

Reverse Osmosis Rejection by Hydrous Inorganic Precipitate-Cellulose Composite Membrane

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Synopsis

Composite membranes were prepared by impregnating hydrous inorganic precipitates (Fe and Cr oxides, nickel chromate or molybdate) into a cellulose acetate membrane which serves as a support. In these membranes, the hydrous iron oxide composite membrane showed high reverse osmosis properties. The permeability of the composite membrane did not decline with time, and the rejection of organic solute was not appreciably affected by impregnation. However, the rejection of electrolyte increased with impregnation. The measurements of membrane potential revealed that salt rejection is primarily attributable to the effect of membrane charge, i.e., to ion exclusion effect. In electrolyte solutions of 1:1 and 2:1, the membrane was anion selective; on the other hand, in electrolyte solution of 1:2, the membrane was cation selective. These results are characteristic of impregnated hydrous metal oxide.

INTRODUCTION

The cellulose acetate membrane has been widely used as a membrane for reverse osmosis desalination. However, improved membrane materials are continually being sought. Upon circulating a dilute solution of a colloid (either inorganic or organic) over a nonselective microporous support, a gel layer may build up on the support membrane.^{1,2}

Such membranes are referred to as dynamically formed membranes.² The membrane formation is very easy. However, the permeability and rejection are not reproducible. On the other hand, a few articles have been published on hydrous iron oxide membranes produced artificially in relation to the corrosion of iron and steels, in which the membranes were anion selective.³ Composite membranes, formed by impregnating hydrous inorganic precipitates into cellulose acetate membrane, have been investigated as reverse osmosis membranes. Simultaneously, the measurements of membrane potentials have been conducted for the composite membranes to evaluate the ion selectivity and the fixed ion concentration on the membrane.

EXPERIMENTAL

The hydrous metal oxide composite membrane was formed on a cellulose acetate membrane sealed tightly between two compartments of a cell: one compartment with 0.1N $\text{Fe}(\text{NO}_3)_2$ [or $\text{Cr}(\text{NO}_3)_2$] and the other compartment with 0.1N NaOH.⁴ Nickel chromate and nickel molybdate composite membranes were prepared by filling one compartment with 0.5M $\text{Ni}(\text{NO}_3)_2$ and the other compartment with 0.5M Na_2CrO_4 or Na_2MoO_4 . Hydrolyzed cellulose acetate

membrane (HCA) was prepared with 0.1N NaOH and pure water.⁴ For the precipitation, the solutions were kept at room temperature for three days.

The procedure for preparation of cellulose acetate (CA) membrane as a support membrane was the same as that described previously.⁵ The casting solution was prepared by mixing 39.8% acetyl content cellulose acetate (Wako Pure Chemicals), formamide, and acetone in a proportion of 25–30–45 by weight. This solution was cast on a glass plate at room temperature by using a casting knife. After an evaporation period of 90 s, the membrane assembly was immersed in ice-cold water for 3 h.

The apparatus and experimental procedure in reverse osmosis experiments were the same as those reported earlier.^{4,5} The cell volume is 1 L and effective membrane surface area is 10 cm². The operating pressure used was 50 atm in all cases. The membrane surface, which was in contact with air during casting, was directed to the high-pressure side of the feed solution. The solute concentrations used were in the range 10⁻⁴–5 × 10⁻² M for organic solute and 0.5N for inorganic solute. All reverse osmosis data are for single solution systems.

The Tōshiba Beckman total carbon analyzer, model 102A was used to determine the concentration of organic solute. The total carbon content in the solution was obtained from predetermined calibration curves. The concentrations of the inorganic solutes were obtained by means of a conductivity meter. Solute rejection *R* is defined as follows:

$$R(\%) = \left(1 - \frac{C_2}{C_1}\right) \times 100$$

where *C*₁ and *C*₂ are the concentrations in the feed solution and product water, respectively.

Membrane potentials arising across the membrane were measured to evaluate the ion selectivity and the fixed ion concentration on the membrane. Apparatus for measurements of membrane potential is shown in Fig. 1. The solutions in both compartments separated by a membrane were well stirred with a magnetic stirrer. The volume of the compartment was 80 cm³ and the membrane area is 0.5 cm². An electrometer model Tr-8651 made by Takeda Riken Co. was used for the potential measurements. The temperature for measurements was 20–23°C. The time necessary to obtain a stationary membrane potential was 10–20 min, depending on the kind of salt.

