ION-EXCHANGE MEMBRANES—CORRELATION BETWEEN STRUCTURE AND FUNCTION

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The study of a complex system such as an ion-exchange membrane can be approached from two directions, which are not mutually exclusive. We can make use of the theoretical framework of irreversible thermodynamics as first applied by Staverman[1] to membrane systems, and as amplified by a number of other investigators, particularly Kedem and Katchalsky[2–4]. Here, we measure fluxes and generalized forces (the latter all too often involving the estimation of thermodynamic activity coefficients) and compute the phenomenological coefficients. This is essentially a "black box" approach which must give us correct and exact answers, provided the requirement of linearity between flux and force is obeyed, as they seem to be under the conditions which obtain in these systems.

The other approach is a mechanistic one, where we employ models and appropriate theoretical treatments to predict the behaviour of real systems. The two approaches are not independent of one another, but complimentary; both require the measurement of a number of different, independent parameters of the same system.

MEMBRANE STRUCTURE

In this contribution, we are concerned entirely with the so-called "tight" membranes which possess a high concentration of fixed-charge groups in a dense, porous gel. These are the ion-exchange membranes of commerce, which demonstrate a high and nearly ideal selectivity for the counter-ion species at all but the higher ($>0{\cdot}2$ M) concentration levels.

The membranes upon which most of the experimental measurements described herein were performed are those available commercially from Asahi Chemical Industries (ACI). These are prepared by the dissolution of linear polystyrene (or a copolymer with styrene as the principal constituent) in a mixture of styrene and divinylbenzene (or another difunctional agent) which is then polymerized to form a cage polymer system, but where both the cross-linked and linear portions are principally of polystyrene. Blocks of these materials are then treated as follows: a microtome knife shaves off large sheets, which are then sulphonated to produce the cation-exchange material or treated with chloromethylether (or by an analogous reaction to form the benzyl chloride derivative), followed by treatment with trimethylamine to produce the anion-exchange membranes[5]. These membranes are "tight", and they are unusually uniform. Pieces taken from the same sheets are usually reproducible to within ±10%, and materials obtained from the manufacturer at times separated by several months or even a year are as nearly alike, although samples obtained 4 years apart do show substantial differences in capacity but not in their intrinsic properties.

These membranes are also reasonably free of imperfections. Before all experiments they were examined for the absence of pinholes by placing the blotted membrane on a piece of dry filter paper, wetting the top of the membrane with a dye solution and examining the white filter paper for dye spots. This is a sensitive test, particularly so because the dry paper draws solvent through the membrane. While the work of Gluekauf *et al.*[6] has indicated that there are undoubtedly voids in most if not all ion-exchange resin and membrane systems, these usually constitute but a small fraction of their volume and do not extend through the structure; thus, these voids have no functional importance.

These ACI membranes show an exchange capacity which is the same to all of the ions studied herein, with the possible exception of a small deviation from full capacity exhibited by the cation-exchange membranes to the tetrabutylammonium (TBA) ion[7], or to the alkylbenzesulphonate (ABS) anion in the case of anion-exchange membranes[8]. Because of their high selectivity, these membranes exhibit nearly the same behaviour in dilute solutions ($<0{\cdot}2$ M); this applies to measurements of the electrical conductivity, electro-osmotic flux, diffusion coefficient of neutral molecules or counter-ions, and the like.

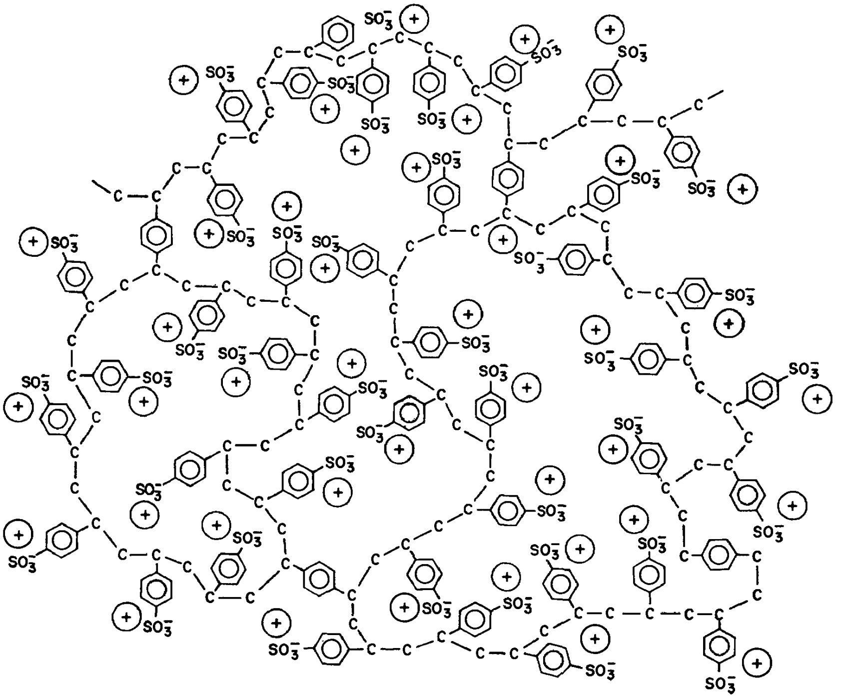

Figure 1

Figure 1 shows diagrammatically a cross-linked, completely sulphonated polystyrene polymer. The drawing is approximately to scale, for later calculations will show that the effective pore diameters are approximately 10 Å. The diagram is of a typical 5–8% DVB polystyrene sulphonic acid (PSSA) resin. Our view of the analogous membrane system is shown in *Figure 2*, where there are both cross-linked and linear polymer domains.

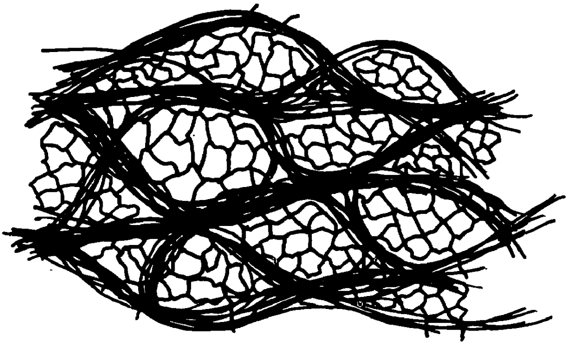

Figure 2

Figure 2 is purely conceptual: we have no direct but only indirect evidence as to the microscopic nature of the membrane. However, as will be shown later, the pore spectrum appears to be fairly narrow and the effective path length across the membrane is not too different from the actual membrane thickness (lack of tortuosity). This would suggest that the more amorphous, cross-linked portions of the membrane are preferentially sulphonated or chloromethylated-aminated to produce ion-permeable regions.

