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Transport of Halogen Ions through Synthetic Polymer Membranes Containing Pyridine Moieties

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ABSTRACT: Halogen ion transport through poly(4-vinylpyridine-*co*-acrylonitrile) membranes and a poly(4-vinylpyridine-*co*-styrene) membrane was investigated. Active transport of halogen ions was observed. For poly(4-vinylpyridine-*co*-acrylonitrile), both antiport and symport mechanisms were observed; for poly(4-vinylpyridine-*co*-styrene) only a symport mechanism was observed. The transport mechanisms and selectivities are explained in terms of membrane polarities based on Dimroth's solvent polarity value (E_T(25 °C)).

Introduction

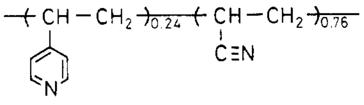
We have been studying halogen ion transport by synthetic polymer membranes having heterocycles as fixed carriers.[1-4] Poly(*N*-propenoyl-9-acridinylamine-*co*-acrylonitrile) membranes actively transported halogen ions by antiport mechanism, i.e., against a concentration gradient. Hydroxide ion transfer was the driving force.[3] In contrast, poly(1-vinylimidazole-*co*-styrene) transported halogen ion not only by an antiport mechanism but also by a proton-driven symport mechanism.[4] Transport mechanisms of halogen ions in the present paper are shown in Figure 1 for the benefit of easy understanding. Symport mechanism is when anionic substances are transported with simultaneous transfer of H^+ (1), while antiport mechanism is when they are transported with transfer of OH^- (2). In a previous paper we described the transport mechanism of halogen ions in terms of membrane polarity as reported by Dimroth's solvent polarity value (E_T(25 °C)).

In the present paper, 4-vinylpyridine was employed as a carrier. In order to obtain membrane with high or low polarities, acrylonitrile or styrene, respectively, were used as comonomers. We describe the relationship of halogen ion transport to membrane polarity, E_T(25 °C), and to the ratio of salt formation constants of the carrier with HCl and HBr.

Experimental Section

Materials. 4-Vinylpyridine (**3**), acrylonitrile (**4**), styrene (**5**), 2,2′-azobis(isobutyronitrile) (AIBN), benzene, *N*,*N*-dimethylformamide (DMF), and chloroform were purified by conventional methods.

Poly(**3**-*co*-**4**) (**1**) or poly(**3**-*co*-**5**) (**2**) were prepared by radical copolymerization initiated by AIBN at 60 °C. The results are summarized in Table I.



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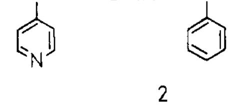

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Preparation of Membranes. Membranes of **1** were prepared as follows: a DMF solution (130 g dm^{-3}) was poured onto a glass plate with an applicator, with the casting thickness being adjusted to 0.254 mm. The solvent was allowed to evaporate at 40 °C for 6 h. The final thickness was 20–23 μm.

Membranes of **2** were prepared as follows: 10 cm^3 of a chloroform solution (140 g dm^{-3}) was poured into a flat laboratory dish (9.0-cm diameter) and the solvent allowed to evaporate at ambient temperature for 12 h. The thickness of the membrane was 20–24 μm.

Transport Measurements. The membrane (3.0 cm^2) was fixed tightly with Parafilm between two chambers of a PMMA cell. The volume of each chamber was 40 cm^3. All experiments were done at 30 °C without stirring.

Concentrations of bromide ion or chloride ion for experiments with **1** membranes were determined by Fajans' method[5] or by the mercuric nitrate method,[6] respectively. Those for experiments with **2** membranes were determined by Mohr's method.[7] In the case of the Br^-/Cl^- binary system, the concentrations of chloride ion for the **2** system were determined by Mohr's method, while Br^- concentrations were determined by Fajans' method. For binary Br^-/Cl^- systems, the components were first separated on a column of "Dowex 1-X8" (2.0 × 22.0 cm, eluant: gradient of $NaNO_3$, 0.1–0.5 mol dm^{-3}) and then analyzed as above.

