

Ionic Membranes. I. Surface Sulfonic Acid

Groups on Porous Glass: a Potentiometric Study

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The cation response of a porous glass is increased by introducing surface phenylsulfonate groups. The treated and untreated glass is characterized using the Meyer-Sievers potentiometric graphical method. The increase in the cation transport number is found to be due to an increase in both the charge density and the cation-to-anion mobility ratio in the membrane phase.

Introduction

Altug and Hair¹ demonstrated that a porous glass behaved as a low-capacity, cation-permeable ionic membrane. The variation of the membrane potential with the external solution concentration was successfully correlated with the Teorell-Meyer-Sievers (TMS) fixed-charge theory. Altug and Hair² also reported that the porous glass surface exhibited a pH titration curve similar to a weak dibasic acid with surface pK_a values of about 5 and 8.

The results of the potentiometric measurements and the pH titrations cited above are consistent with a large volume of spectroscopic studies^{3,4} of the surface of porous glasses. Infrared work indicates that a porous glass surface is heterogeneous and consists primarily of free and hydrogen-bonded hydroxyl groups. These surface hydroxyl groups may be attached to both silicon and boron and would be expected to demonstrate weakly acidic properties.

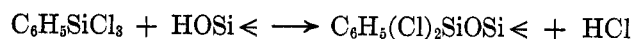
The substitution of strongly acidic or basic groups for the surface hydroxyls would yield a more efficient, higher capacity cation- or anion-permeable ionic membrane. A further advantage of the modified porous-glass system is the nonswelling properties and the good mechanical strength of the porous glass matrix and the large variety of ionogenic groups which can be grafted to the surface. The effect of varying both the nature and concentration of the grafted groups can be studied electrochemically, and the entire system can be accurately characterized using infrared methods and other techniques applicable to solid porous media, such as gas-adsorption isotherms.

This report describes a method for grafting the phenylsulfonate group to the surface of a porous glass. Treated and untreated cation-permeable porous glass membranes are made part of a concentration cell, and the variation of the membrane potential with the external solution concentration is analyzed by the use of the Meyer-Sievers graphical, potentiometric method. Membrane transport numbers are calculated using a

modified Nernst relation and compared with the values determined by the Meyer-Sievers method.

Experimental Section

Preparation of Porous Glass Membranes. Porous glass disks (2.2×0.04 cm) were prepared from glass whose composition is 73% SiO_2 , 1.31% Al_2O_3 , 15% B_2O_3 , 3.6% Na_2O , and 5.8% PbO . The disks were heat treated at 580° for 3 hr followed by $80^\circ/\text{hr}$ cooling. The samples were then leached in 1.0 N HNO_3 for 2.5 hr and washed in 0.1 N HNO_3 for 0.5 hr. Both the leach and wash were performed in a constant-temperature water bath at $95 \pm 1^\circ$. The final composition of the glass was approximately 95% SiO_2 , 4% B_2O_3 , and 1% Na_2O . The surface area and the pore-size distribution of the glass were determined by standard nitrogen-adsorption techniques. The surface area of the untreated glass was $110 \text{ m}^2/\text{g}$ and the average pore diameter was 32 \AA . The pore-size distribution was narrow: 96% of the pores were within $\pm 3 \text{ \AA}$ of the average value. The sulfonic acid groups were grafted⁵ to the surface of the porous glass prepared by evacuation for 12 hr and then refluxing with a 2% (v/v) solution of phenyltrichlorosilane (PTCS) in toluene for 16 hr. The reaction mechanism is probably similar to that proposed by Davydov, *et al.*,⁶ for the reaction between dimethyldichlorosilane and silica. In our case, the main reaction taking place is



The pendant phenyl groups were sulfonated with 30%

- (1) I. Altug and M. L. Hair, *J. Phys. Chem.*, **72**, 599 (1968).
- (2) I. Altug and M. L. Hair, *ibid.*, **71**, 4260 (1967).
- (3) M. L. Hair, "Infrared Spectroscopy in Surface Chemistry," Marcel Dekker, Inc., New York, N. Y., 1967, pp 79-137.
- (4) L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press Inc., New York, N. Y., 1966.
- (5) I. E. Neimark and V. M. Chertov, *Dokl. Akad. Nauk SSSR*, **138**, 877 (1961).
- (6) V. Ya. Davydov, L. T. Zhuravlev, and A. V. Kiselev, *Russ. J. Phys. Chem.*, **38**, 1108 (1964).

