sodium ion concentration was reached on the acidic side.

ESD/40-T) is mainly mediated by the ion-exchange groups. The best results have been achieved with the use of ESD/5-T membrane: the highest effectiveness at the shortest time and the highest relative selectivity. We have to emphasize there that the relative selectivity is the very important parameter. It gives the relative rate of sodium ions transfer with respect to chloride ions. Ideal strongly acid membrane should not be permeable to chloride ions and should guarantee high relative selectivity values. The changes of pH during the experiment are the smallest for the ESD/5-T membrane (fig. 10). This means that the membrane used for the active transport should have

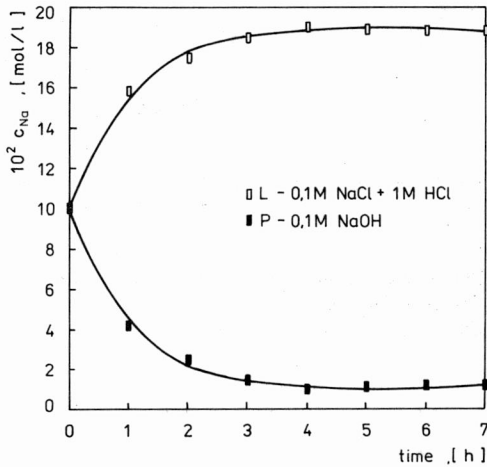


Fig. 5. Active transport of sodium ions through ESD membrane

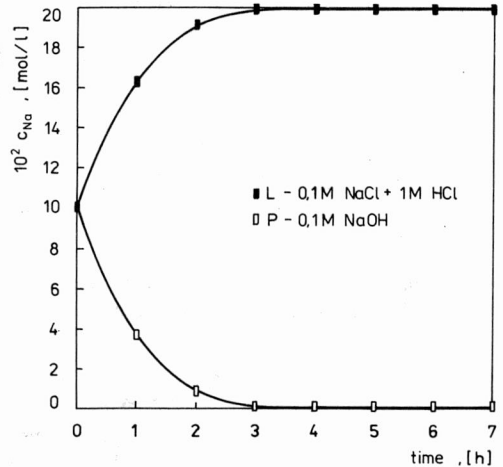


Fig. 6. Active transport of sodium ions through ESD/5-T membrane

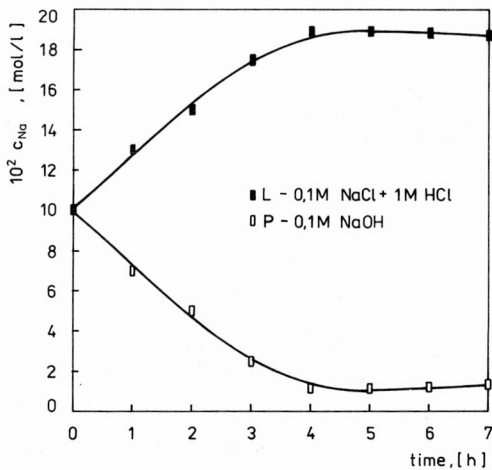


Fig. 7. Active transport of sodium ions through ESD/40-T membrane

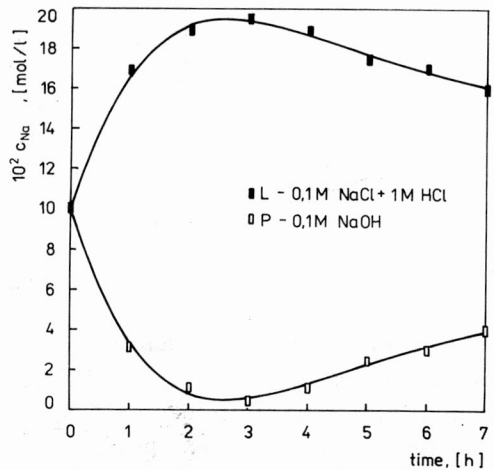


Fig. 8. Active transport of sodium ions through ESD/5-0 membrane

large ion-exchange capacity and appropriate structure assuring the site-to-site type diffusion.

