The transport of salts through cationically charged poly(vinyl alcohol) membranes

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The permeation of simple salts, such as sodium chloride, and sodium salts of five organic acids through cationically charged poly(vinyl alcohol) membranes was determined. The salts with large anions showed an anomalous permeation behaviour, the permeability increasing with decrease in concentration of salt in the outer solution. This behaviour may be attributed to the large difference in ionic mobility w, of cations and anions, w^+ and w^- ($w^- \ll w^+$), in the framework of the Teorell–Meyer–Sievers theory. The effective charge concentration in the polymer has been estimated from permeability and membrane-potential data.

(Keywords: cationically charged poly(vinyl alcohol) membranes; ionic mobility in membrane; effective charge concentration; anomalous permeation; Teorell–Meyer–Sievers theory)

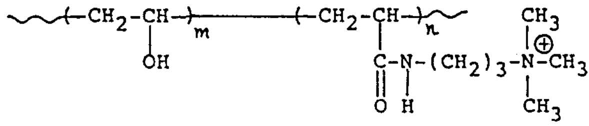
INTRODUCTION

Permeation through charged membranes has been widely investigated and the results have been reviewed in some excellent articles[1]. In water-swollen membranes the ionizable groups of the membrane matrix are dissociated. Small mobile ions are distributed in the membrane phase and the whole is electrostatically neutral. When the membrane is regarded as being homogeneous, permeation phenomena can be described basically by the Teorell–Meyer–Sievers (TMS) theory. Kobatake *et al.* developed the theory further, making a prominent contribution in this field[2]. All this work was concerned with the elucidation of the effect of fixed charges on ion transport. The structural effect of mobile ionic species on permeation was treated less systematically. For this reason we decided to clarify the transport behaviour of ions of different sizes and shapes permeating through charged membranes. Sodium organic sulphonates provide a variety of ions for such work. Therefore cationically charged membranes were used in this investigation.

EXPERIMENTAL

Materials

Cationic poly(vinyl alcohol-*co*-[*N*-(3-trimethylpropylammonium)acrylamide chloride]) (PVA-N) was mainly used. The polymers were prepared and kindly supplied by the Kuraray Co.



PVA-N contains 0.23 mol% of charged monomer units, its degree of saponification is 99.5 mol% and the degree of polymerization is 1620. An identical copolymer (PVA-N-2) containing 2 mol% of charged monomer was also used.

PVA was obtained from Nakarai Chemicals Ltd. Its degree of saponification was 99–100 mol% and the degree of polymerization was 2000. All polymers were Soxhlet extracted with methanol for 16 h before use.

The salts used were sodium chloride (NaCl), sodium tetraphenylborate ($NaBPh_4$), sodium benzene sulphonate ($NaSO_3Ph$), sodium β-naphthalene sulphonate ($NaSO_3Nph$), sodium *p*-toluene sulphonate ($NaSO_3Tlu$), sodium ethane sulphonate ($NaSO_3Eth$) and tetra-n-butylammonium bromide (TBAB). NaCl ('Guaranteed Reagent') and $NaBPh_4$ ('Specially Prepared Reagent') were both supplied by Nakarai Chemicals Ltd. Tokyo Kasei Kogyo Ltd supplied $NaSO_3Ph$ ('Extra Pure'), $NaSO_3Nph$ ('Pure Chemical'), $NaSO_3Eth$ ('Guaranteed Reagent') and TBAB ('Extra Pure'). $NaSO_3Tlu$ was obtained from Eastman Chemicals Co. KCl ('Guaranteed Reagent') for membrane-potential measurements was obtained from Kanto Chemical Co. $NaSO_3Ph$, $NaSO_3Tlu$, $NaSO_3Nph$ and TBAB were recrystallized from aqueous ethanol. The other salts were used without further purification. Distilled deionized water was used throughout.

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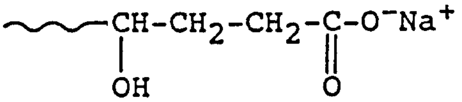
Membrane preparation and characterization

The 10% aqueous solutions of PVA-N or PVA-N-2 were prepared by dissolving the required amounts of polymer in water at 100°C for 4 h with gentle stirring, then allowing them to stand at 21°C to remove air bubbles completely. The membranes were prepared by casting on clean glass plates and drying at $21 \pm 2°C$ for one week.

Commercially available PVA contains carboxyl end-groups[3], amounting to 25% of the total end-groups, as:



$$\sim\sim\sim\underset{\substack{| \\ OH}}{CH}-CH_2-CH_2-\underset{\substack{\| \\ O}}{C}-O^-Na^+$$

To prepare uncharged PVA membranes, commercial PVA was treated with HCl to convert the carboxyl groups to γ-lactone.

Before crosslinking, all membranes were kept in a desiccator containing silica gel. They were then swollen in a saturated aqueous Na_2SO_4 solution and crosslinked in an aqueous solution of 20% Na_2SO_4, 1% H_2SO_4 and 0.1% glutaraldehyde at $25 \pm 0.02°C$. Various degrees of crosslinking were obtained by changing the reaction time and varying the water contents of the membranes. The hydrogel membranes thus obtained were preserved in distilled deionized water at 21°C, the water being renewed every day.

The thickness of the membranes was measured with a precision micrometer, Minicom GST-E100D (Tokyo Seimitsu Co. Ltd), the sample being sandwiched between two cover glasses (1.5 cm × 1.5 cm) of known thickness. The average of 10 thickness measurements was used.

The water content of the membrane, H (g water/g swollen membrane), was determined by weighing the Cl-form membranes before and after drying. After immersion, the sample was taken out of the water and the surface water removed by careful blotting with a filter paper. It was then dried *in vacuo* at 100°C for 24 h.

PVA-N membranes with $H = 0.774$, 0.658, 0.499 and 0.355 were prepared and designated as PN-77, PN-66, PN-50 and PN-36, respectively.

