from rupture of the C–N bond. Mechanisms by which the C–N bond may be broken have been discussed elsewhere.[10] Whereas the free radicals produced in alanine and α-aminoisobutyric acid by C–N bond breakage are stable at room temperature, those produced in glycine apparently are not. Considerable alteration in the esr spectra occurs at room temperature. Interpretation of the final spectra appears still to be a matter of lively controversy.[4]

Perhaps the most significant result of this research is to show that esr studies of single crystals at controlled temperatures, after irradiation at low temperature, offer considerable promise for following radiation damage processes.

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Solvent Mass Transfer across Ion-Exchange Membranes

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Abstract: A study of water diffusion across polystyrenesulfonic acid ion-exchange membranes, induced by osmotic pressure and cation diffusion potentials, has been made. The experimental results have been interpreted in terms of viscous interactions within the membrane during the transport process, between the ion and water, and between the water and membrane pore wall. Equations have been derived which relate solvent and ion transport rates with the viscous interactions within the membrane. These relationships were used to estimate friction coefficients for the interchange processes. The dependence of the ion–water interaction coefficient on inorganic and organic counter-ion diameter was determined.

Previous determinations of water transport across polystyrenesulfonic acid ion-exchange membranes by electroosmosis and ion interchange have been reported.[2–4] The results of measurements of water transport across similar membranes by osmosis (with solutions of HCl, KCl, NaCl, LiCl, $(CH_3)_4NCl$, and $(C_2H_5)_4NCl$ in the concentration range 0.1 to 1.0 *M*) and counter-diffusion of univalent inorganic and organic cations are given in this report. The results are consistent with theoretical considerations[5] of solvent transport phenomena through ion-exchange membranes. The dependence of solvent transport on membrane properties and the interchanging ion species has been determined.

Experimental Section

(A) **Membranes.** The membranes were prepared by the bulk copolymerization of the methyl and *n*-propyl esters of *p*-styrenesulfonic acid with styrene, divinylbenzene, and benzoyl peroxide as catalyst and subsequent hydrolysis in 5% caustic soda solution to produce polystyrenesulfonic acid.[3,6,7]

The methods used for the determination of membrane moisture content, exchange capacity, and thickness have been described previously.[6] In Table I are given the characteristics of the membranes and the membrane moisture contents in various ionic forms in contact with pure water at 25°.

(B) **Solvent and Cation Transfer.** A two-compartment Lucite cell was used to measure the rates of solvent and cation transfer. The compartments, each with a volume of 35 ml, were separated by a membrane with an area of 3.14 cm². The capillary tubes fitted into the cell were each 0.0856 cm in diameter. At the time of filling the cell, the solutions were adjusted to about the same level in both capillary tubes and the heights were measured using a cathetometer. After 1 hr the changes in the heights of the solutions were observed and the contents of the compartments were analyzed by titration. The procedure was repeated with fresh solutions until constant flux was obtained. The data reported here are average values for four individual measurements. All measurements were taken at 25 ± 0.1° with the solutions at rest in the cell. These data were used to calculate solvent transfer rates.

Results and Discussion

The osmotic flow rates are given in Table II. These measurements were made using various solutions of hydrochloric acid, potassium chloride, sodium chloride, lithium chloride, tetramethylammonium chloride, and tetraethylammonium chloride. The results were calculated from the experimental data using the relationship

$$J = \frac{(\Delta V)L}{tA} \qquad (1)$$

where J is the solvent flow rate in ml/cm hr; (ΔV) is the volume change in ml in t hr; L is the membrane thickness, 0.1334 cm; and A is the membrane cross section, 3.14 cm². Graphical representation of the increase of osmotic flow rate with increasing osmotic potential difference gave linear plots. The slopes of the straight lines correspond to osmotic permeability coefficients for the membrane in the given ionic forms. The observed values of the osmotic permeability coefficients are given in Table II. It may be noted that the osmotic permeabilities of the membrane in the various ionic forms decrease in the order hydrogen, potassium, sodium, lithium, tetramethylammonium, and tetraethylammonium, although the radius of the hydrated

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Table I. Membrane Characteristics

Membranes No.	Membranes Ester form	Mole % DVB	Capacity, mequiv/g of dry resin, H form	Moisture content, moles of H_2O/equiv K^+	Na^+	H^+	Li^+	$(CH_3)_4N^+$	$(C_2H_5)_4N^+$	Thickness, cm (±0.0002)
1	Methyl	4	1.89	23.4	24.0	24.6	24.9	21.7	24.2	0.1334
2	Propyl	4	1.45			20.3	20.7	18.0		0.1402

