

Membrane Potential Differences with the Polyelectrolyte Complex— Poly(Vinylbenzyltrimethylammonium)—Poly(Styrenesulfonate)

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Concentration potential differences were measured for KCl, CaCl₂, and NaBr across films cast from stoichiometric and nonstoichiometric mixtures of poly(vinylbenzyltrimethylammonium chloride) and poly(sodiumstyrene sulfonate) in solution. With KCl, the nonstoichiometric films behave rather closely as ion-exchange membranes with a fixed charge of 3*N* for both the anion and cation exchangers, whereas the ostensibly neutral membrane behaved as a weak (*ca.* 0.06*N*) anion exchanger with both KCl and CaCl₂. Possible reasons for the latter result are slight deviations from stoichiometry in the reaction mixture or burial of some of the less bulky sulfonate groups (with associated microions) in the gelation step.

The membrane potential differences of stoichiometric film with NaBr indicated considerable site-binding and/or decrease of the mobility of the Br⁻ ion.

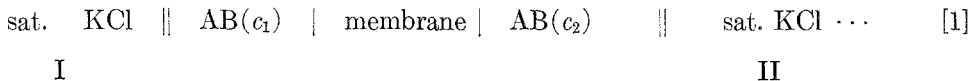
INTRODUCTION

Michaels and Miekka (1, 2) found that membranes consisting of complexes of a polyanion, poly(styrenesulfonate), and a polycation, poly(vinylbenzyltrimethylammonium), could be formed by mixing, in stoichiometric ratio, solutions of the individual polyelectrolytes (as the Na⁺ and Cl⁻ salts, respectively) in a ternary solvent consisting of 60% (by weight) water, 20% acetone, and 20% NaBr, casting thin films from this solution, and allowing the acetone to evaporate so that the complex, called *polysalt*, would precipitate. By the use of an excess of one of the polyelectrolytes, non-neutral polysalt could be prepared. Washing the films thoroughly with water after the casting procedure removed essentially all microions in excess of the Na⁺ or halide ions necessary to preserve electroneutrality within the film.

Subsequent investigations on polysalt, its swelling, ion sorption, and its electrical and mechanical behavior (Michaels, Mir, and Schneider (3), Michaels, Falkenstein,

and Schneider (4), Kwon (5), Gray (6)) led to models for polysalt, the preferred one of which considered polysalt as a randomly interwoven three-dimensional network of the backbones of the individual polyelectrolyte molecules, in which the ionic groups kept the network together either by the formation of ion pairs ("ionic cross-link model") or by their general coulombic interaction ("diffuse interaction model"). Polysalt membranes were also found to have interesting desalination properties (Kwon (5), Michaels *et al.* (7)). Since the desalination might be due to the ionic properties of the membrane, it was obviously of interest to study membrane concentration potential differences with polysalt.

The membrane concentration potential difference is defined as the electric potential difference between two identical electrodes connected via saturated KCl salt bridges to two solutions of the same salt, but of different concentration, separated by a membrane. The essential part of a concentration cell for the salt AB may therefore be represented as:



The sign convention used throughout this work is that the potential difference between the two KCl solutions is positive if the right-hand solution is positive with respect to the left-hand one.

There is a great deal of literature on membrane potential differences in general and on concentration potential differences in particular. We mention here only the fundamental work by Scatchard (8, 9) and some articles of a review nature (10-13).

The potential difference between the two saturated KCl solutions I and II is given by reference 14:

$$\phi^{\text{II}} - \phi^{\text{I}} = -\frac{1}{F} \int_{\text{I}}^{\text{II}} \sum_i \left(\frac{t_i}{z_i} \right) d\mu_i, \quad [2]$$

in which F is the Faraday and t_i , z_i , and μ_i are, respectively, the transference number, valence (with sign included), and chemical potential of the species i and the summation has to be taken over all species in solution. If μ_i refers to an uncharged molecule, t_i/z_i has to be replaced by the number of moles transported in the direction of the positive current per Faraday.

Applying Eq. [2] to the case of a single electrolyte dissolved in water, neglecting the influence of solvent transport and the difference in the two l.j. potential differences at the KCl bridges, we can simply integrate Eq. [2] to give

$$\phi^{\text{II}} - \phi^{\text{I}} = -\frac{RT}{z_+ F} \left\{ \ln \frac{a_{\pm 2}}{a_{\pm 1}} - \frac{\bar{t}_-}{z_-} \cdot (z_- + z_+) \ln \frac{a_{\pm 2}}{a_{\pm 1}} \right\}, \quad [3]$$

where the a_{\pm} 's are single ion activities; the a_{\pm} 's are mean electrolyte activities; z_+ and z_- are the absolute values of the valence of the ions; and \bar{t}_- is the transference number of the anion in the membrane averaged over the range of activities from $a_{\pm 2}$ to $a_{\pm 1}$.

