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Diffusion Dialysis. Effect of Membrane Composition on Acid/Salt Separation

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Abstract

In order to highlight the relationship between membrane composition and ability to separate acid/salt mixtures by diffusion dialysis, a few anion-exchange membranes were examined. Experiments on solubility/diffusivity phenomena were carried out in contact with hydrochloric acid and sodium chloride solutions (single- and two-solute experiments). Computations using Glueckauf and Tye models have indicated high nonuniformity in the distribution of fixed charges within the membranes and different accessibilities of the internal membrane volumes for the acid and salt. The Neosepta AFN-7 membrane (Tokuyama Soda Co.) has proved effective in differentiating the permeants by sorption ($k_{HCl}/k_{NaCl} \approx 2$) and diffusivity ($\overline{D}_{HCl}/\overline{D}_{NaCl}$ up to 10). This membrane is also the only one which, when in contact with two-solutes solutions, absorbs the acid preferentially to the salt. For this membrane the perferential sorption and transport of the acid depends not only on the physical structure of the membrane but also on the chemical nature of the polymer which contains pyridine moieties.

INTRODUCTION

Diffusion dialysis is an energy-saving separation technique. The only thermodynamic force acting in the system is the difference in chemical potential of the permeants on opposite sides of a membrane (*1*).

Following early laboratory experiments (*2*, *3*), diffusion dialysis was shown to be effective in the recovery of sulfuric and other acids from wastes in the steel-making, metal refining, electroplating, and chemical industries (*4–10*). Tokuyama Soda Co. and Asahi Glass Co. made efforts to fabricate membranes for diffusion dialysis and to advance the technique (*11–15*). With the Neosepta and Selemion anion-exchange membranes, the separation factors for separating some acid/salt mixtures could be up to 100 (*15*).

In up-to-date papers (*11–17*), the preparation of membranes and the practical aspects of the technique predominated studies on the permeability/selectivity phenomena and the effect of membrane composition on separation. This paper deals with an experimental examination of the solubility/diffusivity of acid and salt in a few ion-exchange membranes and at relating those phenomena to dialytic separations of the mixtures. The Glueckauf and Tye models (*18–21*) have been used to describe quantitatively the local distribution of fixed charges within membranes. The distribution affects the Donnan sorption and the volume fraction of a membrane accessible for diffusion. Experiments have been carried out with single and two-solute solutions.

EXPERIMENTAL

Membranes

The Neosepta AFN-7 membrane, devised for diffusion dialysis and standard strong basic anion-exchange membranes (Neosepta AM1, AM2, AM3, and ACS, Tokuyama Soda Co., Japan), were selected for our experiments. The characteristics of these membranes, as determined by routine methods (*22*), are collected in Table 1. It is known from the paper by Kobuchi et al. (*13*) that the Neosepta AFN-7 membrane is prepared from the styrene–divinylbenzene–vinyl pyridine copolymer, whereas the other membranes are mainly based on the styrene–divinylbenzene–chloromethylstyrene copolymer. After polymerization, the polymers are quaternized.

Some additional experiments have been performed with the cation-exchange membranes Neosepta CM1 and CM2. All Neosepta membranes are produced by the paste method with PVC powder added (*29*).

TABLE 1
Characteristics of Neosepta Membranes

Membrane	Water content ($g_{H_2O}/g_{dry\ membrane}$)	Exchange capacity ($mval/g_{dry\ membrane}$)	Thickness (mm)
	Anion-Exchange Membranes		
AFN-7	0.544	3.44	0.17
AM1	0.287	2.05	0.13
AM2	0.217	1.87	0.12
AM3	0.158	1.64	0.12
ACS	0.224	1.89	0.13
	Cation-Exchange Membranes		
CM1	0.484	2.57	0.15
CM2	0.372	2.02	0.12