Table II. Osmotic Solvent Transport

Membrane no.	System	Flow rate (J), ml/cm hr × 10^4 0.1 N	0.5 N	0.9 N	1.0 N	Osmotic permeability coeff, ml/cm hr atm × 10^4
1	$HCl-H_2O$	4.37	19.2	36.9		0.76
	$KCl-H_2O$	3.13	10.3		17.9	0.40
	$NaCl-H_2O$	2.11	7.61		13.9	0.27
	$LiCl-H_2O$	1.59	6.56		11.6	0.22
	$(CH_3)_4NCl-H_2O$	1.54	5.86		10.2	0.21
	$(C_2H_5)_4NCl-H_2O$	1.17	4.67		8.85	0.18

lithium ion is greater than that assigned to tetramethylammonium ion.[8] This indicates that the resistance to osmotic flow experienced in the membrane by the stationary organic cations is greater than that for inorganic cations of the same valence and size. As one might expect, the osmotic solvent transport across an ion-exchange membrane showed similar variations with ionic size[8] in solution to that experienced with the conductance[9] of solutions of these ions as shown in Figure 1.

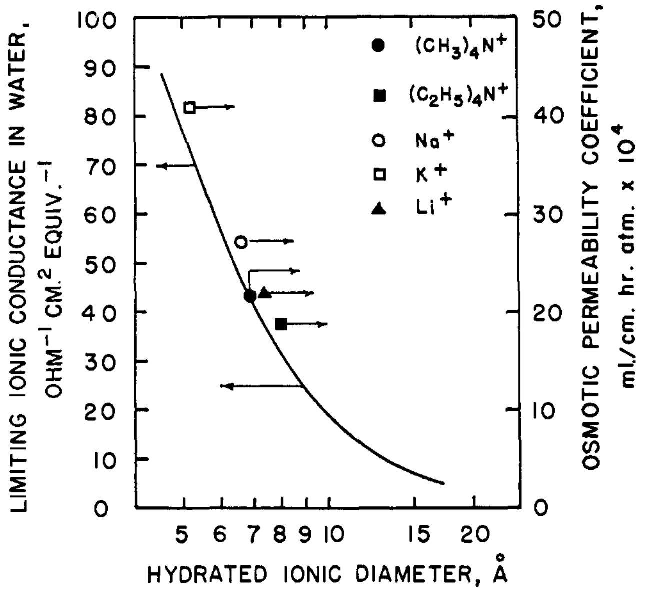

Figure 1. The curve shows the variation of limiting ionic conductance in water of univalent inorganic and organic cations with hydrated ionic diameter in solution; the points show the variation in the osmotic permeability coefficient of the methyl membrane in the ionic forms with hydrated ionic diameter in solution.

The values of water transport which have been obtained during cation interchange between isotonic solutions for various exchange systems are given in Table III. It may be noted from Table III that the net water transport attending the interchange between the various univalent inorganic and organic cations is always in the direction of the larger ion. The results indicate that high water transport during ion interchange is associated with low ionic mobility of the counterion and low osmotic permeability of the membrane in that ionic form. The mobility of an ion in the membrane is an inverse measure of the ion–water interaction experienced in the membrane. Solvent transport across the membrane by cation interchange is the greater the higher the frictional interaction between ion and solvent in the membrane. No net solvent transport should occur when the mobilities of the interchanging ions are equal. This effect may be illustrated by the interchange process $K^+-NH_4^+$ for which the net water transport across the methyl membrane was only 0.23 × 10^{-4} ml/cm hr. The limiting ionic mobilities[9] of K^+ and NH_4^+ in water at 25° differ less than 0.5%.

Table III. Water Transport during Cation Interchange

Membrane no.	System Half-cell 1 0.1 M	System Half-cell 2 0.1 M	Net water transfer into half-cell 2 Flow rate (J), ml/cm hr × 10^4	Net water transfer into half-cell 2 Transference no., moles of H_2O/equiv of ion interchange
1	KCl	HCl	8.75	8.0
	NaCl	HCl	9.15	11.8
	LiCl	HCl	9.75	17.8
	$(CH_3)_4NCl$	HCl	10.1	19.8
	$(C_2H_5)_4NCl$	HCl	8.53	25.0
	$(C_2H_5)_4NCl$	KCl	6.49	(19)[a]
	$(C_2H_5)_4NCl$	NaCl	4.33	(15)
	$(C_2H_5)_4NCl$	LiCl	2.48	(9)
	KCl	NH_4Cl	0.23	(0.4)

[a] The values in the brackets are based on calculated cation-interchange fluxes: J. Ciric and W. F. Graydon, *J. Phys. Chem.*, **66**, 1549 (1962).

