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M. Ersoz[a]; A. Keles[a]; S. Yildiz[a]
[a] DEPARTMENT OF CHEMISTRY FACULTY OF ARTS AND SCIENCES, SELCUK UNIVERSITY, KONYA, TURKEY

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Diffusion of Amines through Polysulfonated Ion-Exchange Membranes

M. ERSOZ,* A. KELES, and S. YILDIZ
DEPARTMENT OF CHEMISTRY
FACULTY OF ARTS AND SCIENCES
SELCUK UNIVERSITY
42079 KONYA, TURKEY

ABSTRACT

The permeabilities and diffusion behaviors of aniline, *p*-chloroaniline, and *p*-nitroaniline were investigated in polysulfonated ICE-450 ion-exchange membranes as a function of pH at 25°C. The permeabilities for these compounds increased with decreasing of receiver side pH. The modes of membrane/solution distribution and diffusion of amines, as a controlling factor to the membrane permselectivity in terms of basicity value, molecular size, and electrophilic groups of amines, were correlated consistently with the flux data as well as with the estimated membrane permselectivity parameters. The transport system depends on the basicity values of amines, and the pH gradients were the main driving force. It is shown that the diffusion parameters measured on single component experiments provide a good prediction of behavior.

INTRODUCTION

The diffusion of ions and molecules through Nafion have been extensively reported (1–4). Only a few studies have been reported on the diffusion of organic compounds through ion-exchange membranes (5–8). In this study the transport of amines through ICE-450 membranes was investigated at various pH values.

Transport properties of low molecular weight organics in ion-exchange membranes have recently been explored. The transport rates of low molecular weight organic acids (6) and amino acids (5) were faster than for

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* To whom correspondence should be addressed.

water and were highly dependent on the pH of the external solution. Furthermore, the activation energy for transport was higher than would be expected for simple diffusion (9).

Amines are of interest because their chemical interactions with ionomers have been well established. Protonated amines can be ion exchanged into cationic-exchange polymers and exist in the ionomers as a cation (9). Hydrogen ions in cationic-exchange polymers are very reactive and have a behavior similar to that in aqueous solutions of pH 1 or lower (10). The amines also exists as ammonium ions in the acid form of cationic-exchange polymers (10), and the $-NH_2$ group in aromatic amines is about 10^6 less basic than in aliphatic amines. They are of practical value and are often used as intermediates in various industrial products such as dyestuffs, drugs, and perfumes.

The purposes of the present study were to investigate the effect of the external solution pH on the transport process and transport properties of new ion-exchange membranes produced for posttreatment processing of low organic molecules, to correlate these results systematically with results based on linear phenomenological analyses in transport systems with a cation-exchange membrane, and to extend the transport data set to amines.

EXPERIMENTAL

Materials

All chemicals were purchased from Merck and were reagent grade. ICE-450 polysulfonated membrane with polyester support (SA_3T) and without polyester support (SA_3S) was obtained from Gelman Sciences. Spectrapor Dialysis membrane (Spectrum Medical Industries Inc., wet cellulose dialysis tubing in 1% sodium azide composed of cotton cellulose, 0.05 mm thick, with a nominal molecular weight cutoff of 3500) was used for comparison.

ICE-450 ion-exchange membranes are true microporous membranes. They are strongly acidic cation-exchange polysulfone membranes and have an ion-exchange capacity of 0.19 meq per 47 mm disk and a thickness of 152.4 μm in the hydrogen form. The membrane disks in the H^+ form were pretreated in boiling water for 1 hour and then conditioned by a cycle of equilibrations with, in turn, HCl, distilled water, NaOH, and finally distilled water. The protocol for treating with HCl and NaOH is to remove any base- or acid-soluble impurities. The membrane disks were then pretreated with 0.1 M HCl to be used in the measurements.