The aromatic nature of these membranes deserves special mention. In spite of their high concentration of polar groups, these systems are still strongly aromatic and capable of strong adsorptive phenomena. This is particularly demonstrable with ions of an organic nature, particularly with the higher-molecular-weight quaternary ammonium cations and with the aromatic anions. Reference should also be made to the strong effects observed by Sakurada (see pp. 263–84) in his catalytic studies involving PSSA polymers, described elsewhere in this volume. While these adsorptive processes evidence themselves principally in thermodynamic measurements such as that of the selectivity coefficient[9, 10], they do affect the permeability of membrane systems appreciably.

A few of the properties of the ions examined in this study are listed in *Table 1*. The equivalent ionic conductance at infinite dilution is certainly a reliable although only a semi-quantitative index of the ion size because of the inapplicability of Stokes' hydrodynamics to these molecular systems. The crystal radii are well established, as are those obtained from model studies for the quaternary ammonium ions. The application of the hydrodynamic equations for the calculation of effective ionic radii in solution is discussed by Robinson and Stokes[11]. On the basis of both experimental and theoretical investigations, it appears that the numerical constant in the

Table 1. Ionic properties

	λ°	*r in* Å	*Crystal radii* Å
H	350		
Li	39		0·68
Na	50		0·98
K	74	2·1†	1·33
Me_4N	45	3·47	
Et_4N	33	4·00	
Pr_4N	23	4·52	
Bu_4N	20	4·94	
OH	195		
Cl	76	2·3*	1·81
Br	76		1·96
I	77		2·19
SCN	72		
*p*TS	34		
IO_3	40	3·7*	
NO_3	71		

† From distance of approach in solution. λ° is the equivalent ionic conductance at infinite dilution.

Stokes' equation is apparently nearly 6 for large ions, decreasing to approximately 3 for ions having approximately the same radius as that of the solvent. However, the recent work of Zwanzig[12] has served to indicate that an additional correction may be required in correlating the ionic radii of the large quaternary ammonium ions with measurements of their electrical conductivity. Further, we know that the activity of water in solutions of quaternary ammonium ions is not that predicted from a consideration of ionic concentrations and radii, employing the Debye–Hückel equations. Measurements of several authors[13–15] confirm the general concept of Frank[16, 17] who views water as existing in a "normal" water state, a hydrogen-bonded "ice-like" state (which may be reinforced by the mirror effect) and another state of low entropy, the ion-hydrate state. Accordingly, ions are classified into "structure-breaking" and "structure-making" species, the structure referring to the ice-like state.

Theoretical studies have indicated that it is the radius of curvature of solvent and solute molecules which determines the extent of momentum transfer on collision and therefore the coefficient of Stokes' equations. When we later apply the classical hydrodynamic equations to the kinds of molecular structures shown in *Figure 1* and its counter-ions, we feel some confidence in this extrapolation because the radius of curvature of the molecules making up the pore walls is of the same magnitude as those of the ions passing through these pores. Under these circumstances, it appears reasonable to apply the classical hydrodynamic equations with a correction for the "hydrodynamic radius"[11].

Table 2 summarizes a number of the properties of the ACI cation-exchange membranes. Using the potassium state as the base for comparison, we see that the membrane swells slightly when larger (hydrated) exchange cations (Na and Li) are present, but appreciably and regularly as the size of the

Table 2. Properties of ACI cation-exchange membranes
(Capy.—2·84 meq/g)

Ion	*Vol.* (ml)	*L* (μ)	φ_p	$\bar{c}$	$\bar{m}$
H	1·42	220	0·44	2·0	4·6
Li	1·50	218	0·45	2·0	4·3
Na	1·42	217	0·41	2·0	4·9
K	1·40	221	0·41	2·0	5·1
A	1·40	216	0·42	2·0	5·1
TMA	1·78	239	0·58	1·6	3·9
TEA	1·94	247	0·63	1·5	3·8
TPA	2·07	245	0·64	1·4	4·3
TBA	1·97	244	0·68	1·4	5·1
Dowex 50-X8			0·50		5·5

Vol.—ml/g of H-form membrane.
L —thickness in microns (μ).
φ_p —pore volume fraction (including exchange ion).
$\bar{c}$ —molar concentration of fixed charge.
$\bar{m}$ —molal concentration of fixed charge.
A, TMA, TEA, TPA and TBA are the ammonium, tetramethyl-, ethyl-, *n*-propyl- and *n*-butyl ammonium ions.

quaternary ammonium counter-ion is increased. There is a 40 per cent increase in membrane volume on going from the potassium to the TBA state, but only a 10 per cent increase in thickness; most of the volume increase is therefore a consequence of increases in pore diameters, if we consider these macro-pores as having their axes normal to the face of the membrane. This anisotropic swelling is one basis for our picture of these membranes as having macro-pores of cross-linked polyelectrolyte extending through the membrane, with the diameter of the macro-pores contained therein being controlled by the extent of cross-linking.

In *Table 2* we note that the pore volume fraction (which includes the counter-ion volume) also increases with (hydrated) ionic size for the inorganic ions, and more strongly as the size of the quaternary ammonium ion increases. The volume of the exchange ion, as will be seen later, constitutes an appreciable fraction of the total volume of the pore solution. Accurate volume and density measurements[18, 19] have shown that with most monovalent ionic species the matrix volume plus the volume of the imbibed solvent and that of the exchange ions very nearly adds up to the total, measured volume of the system. The molality or concentration in terms of imbibed solvent (*Table 2*) usually falls with increasing counter-ion size, because more water is sorbed as its concentration is reduced, due to the size of the exchange ion itself. A comparison with one of the commercial cation-exchange resins (Dowex 50-X8) shows it to be reasonably analogous with the ACI cation-exchange membranes.