Permeability measurements

Permeability was measured in a conventional cell[4,5] consisting of two chambers separated by a membrane. The volumes of the up- and downstream sides were 246 and 68 ml, respectively. The effective membrane area A was 7.28 cm^2. During measurement the solutions on both sides were stirred vigorously to minimize the thickness of stagnant boundary layers on the surface of the membrane. The downstream concentration of salts, C_2, was monitored with an electronic conductometer (FU-22A Toa Electronic Ltd, Japan) and recorded by a multi-pen recorder (R-10, Rikadenki Kogyo Ltd).

Permeation measurements were carried out with an upstream salt concentration, C_1, of 0.005–0.15 mol l^{-1} in a thermostat at $25 \pm 0.05°C$. The downstream side was filled with distilled water at the beginning of the experiment. During the experiment the ratio C_2/C_1 did not exceed 0.01 and C_1 was therefore regarded as constant.

Membrane-potential measurements

The membrane-potential cell consisted of two chambers of equal volume (approximately 250 ml) separated by a membrane, 0.78 cm^2 of which was exposed. In this investigation the concentration ratio of the solutions on the two sides, C_s'/C_s'' was kept at 5.0. The concentration C_s' was changed from 1.5×10^{-4} to 2.0 mol l^{-1}.

The potential was measured with an electrometer (HE-103, Hokuto Denki Ltd) with Ag–AgCl electrodes (TOA HS-205C, Toa Electronics Ltd) and a salt bridge. For all salts, except $NaBPh_4$, a saturated aqueous KCl solution was used in the salt bridge. In the case of $NaBPh_4$ a saturated aqueous NaCl solution was used to avoid precipitation of $KBPh_4$. Using aqueous $NaSO_3Tlu$ solution, different salt bridges did not cause different effects. The solution was stirred on both sides during measurement.

The mean value of two potential determinations in a thermostat at $25 \pm 0.05°C$ was taken, exchanging the electrodes in the two chambers.

Equilibrium sorption measurements

The partition coefficient K, defined as the ratio of the salt concentrations in the membrane, C_{in} (moles per litre of imbibed water), to that in the outer solution, C_{ex} (mol l^{-1}), as equilibrium, was determined by desorption. Sorption equilibrium with the salt solution of appropriate concentration C_{ex} was attained in 8 h at $25 \pm 0.05°C$ and the membrane was removed from the solution. It was carefully wiped with a filter paper and then immersed in distilled water for 8 h at $25 \pm 0.05°C$. Times to attain equilibrium were determined by preliminary experiments. Concentrations higher than 1×10^{-4} mol l^{-1} in the desorbing solution were determined conductometrically and assigned to co-ion concentration in the membrane. The conductometer used was the same as that used in the permeability experiments. Lower sodium concentrations ($< 1 \times 10^{-4}$ mol l^{-1}) were determined with an atomic absorption spectrometer (A.A.-640-12, Shimadzu Co.) to avoid errors caused by atmospheric CO_2. Thus the equilibrium sorption, C_{in}, was obtained as a function of C_{ex}, from 0.005 to 0.15 mol l^{-1}, which is the range of concentrations on the upstream side of the permeability measurement.

In the case of NaCl and $NaBPh_4$, to obtain further information about the effect of the fixed charge in the membranes, the concentrations of the counter-ion as well as the co-ion were measured in the C_{ex} range from 1.5×10^{-3} to 1.5×10^{-2} mol l^{-1}, where the Donnan effect clearly shows. The concentrations of the counter-ions Cl^- and BPh_4^- were determined by desorption. Chloride ions sorbed by the membranes were desorbed with an aqueous $NaCO_3Eth$ solution of high concentration, 1×10^{-2} mol l^{-1} at $25 \pm 0.05°C$ for 8 h. The desorbed Cl^- concentration could be determined by the $Hg(SCN)_2$ method[6] without interference from the ethane sulphonate ion. The absorbance of the developed colour ($\lambda_{max} = 460$ nm) was determined with a u.v.-vis. spectrophotometer (Hitachi 556, Hitachi Ltd).

In the case of $NaBPh_4$, the tetraphenylborate ion was desorbed from the membrane with aqueous NaCl solution at 0.1 mol l^{-1}, and the concentration was determined spectrophotometrically at 273 nm. Complete desorption of BPh_4^- by the above procedure was confirmed for the membrane equilibrated in $C_{ex} = 0.005$ mol l^{-1} by desorbing in 0.1 mol l^{-1} NaCl for 8 h.

RESULTS AND DISCUSSION

Effect of ionic size

The permeability coefficients P of NaCl, $NaSO_3Eth$, $NaSO_3Ph$, $NaSO_3Tlu$, $NaSO_3Nph$ and $NaBPh_4$ through PVA-N membranes, determined at various salt concentrations C_1, are shown in *Figures 1–4*. The water content H in the presence of salts was found to change only negligibly, and therefore its effects on permeability were neglected.

In the case of NaCl, for all membranes, P decreases with decreasing C_1 in the low concentration range 0.005–0.05 mol l^{-1}. This is the usual pattern of the concentration dependence of P. In the low concentration range, P is small because of Donnan exclusion, whereas in the case of $NaBPh_4$, P increases with decreasing C_1. In the case of the other sodium salts investigated, permeation behaviour lies between the two extremes, depending on anion size. *Figure 5* shows equilibrium sorption of C_{in} with C_{ex}. A linear relationship is obtained for all sodium salts and membranes, giving the partition coefficient K by the least-squares method. The intercept on the C_{in} axis is negative. This is attributed to co-ion exclusion effects in the low concentration range on the sorption isotherm and will be discussed later. The partition coefficients are given in *Tables 1–3*. In *Figure 6* the dependence of partition coefficients on the water content of the membrane is shown. Large ions tend to increase K. With the exception of PN-36, K of NaCl and $NaSO_3Eth$—which form relatively small anions—is constant irrespective of the water content of the membranes, while salts forming large anions, such as $NaBPh_4$ and $NaSO_3Nph$, cause an increase in K with decreasing water content. The hydrophobic nature and the capability of proton acceptance of