Methods

The diffusion experiments were performed according to a method described previously (11). The apparatus used for diffusion measurements consisted of two borosilicate half cells. The membrane was set in the middle of the two parts of the cell. The donor and receiver solutions were each 13 mL, the effective membrane area (A) was 2.05 cm^2, and the cell was maintained at 25 ± 1°C. The donor solutions were amines of 0.01 mol·dm^{-3} concentrations (the solvent was 25% methanol and 75% water) and the receiver solutions were H_2SO_4 applied at different pH values (1.0–4.0). Samples were withdrawn from the receiver solution at regular intervals. The concentrations of aromatic amines were determined by UV spectrophotometer (UV 160A Shimadzu) at 238 nm for aniline, 296 nm for *p*-chloroaniline, and 290 nm for *p*-nitroaniline.

RESULTS AND DISCUSSION

The values of the diffusion coefficient and permeabilities of aromatic amines across the membrane are presented in Table 1. The diffusion coefficients of aromatic amines, calculated as described previously (11), were calculated from the slopes of the linear relationship between concentration and time by using

$$\ln\frac{C_{1(t_0)}}{C_{2(t)}} = \frac{2DA}{Vl}t \qquad (1)$$

where $C_{1(t0)}$ is the solution concentration in the source side at time zero, in mol·dm^{-3}; $C_{2(t)}$ is the concentration difference between $C_{1(t0)}$ and the solution concentration in the receiver side at time t, in mol·dm^{-3}; V is the volume of the receiver side (the volumes of solution on both sides were equal), in cm^3; D is the diffusion coefficient, in $\text{cm}^2\text{·s}^{-1}$; A is the active area of the membrane, in cm^2; and l is the membrane thickness, in cm.

The permeation process across membranes is usually described in terms of Fick's law. The flux (J) is proportional to D and to the driving force dC/dx, where C is the concentration and x is the space coordinate in the direction of flow. Steady-state conditions were generally obtained within 5 minutes. In the steady state,

$$J = D\Delta\bar{c}/l = P\Delta c \qquad (2)$$

where $\Delta\bar{c}$ is the difference in permeant concentration in the membrane phase, and P, which defines the permeability, is calculated from the flow of a penetrated solute across a membrane as a function of driving force:

$$P = (D\Delta\bar{c}/\Delta c)/l \qquad (3)$$

In our system the permeability of aromatic amines increased with increasing basicity values and lower pH values on the receiver side. The receiver side solution was sulfuric acid (pH 1–4). The highest transport was observed when the receiver side solution was at pH 1. Since this experiment is designed with no supporting electrolyte on the source side, the amines apparently enter and leave the membrane through reaction with solvated protons. When discussing the diffusion of aromatic amines through membranes, cations (the anilinium ion) should be taken into consideration. Amines are capable of forming hydrogen bonds with methanol (or water) and are therefore partially protonated in solution (methanol). Thus, amines enter the membrane through protonation and leave by ion exchange. A description of the system is shown in Fig. 1.

The transport process for aromatic amines through ion-exchange membranes can be assumed to occur according to the following sequence.

1. Diffusion of amine to the surface of the membrane. In a stirred system this diffusion occurs across the unstirred boundary layer (Nernst layer) adjacent to the interface.
2. The amine diffuses into the surface of the membrane and reacts with a proton in the membrane phase to form a cation (anilinium ion).
3. The anilinium ion diffuses through the membrane by a ion-exchange mechanism.
4. The substrate is released at the membrane/aqueous interface (receiver side).

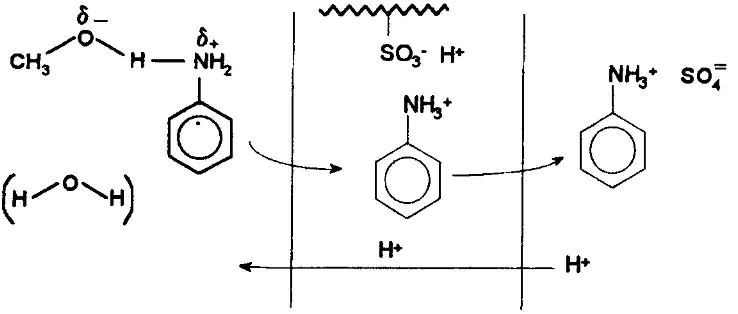

FIG. 1 Description of the transport system for aromatic amines through ICE-450 membranes.