The membrane potential thus gives information on the transference numbers in the membrane. These transference numbers can be written as:

$$t_{\pm} = \frac{z_{\pm} x_{\pm} \lambda_{\pm}}{z_+ x_+ \lambda_+ + z_- x_- \lambda_-}, \quad [4]$$

where the x 's are the molar concentrations of ions *in* the membrane and the λ 's are the equivalent conductances *in* the membrane.

It is often assumed that the ratio of equivalent conductances in the membrane is the same as that in free solution, so that the transference numbers reflect changes in concentration in the first place, but one should keep in mind that an unequal influence of the membrane on the two conductances would also produce "abnormal" transference numbers.

A simple way to estimate the values of the ion concentrations in an ion-exchange membrane is given in the theory of Meyer-Sievers-Teorell (15, 16) and is based upon considering the equilibria between membrane and salt solutions as ideal Donnan equilibria.

If we restrict the treatment to symmetrical electrolytes and neglect activity coefficients, the distribution of ions has to obey the two equations

$$x_+ x_- = c^2 \quad [5]$$

and

$$x_+ + A = x_-, \quad [6]$$

where c is the concentration in the solution in equilibrium with a membrane containing the concentrations x_+ and x_- of mobile z valent ions and a concentration of zA fixed elementary charges. Here A is positive for an anion-exchange membrane and negative for a cation-exchange one. Equations [5] and [6] can be solved for x_+ and x_- giving

$$x_{\pm} = \pm \frac{A}{2} + \sqrt{c^2 + A^2/4} \quad [7]$$

with which the transference numbers can be calculated from Eq. [4], assuming that λ_+ and λ_- have their normal bulk solution values. If the fixed charge is much larger than the equilibrium concentration c , ($|A| \gg c$), one of the transference numbers

is zero, the other equal to one, and the membrane potential differences equal to 59 mv (at 25°C) per decade concentration difference. If the fixed charge is low ($|A| \ll c$), the transference number is equal to that in free solution and the membrane potential difference is equal to the free diffusion potential difference. The transition between these extreme cases occurs around the concentrations where A and c are of the same order of magnitude. Consequently, a membrane potential difference may be used to find the amount of fixed charge in the membrane.

It should be kept in mind, though, that this is a highly idealized treatment neglecting activity effects, the nonideality of Donnan distributions, and the possible influence of the membrane on ion mobilities.

EXPERIMENTAL

Apparatus. The apparatus used for this work was fabricated in accordance with reference (17). A closed insulated cell block was used to hold the membrane in place, with the salt solutions on either side. Such a cell block requires saturated KCl salt bridges to connect the calomel electrodes to the solutions in the cell compartment. The salt bridges were prepared approximately according to the Findlay formula (18). Four grams of KCl and 0.3 gram of agar-agar were used for each 10 grams of triple distilled water. These materials were mixed in the above proportions in a beaker and heated in a steam bath until visible salt particles appeared in the gel.

The electrodes used were saturated calomel electrodes, either sleeve-type or fiber tip, both made by Beckmann Instruments. The instruments used for the measurement of the potential difference were the Model 610B Electrometer by Keithley Instruments and the Model MR Sargent Recorder. The latter instrument was used to follow and to record any transients obtained during the measurements. The entire system, except for the recorder, was insulated inside a large Faraday cage to eliminate any a.c. noise pickup from the surroundings. This noise had to be eliminated because the measurements were very sensitive owing to a very

high resistance inherent in the polysalt membrane.

Membranes. The major portion of the research was done using the neutral polysalt complex membrane. These membrane samples were prepared as reported in reference (7). Some samples of 100% excess VBTACl (polycation chloride) and of 100% excess NaSS (sodium-polyanion) membranes were also prepared for the measurements using nonneutral polysalt films. All membrane samples were equilibrated in the required solution for at least 48 hours prior to use.