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Table IV. Solvent and Cation Transport under Combined Osmotic and Cation Diffusion Potential Differences

Membrane no.	Expt no.	Soln concn, mole/l. Half-cell 1 NaCl	Soln concn, mole/l. Half-cell 2 HCl	Cation interchange flux, g equiv/cm² hr × 10^5	Net solvent[a] flow rate (J) into half-cell 2, ml/cm hr × 10^4	Osmotic solvent flow rate (J), ml/cm hr × 10^4	
						Obsd	Calcd
1	A	0.1	0.1	3.20	9.15		
		0.3	0.3	7.53	18.5		
		0.5	0.5	10.5	27.0		
		0.7	0.7	13.6	31.4		
	B	0.1	0.3	4.70	18.6	5.3	5.3
		0.1	0.5	5.67	26.8	10.6	10.2
		0.1	0.7	6.24	32.1	14.3	15.1
	C	0.3	0.1	4.37	7.86	2.9	4.6
		0.5	0.1	4.73	5.17	7.0	9.3
		0.7	0.1	5.04	1.54	9.9	14.2
		0.9	0.1	5.38	−0.75		

[a] The solvent movement from half-cell 2 into half-cell 1 is considered negative.

In order to determine the extent to which the water molecules present in the membrane accompanied the migrating counterions during cation interchange, the water transference numbers listed in Table III were divided by the respective equivalent moisture contents of the membrane (moles of water per equivalent of ion-exchange capacity). For the various exchange systems, these ratios of water transport to membrane equivalent moisture content may be calculated: for K^+–H^+, 0.34; Na^+–H^+, 0.50; Li^+–H^+, 0.73; $(CH_3)_4N^+$–H^+, 0.87; and $(C_2H_5)_4N^+$–H^+, 1.04. It is of interest to compare these values with similar ratios of electroosmotic water transport to membrane equivalent moisture content for single ions:[3] for H^+, 0.11; K^+, 0.37; Na^+, 0.46; and Li^+, 0.59. It may be noted from the data that the movement of hydrogen ion against the counterions does not reduce the quantity of water transport by counterion migration during the interchange. The large counterion exerts the major control over the magnitude of net water transport during ion interchange.

A graphical representation of the dependence of the ratio of water transport to membrane equivalent moisture content on counterion diameter for univalent inorganic and organic cations is given by straight lines with slope +0.17. The plots illustrate the increase in the amount of water carried per cation with increasing counterion diameter. Water transport is much greater for organic than inorganic cations. This indicates that the ion–water interaction experienced by the mobile organic counterions in the membrane during ion interchange is greater than that for inorganic cations of the same valence and size. It will be noted that the data indicate a higher interaction between tetramethylammonium ion and water than is observed between the larger lithium ion and water. These data would lead one to expect that in a Li^+–$(CH_3)_4N^+$ exchange the flow of water would be in the direction of the smaller tetramethylammonium ion and counter to the larger lithium ion. This direction of water flow has been verified in such an experiment and was found to be about 10^{-4} ml/cm hr across a propyl membrane (no. 2).

The effect of osmotic potential on water and cation transfer during ion interchange also was determined using symmetrical and unsymmetrical external solution concentrations. Examples of the results of water and cation transfer, which have been obtained during the interchange of sodium with hydrogen in three series of experiments (A, B, and C) over a wide range of solution concentration, are given in Table IV. In experiments A, where there was no great osmotic pressure difference between the equimolar solutions of NaCl and HCl, the cation diffusion potential produced convection of the membrane pore liquid. This water was transported in the direction of sodium ions, and the amount transported per equivalent of ion was only slightly dependent on external solution concentration. For experiments B, in which the osmotic potential gradient caused the flow of solvent in the direction of the net convection produced by the cation diffusion potential, the values of cation and solvent transport are large and increase with increasing external solution concentration. In experiments C, where the osmotic potential gradient moved the solvent in opposite direction to the net convection produced by cation diffusion potential, the values of cation and solvent transport are low and decrease with increasing external solution concentration. No net displacement of solvent should occur when solvent transport due to osmotic potential and cation diffusion potential balanced. Indeed, the data of Table IV indicate that there would be no net solvent transport across the methyl membrane separating 0.1 *M* solution of HCl from approximately 0.8 *M* solution of NaCl.

It is of some interest to note the extent to which the osmotic and cation-interchange water flux values are simply additive. An estimate of the osmotic permeability coefficient of 0.51 × 10^{-4} ml/cm hr atm for the mixed sodium–hydrogen form of the ion-exchange resin was obtained by simple numerical averaging of the permeabilities of the pure ionic forms. This value permitted the calculation of osmotic flux which when added to the value obtained for cation-interchange flux in isotonic solutions gave the values listed in the last column in Table IV.