The concentration of sodium ion was determined by atomic absorption spectrophotometry (Daini Seikosha, SAS-727).

Dimroth's solvent polarity values, E_T(25 °C), were measured as described previously, using 1-octadecyl-3,3-dimethyl-6′-nitrospiro[indoline-2,2′-2*H*-benzopyran] as an indicator.[8] A 250-W high-pressure mercury lamp was used as a light source. Absorption spectra were measured with a Shimadzu UV-240 UV–visible recording spectrophotometer.

Results and Discussion

Time Dependence of Halogen Ion Transport. Figure 2 shows typical time–transport curves of Cl^-. The concentration of Cl^- on the right side increased while that on the left side decreased. Some transfer of sodium ions occurred in every run. We observed no relation between the transport of sodium ion and that of halogen ion. During the initial stage of transport, changes in surface level were negligible. At later times, water was transferred from left to right. Hereafter, data presented are for the initial stage only.

Transport of Halogen Ions through Membrane 1. Halogen ion transport through membrane **1** was investigated in terms of the dependence of flux on the initial concentration of H^+ placed on the left side and the initial concentration of OH^- placed on the right. The results for Br^- (J) and Cl^- (J') transport through poly(4-vinylpyridine-*co*-acrylonitrile) (**1**) membrane are shown in Figure 3. The dependence of flux on the H^+ concentration on the left in HX–neutral (NaX) systems followed Michaelis–Menten type behavior, as was previously observed in the case of a poly(1-vinylimidazole-*co*-styrene) membrane.[4] In other words, the flux reached a maximum with increasing H^+ concentration. This result strongly supports a carrier-mediated mechanism for halogen ion transport. We conclude that halogen ions were transported against

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Table I
Results of Copolymerization[a]

polym	monomer/g 3	4	5	AIBN/g	benzene/cm^3	time/h	yield/g	mol fraction of 3 monom	polym	η_{sp}/dm^3 g^{-1} [b]
1	8.20	34.17		0.64	200	60	42.0	0.11	0.24	0.179
2	10.93		39.99	0.39		48	37.0	0.21	0.18	0.115

[a] Polymerization temperature was 60 °C. [b] Reduced viscosity was measured at c = 10.0 g dm^{-3} in DMF for 1 or in chloroform for 2 at 30 °C.

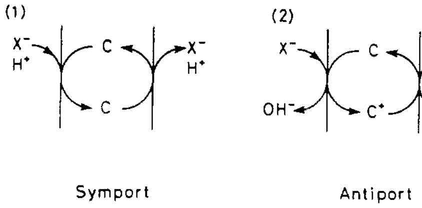

Figure 1. Anion transport mechanisms.

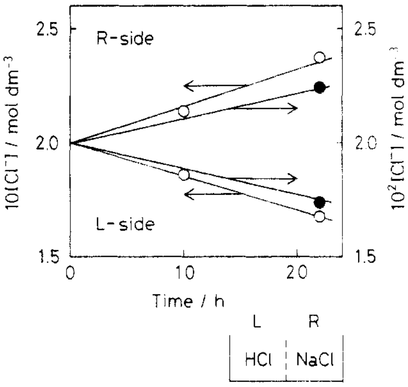

Figure 2. Time transport curves of Cl$^-$ through membranes 1 and 2: (●) membrane 1; (○) membrane 2. $[HCl]_{L,0} = [NaCl]_{R,0}$.