Permeation Experiments

In single electrolyte/membrane systems, the permeabilities were measured using an automatic set devised in our laboratory. It consists of a membrane cell, a measuring block and a microcomputer (*23*). The set measures the resistance of a receiver solution against time t.The data are stored and processed automatically. The permeability coefficient P is calculated from the curve relating the concentrations of permeants to time:

$$\frac{l}{h} \ln \frac{c_1^0 - (1 - k)c_2^t}{c_1^0} = -Pt \tag{1}$$

Equation (1) is a recasting of Fick's first law. The symbols denote:

l = membrane thickness (m), 1.2–1.7 × 10^{-4} m
S = membrane area (m^2), 3.8 × 10^{-4} m^2
$k = V_2/V_1$, 7.2 × 10^{-2}
c_2, c_1, V_2, V_1 = concentrations and volumes of receiver and feed solutions, respectively (mol/dm^3), (m^3)
$h = (1 + k)S/V_2$

Superscripts 0 and t refer to the beginning of the experiment ($t = 0$) and to time t. Aqueous hydrochloric acid and sodium chloride solutions with concentration of 0.1–1 mol/dm^3 were used as feed solutions.

In experiments with two solutes, the concentrations of permeants in a receiver (H^+ and total Cl^-) were determined by titration of the diffusate samples.

With the known permeability coefficients and sorption, the diffusion coefficients $\overline{D}$ have been calculated:

$$P = \overline{D}(\bar{c}/c) \tag{2}$$

where c and $\bar{c}$ are the molar concentrations of a permeant in an external solution and in a membrane (in mol/dm^3 and mol/dm^3 of a swollen membrane, respectively).

To compute the dialysis separation factor S_A^B, the transfer rate of a permeant is usually expressed by the simplified formula (*2*)

$$W = US\Delta c \tag{3}$$

where W = the number of moles of a permeant transferred per time unit (mol/s)
U = the overall dialysis coefficient (m/s)

S = membrane area (m^2)
Δc = logarithmic mean concentration difference of the solutions on the two sides of a membrane (mol/dm^3)

The dialysis separation factor is defined as a ratio of dialysis coefficients of the permeants:

$$S_A^B = U_A/U_B$$

Donnan Sorption from Single and Bicomponent Solutions

For sorption experiments the membranes were put into stirred single or bicomponent (HCl, NaCl) aqueous solutions with concentrations of 0.1–1 mol/dm^3. After 14 h the samples were wiped dry with filter paper. The absorbed electrolyte was eluted with distilled water and determined either by measuring the conductivity of the eluate or by using an ionometer N-517 (produced by Mera Elwro, Poland) and commercially available glass and silver chloride electrodes (produced by Wytwórnia Przyrządów La-

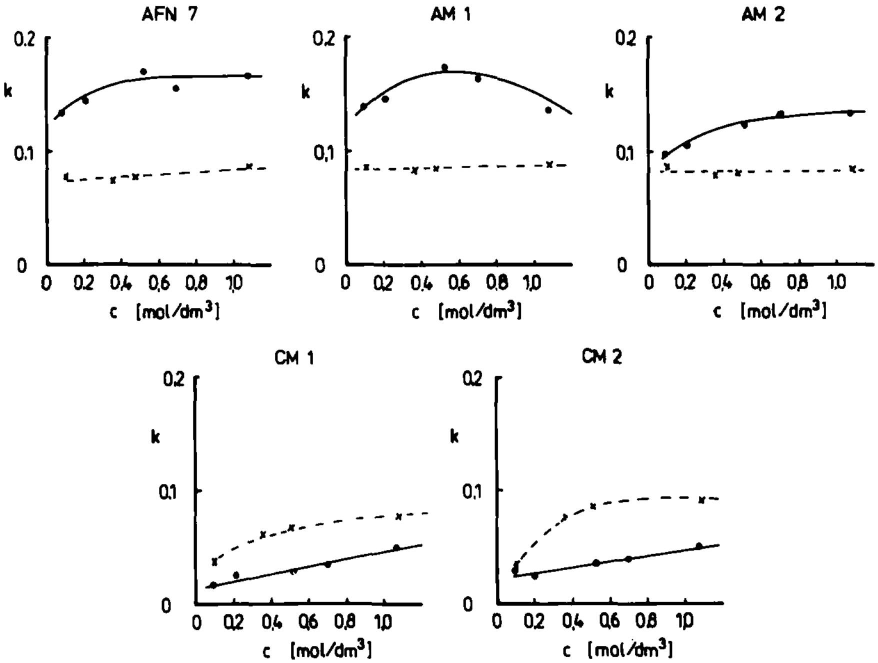

FIG. 1. Molar distribution coefficients of hydrochloric acid (●) and sodium chloride (×) in Neosepta membrane (single-solute experiments).

boratoryjnych, Gliwice, Poland). The computed molar distribution coefficients $k = \bar{c}/c$ are plotted in Fig. 1 against the molarity of the equilibrated solutions. The results for sorption measured in contact with bicomponent solutions are compiled in Table 7.

