GRYZELDA POŹNIAK*, WITOLD TROCHIMCZUK*

TUBULAR INTERPOLYMETER ION EXCHANGE MEMBRANES. ACTIVE TRANSPORT OF SODIUM IONS THROUGH CATION EXCHANGE MEMBRANES**

Active transport of Na^+ ions through tubular strong acid cation exchange membranes prepared from polyethylene–poly(styrene-co-divinylbenzene) systems [PE–poly(St-co-DVB)] was investigated. The membranes are formed from various amounts of DVB, i.e. 0.5, 2 and 10 wt.-%, in the aromatic component of the polymeric material. The active transport of Na^+ ions through these membranes was examined in the following system: 0.1 M NaOH (alkaline side)//membrane//0.1 M NaCl in HCl solution (acidic side). Transport experiments were carried out at four different starting concentrations of HCl solution: 0, 0.01, 0.1 and 1.0 mol/dm^3.

The best results were obtained for the membrane with 2 wt.-% of DVB and for the initial concentration of H^+ ions equal to 1 mol/dm^3.

1. INTRODUCTION

In recent years, active or uphill transport of matter through artificial membranes has received much attention as simulation of biological membrane systems and development of a new separation technology are taken into account.

Different types of chemical compounds have been employed in such membrane systems as carriers, e.g., cyclic polyethers [1], chelating agents [2], redox agents [3].

Transport of various substrates through synthetic membranes using carriers can occur in two different ways, the carrier being either mobile in the membrane phase or immobile and fixed to the membrane. The latter case is illustrated by ion exchange membranes with functional groups as fixed carriers [4]–[12].

TEORELL [13] was the first who studied active transport qualitatively and used a cation exchange membrane of this type. He discussed ion transport in terms of the steady state of the diffusion system.

This work is concerned with the active transport of sodium ions through tubular cation exchange membranes obtained from polyethylene/poly(styrene-co-divinylbenzene) [PE/poly(St-co-DVB)] system with varing content of the crosslinking agent (DVB).

2. EXPERIMENTAL

2.1. MEMBRANE PREPARATION AND CHARACTERISTIC

Tube-shaped samples of PE/poly(ST-co-DVB) system were obtained according to a procedure described elsewhere [14]. Weight percentage of DVB in the aromatic component of the polymer material (crosslinking degree of the interpolymer system) was 0.5, 2 and 10. The PE/poly(ST-co-DVB) tubes were chlorosulfonated with a 30 vol.-% solution of chlorosulfonic acid in 1,2-dichloroethane at room temperature for 4 h and then hydrolysed with a 20 wt.-% NaOH aqueous solution for 18 h.

The cation exchange interpolymer membranes were conditioned in the usual way and the total ion exchange capacity and water content were determined using standard methods [15, 16].

2.2. SYSTEM AND PARAMETERS

The active transport experiments were carried out at 25°C in a laboratory dialyser as described previously [17]. 0.1 M NaOH solution was pumped inside the ion exchange tube (alkaline side) and 0.1 M NaCl in HCl aqueous solution was fed to the jacket surrounding the ion exchange tube (acidic side). The solutions circulated in parallel at the same rate of 95 cm^3/min (linear rate, 0.224 m/s). The active surface of the membrane was 30 cm^2, the wall thickness of membrane was 0.025 cm, and the outer diameter of the cation exchange tube was 0.5 cm.

The experiments were carried out at four different starting concentrations of HCl solution on the acidic side, i.e. 0, 0.01, 0.1 and 1.0 mol/dm^3. The changes in concentration of sodium ions on both (alkaline and acidic) sides of the membrane were determined using atomic absorption photometry.