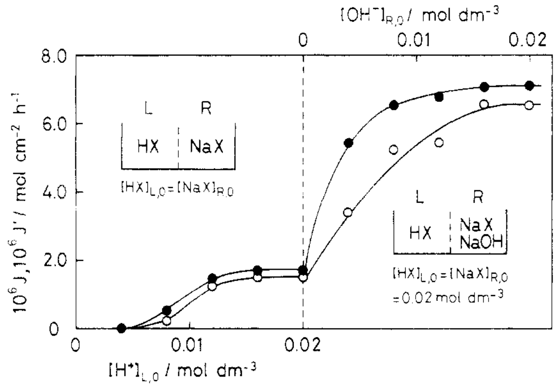

Figure 3. Effect of H$^+$ concentration and OH$^-$ concentration on Br$^-$ (J) and Cl$^-$ (J') fluxes through membrane 1: (●) X$^-$ = Br$^-$; (○) X$^-$ = Cl$^-$.

their concentration gradients, i.e., actively transported by a symport mechanism with H$^+$ transfer as a driving force.

The addition of NaOH on the right caused the fluxes to increase, as also shown in Figure 3. These fluxes were greater than the maximum fluxes observed when NaOH was not added. The increase resulted from an antiport mechanism in which OH$^-$ transfer was the driving force. In a previous work, fluxes through poly(N-propenoyl-9-acridinylamine-*co*-acrylonitrile) and poly(1-vinylimidazole-*co*-styrene) membranes increased linearly with increasing OH$^-$ concentration on the right (see ref 3 and 4), while fluxes through membrane 1 were nonlinear.

Presumably, the effective carrier complex concentration might diminish in the presence of OH$^-$ on the right, since the penetration of OH$^-$ into the membrane from the right prevented the formation of a carrier–HX complex (salt).

Table II
Obtained D and D' Values, λ_{max}^{vis}, and Dimroth's Solvent Polarity Values (E_T(25 °C)) for Membranes 1 and 2

membrane	[C]$_0$/mol dm^{-3}	D/cm^2 h^{-1}	D'/cm^2 h^{-1}	$\lambda_{max}{}^{vis}$	E_T (25 °C)/kcal mol^{-1}
1	3.20	1.18 × 10^{-6}	1.03 × 10^{-6}	543	54.0
2	2.34	3.43 × 10^{-6}	5.64 × 10^{-5}	599	33.2

As a result, the flux lines curved with increasing OH$^-$.

The low H$^+$ concentration region in the HX–neutral system using membrane 1 did not fit Michaelis–Menten type profiles. This might be due to the membrane not appropriately swelling to form carrier complex under these conditions.

The fluxes of Br$^-$ (J) and Cl$^-$ (J') are represented by the equations[4]

$$J = \frac{D}{l}\left(\frac{K[C]_0[HBr]_L}{1 + K[HBr]_L}\right) + \frac{k}{l}\left(\frac{K[C]_0[HBr]_L}{1 + K[HBr]_L}\right)[NaOH]_R \tag{1}$$

$$J' = \frac{D'}{l}\left(\frac{K'[C]_0[HCl]_L}{1 + K'[HCl]_L}\right) + \frac{k'}{l}\left(\frac{K'[C]_0[HCl]_L}{1 + K'[HCl]_L}\right)[NaOH]_R \tag{2}$$

symport antiport

where l is the membrane thickness, K and K' are the complex formation constants between the pyridine moiety (fixed carrier) and HBr or HCl, respectively, D and D' are the diffusion coefficients in the membrane for Br$^-$ and Cl$^-$, respectively, $[C]_0$ denotes the carrier concentration in the membrane, and $[HBr]_L$ and $[HCl]_L$ are the HBr and HCl concentration on the left. k and k' are apparent reaction constants, which are related to the exchange reaction between halogen ions and OH$^-$ at the right of the membrane, respectively, and $[NaOH]_R$ is the NaOH concentration on the right. The first terms on the right side of eq 1 and 2 represent the fluxes by a symport mechanism, carried out by H$^+$ transfer, and the second term the fluxes obtained by an antiport mechanism, carried out by OH$^-$ transfer. In the HX–neutral systems, maximum fluxes of Br$^-$ (J) and Cl$^-$ (J') are represented by

$$J_{max} = (D/l)[C]_0 \tag{3}$$

$$J'_{max} = (D'/l)[C]_0 \tag{4}$$

Limiting fluxes, J_{max}, J_{max}', $[C]_0$, and l allow the calculation of D and D'. The values, calculated in this way, are summarized in Table II.