The properties of ACI anion-exchange membranes, shown in *Table 3*, show a rather different correlation with the properties of exchange anions, as compared with the cation-exchange materials. Their pore volumes are substantially less, with that for the chloride state being approximately half that for the potassium state. Further, the pore volume is relatively independent of the size of the exchange anion; in fact, it is often lower with

Table 3. Properties of ACI anion-exchange membranes (Capy.—1·35 meq/g)

Ion	*Vol.* (ml)	L (μ)	φ_p	$\bar{c}$	$\bar{m}$
Cl	0·94	214	0·23	1·1	5·0
I	0·93	218	0·18	1·1	6·2
SCN	0·92	211	0·18	1·2	6·4
NO_3	0·94	212	0·20	1·1	5·6
*p*TS	1·00	220	0·17	1·1	6·5
IO_3	0·99	216	0·32	1·1	4·3

*p*TS, *p*-toluenesulphonate.

the large organic exchange anions, similar to what is observed with the analogous anion-exchange resin systems[20]. The pore volume only increases substantially with the iodate anion. Anionic pore volumes are approximately half those for the cation-exchange membranes; the molalities for both types of membranes are approximately the same, because of the lowered water content of the anion-permeable membranes.

DIFFUSION OF NEUTRAL SPECIES

The rate of transport across these "tight" ion-exchange membranes is controlled, in large measure, by the frictional or hydrodynamic resistance which obtains. We prefer to calculate this frictional resistance in terms of a pore model. The classical work of Collander[21] first showed that pore diameters can be estimated from the relative rates of permeation of solutes of different molecular weight (and presumably size) across a porous membrane. Collander pointed out that the sorption or adsorption of solutes by the membrane could lead to erroneous conclusions, and it was therefore important to avoid solutes where such phenomena were pronounced. In dealing with "tight" membranes, we unfortunately have relatively few permeating, non-ionic solutes available and very few of these may be regarded as reasonably spherical.

The diffusive flux (J_i) of a neutral molecule across a unit area of a membrane system is given by

$$J_i = -\bar{D}_i\,(\bar{c}_i'' - \bar{c}_i')/L,$$

where $\bar{D}_i$ is the diffusion coefficient of the neutral species in the membrane, L is the measured thickness of the membrane, and the driving force is computed in terms of differences in the bulk (molar) concentration ($\bar{c}_i$) of the species on the left ($'$) and right ($''$) sides of the membrane.

If one assumes a model wherein n tortuous paths, each of uniform radius R and length $L_p = L/h$, connect the opposite sides of a unit area of membrane, then the pore volume φ_p and the corresponding pore area a_p are related by,

$$\varphi_p = n\pi R^2 L_p/L = a_p L_p/L = a_p/h$$

where h is the "tortuosity" factor. The flux can now also be described in terms of the solution phase-diffusion coefficient D of the solute and its concentration c. If the distribution coefficient of the solute between equal pore (c_p) and solution volumes is $k = c_p/c$, then, if no membrane resistance terms are present,

$$J = -Dk\,(c'' - c')\quad \alpha_p\, h/L = -Dk\,(c'' - c')\, h^2\varphi_p/L.$$

Here we assume that in a porous membrane it is necessary for the diffusing species to travel a path length which is tortuous on a macroscopic level and which is greater than that of the measured thickness of the membrane. The tortuosity factor has been discussed at length by several authors, particularly Carman[22]. For systems where the pore length is considerably larger than the diameter of the diffusing species, tortuosity is often taken as $\frac{1}{3}$.

The latter equation must also include two resistance factors, the so-called Ferry–Faxen terms. The former is a purely geometrical one, describing the probability that when the centre of the solute molecule of radius r strikes part of the pore area, it will pass into the pore and not be deflected. The Ferry[23] term is $F' = (1 - r/R)^2$ for a crylindrical pore and $(1 - r/R)$ for a parallel plate or rectangular pore.

The second resistance term is that due to Faxen[24], and describes the hydrodynamic resistance to the flow of a spherical particle in the centre of a pore filled with a homogeneous liquid, assuming the validity of Stokes' hydrodynamics. The employment of these latter terms has been discussed by many authors, particularly by Pappenheimer[25] and by Renken[26], and the flux equation becomes,

$$J = -Dk\,F'Fh^2\varphi_p\,(c'' - c')/L.$$

In the employment of the Ferry–Faxen equations, most authors have assumed cylindrical pores. The equations which obtain here are,

$$F'F = (1 - r/R)^2\,[1 - 2{\cdot}014\,(r/R) + 2{\cdot}09\,(r/R)^3 - 0{\cdot}95\,(r/R)^5].$$

However, with pore diameters which are of molecular dimensions it is obvious that nature has not provided us with cylindrical pores, not at least in the world of organic macromolecules. Instead, these pores must be highly irregular as indicated in *Figure 3*. It is only with pores having a diameter several times the molecular diameters that one could employ the equations for cylindrical pores with reasonable confidence. Accordingly, since the diffusing species usually is passing between two points of contact, we have preferred to employ the parallel plate or rectangular pore. Faxen has derived expressions which apply here[27],

$$F'F = (1 - r/R)\,[1 - 1{\cdot}004\,(r/R) + 0{\cdot}418\,(r/R)^3 - 0{\cdot}169\,(r/R)^5 - 0{\cdot}245\,(r/R)^7].$$

Because in Faxen's treatment the integration was performed starting at the centre, with insufficient terms in the expansion employed to describe

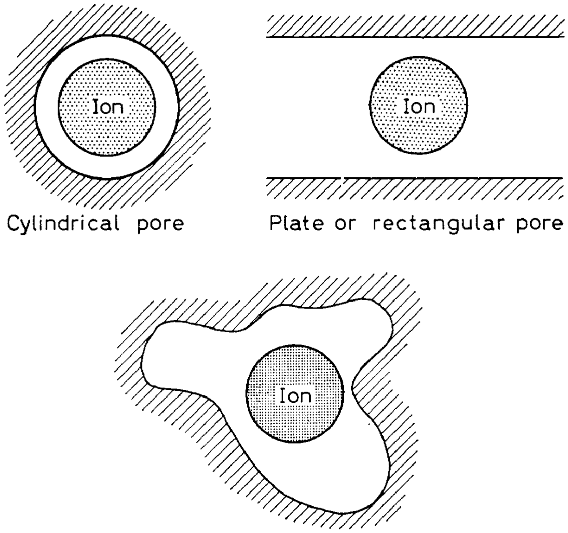

Figure 3

accurately the situation where the radius of the ion approaches that of the pore, we have arbitrarily corrected the last term of the function so that it goes to the proper limit at $r = a$. The difference in the two Ferry–Faxen equations is shown in *Figure 4*; the function is much more shallow in the case of the plate-like pore, and we have found that it fits the data very much better.