The active transport was characterized by:

1. The transport fraction of Na$^+$ ions

$$TF = \left[\frac{c_{max}^{Na} - c_0^{Na}}{c_0^{Na}} \right] \cdot 100 \quad [\%].$$

(1)

2. The mean transport rate of Na$^+$ ions

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

(2)

where c_0^{Na} and c_{max}^{Na} are the initial and maximum concentrations of Na$^+$ ions, respectively,

tively, on the acidic side (mol/dm^3); t_{max} is the time in which c_{max}^{Na} is achieved (h); S is the active surface of the membrane (m^2).

3. RESULTS AND DISCUSSION

The tubular PE/poly(ST-co-DVB) system was obtained as a result of interpolymerization of St and DVB within PE granulates and subsequent extruding the interpolymeter
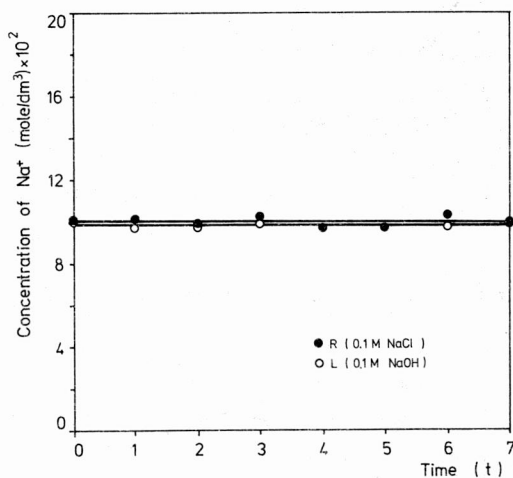

Fig. 1. Na^+ ion concentration on both sides of the membrane made from 2 wt.-% DVB versus time
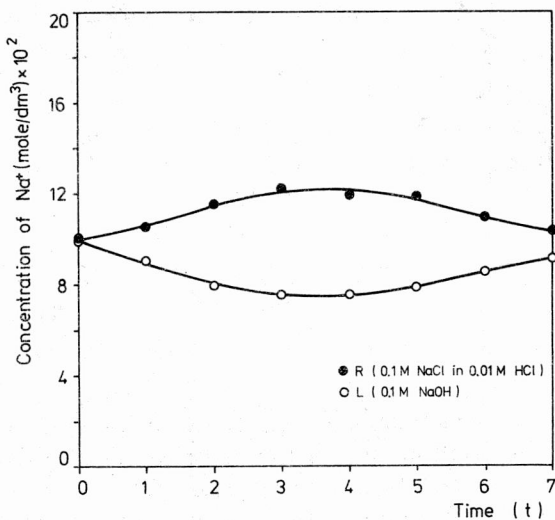

Fig. 2. Na^+ ion concentration on both sides of the membrane made from 2 wt.-% DVB versus time

Fig. 3. Na$^+$ ion concentration on both sides of the membrane made from 2 wt.-% DVB versus time