Procedure. The following is the detailed procedure used for the measurements of the membrane potential differences. The first task was to measure the asymmetry potential difference. The asymmetry potential difference allows for any difference in potential between the two calomel electrodes across the KCl salt bridges and any difference in junction potential difference between the two gel phases when in contact with the same electrolyte solution. The measurement of the asymmetry potential difference was carried out by filling the cell block with one of the solutions being used, without inserting the membrane. Then the saturated KCl salt bridges were inserted into the cell block. The salt bridges were held firmly in place by small rubber o-rings, which also prevented leakage of the solution from the cell compartments. With the use of this system, the asymmetry potential difference could easily be measured. It never amounted to more than 0.3 mv.

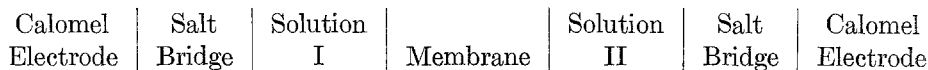
Once the asymmetry potential difference had been measured, the next step was to measure the required membrane potential difference. With the salt bridges left in place, the solution inside the cell block was allowed to drain away and the cell block was taken apart. Rubber tubes were then connected so that the solutions would flow from 2-liter flasks into the proper cell compartments. The two compartments were flushed with the correct solutions and the cell block halves thoroughly dried. Then the membrane sample was inserted in place and the cell block carefully reassembled. By opening the small control valves, the cell compartments were next filled with their respective solutions, ensuring that no air was trapped in the

compartments. The flow of the solutions was turned on until a steady stream came out of the small effluent tubing. The effluent was collected in 400-ml beakers, which were continually replaced when they became full.

All the 2-liter flasks containing electrolytic solutions were placed in a large water bath, and the solution temperature was brought up to $25^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. When a particular

found that the solution temperature did not vary by more than 0.5°C from the time the flask was removed from the water bath to the time the flask was empty. In general, this method of temperature control worked very satisfactorily.

By means of the procedure described above, potential differences were measured across the following cell:



solution was required for a measurement, it was removed from the water bath and placed in the system. This was done to avoid electrical leaks to the water bath. Although the reservoir-flask was now in the open air, it was

This reading was corrected for the asymmetry potential difference previously measured. The resultant value was the required membrane potential difference.

Results. The concentration potential differences of KCl, CaCl_2 , and NaBr with neutral and nonneutral polysalt membranes appear in Table I and Figs. 1 to 7.

TABLE I

CONCENTRATION POTENTIAL DIFFERENCES OF KCl ACROSS NEUTRAL POLYSALT MEMBRANES*

System	Conc. potential difference with 95% conf. limit (mv)	t_-	t_+
1.0N KCl/0.5N KCl	-1.8 ± 0.2	0.56	0.44
1.0N KCl/0.2N KCl	-5.1 ± 1.0	0.57	0.43
1.0N KCl/0.1N KCl	-9.7 ± 0.7	0.59	0.41
1.0N KCl/0.01N KCl	-20.4 ± 2.9	0.60	0.40
1.1N KCl/0.001N KCl	-24.3 ± 5.7	0.57	0.43
0.1N KCl/0.05N KCl	-4.6 ± 0.2	0.64	0.36
0.1N KCl/0.02N KCl	-11.8 ± 1.0	0.65	0.35
0.1N KCl/0.01N KCl	-20.4 ± 2.1	0.69	0.31
0.1N KCl/0.001N KCl	-44.9 ± 7.2	0.70	0.30
0.01N KCl/0.005N KCl	-7.6 ± 2.4	0.72	0.28
0.01N KCl/0.002N KCl	-21.0 ± 5.7	0.76	0.24
0.01N KCl/0.001N KCl	-39.1 ± 9.1	0.84	0.16

* The data of MacInnes (19) was used to estimate mean KCl activities, f_{KCl} , from which single ion activities, f_{K^+} , were calculated from the relation $f_{\text{K}^+} \cdot f_{\text{Cl}^-} = f_{\text{KCl}}^2 = f_{\text{KCl}}$.

Conc. →	1.0 0.1 0.01 0.001	$\Sigma = -69.2$ mv
Pot. diff. →	$\underbrace{-9.7}$ $\underbrace{-20.4}$ $\underbrace{-39.1}$	direct = -24.3 mv
or		
Conc. →	0.1 0.01 0.001	$\Sigma = -59.5$ mv
Pot. diff. →	$\underbrace{-20.4}$ $\underbrace{-39.1}$	direct = -44.9 mv

DISCUSSION

KCl Concentration Potential Differences across Neutral Polysalt. The initial series of experiments was concerned with the measurement of concentration potential differences of KCl systems across several samples of neutral polysalt membrane. About twenty different samples were used in this section of the research. The large number of samples allowed an examination of the reproducibility of the measurements. The results of the KCl measurements are listed in Table I. Also shown in Table I are the 95% confidence limits for each point, and it can be seen that, in general, the confidence limits are quite satisfactory, excepting possibly those corresponding to experimentation at high dilution. With the view that the membrane potential differences of systems with larger concentration drops might be additively estimated from systems with smaller drops, decade by decade, these calculations were made with the aid of Table I to yield the results shown below.