The diffusive flux of several low-molecular-weight, neutral species was measured across cation-exchange and anion-exchange membranes, taken from the measurements of D'Alessandro[8]. Here, Fick's law was obeyed, presumably because the concentration of diffusing species was low ($c = 0{\cdot}1$ M)

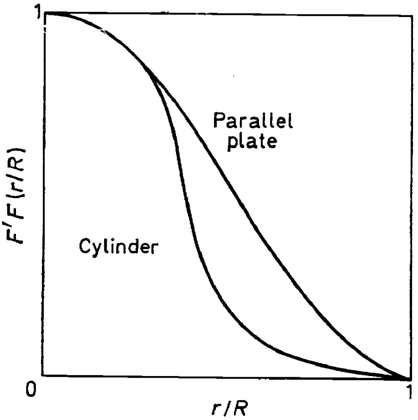

Figure 4

in all cases. *Table 4* summarizes some of these experimental results and also lists solute radii, as estimated by various authors[25, 26]. It shows too that urea and ethyleneglycol are salted-in or absorbed by these membranes, but glycerol is somewhat salted-out. We observe that while the diffusive flux decreases with increasing molecular weight, the relative diffusion coefficient $\bar{D}/D$ does not decrease regularly. There are probably two reasons for this. First, ethylene glycol is a reasonably symmetrical molecule but glycerol is not and probably diffuses in an oriented position, thus giving it an anomalously high diffusion coefficient. For example, in free solution the relative diffusion coefficient of these two species is 1·3, while in most ion-exchange membrane systems it is approximately 1·05, and this demonstrates the problem of evaluating pore diameters on the basis of the diffusion of non-symmetrical molecules. Some authors have employed hydrophilic polymers of different molecular weight for pore size determinations, with results that do not often have even qualitative significance.

Table 4. Diffusion of neutral molecules

Solute	*Ion*	$\bar{D} \times 10^7$ (cm²/sec)	$\bar{D}/D$	*R* (Å)	*R′* (Å)	$\bar{m}/m$†	*r* (Å)	$D \times 10^5$ (cm²/sec)
Urea	K	7·8	0·060	3·3	5·7	1·9	2·6	1·37
Glycol		4·3	0·043		5·5	1·4	2·8	1·00
Glycerol		4·1	(0·052)	3·8	6·4	0·8	3·1	0·78
Glucose		3·3	0·047	4·3	7·1	—	3·6	0·69
Urea	Cl	3·8	0·030	3·1	4·7	2·2		
Glycol		4·1	0·036		5·3	1·7		
Glycerol		3·9	(0·041)	3·5	6·1	0·7		
Glucose		0·84	0·010	3·7	5·2	—		

† $\bar{m}/m \approx c_p/c$.

We have made the assumption of uniform pores; this is obviously not correct, but difficult to subject to experimental test. If one assumes a normal, Gaussian distribution of pore radii and then applies the Ferry–Faxon equation, one finds the experimental predictions substantially unchanged, i.e., the Ferry–Faxon equations yield an average pore diameter, with little or no information on pore diameter spectra.

The relative diffusion coefficient is related to the parameters of these systems by,

$$\bar{D}_i/D_i = h^2 F_i' F_i \, (r_i/R)$$

an expression with two unknowns, the tortuosity factor h and the pore radius R. However, by using a second diffusing solute of a different radius r_j, and making the reasonable assumption that h is unchanged, we can obtain unique values of the effective pore radius R and also the tortuosity factor. A simple procedure for carrying out this computation is to calculate $F'F\,(r_i/R)/F'F\,(r_j/R)$ for different values of R and the two known values of

r_i and r_j; when this ratio is equal to $(\bar{D}_i/D_i)/(\bar{D}_j/D_j)$, the value of R is read from the curve. Using urea and ethylene glycol as the two solutes, and then making the other computations based upon these comparisons, we obtain the data given in *Table 4*. Here we also obtain the unexpected result that the tortuosity factor is near unity for these systems; to this point we will return later.

The diffusion coefficients of neutral species across these membranes lead us to computed pore diameters of approximately 3·3 Å for the potassium form membrane and 3·1 Å for the chloride form. The diffusion of DHO in these membranes as measured by Leszko[8] also yielded similar information on pore sizes and tortuosity.

TRANSPORT OF IONS

Since the transport of counter-ions in ion-exchange membrane systems is necessarily different, in many important respects, from that of neutral species because of the high coulombic fields present in these systems, a discussion of these transport processes is best introduced by consideration of the polyelectrolyte nature of these membranes. It was pointed out some time ago by the author[28] that ion-exchange resins and membranes are best viewed as cross-linked polyelectrolytes, with no fundamental differences in the fundamental physical parameters which obtain in both systems. Examinations of the properties of the two systems from the same point of view has shown that their behaviour is quite analogous. For example, Leszko and Gregor[8] measured the mean activity coefficient of potassium chloride in mixtures of the potassium salt of polystyrene sulphonic acid (PSSK) with potassium chloride, employing an electromotive chain containing a cation-selective glass membrane and a silver–silver chloride reference electrode. Solutions varying in total molality from 0·001 to about 3 were studied in this manner, and it was found that Harned's rule was obeyed over the entire range of concentration. Harned's rule applies for almost all simple electrolytes, but 2-1 electrolytes do not obey the rule in many cases; this makes the conformity of the PSSK–potassium chloride system the more surprising.

In relatively concentrated polyelectrolyte solutions (1–3 M) and with low concentrations of potassium chloride, the mean activity coefficient of the latter species is approximately 0·45; this value should also obtain in calculating the concentration of diffusible electrolyte in comparable ion-exchange resin and membrane systems. Unfortunately, most of these systems contain voids[6] which produce an anomolously high content of diffusible electrolyte and therefore a low, calculated mean activity coefficient.

Leszko and Gregor[29, 8] also have reported the diffusion coefficients of counter-ions, co-ions and water in the PSSK–KCl system. *Table 5* summarizes these results, wherein the parameters for the polymer solution are those measured by direct experiment, divided by the solution volume fraction to yield the "effective" value, one which should be the basis for comparison with the free solution values. The presence of the fixed anionic sites has the effect of decreasing the mobility of counter-ions, with a much smaller effect upon the co-ions, as is observed with ion-exchange resin and membrane systems[30]. From the measurements of Leszko and Gregor[29] we

Table 5. Diffusion coefficients
(3M PSSK, 0·1M KCl, 25°C)

	Polymer solution × 10^5	*Free solution* × 10^5
D+	0·76	2·2
D−	1·1	2·2
D_{HDO}	1·94	2·45
φ†	0·78	1·00

† φ is the solution volume fraction.

find that the diffusion coefficient for water in the polymer solution is substantially less than for water in free solution, probably because of solvation of the highly-polar polyelectrolyte. Thus, in general we can apply the pore or "free solution" volume correction term to membrane, resin and dissolved polyelectrolyte systems, alike.