Despite the fact that the experiments were performed with all the membranes listed in Table 1, in the succeeding part of the paper only the results which help in the discussion are presented.

RESULTS AND DISCUSSION

Single-Solute Experiments

Acid and Salt Permeabilities

For each permeant/membrane system the permeabilities increase with the concentration of a solute; however, the transfer rates of the acid and salt differ (Table 2).

The AFN-7 membrane is the most permeable for both solutes, with the permeability coefficient for hydrochloric acid being roughly up to 10 times that for sodium chloride.

In the case of the other anion-exchange membranes (including the AM3 and ACS membranes, which are not displayed in Table 2), the permeation of the acid exceeds that of the salt. However, the absolute values of the permeability coefficients are lower.

In the case of cation-exchange membranes, $P_{HCl} \approx P_{NaCl}$ or even $P_{HCl} <$

TABLE 2
Permeability Coefficients for the XCl/Neosepta Membrane System (single-solute experiments) (X = H, Na)

	$10^{11}P$ (m^2/s)				
c (mol/dm^3)	AFN-7	AM1	AM2	CM1	CM2
		Hydrochloric Acid			
0.08	4.29	2.50	1.45	0.048	0.077
0.18	15.6	5.20	2.98	0.085	0.079
0.35	26.2	8.10	4.87	0.149	0.110
0.57	43.3	12.0	7.09	0.231	0.125
0.98	52.7	19.7	15.8	0.813	0.212
		Sodium Chloride			
0.10	0.43	0.19	0.12	0.106	0.077
0.36	1.05	0.30	0.16	0.223	0.125
0.50	1.35	0.34	0.23	0.268	0.142
1.08	2.43	0.46	0.28	0.558	0.262

P_{NaCl}. Since the CM1 and CM2 membranes were prepared in hydrogen and sodium forms, respectively, for the experiments with acid and salt, the different swellings of the membranes might affect the observations. Still, in the case of cation-exchange membranes, the diffusion coefficients of the acid in aqueous media, which are twice that of a salt, are not reflected in the observed permeations.

Since the permeabitities are affected by the solubility and diffusivity of the species, both phenomena will be discussed.

Donnan Sorption

The main effect of a charged network of ion-exchange membranes in dilute and mean-molality solutions should be the Donnan rejection of an electrolyte. Because of the nonideal structure of membranes, sorption depends on the concentration and distribution of charged groups within a membrane. The lower the concentration and the less uniform the distribution of charges, the less effective is a membrane in rejecting electrolytes.

The results of sorption experiments displayed as the molar distribution coefficients are plotted in Fig. 1.

In the case of anion-exchange membranes, the molar distribution coefficients for both solutes are rather high, and the ones found for the acid exceed those for the salt. For the AFN-7 membrane, k_{HCl} is roughly twice that of k_{NaCl} and does not change much with concentration. The easy sorption supports the high permeability of the acid (see Table 1). It is also remarkable that while the sorption of acid decreases from AFN-7 to AM2, the sorption of sodium chloride is almost the same for all the membranes.

In the case of cation-exchange membranes, the sorption of both solutes is low, confirming that the charged sulfonated network is much more effective in Donnan rejection than the positive charge network of anion-exchange membranes. It was rather unexpected, however, to find for CM1 and CM2 membranes that the distribution coefficients are reversed; that is, lower for the acid than for the salt. The comment about the different swellings of membranes with H^+ and Na^+ counterions should be remembered here.

Diffusion Coefficients

In 0.1 *M* aqueous solutions, $D_{HCl} = 3.05 \times 10^{-9}$ m^2/s and $D_{NaCl} = 1.48 \times 10^{-9}$ m^2/s ($T = 298$ K) (*24*). Normally the internal diffusion coefficients for the solutes absorbed into charged gel membranes are usually one order lower. The same order or an even lower order has been found here.