Transport of Halogen Ions through Membrane 2. Figure 4 shows the halogen ion flux dependence on [H$^+$] on the left and [OH$^-$] on the right. As in the case of membrane 2, the flux dependence on HX–neutral system followed Michaelis–Menten behavior, although this was not true at low H$^+$ concentrations. The flux dependence on OH$^-$ concentration for membrane 2 was different from that observed for membrane 1. The fluxes did not change

Table III
Fluxes and Carrier Complex Concentration of Membranes 1 and 2

membrane	$[HBr]_{L,0}/([HBr]_{L,0} + [HCl]_{L,0})$	J/mol cm^{-2} h^{-1}	J'/mol cm^{-2} h^{-1}	[C–HBr]/mol dm^{-3}	[C–HCl]/ mol dm^{-3}	[C–HBr]/ ([C–HBr] + [C–HCl])
1	0.2	1.71×10^{-7}	1.23×10^{-6}	0.32	2.62	0.11
	0.5	5.23×10^{-7}	9.99×10^{-7}	0.99	2.13	0.32
	0.8	1.14×10^{-6}	4.79×10^{-7}	2.13	1.02	0.68
2	0.2	2.45×10^{-6}	5.93×10^{-6}	1.57	0.23	0.87
	0.5	3.11×10^{-6}	1.94×10^{-6}	1.99	0.08	0.96
	0.8	3.74×10^{-6}	5.87×10^{-7}	2.39	0.02	0.99

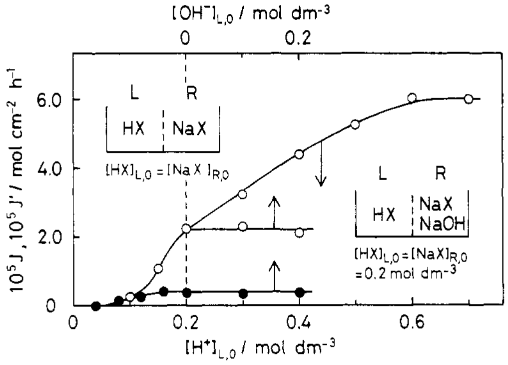

Figure 4. Effect of H^+ concentration and OH^- concentration on Br^- (J) and Cl^- (J') fluxes through membrane 2: (●) $X^- = Br^-$; (○) $X^- = Cl^-$.

with changing OH^- concentration. Therefore, halogen ions were actively transported through membrane **2** by only a symport mechanism, with H^+ transfer as the driving force. Thus, the fluxes through membrane **2** can be written as

$$J = \frac{D}{l}\frac{K[C]_0[HBr]_L}{1 + K[HBr]_L} \tag{5}$$

$$J' = \frac{D'}{l}\frac{K'[C]_0[HCl]_L}{1 + K'[HCl]_L} \tag{6}$$

In the HX–neutral systems, maximum fluxes are represented by eq 3 and 4. Derived D and D' values are listed in Table II.

Effect of Membrane Polarity on Transport Mechanism. In a previous paper,[4] the transport mechanism of halogen ions was related to a degree of membrane polarity that was based on Dimroth's solvent polarity value (E_T(25 °C)) of the membrane. In that work, imidazolyl and acridine moieties were the fixed carriers. Carrier contents in the membrane also differed. In this work, the same fixed carrier is used for both membranes. Therefore, the effect of membrane polarity on the transport mechanism can be examined independent of fixed carrier type.