The selective uptake of one ionic species over another by an ion-exchange resin or membrane gives us a further insight into the system and the processes occurring therein. Selectivity in ion-exchange systems is determined by a number of factors. First, there is the straightforward coulombic interaction between the fixed-charge group and the mobile ion species. Selective uptake under these circumstances is determined by differences in the distance of closest approach of ions to the charged rod. This has been investigated theoretically by Miller and Gregor[10] following an earlier study by Kagawa and Gregor[31] based upon the charged rod model (Fuoss, Katchalsky and Alfrey). Here, one must employ (hydrated) ionic radii, so under these circumstances the interactions between ions and solvent come into play. *Figure 5* shows the model assumed by Miller and Gregor and their

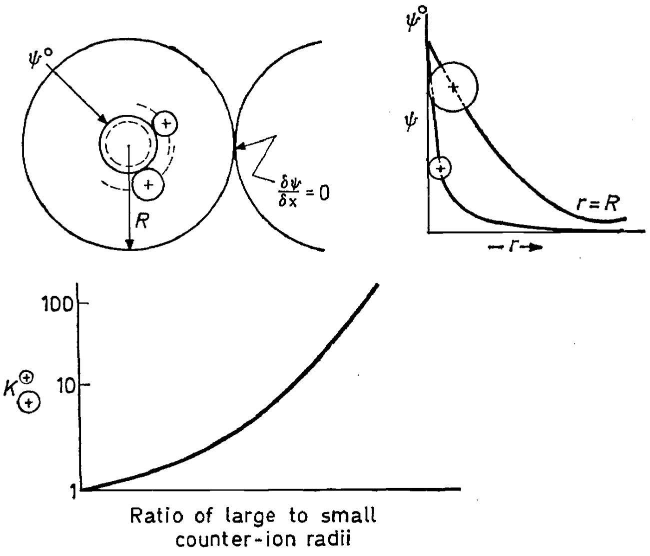

Figure 5

calculated results. This theory was compared with the data of Gregor and Bernstein[10, 32]; an excellent correspondence between theory and experiment was obtained for a number of polymethacrylic acid polymers and the exchange of potassium against a number of quaternary ammonium cations. This system was studied at complete neutralization to produce a highly polar polymer and accordingly, in minimum of adsorptive interactions. In these polymer systems, which were cross-linked by divinylbenzene (DVB), a substantial deviation from the theory was encountered at high degrees of cross-linking, undoubtedly due to adsorptive forces between the apolar cations and the aromatic ring. Later experiments by Gregor and Greff[8] on a copolymer of methacrylic acid and ethyleneglycoldimethacrylate do not demonstrate this adsorptive effect.

The role of adsorption in ion-exchange interactions has been recognized for some time. In general, ion-exchange polymers of low capacity (and low polarity) show a strong preference towards organic ions. The study by Bregman and Gregor[9] on the selective uptake of potassium against a number of quaternary ammonium cations with PSSA resins of different degrees of cross-linking (see *Figure 6*) showed that at low degrees of cross-linking (when pressure–volume effects are minimal), the organic cations are preferred, approximately in the order of their increasing molecular weight. Much greater adsorption is encountered with the aromatic benzyltrimethylammonium cation, as expected. Some recent studies have shown that the changes in enthalpy accompanying these reactions are small, consistent with our knowledge of hydrophobic bonding. These adsorptive effects are different in character from the coulombic effects, but a clear-cut distinction between site-binding and non-specific coulombic binding is not easy to obtain because in many systems they differ only in degree but not in kind, and are difficult to demonstrate by reasonably absolute and independent means. In general, we may say that when the selective uptake of an ion is well in excess of that predicted from considerations of size, one may consider ion-pair formation or site-binding. *Figure 7* shows the selective uptake of a

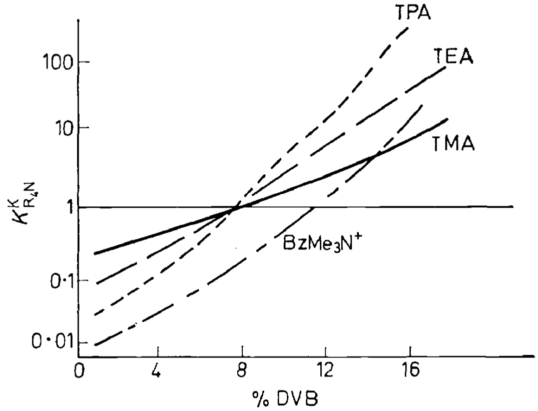

Figure 6

number of anions by the ACI anion-exchange membranes and a cross-linked aliphatic polyethyleneimine (PEI) resin, taken from the study of Konrad, Saber and Gregor[8]. Here it is seen that the order of selective uptake is SCN > *p*TS > I > Cl > IO_3 (the latter not shown) with the ACI membrane. This is the familiar Hofmeister or Lyotropic series. It is apparent that the polarizability of the halogens anions is an important factor here, as was also shown by Gregor, Belle and Marcus[20]. Adsorptive forces undoubtedly come to play in exchange with the aromatic *p*-toluenesulphonate anion. It is also evident that the selective uptake of adsorbable anions increases with the increasing chain potential. For a system of two anions of the same size differing only in polarizability, the theory of Miller and Gregor[10] predicts selectivity (through different degrees of closest approach) and also an increase in the selectivity of the more polarizable anion as the mole fraction of the less polarizable anion increases; this is also confirmed by the study of Konrad *et al.*[8].