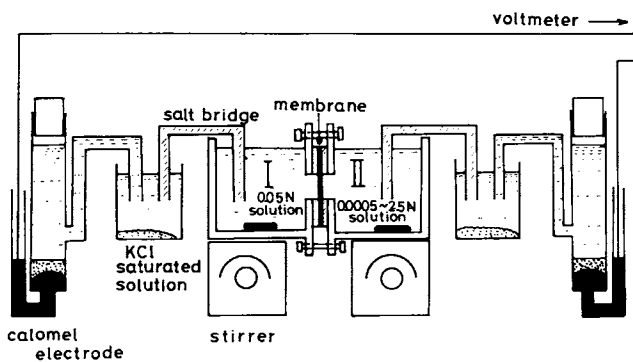


Fig. 1. Apparatus for measurement of membrane potential

The membrane was cut in small pieces to observe the cross section. The piece was immersed in 1% osmic acid solution for 48 h. It was then immersed in a series of five ethanol/water baths until the water had been exchanged for pure ethanol. Next, the membrane structure was preserved with spurr-low-viscosity embedding media (Polyscience Inc.). The embedded membrane was then cross sectioned using an ultramicrotome to approximately 500 Å. It was coated with a layer of evaporated carbon and then observed in the transmittance electron microscope (Hitachi H-500).

All reagents and chemicals used that were commercially available were either of analytical or reagent-grade purity and were used without further purification.

RESULTS AND DISCUSSION

Figure 2 is an electron micrograph of a cross section of the hydrous iron oxide composite membrane. The top photo shows the dense layer which was in contact with air during casting, while the bottom photo shows a highly porous layer which was in contact with the glass plate during casting. It is seen that the oxide precipitate is distributed in fine particles and the distribution increases gradually from porous layer to dense layer. From x-ray diffraction analysis, the hydrous iron oxide was identified as amorphous and a mixture of FeOOH (goethite) and Fe₂O₃ (hematite). The composite membrane had $\chi = 1.51 \times 10^{-5}$ emu/g of magnetic susceptibility which was determined by magnetic balance.

The composite membrane is paramagnetic. Nickel molybdate formed in this manner is NiMoO₄·xH₂O and the chromate is amorphous.⁶ From IR spectra, the hydrolyzed cellulose acetate (HCA) membrane is to some extent hydrolyzed by NaOH. That is, the band due to stretching of carbonyl group at 1700 cm⁻¹ is reduced in strength. In contrast, the band due to stretching of OH group at 3500 cm⁻¹ is increased in strength.

Reverse osmosis data are summarized in Table I for cellulose acetate (CA) membrane and hydrolyzed cellulose acetate (HCA) membrane as support membrane and composite membranes. On the whole, the divalent ions are rejected more effectively than monovalent ions, and hydrophobic solute more often than hydrophilic solute. In addition, permeability decline with time (compaction effect), as usually observed in cellulose reverse osmosis membrane,⁷ was not observed. This may be due to the impregnation into the porous layer of the support membrane. Rejection of organic solute by hydrous iron oxide composite membranes is nearly equal to that by HCA membrane. However, the composite membrane shows higher rejection for inorganic solute, as compared to the HCA membrane. The permeability was not appreciably affected by impregnation. The hydrous chromium oxide composite membrane shows lower rejection for both organic and inorganic solutes, and lower permeability. This behavior results in part from the low charge density on the membrane as presumed from the membrane potential.

The lower permeability may be attributed to thickening of the membrane by impregnation of hydrous chromium oxide into the porous layer. In this case, plugging effect may be caused by the impregnation. On the other hand, both salt rejection and permeability for NiMoO₄ composite membrane increased compared to CA membrane as a support membrane. NiMoO₄·xH₂O enters into