E_T(25 °C) values of membranes 1 and 2 are summarized in Table II. Membrane 1 had a higher membrane polarity than membrane 2. When compared to small molecules,[9] the polarity of membrane 1 is equivalent with that of *N*-methylformamide and the polarity of membrane 2 is equivalent with that of toluene.

Our findings can then be interpreted as follows: in highly polar membrane 1, HX and the carrier (pyridine moiety) formed a relatively stable salt. As a result, transport requires that halogen ions are released by exchange with OH^-. An antiport mechanism was observed for membrane 1. Though membrane 1 had such a high polarity, a part of the salt dissociated into HX and carrier on the right without exchange of halogen ion with OH^-. This yields the symport mechanism.

In contrast, the salt formation in membrane 2 was unfavorable because of the low membrane polarity. As a result, only the symport mechanism was active.

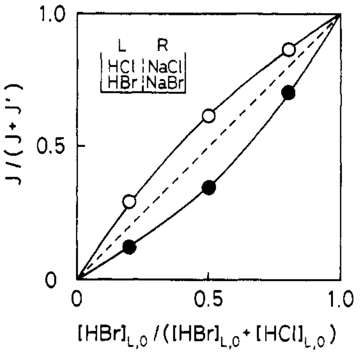

Figure 5. Effects of feed fraction on selectivities for the transport of anions through membranes 1 and 2. ($[HBr]_{L,0} = [NaBr]_{R,0}$; $[HCl]_{L,0} = [NaCl]_{R,0}$); (●) membrane 1, $[HBr]_{L,0} + [HCl]_{L,0} = [Na_{Br}]_{R,0} + [NaCl]_{R,0} = 0.02$ mol dm^{-3}; (○) membrane 2; $[HBr]_{L,0} + [HCl]_{L,0} = [NaBr]_{R,0} + [NaCl]_{R,0} = 0.2$ mol dm^{-3}).

These results, combined with previously reported results,[4] lead to the conclusion that the membrane polarity was the dominant factor in determining transport mechanism. The type of carrier has little influence. This suggests that transport mechanism can be controlled through the membrane polarity.

Selective Active Transport in a Br^-/Cl^- Binary System. To study selectivity, we tested binary Br^-/Cl^- solutions. The total initial concentration of anions was the same on both sides of the membrane (0.02 mol dm^{-3} for membrane 1, 0.2 mol dm^{-3} for membrane 2); the cations were H^+ on the left and Na^+ on the right. The observed initial flux of Br^- and Cl^- is plotted against the mole fraction of Br^- in Figure 5.

Membrane 1 preferentially transported Cl^-, which was considered to be more hydrophilic than Br^-,[10] while membrane 2 preferentially transported Br^-, which was considered to be more hydrophobic than Cl^-.[10] In this system, the fluxes of Br^- and Cl^- are represented by eq 7 and 8,

$$J = (D/l)[C\text{–}HBr] \tag{7}$$

$$J' = (D'/l)[C\text{–}HCl] \tag{8}$$

which are simplifications of eq 5 and 6. In eq 7 and 8, [C–HBr] and [C–HCl] represent the carrier–complex concentrations of C–HBr and C–HCl, respectively. From the observed flux values and diffusion coefficients (summarized in Table II), we can calculate the carrier–complex concentration for any experimental conditions. In Figure 6, the mole fraction of C–HBr in the membrane ([C–HBr]/([C–HBr] + [C–HCl]) is plotted against the mole fraction of HBr initially placed on the left. The values are summarized in Table III. The fraction of C–HBr in the membrane can be represented by using the fraction of HBr on the left side.[2,3]

$$\frac{[C\text{–}HBr]}{[C\text{–}HBr] + [C\text{–}HCl]} = \frac{f_{Br}}{(1-\alpha)f_{Br} + \alpha} \tag{9}$$

where $f_{Br} = [HBr]_L/([HBr]_L + [HCl]_L)$ and $\alpha = K'/K$. By

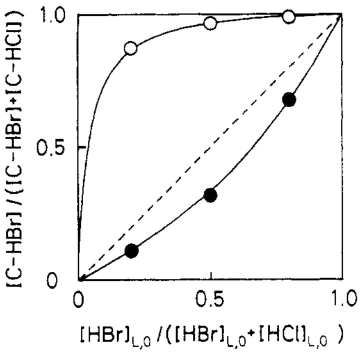

Figure 6. Relationship between the fraction of C–HBr in the membrane and the feed fraction: (●) membrane 1; (○) membrane 2. Experimental and calculated values are summarized in Table III.