Figure 7 also presents data on the selectivity of aliphatic anion-exchange polymers for similar pairs of ions, and here we see a marked decrease in

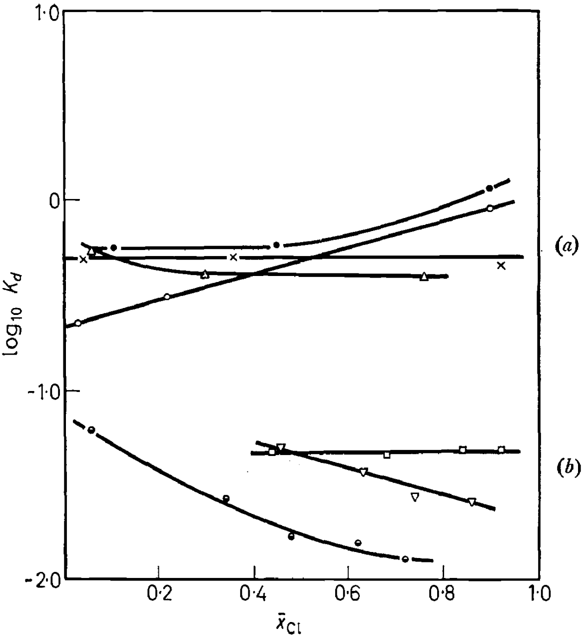

Figure 7. Selectivity coefficients measured against chloride for the following ions
(*a*) PEI-ECH resin — iodide (×); thiocyanate (○); perchlorate (△); *p*-toluenesulphonate (●)
(*b*) Asahi anion-exchange membrane — iodide (□); thiocyanate (◒), *p*-toluenesulphonate (▽)

preference. With iodide, its selectivity over chloride is about 50 with the benzyltrimethylammonium polymer, and only about 5-fold with the (analogous) diethylammonium group. This result is unexpected in its magnitude and suggests that a charge-transfer mechanism may be involved with the former. With the thiocyanate and *p*TS anions it is evident that hydrophobic bonding is the most significant causative factor in their selective uptake.

Self-diffusion coefficients in chloride–iodide from anion-exchange membranes (also of aromatic character) were measured by radio-tracer techniques by Andelman and Gregor[33] who found that the individual diffusion coefficients did not vary significantly over the entire range of composition varying from iodide to chloride forms, and that the self-diffusion coefficient of chloride was greater than that of iodide by a factor of 4·5. Employing the Nernst–Einstein theory which relates self-diffusion coefficients to limiting ionic conductivities (at infinite dilution) one calculates the same equivalent conductivity ratio for these ions. This composition-independent behaviour may be explicable on the basis of a chain mechanism, as postulated by Belgovskiy[8].

The measurement of the diffusion coefficient of an ion in a membrane system is not as simple and unequivocal as one would desire, because there is always resistance due to the solution boundary layer adjacent to the membrane face. One can make measurements on "sandwiches" of membranes with one pressed firmly to the other to minimize the solution resistance term or make appropriate computations. In general, the self-diffusion coefficient of counter-ions in "tight" membranes is relatively independent of concentration in solutions more dilute than 0·1 M, as was shown by Kawabe *et al.*[7].

The conductances of ACI cation-exchange and anion-exchange membranes are listed in *Table 6*. Here we find that the relative conductivity ratio $\bar{\lambda}/\lambda^0$ does not vary greatly for the univalent, inorganic ions but does fall off sharply as the molecular weights of the quaternary ammonium ions increase. The energies of activation for conduction are not very different from those in free solution (3·3–3·7 kcal/mole) with the exception of

Table 6. Conductance of ACI ion-exchange membranes

Ion	*RA* (ohm cm^2)	$\bar{\kappa} \times 10^3$ (ohm^{-1} cm^{-1})	$\bar{\lambda}$ (cm^2/ohm eq)	$\bar{\lambda}/\lambda^0$	E_a (kcal/mole)
H	0·3	60	30	0·085	—
Li	2·3	9·3	4·6	0·12	4·1
Na	1·5	16	8·0	0·16	4·6
K	0·9	24	12	0·16	3·8
A	0·9	24	12	0·16	—
TMA	4·3	5·6	3·5	0·078	—
TEA	13·2	1·7	1·2	0·036	3·4
TPA	49·5	0·41	0·30	0·013	4·7
TBA	469	0·047	0·032	0·0017	5·9
Cl	4·7	4·6	4·2	0·055	4·8
I	19·7	1·1	0·98	0·013	—
SCN	26·8	0·79	0·69	0·0096	6·8
NO_3	6·8	3·1	2·8	0·040	—
*p*TS	717	0·031	0·031	0·00090	—
IO_3	11·2	1·9	1·9	0·046	5·5

RA—areal resistance, equal to $L/\bar{\kappa}$.
$\bar{\kappa}$ —specific conductivity.
$\bar{\lambda}$ —equivalent conductance.

those for the larger quaternary ammonium cations. In the case of the anion-exchange membranes, the equivalent conductance falls with increasing atomic weight of the halide anions, but several anomalies appear and will be discussed later. A comparison of the relative equivalent conductivities of cation and anion-exchange membranes show that the former have much larger relative equivalent conductivity, with that for potassium being approximately three times that for chloride. The energy of activation for conductivity in the anion-exchange membranes is appreciably higher than in free solution for all anions measured, particularly with the strongly adsorbed thiocyanate ion. This suggests that a different energetic process is involved in transport in anion-exchange membranes.

With the cation-permeable membranes, the Ferry–Faxen equation can be employed to estimate effective pore radii from the conductivity of ions of different size. As discussed by Kawabe[7], there are two ways of calculating pore radii. One may make the assumption that the pore volume of the system is directly proportional to the square of the pore radius (because swelling is anisotropic), and calculate individual pore radii which pertain to those for the smaller ion, given as *R′* values in *Table 7*. One can also compare ions of different size and calculate mean pore radii (shown *R″* in *Table 7*). The two methods naturally yield comparable results, with radii from the latter method favouring those for the larger ion.

Table 7. Parameters of ACI cation-exchange membranes

	R′ (Å)	*R″* (Å)	*R‴* (Å)	*r of ion* (Å)
K	3·6		3·5	2·1
Me_4N	4·4		4·1	3·5
		4·9		
Et_4N	5·1		4·6	4·0
		5·1		
Pr_4N	4·9		4·8	4·5
		5·2		
Bu_4N	5·1		5·0	4·94

λ + *EO.*

ELECTRO-OSMOTIC WATER TRANSPORT

The electro-osmotic (EO) permeability of membranes was measured by D'Alessandro, Bagner and Breslau[8]; *Table 8* summarizes some of these results. It is usual to express electro-osmotic transport in terms of moles of water transported per Faraday of ions, but here it is more correct to report electro-osmotic volume transport because such a large fraction of the solution volume transported consists of the exchange ion itself. *Table 8* shows that in the case of cations, the electro-osmotic volume transport increases with (hydrated) ionic size. Turning first to the non-hydrated quaternary ammonium ions, one finds that the amount of water transported per ion begins to level off as the size of the cation increases, and with the TPA and TBA ions equals, within experimental error, the water content of the membrane.