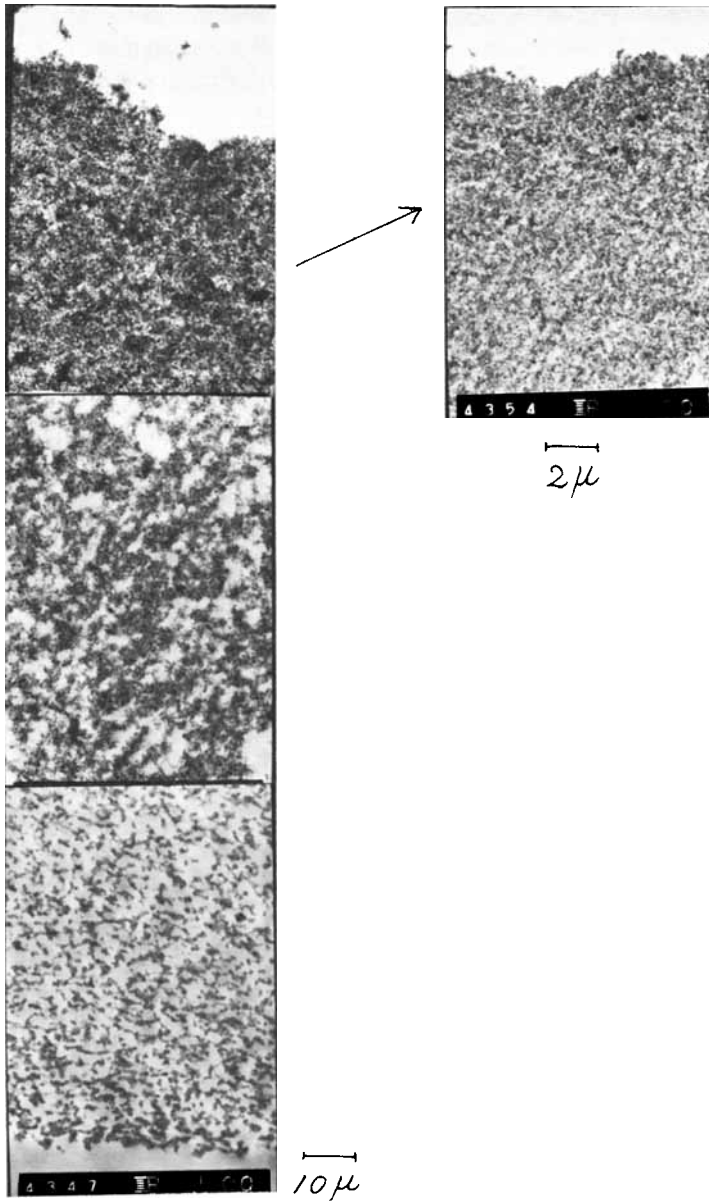


Fig. 2. Cross section of hydrous iron oxide composite membrane.

the pore of the support membrane, grows in it, and broadens the pore whereas amorphous NiCrO_4 only enters into the large pore.

NiCrO_4 or NiMoO_4 in the membrane has a tendency to dissolve in limited amounts under pressure. The stability of this membrane as a reverse osmosis membrane is not as good as the hydrous metal oxide composite membrane.

A series of different molecular weight polyethylene glycols was used in order to determine the porosity of the membrane at a pressure of 50 atm (Fig. 3). NiCrO_4 composite membrane shows a sharp molecular weight cut, compared with the HCA membrane (Fig. 3). This may indicate plugging by the NiCrO_4