Fig. 4. Na$^+$ ion concentration on both sides of the membrane made from 2 wt.-% DVB versus time
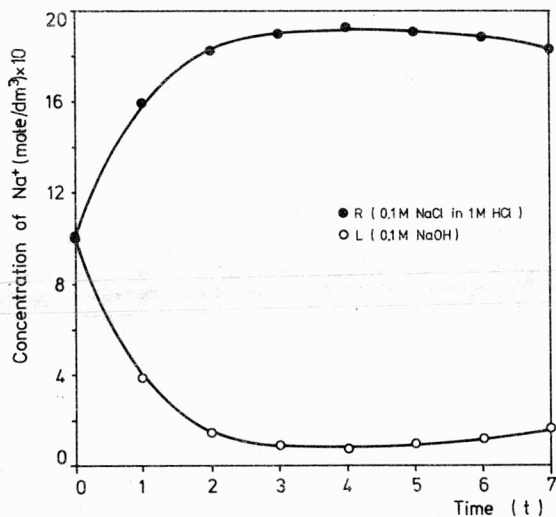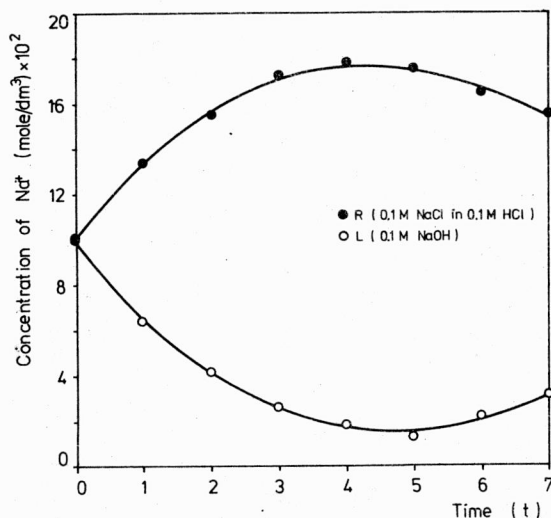
granulates to tube shape [14]. This procedure leads to formation of a microheterogeneous structure [18], [19]: isolated microdomains of poly(ST-co-DVB) are distributed within PE network [20]. After chlorosulfonation of the PE/poly(ST-co-DVB) system, cation exchange membrane was obtained. In this type of membrane PE served as the matrix and poly(St-co-DVB) with sulfonic groups as the crosslinked polyelectrolyte. It was assumed that the properties of poly(St-co-DVB) in this interpolymer system are similar to those of

a poly(St-co-DVB) copolymer obtained by suspension copolymetrization [19]. It is well known that the amount of DVB in the copolymer is the main factor that determines the properties of ion exchange materials [21]. The characteristics of the membranes are shown in tab.1.

Table 1

Characteristics of cation exchange membranes

Membrane wt.-% of DVB	Exchange capacity mmol/g dry membrane	Water content g/g dry membrane
0.5	1.95	0.768
2	1.98	0.625
10	1.85	0.355

The ion exchange capacities of the membranes are similar, but their equilibrium swelling in water depends strongly on the content of DVB in the membrane polyelectrolyte.

Changes in the concentration of Na^+ ions on both sides of the membrane with 2 wt.-% of DVB depending on time are shown in figs. 1–4. In the system where the membrane separated NaCl and NaOH solutions only (fig. 1), transport of Na^+ ions did not occur. When H^+ ions were added to NaCl solution (R-acidic-side), conditions changed drastically. The concentration of Na^+ ions on the R-side increased with time of transport, whereas on the L-side (alkaline side) it decreased with time. Because the initial concentration of Na^+ ions was identical on both sides, they were actively transported through the membrane from the alkaline side to the acidic side against its concentration gradient. The transport rate was dependent on the initial concentration of H^+ ions on the acidic side (figs. 2–4). The best results were obtained in the case when the initial concentration of H^+ ions on the acidic side was equal 1 mol/dm^3 (fig. 4). In this case the transported fraction of Na^+ ions (tab. 2) attained 90% and it is kept almost constant on this level.

On the other hand, URAGAMI et al. [11] investigated active transport of K^+ ions through cation exchange membranes from the poly(styrene sulfonic acid)–poly(vinyl alcohol) system and observed that transport fraction of K^+ ions equal 90% at initial concentration of H^+ ions exceeding 0.1 mol/dm^3 on the R-side.

In the system investigated, where one side is acidic and the other alkaline, the driving force of the active transport of alkali metal ions is a pH difference between the two sides of the cation exchange membrane. The increase of H^+ ion concentration on the acidic side leads to the greater transport fraction and mean transport rate of Na^+ ions.

This phenomenon may be explained (URAGAMI et al. [11]) by a tentative mechanism of the active transport of alkali metal ions through the membrane with sulfonic acid groups shown in fig. 5. Alkali metal ions incorporated into the membrane on the alkaline side are transferred by the sulfonic acid groups through the membrane and released by H^+ ions on the acidic side, while H^+ ions are easily counter-flowed by a proton jump mechanism [22]. Moreover, OH^- ions on the L-side and H^+ ions on the R-side diffuse through the

membrane due to concentration gradients of ions between both sides and the neutralization occurs in the membrane.