Table 8. Electro-osmosis

Ion	λ/λ°	φ_p	*EO* (ml/*F*)	*EO'* (H_2O/*ion*)	$(18\,\bar{m})^{-1}$ (H_2O/*ion*)	V_{ion} (ml)
H			45			
Li	0·12	0·45	163			
Na	0·16	0·41	116	6		
K	0·16	0·41	105	4	11	33
TMA	0·078	0·58	267	8·6	15	116
TEA	0·036	0·63	368	10	15	172
TPA	0·013	0·64	463	12	13	255
TBA	0·0017	0·68	632	17	14	326
F	—	—	170	9		—
Cl	0·055	0·23	90	3		30
Br	—	—	90	3		30
I	0·013	0·18	95	3		30
IO_3	0·046	0·22	159	2		140
ClO_4	—	—	105	—		—
*p*TS	0·001	—	224	—		—

ml/*F* —ml of water transported/Faraday of current.
EO' —moles of water per ion.
$(18\,\bar{m})^{-1}$—moles of water present/counter-ion.
V_{ion} —molar volume of counter-ion.

In other words, these ions sweep *all* of the water contained in the membrane along with it under electro-osmotic flow, equalling the "plug-flow" of engineers. This result indeed suggests that these ions very nearly approximate the size of the pores through which they move, and also suggests that there is little solvent contained in pores not penetrated by the exchange ions. It suggests, then, a remarkably homoporous system, but this conclusion may readily be erroneous. The stress placed upon the membranes by the electro-osmosis of the TBA ion was considerable; several split during the experiment and all swelled, so that the apparent discrepancy in *Table 8* wherein more water was transported than present is the result of increased swelling (and water content) during this procedure.

The electro-osmotic transport shown by the lithium and sodium forms of the membrane are not nearly as high as one would predict from their apparent hydrated diameters as estimated from their conductivity in solution[11]. For example, one should compare Li with the mean of the TMA–TEA ions on the basis of solution sizes, but it has only half the predicted EO value. The obvious conclusion is that it has lost half its water of hydration, and that the same process has occurred with Na, to a lesser extent. This conclusion reinforces the work of Kawabe[7] who calculated pore radii for the alkali metal cations by extrapolation (using φ_p data) from *R* values for the TMA ion, and came to the conclusion that there was considerable dehydration of the Li ion, less for Na and little for the K or A ions, as they move from the solution to the membrane phase. The constancy of λ/λ^0 values with these ions is then the result of a decrease in size and a lowered *F'F* drag factor.

It is interesting to note that while in exchange and other equilibrium phenomena (such as hydration[34, 35]) the hydrogen ion has apparently the same volume as does the lithium ion, presumably because its organization of water structure gives it the same effective size under these circumstances; under electro-osmosis the different transport mechanism for the hydrogen ion results in a low EO value.

Breslau[8] also measured the temperature coefficient for EO with Li and K-form membranes, and obtained the most interesting result, that the energy of activation almost exactly corresponded with that for the viscosity change of water. In other words, no significant change in hydrated size took place, unless different effects compensated for one another. Under equilibrium conditions hydration numbers are larger and more influenced by temperature changes, as was observed by Gregor and Bregman[9].

Electro-osmotic fluxes across anion-exchange membranes demonstrate a rather different behaviour than is observed with cation-exchange membranes. First, EO for the halide anions (except fluoride) are nearly the same, while that for the iodate ion is approximately doubled. A comparison with the behaviour of cation-exchange membranes shows the unexpected result that the potassium and chloride ions demonstrate approximately the same electro-osmotic transport, but their relative equivalent conductivities differ by a factor of 3. We have seen earlier that their pore diameters, as measured by the diffusion of neutral species, are but slightly different, from the magnitude which one would expect from their relative electro-osmotic water transports, but quite different from what one would anticipate from their relative equivalent conductivities. In other words, a large difference in pore diameters would be required to account for the different conductivities. On the other hand, the comparison between iodate and the TMA ion is "normal" in that their relative equivalent conductances are in approximately the same ratio as their electro-osmotic water transport terms. We must conclude that the halide ions show yet another effect.

The fluoride ion shows an EO which is very much higher than for the other halides, undoubtedly the result of changes in water structure. This is classified as a "structure breaking" ion, and its EO transport reflects this.

DISCUSSION

One can attempt to correlate these data on the basis of model studies reported in the literature. In particular, Schmid (see reference 30 for an excellent discussion of his papers) has correlated self-diffusion coefficients, equivalent ionic conductivities and hydraulic permeabilities for fine-pore membrane systems—ones where the Debye radius is large compared with the pore radius. This is obviously the case for the tight membranes with which we are concerned here. Schmid derived his equations by considering the relative velocities of the ions, the solvent and the membrane; essentially, his treatment is based upon the choice of a stationary frame of reference, in this case the membrane. Under these circumstances, the moving ion carries along with it electro-osmotic water, which in turn contributes to the conductivity of other ions in the system. The total conductivity $\bar{\kappa}_t$ is then equal to the intrinsic conductivity (velocity of water zero) plus the contribution to the specific conductivity of the electro-osmotic flow, $\bar{\kappa}_{EO}$. The intrinsic conductivity is assumed to be described by the Nernst–Einstein equation, for here we neglect the time of relaxation effect because at the usual frequency of measurement the ion traverses several fixed-charge sites in the membrane. Schmid defines a specific flow resistance term, and the ratio of the electro-osmotic specific conductivity to the "true" conductivity can be calculated in terms of the electro-osmotic flux or the ratio of the electro-osmotic and hydraulic permeability fluxes, $\bar{\kappa}_{EO}/\bar{\kappa}_t = 1 - \alpha = 1 - F\bar{c}\,(EO)\,\varphi_p$. One can determine α directly by self-diffusion coefficient measurements and then employ the Nernst–Einstein equation for comparison with the conductivity value. It should be emphasized that the theory of Schmid does not allow for specific interaction; it treats all ions as moving at the same velocity with the same electro-osmotic flow.

A test of the Schmid relationships, both from electro-osmotic fluxes and also from a combination of electro-osmotic and hydraulic permeability fluxes has been made[36]. For the potassium ion the discrepancy between theory and experiment is substantial (0·48 cf. 0·61) but not impossible. However, the correction term α falls sharply as the size of the ions increases, until for the TPA ion we find that 0·99 of the specific conductivity is that due to electro-osmosis, a most unlikely event. Further, the equation gives negative values of the coefficient with the TBA ion. The model upon which the Schmid theory is based obviously cannot be employed with these very tight membranes, particularly where the diameter of the counter-ion is an appreciable fraction of the total pore diameter.