The interactions which exist during transport processes through ion-exchange membranes between ions, water, and organic membrane material may be considered in terms of "friction coefficients."[10] If the force of interaction is assumed proportional to the relative velocity, a simple force balance for a fully developed (steady-state) flow of solvent through an ion-exchange membrane induced by osmotic pressure difference yields

$$(\Delta P)A = (f_{\mathrm{IW}} + f_{\mathrm{Ww}})U_{\mathrm{w}} \qquad (2)$$

where ΔP is the osmotic pressure difference across the ion-exchange membrane, atm; U_{w} is the velocity of solvent relative to the membrane pore wall ($=\Delta V/At$), cm/sec; f_{IW} and f_{Ww} are the interaction coefficients (dynes sec/cm) between ion-water and water-membrane, respectively. Similar considerations for ion and water transport during the interchange of univalent cations with hydrogen lead to the relationship[3]

$$\frac{w_{\mathrm{T}}}{W_{\mathrm{D}}} = \frac{f_{\mathrm{IW*}}}{f_{\mathrm{IW*}} + f_{\mathrm{Ww}}} \qquad (3)$$

where $w_{\mathrm{T}}/W_{\mathrm{D}}$ is the ratio of net water transport (in the direction of the large counterion) to membrane equivalent moisture content, and $f_{\mathrm{IW*}}$ is the interaction coefficient between the large counterion and water. (Since the large counterion exerts the major control over the magnitude of net water transport during ion interchange, the interaction coefficient between hydrogen-water is assumed negligible in this development.) By combination of eq 2 and 3 individual interaction coefficients between counterion-water and water-membrane pore wall may be estimated.

Samples of such values of friction coefficients calculated by eq 2 and 3 for the interchange of potassium, sodium, and lithium with hydrogen are given in Table V. It may be noted that the value for the interaction between the water and the membrane pore wall does not vary markedly over a change of fourfold in the ion-water interaction for the inorganic cations. A similar calculation for the organic cations yields considerably higher values for the ion-water interaction coefficient and much lower values for the water-membrane pore wall interaction term. These results may indicate a substantial difference in the location of the organic cation from that of the inorganic one relative to the membrane pore wall. Indeed, the heteropolar nature of the organic cation would suggest its location closer to the polymer wall. The increase in the value of the ion-water interaction coefficient with increasing ionic size for the univalent inorganic and organic cations showed linear dependence of ion-water interaction coefficient on counterion diameter.

Table V. Ion-Water and Water-Membrane Interaction Coefficients

Membrane no.	Ion-pair exchange system	Interaction coefficients, dynes sec cm^{-1} × 10^4 $f_{\mathrm{IW*}}$	f_{Ww}
1	K^+-H^+	K^+, 0.98	1.9
	Na^+-H^+	Na^+, 2.2	2.2
	Li^+-H^+	Li^+, 3.9	1.5
		Av	1.9
	$(CH_3)_4N^+$-H^+	$(CH_3)_4N^+$, 4.8	0.6
	$(C_2H_5)_4N^+$-H^+	$(C_2H_5)_4N^+$, >6.3	<0

Acknowledgment. The authors are indebted to the National Research Council, Ottawa, Canada, and the President's Advisory Committee on Scientific Research, University of Toronto, for financial support.

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Conductance of Electrolytes in Anhydrous Acetone

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Received August 30, 1965

Abstract: The conductances of a number of lithium and tetra-*n*-butylammonium salts in anhydrous acetone were measured at 25° and the data analyzed by the Shedlovsky method. The limiting conductances (Λ_0) and the ion-pair dissociation constants ($K_D \times 10^4$) are as follows: LiCl, 214, 0.033; LiBr, 194, 2.19; LiI, 195.0, 69.1; lithium *p*-toluenesulfonate, 172, 0.096; tetra-*n*-butylammonium chloride, 188, 16.6; tetra-*n*-butylammonium *p*-toluenesulfonate, 151.6, 24.6. It is suggested that in the LiCl ion pair the unsolvated ions are in contact, while in LiI the ion pair is formed from fully solvated ions. LiBr represents an intermediate case with some solvent included within the ion pair.

In the course of an investigation of second-order rates for SN2 reactions of lithium and tetra-*n*-butylammonium halides in acetone, Winstein and co-workers[2] observed that the nucleophilicities of the tetra-*n*-butylammonium halides showed the order Cl > Br > I, the exact opposite of the commonly accepted order which was based on the reactions of lithium halides as nucleophiles.[3] Their results could be explained upon assuming an order of Cl > Br > I for the nucleophilicities of the free halide ions and that the reversal of this order, observed when lithium halides are used as nucleophiles, is a consequence of ion association. In order to

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