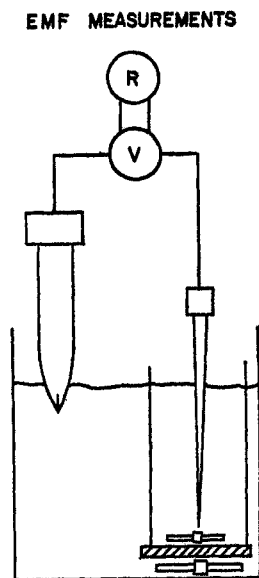


Figure 1. Schematic of experimental setup for potentiometric measurements.

oleum at 23° for 14 hr. The reaction here is presumably



All the chemicals used were reagent grade. The PTCS was made by Dow Chemical and was used as received.

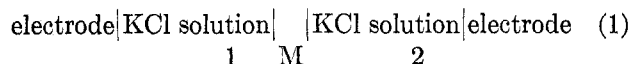
Electromotive Force Measurements. The physical arrangement is shown in Figure 1. The electrodes used were Beckman fiber-junction calomel probes; the emf was measured with a Keithley 150B microvoltmeter and 370 recorder. The membrane potential was obtained by first determining a constant cell emf with identical solutions on both sides of the membrane. The outer solution was changed to the lower concentration and a new voltage value was determined. The difference between the two readings was taken as the membrane potential. For the more concentrated KCl solutions (greater than 0.05 *m*), the emf was read when the drift was less than 0.2 mV/hr during a 20-min period. The solutions were changed until the measured potential was constant to about 0.3 mV. The emf measurements of the more dilute solutions (less than 0.05 *m*) were less precise because of the fluctuations of the potentials at the membrane- and electrode-solution interface caused by vigorous stirring. This was symmetrical and reached a maximum value of ± 0.4 mV at 0.001 *m* KCl.

The membrane disks were cemented to code 7740 glass cylinders (0.625 in. i.d. \times 3 \times 0.125 in.) using epoxy cement and were allowed to age 14 hr before equilibrating with stirring for another 14 hr in the solution having the higher concentration. Further soaking in the KCl solutions had little effect on the potential measurements. All the emf measurements

were made in a constant-temperature room at $23 \pm 0.2^\circ$, and the emf values were converted to 25°. The solutions were made using reagent grade KCl.

Theory

The system we are concerned with is the concentration cell



M represents a cation-permeable membrane which separates the two KCl solutions.

The electromotive force, E_M , of this galvanic cell may be expressed as⁷

$$E_M = -\frac{RT}{F} \int_1^2 (t_{\text{Cd}} \ln a_{\text{C}} + t_{\text{Ad}} \ln a_{\text{A}} + t_{\text{Wd}} \ln a_{\text{W}}) \quad (2)$$

where t is the transference number, a is the activity, and the subscripts C, A, and W refer to the cation, anion, and water. We have considered the fixed anion charge in the membrane to be stationary.

Equation 2 expresses the main problem. In order to relate the membrane potential to the physical properties of the membrane, the transference numbers must be determined as functions of the activities of the various permeating species. Two different approaches can be taken to this problem. The first is the use of a modified Nernstian approach; the second is the use of the TMS fixed-charge theory.