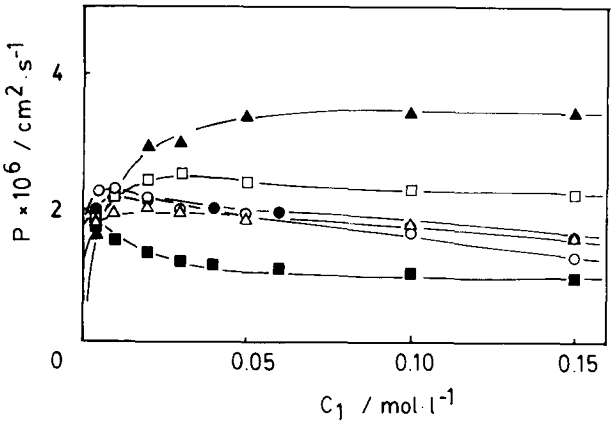


Figure 1 Permeability coefficient through PN-77 *versus* external salt concentration: (▲) NaCl; (□) $NaSO_3Eth$; (△) $NaSO_3Ph$; (●) $NaSO_3Tlu$; (○) $NaSO_3Nph$; (■)$NaPBh_4$

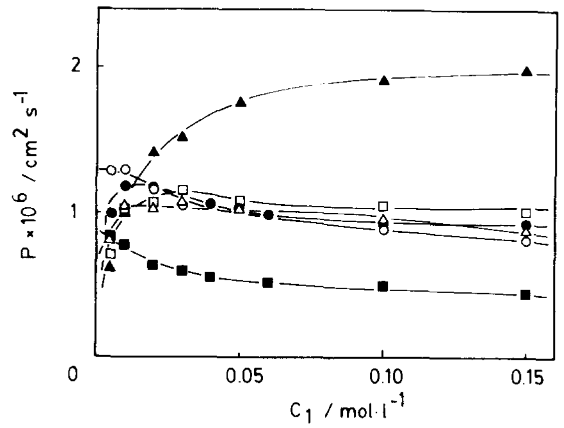


Figure 2 Permeability coefficient through PN-66 *versus* external salt concentration: (▲) NaCl; (□) $NaSO_3Eth$; (△) $NaSO_3Ph$; (●) $NaSO_3Tlu$; (○) $NaSO_3Nph$; (■) $NaBPh_4$

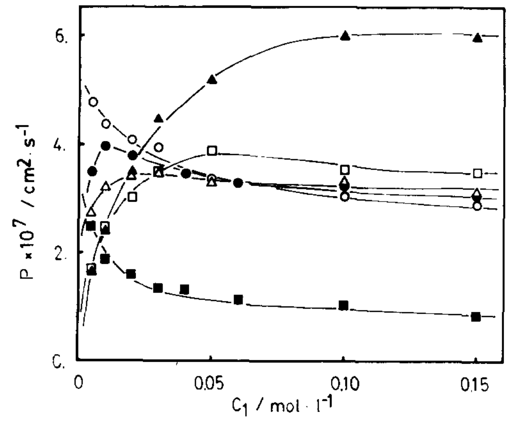


Figure 3 Permeability coefficient through PN-50 *versus* external salt concentration: (▲) NaCl; (□) $NaSO_3Eth$; (△) $NaSO_3Ph$; (●) $NaSO_3Tlu$; (○) $NaSO_3Nph$; (■) $NaBPh_4$

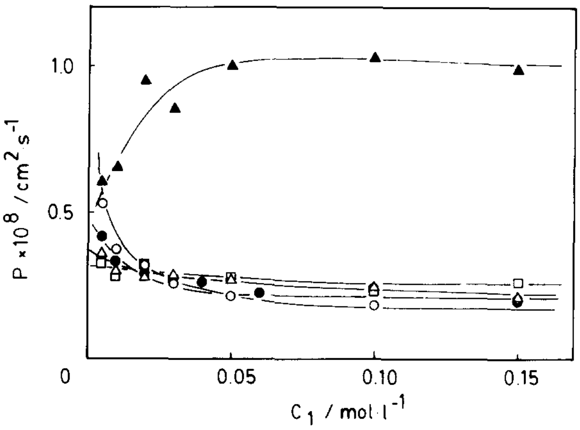


Figure 4 Permeability coefficient through PN-36 *versus* external salt concentration: (▲) NaCl; (□) $NaSO_3Eth$; (△) $NaSO_3Ph$; (●) $NaS0_3Tlu$; (○) $NaSO_3Nph$

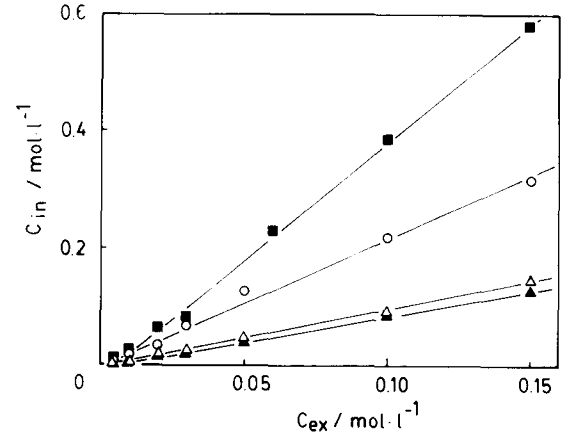


Figure 5 Equilibrium sorption by PN-50 membrane: (▲) NaCl; (△) $NaSO_3Ph$; (○) $NaSO_3Nph$; (■) $NaBPh_4$