Anion-exchange membranes differentiate the diffusivities of both solutes

TABLE 3
Internal Diffusion Coefficients for XCl in Neosepta Membrane (X = H, Na)

	$10^{10}\bar{D}$ (m²/s)				
c (mol/dm³)	AFN-7	AM1	AM2	CM1	CM2
	Hydrochloric Acid				
0.08	5.44	2.06	1.46	0.26	0.29
0.18	9.59	3.44	2.92	0.39	0.33
0.35	15.2	4.85	4.26	0.59	0.39
0.57	26.7	7.05	5.58	0.74	0.36
0.98	31.8	13.8	11.7	1.75	0.45
	Sodium Chloride				
0.10	0.56	0.23	0.14	0.26	0.25
0.36	1.43	0.37	0.22	0.37	0.16
0.50	1.75	0.40	0.28	0.39	0.16
1.09	2.80	0.53	0.33	0.73	0.29

drastically (Table 3). In this respect the AFN-7 membrane is again the most effective one. In contact with dilute solutions, the value for $\bar{D}_{\mathrm{HCl}}$ is one order of magnitude greater than $\bar{D}_{\mathrm{NaCl}}$, and the ratio $\bar{D}_{\mathrm{HCl}}/\bar{D}_{\mathrm{NaCl}}$ still increases for high sorption regions.

For cation-exchange membranes the internal diffusion coefficient of hydrochloric acid is below that found for anion-exchange membranes, and the ratio $\bar{D}_{\mathrm{HCl}}/\bar{D}_{\mathrm{NaCl}}$ is either below or close to that for aqueous media.

Membrane Characteristics

As stated in the Introduction, the aim of this paper was to search for the interrelation between selectivity in diffusion dialysis and membrane chemistry and structure.

In a number of papers it has been proved that the distribution of charged groups within ion-exchange membranes is nonuniform, thus affecting the Donnan sorption and permselectivity.

The models and formulas for describing the nonuniformity quantitatively have been published by Glueckauf and Tye. The Glueckauf nonuniformity factor Z is a "one-figure" factor that increases from 0 to 1 in a direct relationship to nonuniformity (*18–20*). This factor can be calculated by measuring the Donnan sorption against the molality of a solute in equilibrated solutions:

$$\ln \bar{m} = (2 - Z) \ln m + \ln k \tag{4}$$

where Z = nonuniformity factor
k = constant
m and $\overline{m}$ = molalities of an electrolyte in an external solution and within a membrane

The extreme values for Z were reported by Jerome et al. for the AMF C-313 membrane ($Z = 0.06$, low nonuniformity) (*25*) and by Brun for the sulfonated phenol-formaldehyde membrane ($Z = 1.0$, the highest nonuniformity) (*26*).

The Z-factors found here are collected in Table 4. They vary from 0.8 to 1. The high Z-factors for the Neosepta membranes were anticipated since they reflect the heterogeneity of reinforced membranes prepared by the paste method. For example, $Z = 0.915$ was reported by Wódzki et al. for the Ionac MC-3470 membrane (*27*), which is another kind of reinforced paste-method material.

In the Tye model (*21*) the pore space within the swollen ion-exchange membrane is divided into a fraction at zero electric potential β, which is nonselective, and the rest at nonzero electrical potential. The parameter β for a membrane in contact with the 1:1 electrolyte can be calculated from the sorption data, as before:

$$\overline{m}_R(\overline{m} - \beta m) + (\overline{m} - \beta m)^2 - [(1 - \beta)m]^2 = 0 \qquad (5)$$

The symbol $\overline{m}_R$ denotes the concentration of ionic groups in a membrane, whereas m and $\overline{m}$ retain their former meanings.

Although the Tye model can be treated as a simplified representation of physical reality, it seems to be helpful in differentiating membranes of

TABLE 4
The Nonuniformity Factor (Z) for Neosepta Membranes (Glueckauf model)

	Z	
Membrane	HCl[a]	NaCl[b]
AFN-7	0.91 ± 0.01	0.95 ± 0.04
AM1	0.90 ± 0.03	0.96 ± 0.02
AM2	0.88 ± 0.01	0.99 ± 0.04
CM1	0.59 ± 0.04	0.77 ± 0.03
CM2	0.72 ± 0.08	0.54 ± 0.09

[a] Calculated by taking sorption data for HCl, molality range 0.1–1.1 mol/kg.