Consequently, the amine exits the membrane to enter the receiver phase. The proton remains in the membrane and diffuses toward the source side. Finally, the amine diffuses through the liquid-phase boundary layer on the receiver side of the membrane.

Processes 1 and 4 can be altered by adjusting either the pH or the concentration of the external solutions. The reaction in the source phase of the membrane can be stopped by lowering the pH of the solution to a level that insures solute protonation. The amine then enters through the membrane by an ion-exchange mechanism instead of by a reaction; the exit process is similarly affected by the pH of the receiver side. When the pH of the receiver side solution is lower than the protonation pH, the amine exits the membrane through ion exchange. More amine diffused when the pH of the receiver side was at a lower level. Amines are partly protonated in acidic solutions. The methanol used as a solvent (25%) was necessary in order to increase the amine solubility in water and also the protonation of aromatic amines.

The permeabilities and diffusion coefficients were found to be reproducible to within between 5 and 10%. There are no comparable data in the literature about this membrane. The rate of transport of aromatic amines in polysulfonated ion-exchange membranes is controlled by protonation at the surface of the membranes and ion exchange. The rate of protonation determines the species that transports fastest. Transport was largest when the amine entered the membrane through the protonation process and exited the membrane by ion exchange.

Many workers have reported that mass transport through ion-exchange membranes is complicated and that, in addition diffusion, the potential distribution influences inside the membrane (such as migration effects, swelling, hydration) should also be taken into consideration (12, 13). Furthermore, diffusion is complicated by a nonlinear concentration distribution caused by potential distribution inside the membrane. However, the linear concentration gradients of amines passing through the membranes were assumed to be under steady-state conditions.

Molecular diffusion through the aqueous pores of the membrane structure was assumed for the transport of amines within the membrane, and since the pressure difference between the two cells (including the osmotic pressure) was small under the experimental conditions, contributions from convection were considered to be negligible. The membranes were assumed to be microporous films. The micropores correspond to the ionic clusters of Nafion, which contain almost all of the water and ionic species and are thought to be responsible for the diffusion of anilinium cations (7).

The pH level of the receiver side has a large influence on transport which increases at lower pH, as shown in Fig. 2. Transport would also be expected to depend on pK_a. Transport was increased with a decrease of pH on the receiver side, and as would be expected due to protonation of the —NH_2 group, decreased relative to that at higher pK_a. The effect is more pronounced for more basic amines. Since a more basic amine would pass the membranes, K_b would be expected to increase with the basicity of the aromatic amines. This is corroborated by Fig. 3. In this

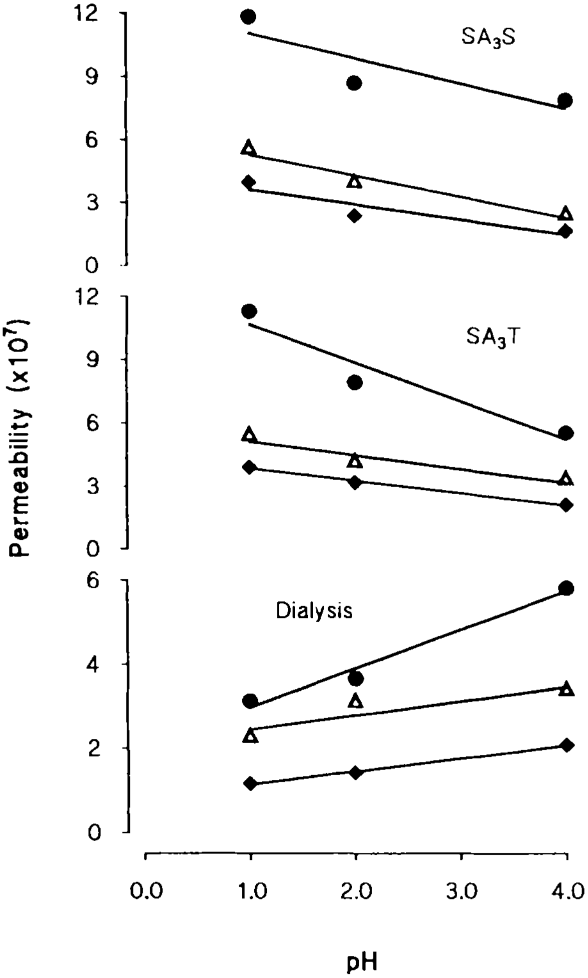

FIG. 2 The permeability of amines against pH: (●) aniline, (△) *p*-chloroaniline, and (◆) *p*-nitroaniline.