Table 1 K, U, X, w^+ and w^- of NaCl and $NaSO_3Eth$

	Membranes	K	U	X (equiv l^{-1})^a	$w^+ \times 10^9$ ($cm^2\,mol\,J^{-1}\,s^{-1}$)	$w^- \times 10^9$ ($cm^2\,mol\,J^{-1}\,s^{-1}$)
NaCl	PN-77	0.811	−0.13	0.005	1.51	1.96
	PN-66	0.845	−0.14	0.0085	0.823	1.09
	PN-50	0.832	-0.12_5	0.0175	0.285	0.367
	PN-36	0.463	−0.12	0.025	0.0089	0.0113
$NaSO_3Eth$	PN-77	0.787	0.06	0.0045	1.29	1.14
	PN-66	0.761	0.11	0.006	0.743	0.593
	PN-50	0.768	0.16	0.012	0.258	0.186
	PN-36	0.346	0.65	0.001	0.0089	0.0019

^{a} Equivalents per litre of imbibed water

Table 2 K, U, X, w^+ and w^- of $NaSO_3Ph$ and $NaSO_3Tlu$

	Membranes	K	U	X (equiv l^{-1})^a	$w^+ \times 10^9$ ($cm^2\,mol\,J^{-1}\,s^{-1}$)	$w^- \times 10^9$ ($cm^2\,mol\,J^{-1}\,s^{-1}$)
$NaSO_3Ph$	PN-77	0.864	0.34	0.002	1.40	0.689
	PN-66	0.942	0.42	0.004	0.753	0.308
	PN-50	0.988	0.48	0.008_5	0.258	0.0907
	PN-36	0.655	0.83	0.003	0.0086	0.0008
$NaSO_3Tlu$	PN-77	1.158	0.53	0.001_8	1.45	0.446
	PN-66	1.177	0.62	0.003_3	0.918	0.216
	PN-50	1.194	0.68	0.006_5	0.317	0.0605
	PN-36	0.769	0.91	0.002_5	0.012	0.0006

^{a} Equivalents per litre of imbibed water

Table 3 K, U, X, w^+ and w^- of $NaSO_3Nph$ and $NaBPh_4$

	Membranes	K	U	X (equiv l^{-1})^a	$w^+ \times 10^9$ ($cm^2\,mol\,J^{-1}\,s^{-1}$)	$w^- \times 10^9$ ($cm^2\,mol\,J^{-1}\,s^{-1}$)
$NaSO_3Nph$	PN-77	1.485	0.70_5	0.001_3	1.72	0.298
	PN-66	1.796	0.72	0.003	0.813	0.132
	PN-50	2.166	0.79	0.003_5	0.291	0.0341
	PN-36	1.902	0.96	0.003	0.0009	0.0002
$NaBPh_4$	PN-77	2.372	0.88	0.001	1.51	0.0962
	PN-66	2.898	0.88	0.003	0.576	0.0368
	PN-50	4.000	0.93_5	0.012_5	0.161	0.0054

^{a} Equivalents per litre of imbibed water

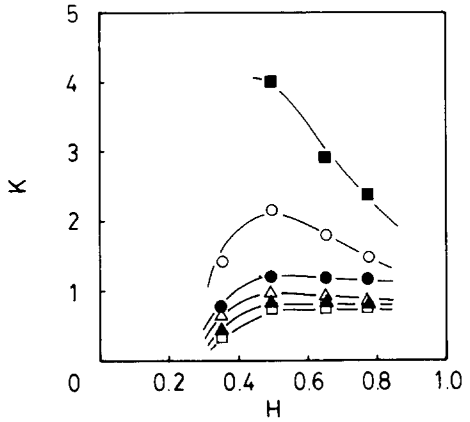


Figure 6 Partition coefficient *versus* water content: (▲) NaCl; (□) $NaSO_3Eth$; (△) $NaSO_3Ph$; (●)$NaSO_3Tlu$; (○) $NaSO_3Nph$; (■) $NaBPh_4$

the π-hydrogen bond are greater in larger anions. Thus with increase in the volume fraction of the polymer, an increase in sorption can be anticipated. The volume fraction of the polymer in PN-36 is thought to be too large to neglect the obstruction effect of the polymer chains and a decrease in K results, particularly for the naphthalene sulphonate ion. The tetraphenylborate ion, the largest anion, is entirely excluded from PN-36.

Figures 7–9 show the relationship between the membrane potential ($\Delta\phi$ and C''_s, when $C'_s = 5C''_s$, for NaCl, $NaSO_3Ph$ and $NaBPh_4$, respectively. In the case of PN-36, $\Delta\phi$ is negative even in the low concentration range of C''_s in which NaCl gives a positive value of $\Delta\phi$. The same phenomenon is observed with $NaBPh_4$ in PN-50 (*Figure 8*). These results can be attributed to the obstruction effect of polymer chains; the large anion hardly enters the membrane.

On the other hand, according to the TMS theory[7], in cationic membranes $\Delta\phi$ is a constant value, 41.3 mV, at low C''_s. In practice, however, $\Delta\phi(C''_s)$ is smaller than the theoretical value, and decreases with increasing water content of the membranes, as can be seen in *Figures 7–9*. All the salts give this result, except when $\Delta\phi$ is negative at low C''_s. These observations are interpreted as follows. The permeability coefficient P increases with increasing water content of the membranes (*Figures 1–4*). Because of the relatively large permeability coefficients, C'_s becomes less than $5C''_s$, giving a smaller absolute estimate of $|\Delta\phi|$ than

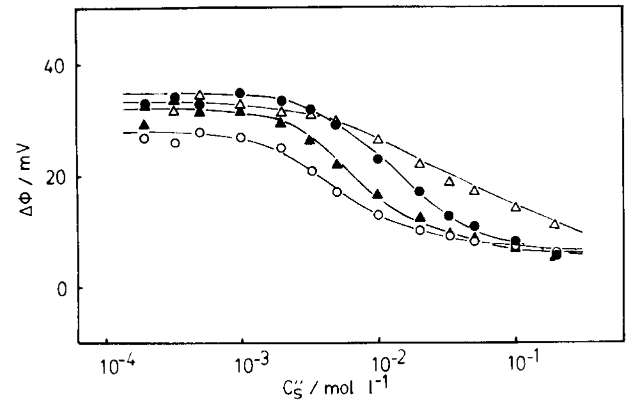


Figure 7 Membrane potential $\Delta\phi$ *versus* C_s'' for NaCl ($C_s'=5C_s''$): (○) PN77; (▲) PN-66; (●) PN-50; (△) PN-36