[b] The same for NaCl and equal molality range.

TABLE 5
Fraction of Zero Potential Domains in Neosepta Membranes (parameter β from the Tye model)[a]

Membrane	β HCl	β NaCl
AFN-7	0.41–0.60	0.23–0.34
AM1	0.35–0.76	0.35–0.46
AM2	0.50–0.75	0.41–0.51
CM1	0.05–0.21	0.12–0.30
CM2	0.10–0.25	0.10–0.39

[a] See Table 4 footnotes.

the same composition but of different permelectivities. Parameters β for some Neosepta membranes are presented in Table 5.

The results confirm that in anion-exchange membranes the volume fraction of a polymer accessible to the acid is larger than that which can be entered by the salt, and that the AFN-7 membrane differentiates the sorption (or imbibition) of HCl and NaCl more than do the other membranes.

In summarizing the results of both models, the following conclusions can be drawn. Despite being prepared by the same method, the anion-exchange membranes are more nonuniform than the cation-exchange ones (Table 4). Considering the absolute figures of the nonuniformity factor, those found from the sorption of HCl are rather lower and suggest a more uniform distribution of the absorbed acid within the membrane than that of the salt. The same follows from the β-parameters. One can conclude that hydrochloric acid penetrates into the volume elements of the anion-exchange membranes which expel the salt.

Chemical Nature of Membranes

The distinct permeability, sorption, and diffusivity of the AFN-7 membrane, which does not differ much in structure compared with the other anion-exchange membranes, implies the importance of the chemical nature of the polymer used for membrane preparation. Figure 2 presents the potentiometric titration of alkali forms of AFN-7 and AM1 membranes. The curve for the AFN-7 membrane corresponds to the one for a weak-base polyelectrolyte material. This finding is rather in contradiction to the information about the quaternized vinyl pyridine group present in the membrane (*11*, *13*). One more argument, however, is that the AFN-7 membrane shows an affinity for the acid exceeding that of the other polymers with quaternary ammonium groups. If this is correct, these results

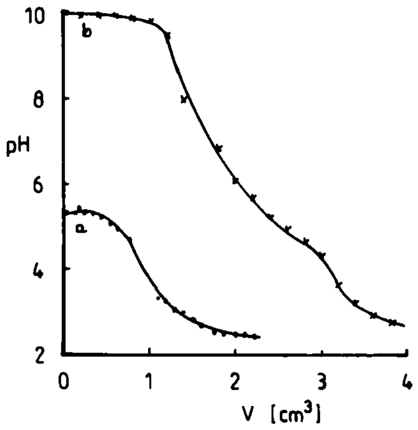

FIG. 2. Titration curves of (a) AFN-7 and (b) AM2 membranes with hydrochloric acid. The masses of membrane samples used for titration are not equivalent.

imply that for differentiating the transport of the permeants, the effect of expulsion of the acid from polymer chains into the volume space filled with water is not the only mechanism underlying the different rates of transport of the acid and salt, and consequently the dialytic separation.

Two-Solutes Experiments

Sorption

The total sorption of the acid and salt found in the two-solute and one-solute experiments (sum of two permeants) is comparable (Table 6). However, the sorption of acid in all the anion-exchange membranes, except for AFN-7, is now below that of the salt. Only in the case of the AFN-7 membrane is the sorption of acid from the two-solute solution above that found in the single-solute experiments. This effect was also reported by Kobuchi et al. (*14*). Once again, the results point to the unique properties of AFN-7 compared to the other anion-exchange membranes.