trial and error, we fitted eq 9 to the data. The solid lines in Figure 6 were calculated by assuming values $\alpha = K'/K = {}^2/_1$ for membrane 1 and ${}^1/_{25}$ for membrane 2. In other words, in membrane 1, the salt formation constant between the carrier and HCl was 2 times greater than that between the carrier and HBr. In the membrane 2 system, the salt formation constant between the carrier and HBr was 25 times greater than between the carrier and HCl. The different membrane polarities may be the reason for the drastic difference in salt formation constants even though membrane 1 and 2 contained the same fixed carrier. Membrane 1 formed a more stable complex with hydrophilic Cl^- than with hydrophobic Br^-. In contrast, membrane 2 formed a more stable complex with Br^- than Cl^-. In conclusion, the membrane polarity not only determined the transport mechanism but also played an important role in controlling affinity between carriers and substrates (halogen ions).

Conclusions

Membrane 1 (highly polar) transported halogen ions not only by an antiport mechanism with OH^- transfer but also by a symport mechanism with H^+ transfer. Membrane 2 (low polarity) transported halogen ions only by a symport mechanism. Membrane 1 selectively transported Cl^-, while the membrane 2 transported Br^-. The values $K'/K = {}^2/_1$ for membrane 1 and ${}^1/_{25}$ for membrane 2 were determined.

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Registry No. 1, 32236-74-1; 2, 26222-40-2; bromide ion, 24959-67-9; chloride ion, 16887-00-6.

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Dichlorocarbene Adducts of 1,4-Polybutadienes. Improved Synthesis and Characterization by High-Field NMR

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ABSTRACT: An efficient method for obtaining the dichlorocarbene adducts of 1,4-polybutadienes is described. The procedure involves mild, nonbasic, and homogeneous reaction conditions to generate dichlorocarbene from the organomercury precursor phenyl(bromodichloromethyl)mercury (Seyferth reagent) in the presence of polybutadienes. This methodology represents a significant improvement over treatment of chloroform with strong base in that strictly neutral conditions are employed; no block structure results and high degrees of conversion can be achieved readily. Complete double bond conversion provides the structural equivalent of 1:1 poly(dichlorocyclopropene-*co*-ethylene). We use high-field NMR to characterize the chemical microstructures of the adducts from both *cis*- and *trans*-1,4-polybutadienes at varying extents of cyclopropanation and verify that carbene addition is stereospecific. Proton NMR (500 MHz) is used to measure the degree of conversion and establish the geometry of the cyclopropyl ring. Carbon-13 NMR (125.7 MHz) is used to probe more detailed microstructural features involving monomer and stereosequence effects. Monomer sequence pentads are observed for olefinic carbons in partially converted materials, whereas the gem-dichloro carbons are less sensitive and reveal triad monomer sequences. These quaternary carbons also reveal triad stereochemical sequences in the trans adducts. The copolymers are almost perfectly random (Bernoullian) in both monomer and stereosequence distribution.

Introduction

Recently we described the synthesis and characterization of a series of novel cyclopropanated fluoropolymers obtained by the addition of difluorocarbene to *cis*- and *trans*-1,4-polybutadienes.[1] The carbon-13 NMR assignments of these copolymers, particularly for the cyclopropyl ring carbons, were complicated by the presence of significant $^{13}C-^{19}F$ scalar couplings, which obscured the fine

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