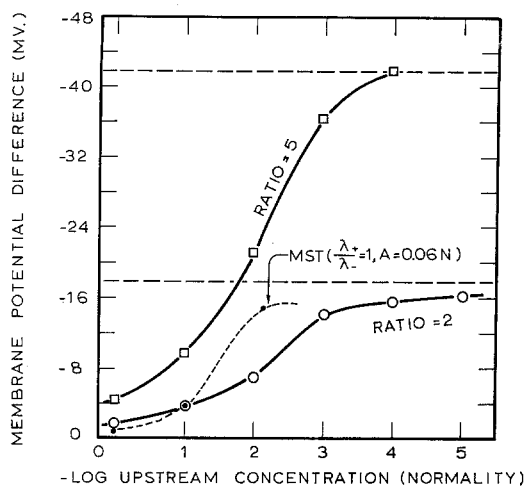


FIG. 1. KCl concentration potential differences across a sample of neutral polysalt.

Noting the discrepancies between the direct measurements and summed estimates, we interpret these results to mean that, with the larger concentration difference, the concentrated KCl penetrated so extensively through the membrane that the concentration at the downstream face was higher than the bulk concentration in contact with it.

Thus, further research was done with concentration ratios of 2, 5, and 10, these results, shown in Fig. 1, provided the data required for an evaluation of the behavior of the membrane with respect to concentration potential differences. It was found that the membrane potential differences were all negative, approaching the theoretical limit when $\bar{L} \rightarrow 1$ (Table I, Fig. 1). Further, as the external solution concentration decreases, the concentration potential difference becomes more negative. Apart from the genuine effect of the more favorable ratio of solution concentration to fixed ion concentration, this is due to the fact that, as the external solution concentration goes down, the neutral polysalt membrane becomes less swollen (6) and consequently the absolute value of the fixed ion concentration goes up. Consequently, the membrane behaves as a weak ion-exchanger with relatively small fixed (+) charge.

With the use of Eq. [3], average ion transference numbers in the membrane were calculated, as already noted. These values

are shown in Table I. From this table, it is seen that differences between transference numbers of cation and anion tend to lessen as the upstream concentration is increased. These results definitely show that the neutral polysalt membrane is affecting the passage of KCl, in that the transference numbers of the chloride ion are significantly greater in the membrane than they are in free solution.

CaCl₂ Concentration Potential Differences across Neutral Polysalt. The concentration potentials with CaCl₂ across neutral polysalt membranes were studied with four different membrane samples. Figure 2 shows that, in all cases, the values of \bar{L}_+ are less than 0.10, indicating that the divalent co-ion, Ca⁺⁺, is significantly excluded and/or retarded by the membrane, more so than K⁺.

Cation Retardation. Since at this point the pronounced effect of concentration has been demonstrated, it seems clear that the major effect is based upon the Donnan exclusion of the cation, more powerful for the higher valent calcium ion. Possible lyotropic influence (14, 20, 21) may be contributing but is not controlling.

NaBr Concentration Potential Differences across Neutral Polysalt. The next series of measurements was concerned with the concentration potential differences for NaBr across various samples of neutral polysalt membrane equilibrated in NaBr solutions of 1.0 N concentration. A distinguishing feature of these systems is the fact that the Br⁻ ion is supposed to be strongly site-bound by such groups as the membrane quaternary ammonium group (6). Since this site-binding can be considered to neutralize some of the positive groups of the matrix, the net fixed charge of the membrane, which was positive, will become less positive and may even change sign. Therefore, the membrane potential with NaBr is expected to be less negative or even positive. Further, experiment shows that site-binding is accompanied by swelling and the membrane becomes spongy and "leaky," so that concentration potential difference tends toward zero with increased Br⁻ concentration (14).