a. Modified Nernstian Relation. There are two main assumptions associated with this approach. The most important one is the use of an average value for the transference number in the integration of eq 2. The other is to neglect the transference of water. The latter quantity is directly related to the hydraulic permeability of the membrane and would be expected to be small for the porous glass systems. With these assumptions and the use of the relations

$$a_{\text{C}} = a_{\text{A}} = a_{\pm}$$

$$\bar{T}_i = z_i \bar{l}_i$$

and

$$\bar{T}_{\text{A}} + \bar{T}_{\text{C}} = 1$$

the integration of eq 2 results in

$$E_M = \frac{RT}{F} (2\bar{T}_{\text{C}} - 1) \ln \frac{a_{\pm}(2)}{a_{\pm}(1)} \quad (3)$$

where z_i is the valence, \bar{T}_{C} is the average transport number of the cation in the membrane, and $a_{\pm}(1)$ and $a_{\pm}(2)$ are the mean activities of the salt in solutions 1 and 2. Equation 3 may be rearranged to

(7) G. Scatchard, *J. Amer. Chem. Soc.*, **75**, 2883 (1953).

$$\bar{T}_C = \frac{E_M + E^\circ}{2E^\circ} \quad (4)$$

where E_M is the measured membrane potential and E° is the ideal Nernstian potential. Equation 4 permits the calculation of \bar{T}_C from the measured values of E_M for the different solution activities.⁸

b. Fixed-Charge Theory. The earliest effort toward developing a membrane model was by Michaelis,⁹ who considered that the charge on the membrane was due to the adsorption of one kind of ion. Later, Teorell¹⁰ and Meyer and Sievers¹¹ (TMS) developed the theory of membranes with charges fixed in the lattice. In the TMS theory there is an equilibrium process at each solution-membrane interface which has a formal analogy with the Donnan equilibrium. In addition, there is an internal salt-diffusion potential which was first represented by the Henderson equation and later by the more nearly correct Planck expression.¹² Further assumptions made are: (1) the cation and anion mobilities and the fixed-charge concentration are constant throughout the membrane phase and are independent of the salt concentration; and (2) the transference of water may be neglected.

In order to use the graphical method of Meyer and Sievers,¹¹ a further assumption must be made that the activity coefficient of the salt is the same in the membrane and solution phase at each interface. The introduction of activities for concentration can only be correctly made for the Donnan potential. The expression for the diffusion potential using either the integration of Planck or Henderson requires concentrations. The membrane potential in the TMS model can be expressed in the following form¹³ for a 1:1 valent electrolyte at external concentrations m_1 and m_2

$$E_M = \frac{RT}{F} \omega \ln \frac{m_2(x_1 + 1)}{m_1(x_2 + 1)} + \bar{U} \ln \frac{x_1 - \omega \bar{U}}{x_2 - \omega \bar{U}} \quad (5)$$

where $\omega = +1$ or -1 for an anion-selective or cation-selective membrane, respectively

$$x = \left[\left(\frac{2m}{\bar{X}} \right)^2 + 1 \right]^{1/2}$$

$$\bar{U} = \frac{\bar{U}_C - \bar{U}_A}{\bar{U}_C + \bar{U}_A}$$

where \bar{X} is the fixed-ion concentration and \bar{U}_C and \bar{U}_A are the cation and anion mobilities in the membrane phase.

The graphical potentiometric method of Meyer and Sievers yields values of \bar{X} and the cation-to-anion mobility ratio in the membrane phase, \bar{U}_C/\bar{U}_A . This procedure will be discussed in the Results section. The results of the above analysis may be used to calculate values of the membrane transport numbers using the relation (eq 6)

$$\frac{\bar{T}_C}{\bar{T}_A} = \frac{\bar{U}_C \bar{m}_C}{\bar{U}_A \bar{m}_A} = \frac{\bar{U}_C \sqrt{4m^2 + \bar{X}^2} + \bar{X}}{\bar{U}_A \sqrt{4m^2 + \bar{X}^2} + \bar{X}} \quad (6)$$

where \bar{m}_C and \bar{m}_A are the molal concentrations of the cation and anion, respectively, in the membrane phase.