TABLE I
Reverse Osmosis Properties of CA, HCA, and Composite Membranes^a

Solute	CA Membrane		HCA Membrane		Hydrous iron oxide composite membrane		Hydrous chromium oxide composite membrane		NiCrO ₄ composite membrane		NiMoO ₄ composite membrane	
	R	P	R	P	R	P	R	P	R	P	R	P
NaCl	38.1	0.680	6.26	0.350	37.2	0.330	25.5	0.123	58.6	0.298	69.5	1.43
KCl	32.1	0.550	4.89	0.382	34.0	0.283	21.7	0.121	42.7	0.216	71.9	1.36
KNO ₃	20.1	0.520	0.78	0.354	17.5	0.271	17.7	0.125	39.2	0.224	54.6	1.18
CaCl ₂	62.8	0.531	11.9	0.375	68.8	0.246	37.3	0.124	76.6	0.241	89.0	1.23
MgCl ₂	62.2	0.503	10.8	0.344	57.3	0.257	34.5	0.123	84.1	0.289	95.4	1.09
Na ₂ SO ₄	75.5	0.378	15.9	0.342	66.3	0.242	25.5	0.115	79.5	0.212	86.8	1.47
<i>n</i> -Butanol	8.63	0.378	17.2	0.355	14.8	0.282			14.4	0.317	23.4	1.54
Isobutanol	13.7	0.334	19.2	0.375	14.2	0.290			26.7	0.302	28.9	1.38
<i>sec</i> -Butanol	16.7	0.329	16.7	0.363	16.6	0.297			28.5	0.294	16.4	1.76
<i>n</i> -Pentanol	11.2	0.302	12.4	0.355	19.7	0.317			7.03	0.313	12.6	1.34
Isopentanol	10.0	0.319	21.1	0.369	21.6	0.323			35.0	0.287	23.0	1.28
<i>sec</i> -Pentanol	22.9	0.331	18.5	0.355	19.4	0.320			28.2	0.304	16.0	1.47
Benzene	92.6	0.327	93.1	0.357	84.9	0.306					66.7	1.40
Toluene	79.6	0.319	88.1	0.394	84.6	0.332					93.7	1.47
Pure water	—	0.437	—	0.338	—	0.358	—	0.120	—	0.354	—	1.39

^a Feed concentration: inorganic solute, 0.05*N*; organic solute; 10^{-4} – 5×10^{-2} . Operating conditions: 50 atm, 25 ± 0.2°C. R = Rejection (%); P = product rate (cm³/cm²·h).

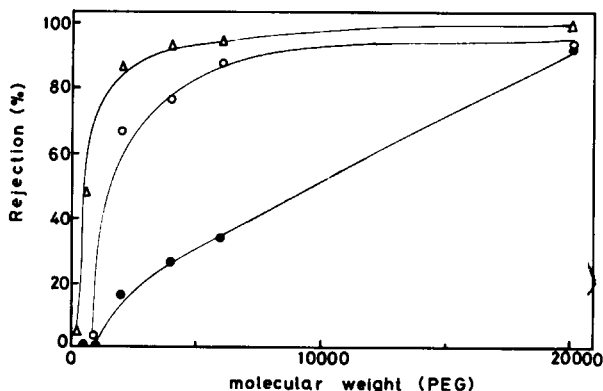


Fig. 3. Relation between molecular weight of PEG and its rejection: (Δ) NiCrO_4 composite membrane; (\bullet) hydrous iron oxide composite membrane; (\circ) HCA membrane.

precipitate which plugs up the large pore. The hydrous iron oxide composite membrane shows a broad molecular cut. Hydrous iron oxide precipitate gel enters into a gap or amorphous region (so-called pore) of the membrane surface of cellulose and broadens the gap. Despite broadening of pore by impregnation, however, this membrane shows high salt rejection (Table I). Hence, the reverse osmosis property of composite membranes is not necessarily determined by porosity. The electrostatic repulsion effect, such as the Donnan effect, may contribute to the salt rejection. Therefore, measurements of membrane potential were conducted to determine the selectivity and charge of the membrane. The ion selectivity is related to the ability of the membrane to reject ion and is reflected in the membrane potential.

In the previous report,⁸ the authors evaluated the permeability ratio from the membrane potential using the equation of Hodgkin and Katz, assuming the Cl^- permeability to be unity. The order of salt rejection was consistent with the order of the permeability ratio determined from the membrane potential. Fig. 4 for HCA membrane, Fig. 5 for hydrous iron oxide composite membrane, and

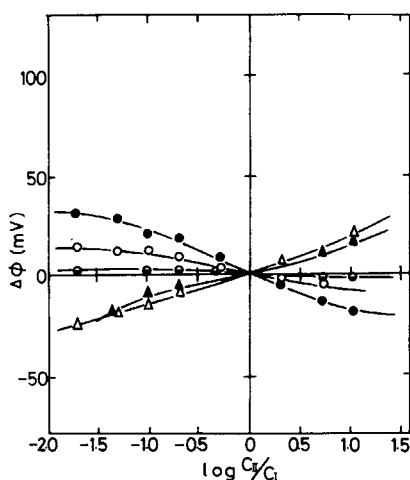


Fig. 4. Membrane potential arising across hydrolyzed cellulose acetate (HCA) membrane with concentration ratio: (\circ) NaCl ; (\bullet) KCl , (\bullet) CaCl_2 ; (Δ) K_2SO_4 ; (\blacktriangle) Na_2SO_4 .