Table 2

Transport properties of cation exchange membranes

Membrane wt.-% of DVB	$10^2 c_{max}^{Na}$	t_{max}	c_0^H	TF*	MTR**
	mol/dm^3	h	mol/dm^3	%	mol/dm^{3}m^{2}h
0.5	17.75	5.5	1	77.5	4.7
	19.0	4	1	90	7.5
2	17.5	4	0.1	75	6.2
	12.5	3.5	0.01	25	2.4
10	15.8	6.5	1	58	3.0

*TF – transport fraction of Na$^+$ ions.

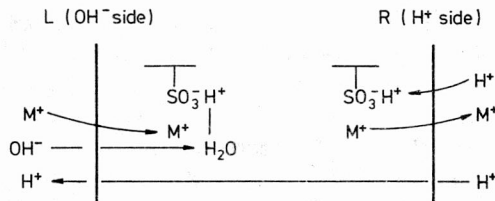**MTR – mean transport rate of Na$^+$ ions.

Fig. 5. Tentative mechanism of the transport of metal ions through the interpolymer cation exchange membrane with sulfonic acid groups

Investigations of the influence of membrane structure on the active transport of Na$^+$ ions can be conducted when the initial concentration of H$^+$ ions on the acidic side (R-side) equals 1 mol/dm^3 (figs. 4, 6, 7 and tab. 2).

The best transport properties are characteristic of the membrane with 2% DVB content; this membrane is characterized by high transport fraction and high mean transport rate of Na$^+$ ions (tab. 2).

For DVB content of 2%, a strong expansion of the crosslinked polyelectrolyte domains initially isolated might cause the polyelectrolyte network to become continuous [20]. The continuous polyelectrolyte network in the membrane makes possible a site-to-site diffusion mechanism [23], [24]. In this case the coupled transport of both ions through the membrane phase, i.e. H$^+$ ions from the R-side to the L-side (proton-jump mechanism [22]) and Na$^+$ ions from the L-side to the R-side (site-to-site diffusion [23], [24]), was easier (fig. 4 and tab. 2).

An increase of DVB content to 10% leads to the decrease of swelling of strong crosslinked polyelectrolyte domains (tab. 1, see water content). These domains are still isolated
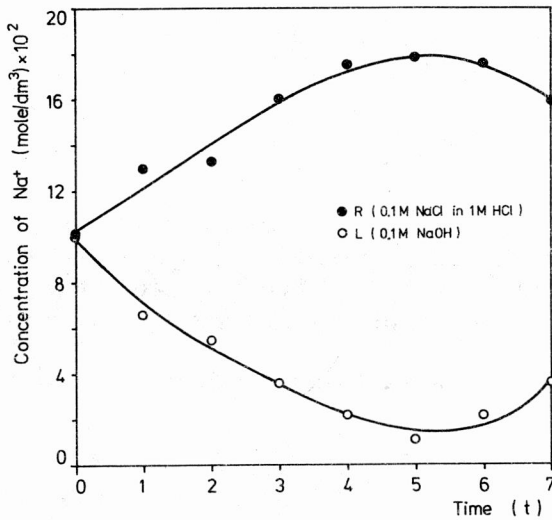
Fig. 6. Na^+ ion concentration on both sides of the membrane made from 0.5 wt.-% DVB versus time
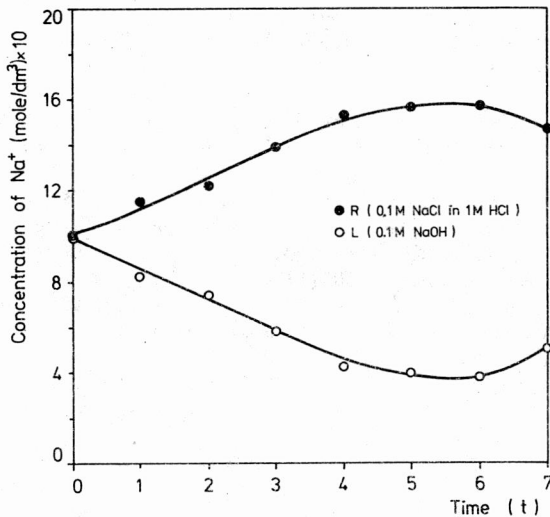