Results and Discussion

The graphical method of Meyer and Sievers determines the fixed-charge concentration \bar{X} and the cation-to-anion mobility ratio in the membrane phase. The set of curves on the left in Figure 2 are the theoretical membrane potentials calculated using eq 5 for a cation-exchange membrane, 1:1 electrolyte and constant solution-concentration ratio $m_1/m_2 = 2$, as a function of $\log 1/m_2$. The different curves are for different mobility ratios, \bar{U}_C/\bar{U}_A , with a constant value of $\bar{X} = 1$ m. Experimental E_M values for treated and untreated porous-glass membranes are plotted in the same graph against $\log 1/m_2$. The shift of the theoretical curves to coincide with the experimental points gave $\log \bar{X}$, and the coinciding curve gave the mobility ratio.

The lower curve in Figure 2 is a graphical representation of eq 5 with $\bar{X} = 0.04$ m and $\bar{U}_C/\bar{U}_A = 1.0$ and corresponds approximately with the experimental values of E_M for the untreated porous-glass membrane. The

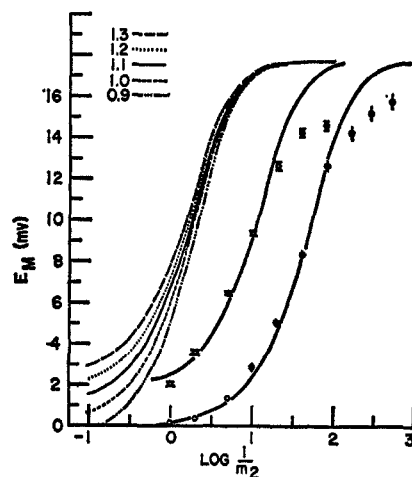


Figure 2. Membrane potentials for various 2:1 m ratios of KCl solutions ($m_1/m_2 = 2$) plotted against $\log 1/m_2$. Broken curves at left are theoretical curves with varying cation-to-anion mobility ratios in the membrane phase and $\bar{X} = 1.0$ m. Solid curves at right are theoretical curves which best fit the data. Experimental points are for untreated porous glass, Φ , and for porous glass with surface sulfonic groups, ϕ .

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(9) L. Michaelis and A. Fujita, *Biochem. Z.*, **158**, 28 (1925).

(10) T. Teorell, *Proc. Soc. Exptl. Biol. Med.*, **33**, 282 (1935).

(11) K. H. Meyer and J. F. Sievers, *Helv. Chim. Acta*, **19**, 649 (1936).

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(13) R. Schlögl and F. Helfferich, *Z. Elektrochem.*, **56**, 644 (1952).

Table I: Membrane Potentials and Calculated Transport Numbers

1 <i>m</i>	2 <i>m</i>	Porous glass membrane				Porous glass-sulfonic acid membrane			
		3 <i>E_M</i> , mV	4 (<i>T_K⁺</i>) _N	5 (<i>T_K⁺</i>) _T	6 <i>Δ</i>	7 <i>E_M</i> , mV	8 (<i>T_K⁺</i>) _N	9 (<i>T_K⁺</i>) _T	10 <i>Δ</i>
0.001	0.0015	16.2	0.97	1.00	-0.03
0.002		15.9	0.96	0.97	-0.01
0.004		15.3	0.95	0.98	-0.03
0.008		14.3	0.93	0.94	-0.01
0.00625	0.0188	12.7	0.88	0.85	0.03	14.7	0.94	0.99	-0.05
0.0125		8.4	0.75	0.72	0.03	14.3	0.93	0.96	-0.03
0.025		5.1	0.66	0.62	0.04	12.7	0.89	0.88	0.01
0.050		2.9	0.59	0.56	0.03	9.4	0.79	0.76	0.03
0.10	0.30	1.4	0.54	0.53	0.01	6.5	0.71	0.66	0.05
0.20		0.37	0.51	0.51	0.00	3.6	0.61	0.59	0.02
0.40		0.14	0.50	0.51	-0.01	2.1	0.56	0.57	-0.01
0.50									
1.0	1.5								
2.0									

upper curve, which provides a good fit of the membrane potentials of the sulfonic acid-porous glass membrane, has $\bar{X} = 0.15 m$ and $\bar{U}_C/\bar{U}_A = 1.2$.