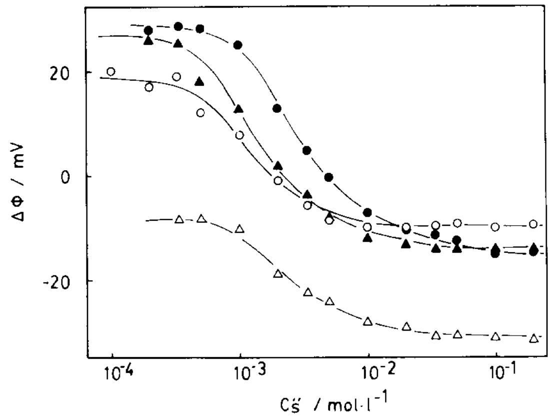


Figure 8 Membrane potential $\Delta\phi$ *versus* C_s'' for NaSO$_3$Ph ($C_s'=5C_s''$): (○) PN-77; (▲) PN-66; (●) PN-50; (△) PN-36

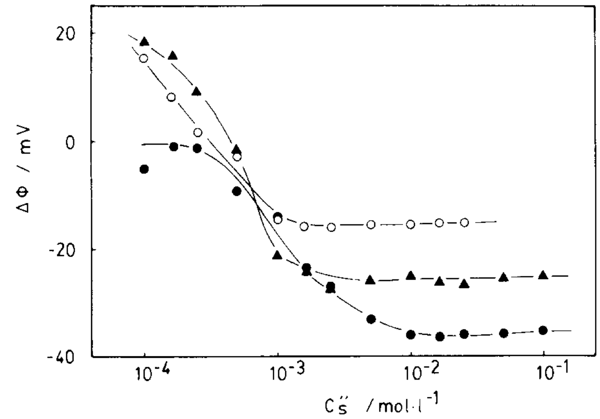


Figure 9 Membrane potential $\Delta\phi$ *versus* C_s'' for NaBPh$_4$ ($C_s'=5C_s''$): (○) PN-77; (▲) PN-66; (●) PN-50

when $C_s'=5C_s''$. In addition, the effect of the fixed charge concentration cannot be neglected; this will be mentioned later.

The TMS theory is used in the interpretation of the present results. According to this theory, the membrane potential and permeability coefficient of a uni-univalent electrolyte can be expressed by equations (1) and (2), which are based on the Nernst–Planck flux equation, assuming that

(i) the total membrane potential $\Delta\phi$ is the sum of the Donnan potential at the two membrane–solution interfaces and the diffusion potential in the membrane,

(ii) the fixed charges carried by the membrane matrix are uniformly distributed and remain constant at all values of external electrolyte concentrations,

(iii) the fluxes of anion and cation are equal in any part of the membrane (for electroneutrality), and

(iv) the pressure term is negligible:

$$\Delta\phi=\frac{RT}{F}\left[\ln\left(\frac{C_s'}{C_s''}\right)\frac{[1+(2C_s''/QX)^2]^{1/2}+1}{[1+(2C_s'/QX)^2]^{1/2}+1}\right.$$
$$\left.-U\ln\left(\frac{[1+(2C_s'/QX)^2]^{1/2}+U}{[1+(2C_s''/QX)^2]^{1/2}+U}\right)\right] \qquad (1)$$

$$P=\frac{w^+w^-RTX}{(w^++w^-)(C_2-C_1)}$$
$$\times\left[[1+(2C_2/QX)^2]^{1/2}-[1+(2C_1/QX)^2]^{1/2}\right.$$
$$\left.-U\ln\left(\frac{[1+(2C_2/QX)^2]^{1/2}+U}{[1+(2C_1/QX)^2]^{1/2}+U}\right)\right] \qquad (2)$$

where $U=(w^+-w^-)/(w^++w^-)$ and $Q^2=\gamma^+\gamma^-/k^+k^-$; X is the effective concentration of fixed charges; γ^+ and γ^- are single-ion activity coefficients in the membrane phase and are assumed to be unity; k^+ and k^- are the partition coefficients and both are assumed to be equal to K, giving $Q=1/K$, where K is the partition coefficient obtained experimentally; w^+ and w^- are the ionic molar mobilities in the membrane phase and w^+ is assumed to be expressed as[8]:

$$w^+=\theta w_0^+ \qquad (3)$$

in which θ is a parameter representing the obstruction effect on the mobility of the cation in the membrane and w_0 is the molar mobility in bulk water. Using equation (3) and U, w^- is given by:

$$w^-=(1-U)\theta w_0^+/(1+U) \qquad (4)$$

Using equation (1), the membrane potential $\Delta\phi$ can be written as a function of C_s'' when $C_s'=5C_s''$, varying X, U and K. On the other hand, equations (2) and (3) can be used to give the permeability coefficient P as a function of the upstream concentration C_1, varying X, U, θ and K. The value of X was found by curve-fitting the $\Delta\phi$ data against C_s'', using equation (1). Subsequently, taking the value of X, U and T were determined by curve-fitting the data for P against C_1, using equations (2) and (3). The ionic molar mobilities in the membrane phase, w^+ and w^-, are obtained from U and θ using equations (3) and (4).

As fitting by equation (1) was not successful in the case of NaBPh$_4$, NaSO$_3$Nph and NaSO$_3$Tlu, the following was attempted. The permeability coefficient, described as P_a, was calculated, using the activity gradient instead of the concentration gradient. In the case of NaBPh$_4$, P_a is obtained from activity coefficients calculated by the Debye–Hückel theory[9]. Plots of P_a against the activity of the salt on the upstream side of the membrane, a_1, are shown in *Figure 10*.