Table 9. Comparative values

	*Cation-permeable** $\bar{c}_K = 2{\cdot}0$, $\bar{m}_K = 5{\cdot}1$			*Anion-permeable*† $\bar{c}_{Cl} = 1{\cdot}1$, $\bar{m}_{Cl} = 5{\cdot}0$		
	K	Li	TMA	Cl	I	IO_3
φ_p	0·41	0·45	0·58	0·23	0·21	0·35
$\bar{\lambda}/\lambda^\circ$	0·16	0·12	0·078	0·055	0·013	0·046
EO	105	259	267	90	90	169
r	2·1	2·5	3·5	2·1	2·1	3·5
$R_{\bar{\lambda}}$	3·3	3·6	4·5	3·0	3·0	4·2
$\%_{\text{Dissoc.}}$	100	100	100	46	10	100

* $\bar{c}_K = 2{\cdot}0$; $\bar{m}_K = 5{\cdot}1$.
† $\bar{c}_{Cl} = 1{\cdot}1$; $\bar{m}_{Cl} = 5{\cdot}0$.
$R_{\bar{\lambda}}$– for TEA is 4·7 Å; TPA is 5·0 Å; TBA is 5·1 Å.

Table 9 summarizes the salient experimental results obtained herein. The potassium, TMA and iodate ions show "normal" behaviour. However, with the halide anions we observe reasonably normal electro-osmotic (and hydraulic permeability[36]) behaviour, but an abnormally-low electrical conductivity. The most reasonable conclusion we can draw is that the halide (and the SCN, *p*TS and ClO_4 anions) are bound at fixed-charge sites and cannot contribute to the conductivity, although under the influence of an electric current they are able to move electro-osmotically and exhibit "normal" behaviour. Accordingly, taking reasonable values for the radii of the halide anions, from their R values we compute that the membrane in the chloride form is 46 per cent dissociated and in iodide form is 10 per cent dissociated.

Should site-binding occur, this will be evident by the selectivity coefficient measurement, as indeed it is. However, as was shown by Miller and Gregor[10], coulombic binding and site-binding show the same general characteristics and are difficult to distinguish one from another. From selectivity coefficient data, the chloride ion is preferred approximately 8 times as strongly as the iodate anion, while from conductivity data the apparent ratio is 2:1. We may then conclude that the difference is due to ordinary coulombic binding, or that *both* occur here. By the same token, the relative binding of iodide to chloride from conductivity data is approximately 5:1, while from selectivity coefficient data the ratio is 25:1. Again, the difference is assumed to be that due to coulombic binding. One may raise the question as to whether there is not a retardation of ionic motion under the influence of an electric field or a concentration gradient as the result of ordinary coulombic binding. One could explain this on the basis that the ion was not travelling through the *centre* of the pore but rather along its periphery, with a correspondingly greater "drag". Unfortunately, the hydrodynamic equations for this case are rather involved and no solution has been published. Further, the simplifications involved are rather severe and we have already made too many approximations.

CORRELATION WITH MEMBRANE TECHNOLOGY

On the basis of our extensive industrial experience in the employment of ion-exchange membranes in electrodialysis, the results which we have just described lead us to certain conclusions. First, consider the all-important problem of the "fouling" of membranes. When natural waters containing high-molecular-weight, adsorbable anions such as the humic acids or ABS (alkylbenzenesulphonate) are electrodialysed, one observes an increasing ohmic resistance of the anion-exchange membrane, such that it ultimately must be replaced. Reversal of the current does not help. This problem is particularly exacerbated when solutions of biological extracts such as fermentation liquors or sugar solutions are treated by electrodialysis; the cation-exchange membranes are quite undamaged even after several weeks or months of use, while the anion-exchange membranes fail rapidly under these circumstances, often in a matter of hours or even minutes. Some of the commercially available membranes show some relatively minor advantage over others with respect to these fouling phenomena, but no membrane is reasonably free of fouling.

Since fouling is the result of site-binding, we can approach its alleviation either by employing solutions not containing strongly polarizable anions, which is obviously impossible, or by making anion-exchange membranes of a less adsorbent character. This obviously calls for elimination of the aromatic ring system. Membranes prepared from polyethyleneimine should show lowered fouling, unless other nonpolar moieties are present in excess.

There is yet another good reason why one should avoid the aromatic ring. The benzyltrimethylammonium compound is relatively unstable; its thermal decomposition occurs rapidly at relatively low temperatures, particularly in the presence of oxygen. Some systematic investigations of the relative stability of different commercially available membranes under different conditions of temperature, acidity and basicity have been carried out by Gregor[8]. Wichterle *et al.*[37] have shown by model studies that only the symmetrical *n*-alkyl ammonium compounds would show the desired stability.

In our search for a stable quaternary ammonium polymer we may look to the work of Okomoto[38] who synthesized 2,6-isopropylmethylpyridinium iodide and found that this quaternary ammonium compound could be distilled at 250°C under reduced pressure without decomposition. Whether this particular compound can be made in the form of a polymer remains to be seen, but pyridinium compounds are highly aromatic in nature and therefore the fouling problem would still persist. The recent report by Gianinni[39] who has prepared and polymerized a variety of aliphatic olefinic tertiary and quaternary ammonium compounds suggests that it may be possible to have a quaternary ammonium polybase of high stability and non-aromatic character.

The availability of a thermally stable anion-exchange membrane would allow electrodialysis to be carried out at elevated temperatures with lowered power costs and at higher allowable current densities; and would thus give further impetus to its application to this particular technology.

It is possible also that another deleterious effect in electrodialysis may be reduced by the availability of non-adsorbing anion-exchange membranes. The Bethe–Toropoff effect is very much in evidence with ion-exchange membranes, as evidenced by a water-splitting phenomenon with hydrogen ions passing in one direction and hydroxide ions in the other. This effect has been studied by several investigators[40]; and Gregor and Miller[41] have proposed that it is a result of the unusual boundary conditions which obtain at the membrane surface, where the electric field acts to retard the recombination of hydrogen and hydroxide ions and increases markedly, in effect, the degree of dissociation of water. Different membrane types, particularly the anion-permeable membranes, show different degrees of polarization, suggesting that the water structure at the surface of these membranes may be different. Almost all anion-exchange membranes show considerably greater water-splitting than their cation-permeable counterparts, and one can only speculate that the availability of an aliphatic technology of anion-exchange membrane may alter this preferred water-splitting and thus add another dimension to the technology of electrodialysis.

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