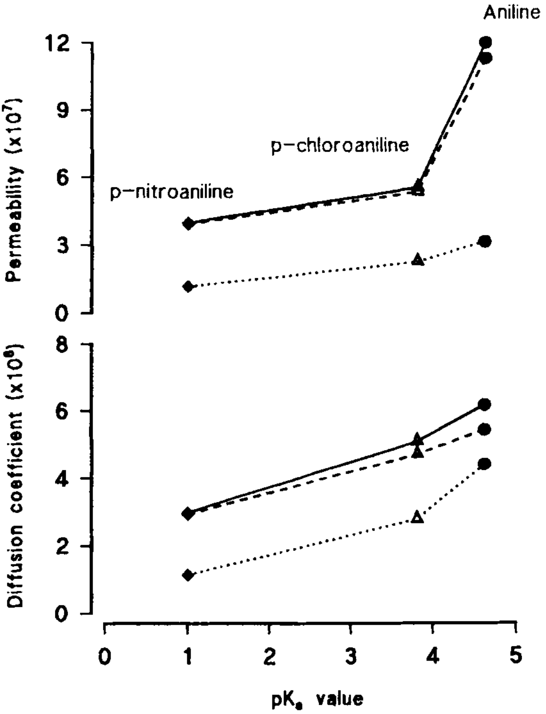

FIG. 3 Effect of pK_a values on the permeability and diffusion coefficients for (——) SA_3S, (- -) SA_3T, and (····) Spectrator Dialysis membranes at pH 1.

study the pK_a values for aniline, *p*-chloroaniline, and *p*-nitroaniline were 4.62, 3.81, and ~1.0, respectively (14). Transport was in the order aniline > *p*-chloroaniline > *p*-nitroaniline, which is in the order of increasing basicity and molecular size of amines. Amines contain an unshared pair of electrons and a NH_2 group which shares its electrons with the ring and can accept a positive charge. Basicity depends upon the ability to accommodate a positive charge. The basicity of an amine depends on the substituent group. The effects influencing the basicity of aromatic amines are the effect of alkyl substitution, the inductive effect, and the resonance effect. The pK_a of an anilinium ion is also directly related to the standard free-energy difference ($\Delta G°$) between it and its conjugate base by the equation $\Delta G° = 2.3RTpK_a$. The tendency for the —NH_2 group to release electrons to the ring through resonance makes the ring more reactive toward electrophilic attack. Electron withdrawal tends to intensify the positive charge of the anilinium ion. The Cl and NO_2 groups are electron-withdrawing substituents (electron acceptors) and decrease the basicity of the aromatic amines. The Cl group can withdraw electrons from the ring by the inductive effect, but at the same time the Cl group can present its electrons to the ring by the resonance effect, and thus the decrease of basicity values of *p*-chloroaniline is somewhat less than that of aniline. Because the NO_2 group withdraws electrons by both the inductive effect and the resonance effect, the decrease of basicity values of *p*-nitroaniline is rather less.

Transport data were obtained for aromatic amines. The results are presented in Table 1 where each entry is the average of three experiments with

TABLE 1

Permeability, Diffusion Coefficients, and Steady-State Fluxes for Amines on Membranes (data are averaged values over three experiments, standard deviations were 5–10%)