A good fit can be established with equation (2) in the low activity range by the use of X, obtained by equation (1). The values of U and θ obtained by this method are the same as those determined by equation (2), when X, U and θ are used as variable parameters. The parameters X, U,

w^+ and w^- are summarized in *Tables 1, 2* and *3*. For the purpose of comparison, the limiting values of the diffusion coefficient, D_0, and molar mobility, w_0, in bulk water were calculated from the respective conductivity data[10,11] and are shown in *Table 4*.

As shown in *Tables 1–4*, the molar mobilities of anions in the membrane become smaller as molecular size increases, with:

$$BPh_4^- < SO_3Nph^- < SO_3Tlu^- < SO_3Ph^- < SO_3Eth^- < Cl^-$$

while the sequence in water is:

$$BPh_4^- < SO_3Nph^- < SO_3Tlu^- < SO_3Eth^- < SO_3Ph^- < Cl^-$$

The reversal in membranes between SO_3Eth^- and SO_3Ph^- may be attributed to the change in hydration in the membrane. The decrease in molecular mobilities with decreasing water content is more marked in the anion than the cation in salts in which the anion is large. This is attributed to geometrical obstruction of the transport of the larger particles. The small molar mobility of anions that give a large U leads to anomalous permeation behaviour, as shown in *Figures 1–3*.

According to the TMS theory for cationically charged membranes, anomalous permeation behaviour is produced by a large U, that is, a small cation and a large anion, whereas in the case of a large cation and a small anion, calculation predicts the relation between P and C_1 to follow the usual pattern, such as is the case with NaCl. This was supported experimentally by the permeability of TBAB, measured under the same conditions as the sodium salts. The permeability of TBAB through PN-77, PN-66 and PN-50 is shown in *Figure 11*.

Effect of fixed charge concentration

The plot of membrane potential $\Delta\phi$ of PVA membranes against salt concentration is shown in *Figure 12*. The membrane used here was prepared from PVA, as described in the 'Experimental' section. Some of this membrane was pretreated with HCl to reduce the number of carboxyl groups. Both membranes had the same water content of $H = 0.794$. KCl was used in this experiment because its diffusion potential in water is zero, as $U_0 = 0$. It was assumed that the above condition applies in the membrane as well as in water. *Figure 12* demonstrates clearly a decrease in the number of fixed charge groups, caused by the HCl treatment. It can be taken that the pretreated PVA membrane contains only a negligible amount of charged groups.

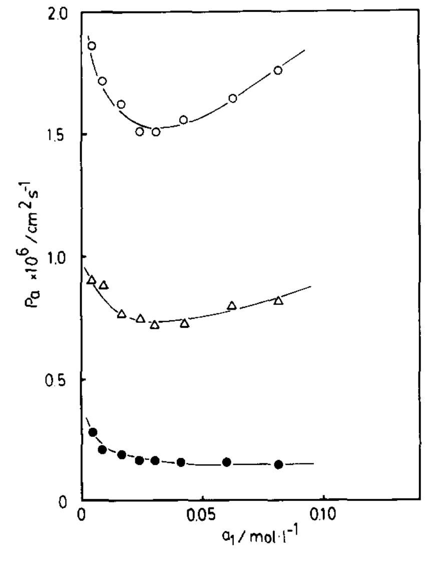


Figure 10 Permeability coefficient P_a *versus* external salt activity a_1 for NaBPh$_4$: (○) PN-77; (△) PN-66; (●) PN-50

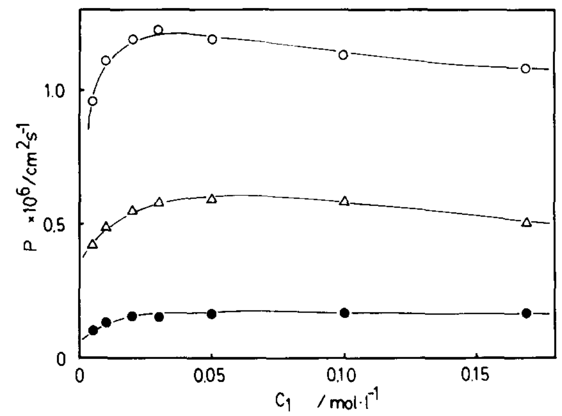


Figure 11 Permeability coefficient P *versus* external salt concentration for TBAB: (○) PN-77; (△) PN-66; (●) PN-50

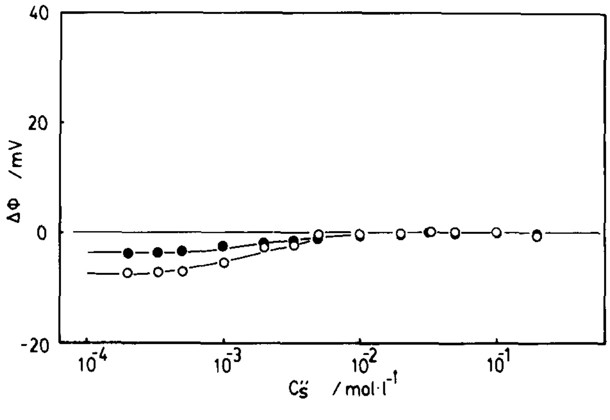


Figure 12 Membrane potential $\Delta\phi$ *versus* C_s'' for KCl ($C_s' = 5C_s''$, $H = 0.794$): (●) PVA treated with HCl; (○) PVA untreated

Table 4 w_0^+, w_0^-, U_0 and D_0 of NaCl, NaSO$_3$Eth, NaSO$_3$Ph, NaSO$_3$Tlu, NaSO$_3$Nph and NaBPh$_4$

	NaCl	NaSO$_3$Eth	NaSO$_3$Ph	NaSO$_3$Tlu	NaSO$_3$Nph	NaBPh$_4$
$w_0^+ \times 10^9$ (cm^2 mol J^{-1} s^{-1})	5.381	5.381	5.381	5.381	5.381	5.381
$w_0^- \times 10^9$ (cm^2 mol J^{-1} s^{-1})	8.201	4.025	5.115	3.512	3.288	2.131
U_0[a]	−0.2076	0.1442	0.0253	0.2102	0.2414	0.4326
$D_0 \times 10^5$ (cm^2 s^{-1})	1.610	1.142	1.285	1.054	1.012	0.757