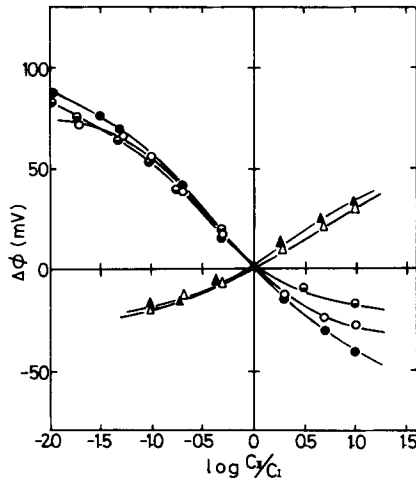


Fig. 5. Membrane potential arising across hydrous iron oxide composite membrane with concentration ratio. Symbols same as those used in Fig. 4.

Fig. 6 for hydrous Cr oxide composite membrane show the relationships between the membrane potentials in the systems of various electrolytes and the concentration ratios referred to the standard concentration of $5 \times 10^{-2}N$. The membrane potentials vary nonlinearly with concentration ratios and are similar. The salt, such as the divalent ion, shows the higher membrane potential. Potential curves for NaCl, KCl, and CaCl₂ solutions represent negative slopes, but the Na₂SO₄ and K₂SO₄ solutions represent positive slopes. A negative slope indicates that the membrane is anion selective. A positive slope indicates that the membrane is cation selective.^{6,11} This may be attributed to the partial replacement of hydroxyl groups on the membrane by SO₄⁻² ion which leads to a stage in which a negative charge is fixed on the membrane.

Such behavior is not peculiar to this system. Siddigi et al. found that the surface charge on ferrocyanide membranes was reversed from negative to positive

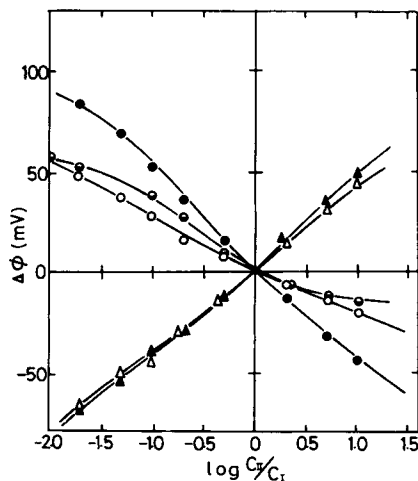


Fig. 6. Membrane potential arising across hydrous chromium oxide composite membrane with concentration ratio. Symbols same as those used in Fig. 4.

by adsorption of di- and trivalent cations.⁹ The composite membrane may consist of a tridimensional polymeric network of hydrated metal oxide containing an ionic group. The membrane may expel the coion by electrostatic repulsion according to the Donnan ion exclusion effect. The apparent transport numbers of cations are calculated from the slope at the point of $\log C_{11}/C_1 = 0$. The results are t_{Na}^+ (NaCl) = 0.20, t_{K}^+ (KCl) = 0.25, t_{Na}^+ (Na₂SO₄) = 0.6 for hydrous iron oxide composite membranes; t_{Na}^+ (NaCl) = 0.28, t_{K}^+ (KCl) = 0.32 for hydrous chromium oxide composite membranes; and t_{Na}^+ (NaCl) = 0.5, t_{K}^+ (KCl) = 0.5 for HCA membranes. The HCA membrane is nearly nonselective. The order of selectivity is: hydrous iron oxide composite membrane > hydrous chromium oxide composite membrane > HCA membrane. This order is in accord with the order of salt rejection Table I.

The fixed charge on the membrane can be estimated from the membrane potential. According to the fixed charge theory of membrane potential,¹⁰ the potential is given by the equation

$$\Delta\psi = \psi_1 - \psi_{11} = \frac{RT}{F} \ln \frac{C_1(\sqrt{4C_1^2 + x^2} + X)}{C_{11}(\sqrt{4C_{11}^2 + X^2} + X)} - \bar{U} \ln \frac{\sqrt{4C_1^2 + X^2} - X\bar{U}}{\sqrt{4C_{11}^2 + X^2} - X\bar{U}}$$