Membrane	pH	Amine	P ($\text{cm}\cdot\text{s}^{-1} \times 10^7$)	D ($\text{cm}^2\cdot\text{s}^{-1} \times 10^8$)	J ($\text{mol}\cdot\text{cm}^2\cdot\text{s}^{-1} \times 10^5$)
SA_3S	1.0	Aniline	12.0	6.17	7.00
	2.0		8.71	3.82	6.94
	4.0		7.92	3.09	6.17
	1.0	*p*-Chloroaniline	5.56	5.09	8.92
	2.0		3.93	3.05	7.21
	4.0		2.42	2.77	4.73
	1.0	*p*-Nitroaniline	3.98	2.97	6.28
	2.0		2.38	2.24	4.55
	4.0		1.69	1.27	3.38
SA_3T	1.0	Aniline	11.3	5.43	9.01
	2.0		7.94	4.72	6.12
	4.0		5.57	3.82	5.71
	1.0	*p*-Chloroaniline	5.37	4.71	8.76
	2.0		4.12	3.27	7.30
	4.0		3.32	3.09	6.22
	1.0	*p*-Nitroaniline	3.92	2.92	6.53
	2.0		3.20	2.24	5.77
	4.0		2.14	1.66	4.16
					J ($\text{mol}\cdot\text{cm}^2\cdot\text{s}^{-1} \times 10^7$)
Spectrapor Dialysis	1.0	Aniline	3.14	4.40	3.67
	2.0		3.67	5.44	5.41
	4.0		5.83	5.96	8.55
	1.0	*p*-Chloroaniline	2.25	2.78	1.65
	2.0		3.09	3.35	2.78
	4.0		3.38	3.82	3.41
	1.0	*p*-Nitroaniline	1.15	1.14	1.24
	2.0		1.41	1.51	1.55
	4.0		2.08	1.77	2.17

each solution. Diffusion coefficients and permeabilities varied between 5 and 10% of the mean values presented. The permeabilities and diffusion coefficients were all of similar magnitude based on the molecular size of aromatic amines and the basicity values. Compared with perfluorosulfonated ion-exchange membranes, the permeabilities of aromatic amines on ICE-450 polysulfonated membranes are very similar. The values for aniline, *p*-chloroaniline, and *p*-nitroaniline are 12.4×10^{-7}, 5.26×10^{-7}, and 3.98×10^{-7} $cm \cdot s^{-1}$ for Sa_3S and 11.3×10^{-7}, 5.37×10^{-7}, and 3.92×10^{-7} $cm \cdot s^{-1}$ for SA_3T membranes, respectively. They compare well with values for perfluorosulfonated ionomer membranes: 6.6×10^{-9}, 6.6×10^{-9}, and 7.6×10^{-9} $m^2 \cdot s^{-1}$, respectively (9). The diffusion coefficients for aniline were 5.09×10^{-8} for SA_3S and 5.43×10^{-8} $cm^2 \cdot s^{-1}$ for SA_3T membranes, while with apparent diffusion coefficient value for Nafion 117 perfluorosulfonate membrane was 1.2×10^{-8} $cm^2 \cdot s^{-1}$ (8). Comparison shows that the data obtained by the ICE-450 membranes are also in good agreement with the Nafion 117 membrane.

Compared with a dialysis membrane, the effect of pH on the receiver side is reversed due to the fixed functional groups in the membranes. This membrane, which is a weak acid cation exchanger and has carboxyl functional groups which are dissociable above pH 4 and has an apparent pK_a value of 4.1 for the carboxyl groups (15), behaves as a cationic-exchange substance in neutral media. At lower pH, where the carboxylic groups are not dissociated, the membrane acts as an uncharged diaphragm.

The measured values of the flux and diffusion coefficients of H_2SO_4 were much greater than those of the amines owing to the higher value of the activity coefficients of H_2SO_4. The larger value for H_2SO_4 is due more to the more swollen state of the membrane than to the high mobility of the proton.

The various factors which control permeability through a membrane are the charge on the membrane, the membrane's porosity, and the charge and size of the diffused material. The process of permeation involves the entry of aromatic amines into the membrane phase by ion exchange followed by diffusion to the other side of the membrane. Obviously, the ionic size, hydration, and association are some of the important factors which affect the process.

In conclusion, the transport of aromatic amines in ICE-450 ion-exchange membranes is controlled by the protonation process and the pH on the receiver side. Transport is also correlated with basicity, molecular size, and electrophilic groups in the aromatic amines. Further investigation is required to elucidate details of the mass transfer of aromatic amines through ICE-450 membranes.

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