[a] $U_0 = (w_0^+ - w_0^-)/(w_0^+ + w_0^-)$

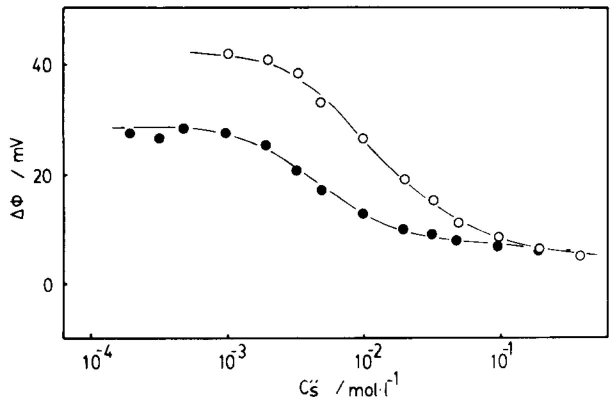


Figure 13 Membrane potential $\Delta\phi$ *versus* C_s'' ($C_s'=5C_s''$): (●) PN-77; (○) PNN-80

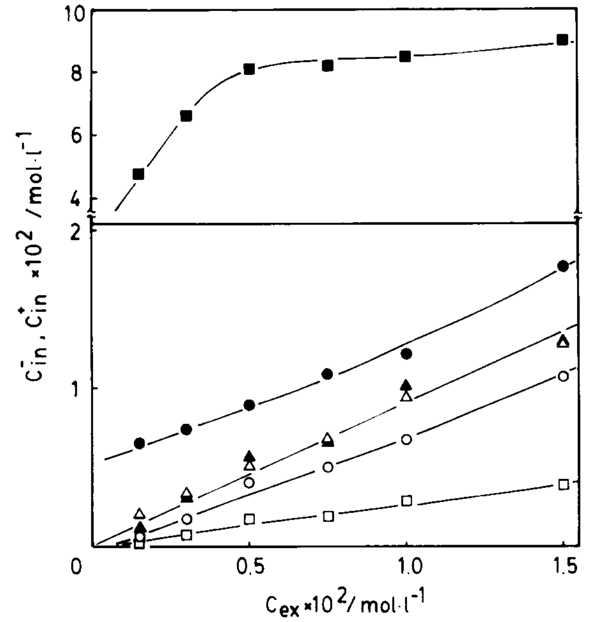


Figure 14 C_{in}^- and C_{in}^+ *versus* C_{ex} of aqueous NaCl solution: filled symbols, Cl^-; open symbols, Na^+; (△, ▲) P-83; (○, ●) PN-77; (□, ■) PNN-80

The membrane potential for PNN-80, the PVA-N-2 membrane with $H=0.800$, as well as for PN-77 is given in *Figure 13*. It can be seen in *Figures 11, 12* and *13* that, at low C_s'', $\Delta\phi$ decreases with fixed charge concentration. As mentioned before, according to the TMS theory, at low C_s'', $\Delta\phi$ should be 41.4 mV, which is in accord with the value for PNN-80. However, at low C_s'', for PN-77, $\Delta\phi$ is smaller than the theoretical value. The reason for this discrepancy remains an open question.

The method described in the 'Experimental' section was applied to elucidate the Donnan effect of both counter-ion and co-ion sorption of NaCl and $NaBPh_4$. PN-77, PNN-80 and P-83, an uncharged PVA membrane with $H=0.828$, were used. The three membranes have approximately the same water contents. The results are shown in *Figures 14* and *15*. In the case of uni-univalent salts, assuming a simple Donnan equilibrium, the effective concentration of the fixed charges, X', is estimated from the following relation:

$$X'=C_{in}^- - C_{in}^+ \qquad (X' \text{ in mol l}^{-1}=\text{equiv l}^{-1}) \qquad (5)$$

Figure 16 shows the constancy of the effective fixed charge concentration in the membranes.

The total fixed charge concentration X_0 can be calculated from the copolymer composition. *Table 5* gives X, X' and X_0. That X and X' are always smaller than X_0 is explained by considering how the charged groups exert their effect; some of them may be buried in the polymer matrix. In addition to this, the activity in the polymer phase should be considered, especially when we deal with high anion concentrations such as, for example, in the system PNN-80/NaCl. Moreover, X is found to depend upon the salt species as well as on the membranes.

The ionic mobility in the uncharged PVA membrane was estimated with a view to ascertaining the fixed charge effect on ionic mobility. The diffusion coefficient in the

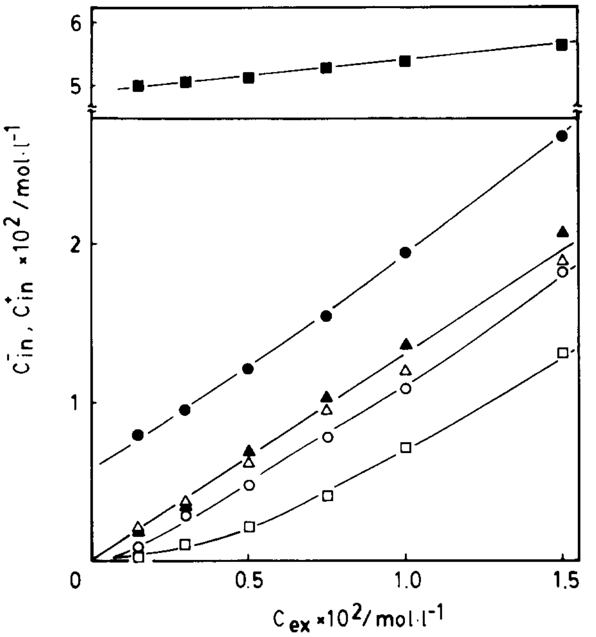


Figure 15 C_{in}^- and C_{in}^+ *versus* C_{ex} of aqueous $NaBPh_4$ solution: filled symbols, BPh^-; open symbols, Na^+; (△, ▲) P-83; (○, ●) PN-77; (□, ■) PNN-80