where $\bar{U} = (u_+ - u_-)/(u_+ + u_-)$; u_+ and u_- are the mobilities of cation and the anion in the membrane, respectively; and X is the charge on the membrane expressed in equiv/L. For a membrane carrying a fixed charge of unity ($X = 1$) in the electrolyte solution at a constant concentration ($C_1/C_{11} = 10$), the theoretical membrane potential can be calculated as a function of C_{11} for different mobility ratio (u_+/u_-) (smooth curves, Fig. 7). The observed values for hydrous iron oxide composite membrane in NaCl and KCl solutions are plotted in the same graph (Fig. 7) as a function of $-\log C_{11}$. Since the theoretical curves of different fixed charge concentrations are shifted by the extent of $\log X$ from the curve of $X = 1$ for each value of u_+/u_- , the values of X and u_+/u_- for a given membrane can be determined by means of a best-fit approach between experimental and theoretical curves.^{11,12} The fixed charge concentration and the mobility ratio estimated from this method are $X = 0.01$ equiv/L and $u_+/u_- = 0.5$ in NaCl solution for hydrous iron oxide composite membrane and $X = 0.001$ equiv/L, $u_+/u_- = 1.0$ for the CA membrane. The concentration ratio is assumed

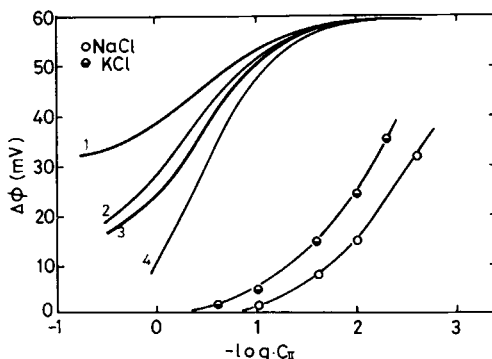


Fig. 7. Theoretical membrane potential in 1-1 electrolyte solution and experimental membrane potential across hydrous iron oxide composite membrane at constant concentration ratio ($C_1/C_{11} = 10$) as function of $\log C_{11}$: (O) NaCl; (●) KCl; 1, $x = 1$, $u_+/u_- = 0.3$; 2, $x = 1$, $u_+/u_- = 0.5$; 3, $x = 1$, $u_+/u_- = 0.6$; 4, $x = 1$, $u_+/u_- = 1.0$.

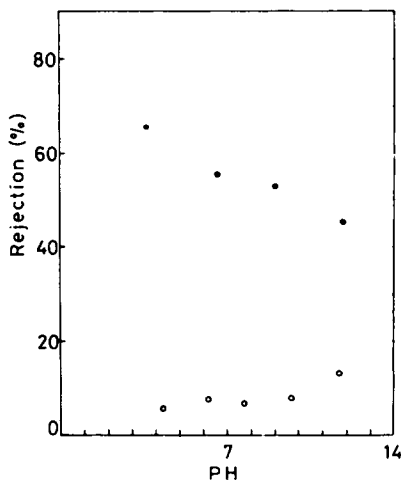


Fig. 8. Effect of pH on NaCl rejection; concentration of NaCl 0.05N: (○) HCA membrane; (●) hydrous iron oxide composite membrane.

to be identical to the mean activity ratio. The fixed charge of the composite membrane is about 10 times that of the CA membrane.

The effect of pH on NaCl rejection by the hydrous iron oxide composite membrane is shown in Figure 8. An increase in salt rejection with pH is observed for the HCA membrane. From the variation of membrane potential with pH, the CA membrane is slightly acidic.¹³ The larger the degree of dissociation of CA, the larger the salt rejection. On the other hand, the fixed charge of hydrous iron oxide precipitate decreases from positive to zero with an increase in pH.⁶ The variation of membrane charge corresponds to that of rejection. Therefore, the electrostatic repulsion effect may also affect the rejection.

CONCLUSIONS

In composite membranes which were prepared from the impregnation of hydrous inorganic precipitates into cellulose support membranes, the hydrous iron oxide composite membrane showed good reverse osmosis properties. This properties may be principally ascribed to the Donnan exclusion effect. In electrolyte solutions of 1:1 and 2:1, the membrane was anion selective. On the other hand, in electrolyte solution of 1:2, the membrane was cation selective. This change in selectivity may be due to the adsorption of divalent anions resulting in a negative charge on the membrane.

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