Dialytic Separation of HCl/NaCl

The separation factors $S_{\mathrm{HCl}}^{\mathrm{NaCl}} = U_{\mathrm{HCl}}/U_{\mathrm{NaCl}}$ determined for exemplary two-solute solutions can be seen in Table 7. For all anion-exchange membranes, the separation factors are above unity, and the value found for the AFN-7 membrane is much higher than the others. For this membrane the separation factor of 11.8 is close to those reported by Kobuchi et al. (*14*) and

TABLE 6
Sorption of Hydrochloric Acid and Sodium Chloride from Two-Solute Solutions ($\bar{c}$ in mol/dm^3 of swollen membrane)

Membrane	Two-solute solutions		One-solute solutions	
	$\bar{c}_{HCl}$	$\bar{c}_{NaCl}$	$\bar{c}_{HCl}$	$\bar{c}_{NaCl}$
	0.2 *M* HCl + 0.2 *M* NaCl		0.2 *M* HCl	0.2 *M* NaCl
AFN-7	0.059	0.034	0.033	0.014
AM1	0.022	0.034	0.031	0.017
AM2	0.018	0.029	0.021	0.015
CM1	0.003[a]	0.010	0.004[a]	0.009
CM2	0.003[a]	0.015	0.005[a]	0.012
	0.5 *M* HCl + 0.5 *M* NaCl		0.5 *M* HCl	0.5 *M* NaCl
AFN-7	0.158	0.079	0.083	0.038
AM1	0.051	0.064	0.085	0.042
AM2	0.034	0.043	0.061	0.041
CM1	0.026	0.052	0.015	0.034
CM2	0.018	0.036	0.016	0.043

[a] Results within experimental error.

by Sridhar and Subramaniam in experiments performed using laboratory unit TSD-2-20 (*28*).

The ratios of the permeability coefficients P_{HCl}/P_{NaCl} in the last column of Table 7 have been calculated by taking the results of one-solute experiments. This ratio can be regarded as a limit separation factor. The experimental separation factors S_{HCl}^{NaCl} are much below the theoretical limits,

TABLE 7
The Overall Dialysis Coefficients (U, m/s) and Dialysis Separation Factor of HCl and NaCl (S_{HCl}^{NaCl}) for the Neosepta Membranes (feed solution: 0.2 *M* HCl + 0.2 *M* NaCl)

Membrane	$10^7 U_{HCl}$	$10^7 U_{NaCl}$	S_{HCl}^{NaCl}	P_{HCl}/P_{NaCl}[a]
AFN-7	13.3	1.12	11.82	25.4
AM1	5.68	1.28	4.45	21.0
AM2	3.38	0.52	6.49	21.7
CM1	0.19	0.23	0.82	0.74
CM2	0.21	0.25	0.85	0.91

[a] P_{HCl}/P_{NaCl} is the ratio of permeability coefficients of HCl and NaCl calculated after taking the results of one solute experiment.

thus pointing to the mutual interactions of the permeants in diffusion dialysis.

CONCLUSIONS

The Neosepta AFN-7 membrane, devised for diffusion dialysis, differs from other standard strong base anion-exchange membranes in:

High permeability, sorption, and diffusivity of the permeants (HCl and NaCl)
Preferential sorption of the acid from the acid/salt solutions, not observed in experiments with other anion-exchange membranes
The separation factor $S_{\mathrm{HCl}}^{\mathrm{NaCl}}$ ranging to 11 against 4–6 for other anion-exchange membranes

This membrane also differs from the others in its high ion-exchange capacity and water content, and also in the chemical nature of its charged groups.

The Glueckauf nonuniformity factor (Z) and the Tye zero potential volume fractions (β) suggest a more uniform distribution of the acid within this membrane as compared with the salt. This effect does not seem to correspond to the model, which assumes that expelling the acid from the polymer chains is the underlying effect of dialytic separation of acid/salt mixtures.

The interaction of the penetrating acid with the polymer matrix and the coupling effects between the permeants are problems for further experiments.

SYMBOLS

$\bar{D}$	internal diffusion coefficient (m^2/s)
Δc	logarithmic mean difference of concentrations on two sides of a membrane (mol/dm^3)
k	molar distribution coefficient
l	membrane thickness (m)
c, $\bar{c}$	molarities of an electrolyte in the external solution and within the swollen membrane (mol/dm^3)
P	permeability coefficient (m^2/s)
S	membrane area (m^2)
$S_{\mathrm{HCl}}^{\mathrm{NaCl}}$	dialysis separation factor
U	overall dialysis coefficient (for bicomponent solution systems) (m/s)
Z	nonuniformity factor (from the Glueckauf theory)

Greek Symbol

β parameter from the Tye model denoting zero potential volume fraction within the swollen membrane

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