In Fig. 3 are plotted the concentration potential differences of NaBr across a

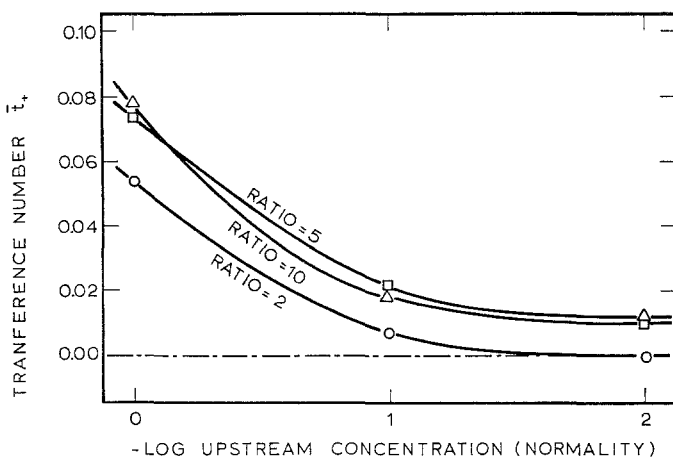


FIG. 2. Values of \bar{t}_+ for CaCl_2 in neutral polysalt membranes.

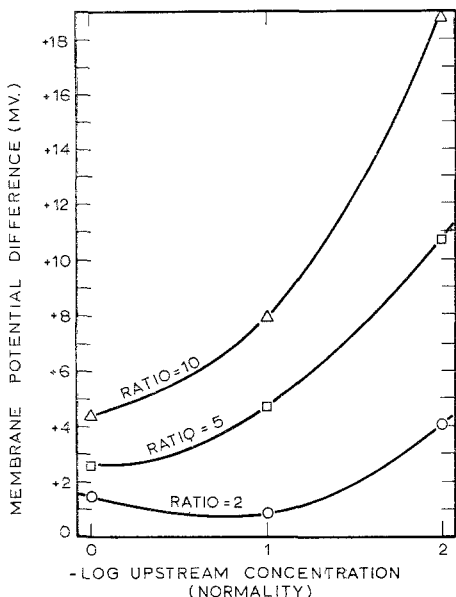


FIG. 3. NaBr concentration potential differences across neutral polysalt equilibrated in 1.0 N NaBr.

neutral polysalt membrane sample previously equilibrated in 1.0 N NaBr. Figure 3 shows that, as the upstream solution concentration increases from 0.01 N to 1.0 N, the concentration potential differences tend toward zero very rapidly. This is in agreement with the charge neutralization/swelling arguments previously advanced.

KCl Concentration Potential Differences across Nonneutral Polysalt. To seek further manifestation of ion-exchange behavior, the

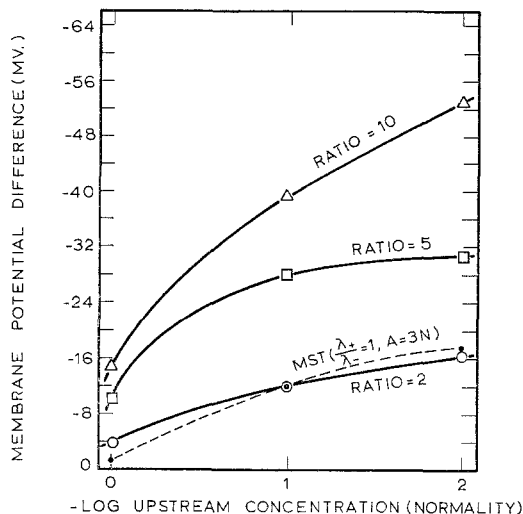


FIG. 4. KCl concentration potential differences across 100% excess VBTACL membranes.

next series of experiments was concerned with the measurement of the concentration potential differences of KCl systems across nonneutral membranes. The membranes used in this section of the research were samples of 100% excess VBTACL and samples of 100% excess NaSS, and it was expected that a change in the sign of the concentration potential difference would be observed, proceeding from a membrane with the excess polyanion to a membrane with the excess polycation.