Fig 7. Na^+ ion concentration on both sides of the membrane made from 10 wt.-% DVB versus time

in the PE matrix [20]. The cation transport through this membrane is much worse because of difficulties in diffusion through the highly crosslinked polyelectrolyte and disconti-nuities of the polyelectrolyte network (fig. 7 and tab. 2).

This may lead to the conclusion that the lower crosslinking degree, the higher trans-port properties should be expected. However, this is in contradiction with the results con-cerning the membrane with 0.5% of DVB (fig. 6 and tab. 2). When the degree of

crosslinking of the membrane polyelectrolyte is low (0.5% DVB), the continuous network might be also created. Because of very strong swelling of polyelectrolyte domains, the wider channels filled with water might be formed [20]. This directs the reverse Na^+ ion diffusion of volume type [23] from R-side to the L-side.

4. CONCLUSIONS

Active transport of Na^+ ions proceeds through the interpolymer tubular cation exchange membranes made from polyethylene/poly(styrene-co-divinylbenzene). The efficiency of the active transport of Na^+ ions is dependent on the crosslinking degree of the interpolymer system and on the initial concentration of H^+ ions on the acidic side.

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TUBULARNE INTERPOLIMEROWE MEMBRANY JONOWYMIENNE. TRANSPORT AKTYWNY JONÓW SODU PRZEZ MEMBRANY KATIONOWYMIENNE

Przedstawiono wyniki badań transportu aktywnego jonów sodowych przez tubularne silnie kwasowe membrany formowane z układu PE/poly(St-co-DWB). Membrany różniły się zawartością DWB, który stanowił 0,5, 2,0 i 10% wag. w składniku aromatycznym układu. Transport aktywny realizowano w następującym układzie: 0,1 M NaOH (strona zasadowa)–membrana–0,1 M NaCl w roztworze HCl (strona kwasowa) o różnym początkowym stężeniu – 0, 0,01, 0,1, 1,0 mol/dm^3.

Najkorzystniejszą charakterystykę transportową (efektywność i szybkość przenoszenia jonu sodowego) uzyskano dla membrany z 2% DWB, pracującej przy 1 molowym początkowym stężeniu jonu wodorowego.

ТУБУЛЯРНЫЕ ИНТЕРПОЛИМЕРНЫЕ ИОНООБМЕННЫЕ МЕМБРАНЫ. АКТИВНЫЙ ТРАНСПОРТ ИОНОВ НАТРИЯ КАТИОНООБМЕННЫМИ МЕМБРАНАМИ

В настоящей работе представлены результаты исследований активного транспорта ионов натрия турбулярными сильнокислотными мембранами, формируемыми из системы PE-poly(St-co-DWB). Мембраны отличались содержанием DWB, а именно 0,5, 2,0 и 10% веса в ароматическом компоненте системы. Активный транспорт был реализован в следующей системе: 0,1 M NaOH (основная сторона)– мембрана–0,1 M NaCl в растворе HCl (кислотная сторона) разной начальной концентрации – 0, 0,01, 0,1, 1,0 моль/дм^3.

Наиболее полезная транспортная характеристика (эффективность и скорость переноса натрия) была получена для мембраны с 2% DWB, работающей при начальной концентрации иона водорода 1 моль.