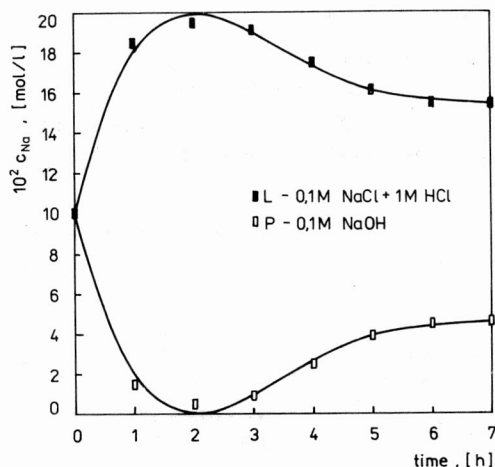


Fig. 9. Active transport of sodium ions through ESD/40-0 membrane

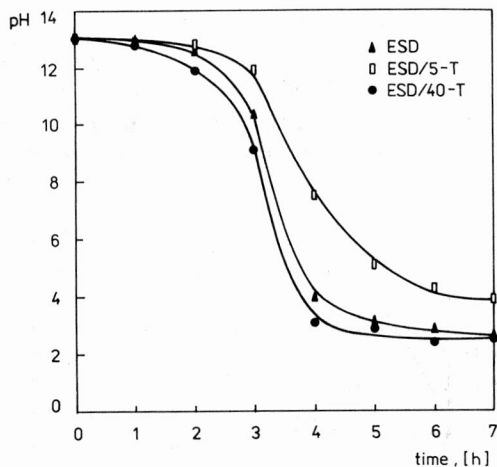


Fig. 10. pH changes on the alkaline side

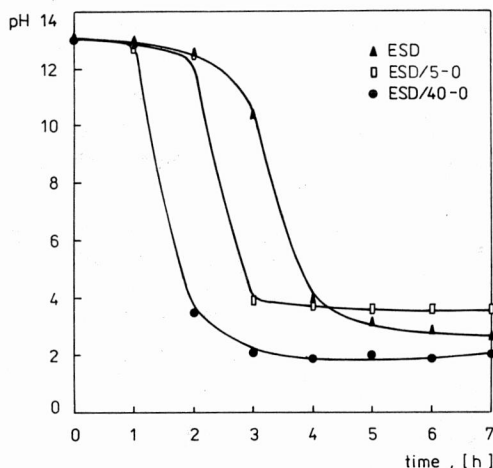


Fig. 11. pH changes on the alkaline side

For the non-sol type membranes (ESD/5-0 and ESD/40-0), the active transport effectiveness is also very good and is reached in a very short time (table 2). However, sodium ion concentration on the acidic side reaches maximum and then starts to decrease (fig. 8 and 9). The porous structure of the non-sol type membranes makes possible the back diffusion of sodium ions through the channels filled with water according to the volume-type mechanism [19]. The change of pH values on the

alkaline side is substantial for ESD/5-0 and ESD/40-0 membranes, so that driving force of process vanishes (fig. 11). Because volume-type diffusion is not ion-selective, the selectivity of the active transport through the non-sol type membranes is small. The respective relative selectivities of ESD/5-0 and ESD/40-0 are over 4 and 6 times smaller than that of ESD/5-T membrane (table 2).

4. CONCLUSIONS

The effectiveness and relative selectivity of active transport of sodium ions through interpolymer strongly acid membranes depends on the kind and amount of inert solvent during the interpolymerization. Carrying out the interpolymerization of St and DVB in LDPE with 5 wt.% of toluene makes possible to obtain the membrane of the structure appropriate for the active transport. This membrane allows predomination of the ion-selective site-to-site type diffusion over the nonselective volume type diffusion.

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AKTYWNY TRANSPORT JONÓW SODOWYCH PRZEZ INTERPOLIMEROWE MEMBRANY KATIONOWE OTRZYMANE W OBECNOŚCI ROZPUSZCZALNIKÓW

Badano aktywny transport jonów sodowych przez silnie kwasowe membrany z interpolimeru polietylen/poli(styren-co-diwinylbenzen). Interpolimery otrzymywano bez udziału rozpuszczalnika lub w obecności 5 i 40% wagowych toluenu (rozpuszczalnik typu zol) lub izooktanu (rozpuszczalnik typu nie zol).

Transport aktywny badano w układzie: 0,1 M NaCl+1 M HCl//membrana//0,1 M NaOH. Najbardziej efektywny i selektywny był transport jonów sodowych ze strony alkalicznej do kwasowej, gdy stosowano membrany z interpolimeru otrzymanego w obecności 5% wag. toluenu.

АКТИВНЫЙ ТРАНСПОРТ ИОНОВ НАТРИЯ ИНТЕРПОЛИМЕРНЫМИ КАТИОННЫМИ МЕМБРАНАМИ, ПОЛУЧАЕМЫМИ В ПРИСУТСТВИИ РАСТВОРИТЕЛЕЙ

Исследован активный транспорт ионов натрия сильно кислотными мембранами из интерполимера полистирол/поли(стирол-ко-дивинилбензол). Интерполимеры были получены без присутствия растворителя или в присутствии 5 и 40% веса толуола (растворитель типа золь) или изооктана (растворитель типа не золь).

Активный транспорт исследован в системе: 0,1 M NaCl+1 M HCl//membrana//0,1 M NaOH. Наиболее эффективным и селективным был транспорт ионов натрия от основной стороны к кислотной, когда применяли мембраны из интерполимера, полученного в присутствии 5% веса толуола.