Figure 4 shows the concentration potential differences across 100% excess VBTACL

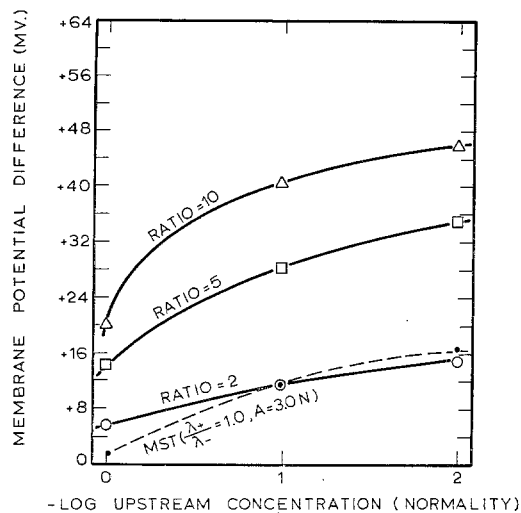


Fig. 5. KCl concentration potential differences across 100% excess NaSS membranes.

membranes. The results show that the concentration potential differences behave in a manner similar to that described for KCl systems across neutral polysalt membranes, except that ion-exchange behavior is more pronounced.

Figure 5 shows the potential differences across 100% excess NaSS. This time, the readings are all positive, showing that the excess NaSS acts as a cation-exchanger membrane. Hence, the expected switch in sign is observed, indicating that nonneutral polysalt films are, in fact, ion-exchanger membranes. This point is further emphasized by the plots of transference numbers (Figs. 6 and 7).

Membrane Fixed Charge. In order to characterize more fully the nonneutral polysalts, a graphical form of the MST theory

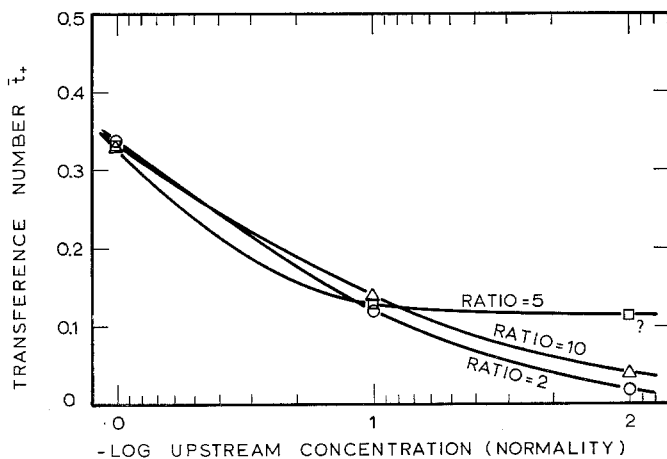


Fig. 6. Values of t_+ for KCl in 100% excess VBTACl membranes.

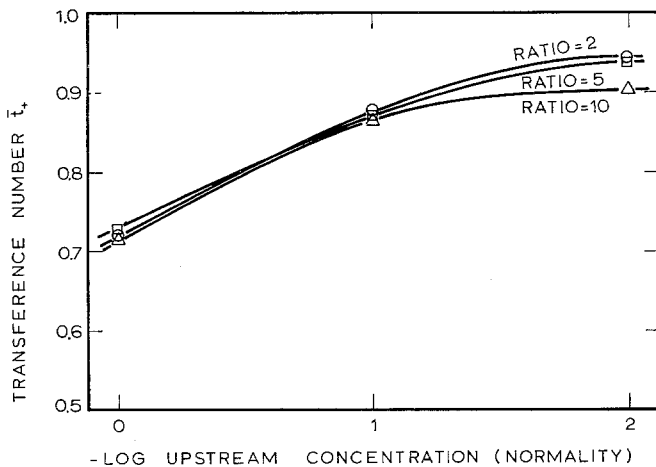


Fig. 7. Values of t_+ for KCl in 100% excess NaSS membranes.

(15, 16) was applied to the concentration potential difference results (for a ratio of 2) as shown in Figs. 4 and 5. The membranes behaved very closely as ion-exchange membranes with a fixed charge of $3N$ for both the anion- and cation-exchangers, in good agreement with the values estimated on the basis of equivalent weights of the individual polyions and nonneutral membrane swelling data (14). Since the ostensibly neutral polysalt had also shown a partial ionic character, the MST theory was applied and as shown in Fig. 1, indicated that the neutral membrane behaves as a weak (*ca.* 0.06 N) anion-exchanger. Thus, the gelation step may result in burial of some of the less bulky sulfonate groups (with cation), leaving a net preponderance of exposed trimethylammonium groups, or the reaction mixture may have been slightly nonstoichiometric. Although the same behavior might be due to mobility effects, the variation in membrane potential difference with concentration points to activity effects, as influenced by membrane fixed charge. The somewhat slower change of the membrane potential difference with concentration than corresponds to the MST theory might be related to some deswelling at high salt concentration or to adsorption of the cation.

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