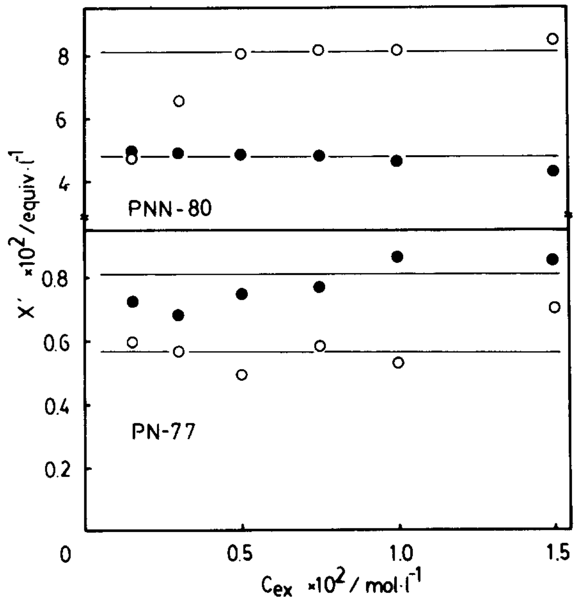


Figure 16 X' *versus* C_{ex}: (●) $NaBPh_4$; (○) NaCl

Table 5 X_0, X and X' (equiv l^{-1})[a] of PN-77 and PNN-80

Membranes	X_0	X^b	X'^b	X^c	X'^c
PN-77	0.015	0.005	0.005_6	0.001	0.007_7
PNN-80	0.113	0.038	0.081	–	0.048

[a] Equivalents per litre of imbibed water
[b] Determined by NaCl
[c] Determined by $NaBPh_4$

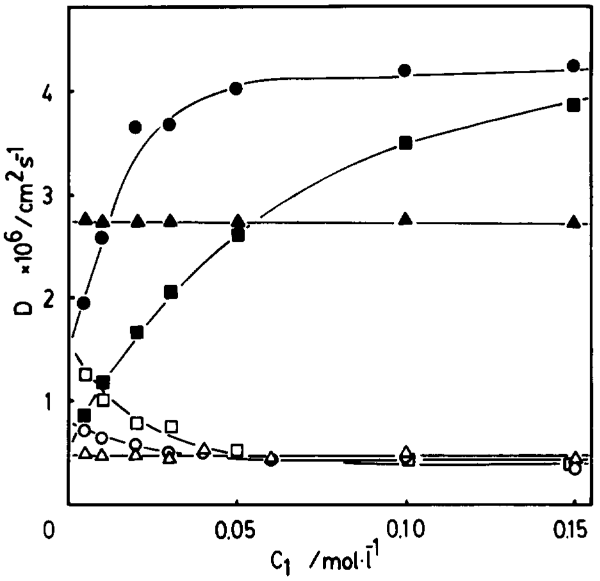


Figure 17 Diffusion coefficient D *versus* C_1: filled symbols, NaCl; open symbols, $NaBPh_4$; (△, ▲) P-83; (○, ●) PN-77; (□, ■) PNN-80

Table 6 $Y\,(=2w^+w^-/(w^+ + w^-))$ of NaCl and $NaBPh_4$ in P-83, PN-77 and PNN-80

	Membranes		
Salts	P-83	PN-77	PNN-80
NaCl[a]	0.83	1.71	1.43
$NaBPh_4$[b]	1.96	1.81	1.88

[a] $\times 10^{-9}\,cm^2\,mol\,J^{-1}\,s^{-1}$
[b] $\times 10^{-8}\,cm^2\,mol\,J^{-1}\,s^{-1}$

uncharged membrane phase is:

$$D' = 2w^+w^-RT/(w^+ + w^-) \qquad (6)$$

However, equation (6) neglects the charge effect. Therefore the diffusion coefficient determined by this equation is denoted as D', to distinguish it from D. The coefficient D' is related to the permeability coefficient P through $P = D'K$.

Equation (6) is derived from equation (2) as a limiting case of $x \to 0$ or $C_1 \to \infty$. The harmonic average of molar mobilities of cation and anion, $2w^+w^-/(w^+ + w^-)$, is denoted here by Y.

Figure 17, the relation between D and C_1 for NaCl and $NaBPh_4$ in P-83, PN-77 and PNN-80, clearly indicates the effects of the fixed charge. The difference in Y can be compared with values of D at high C_1. For comparison of the ionic mobility in PN-77, Y is estimated using the values of w^+ and w^- given in *Tables 1* and *3*. The w^+ and w^- values determined by the TMS theory give Y for PNN-80. Equation (6) is used to calculate Y for P-83. The values thus obtained are summarized in *Table 6*. By inspecting the table, together with the values for mobility given in the previous subsection of this discussion, it can be seen that ionic mobility is affected sterically by the polymer chain and is independent of fixed charge concentration. The values of Y for NaCl in different membranes vary considerably compared with those for $NaBPh_4$. This is attributed to experimental error, which is inevitable in determining the permeability of NaCl in the high C_1 range when the permeability is too large for accurate determination. One should in addition also consider variations in the physical character of the membranes, such as the water content.

CONCLUSIONS

The permeability of six sodium salts through cationically charged poly(vinyl alcohol) membranes was determined with a view to elucidating the effect of membrane charge on the ionic permeation of simple salts. The dependence of permeability on salt concentration was anomalous for salts producing a large anion. The results, together with those of membrane-potential measurements, can be explained satisfactorily by the TMS theory.

In the low concentration range, a simple Donnan equilibrium was found to hold for NaCl in PVA-N ($H = 0.774$). The effective concentration of fixed charges thus obtained is in good agreement with that determined from membrane-potential measurements.

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