In both systems the experimental values of the emf fall below the theoretical curves at low solution concentrations. This divergence may be examined by noting that if we substitute activities for concentration terms in eq 5, we have

$$\lim E_M (25^\circ) = 59.15 \frac{m_1 \gamma_1 \bar{a}_2}{m_2 \gamma_2 \bar{a}_1} \quad (7)$$

for $\bar{X} \gg m$. Here γ_i is the mean molal activity coefficient in the *i*th solution and \bar{a}_i is the activity of KCl in the membrane phase at the *i*th solution-membrane interface. By substituting for E_M the value of the emf measured when m_1 and m_2 are equal to 0.002 and 0.001 *m* KCl, respectively, and using published values for γ_i , we obtain

$$\bar{a}_{(0.001)} = 0.96 \bar{a}_{(0.002)} \quad (8)$$

The inequality expressed by eq 8 implies that in order to account for the difference between the measured and the calculated emf, the activity of KCl in the membrane phase must be highly dependent upon the internal salt concentration and must decrease with decreasing concentration. This is in accord with the conclusions of several investigators who studied the sorbing of salt into various kinds of ion-exchange resins.¹⁴

The values of \bar{X} and \bar{U}_C/\bar{U}_A obtained by the MS

graphical analysis can be substituted into eq 6 to calculate values of \bar{T}_{K^+} . The transport number \bar{T}_{K^+} may also be calculated by the use of eq 4.

The results of the two approaches to the calculation of the potassium ion transport numbers in the membrane phase are presented in Table I. The numbers $(\bar{T}_{K^+})_N$ and $(\bar{T}_{K^+})_T$ were determined by eq 4 and 6, respectively. Two conclusions are apparent from these calculations. The potassium ion transport number at any particular concentration is higher in the sulfonic acid doped porous glass membrane than for the untreated porous glass. Also, a comparison of the two methods of calculating the transport numbers shows an agreement within 5% for all the different concentrations.

The increase in the potassium ion transport number with the attachment of the sulfonic acid group is caused by the increase in the fixed-charge density and the cation-to-anion mobility ratio. The direct effect these parameters have on the transport number may be seen in eq 6.

The agreement between the two methods of calculating \bar{T}_C supports the assumption of an approximately constant transport number for the counterion in the membrane phase used to derive eq 3. This is expected, in terms of the TMS model, in the concentration ranges where $\bar{X} \gg m$ and $\bar{X} \ll m$. Under these conditions, the expression

(14) For bibliography, see C. J. Attridge and J. R. Millar, *J. Chem. Soc.*, 6053 (1964).

$$\lim \bar{T}_C = \lim \frac{\bar{U}_C \bar{m}_C}{\bar{U}_C \bar{m}_C + \bar{U}_A \bar{m}_A}$$

approaches the values of 1 and $\bar{U}_C/(\bar{U}_C + \bar{U}_A)$, respectively, at each membrane-solution interface. The greatest variation of \bar{T}_C should occur across the membrane phase when $\bar{X} \simeq m$, and the difference between the two sets of calculated values of \bar{T}_C should be a maximum at this point. This is approximately true in Table I for the positive values of

$$\Delta = (\bar{T}_{K^+})_N - (\bar{T}_{K^+})_T$$

The negative values of Δ in the low concentration region are due to the poor fit of the TMS theory with the measured values of emf.

The results of the potentiometric analysis indicate that the grafting of sulfonic acid groups to the surface of porous glass increases the fixed-charge concentration and the cation-to-anion mobility ratio in the membrane. The increase in \bar{X} is expected because the sulfonic acids are comparable in strength to sulfuric acid. The apparent pK_a value for a sulfonic acid type resin¹⁵ can be given an upper limit of 1. Unless the pH in the membrane pore is drastically lower than the solution pH, nearly all of the existing sulfonic acid groups would be dissociated. Using the value of \bar{X} obtained for the sulfonic acid type porous glass, 0.15 *m*, and assuming cylindrical pores with a 30-Å diameter, a surface concentration of about 1 dissociated sulfonic acid group/1300 Å² is calculated. According to the work of Davydov, *et al.*,⁶ the number of potentially reactive silanol groups on a silica surface is approximately 2/100 Å². The low coverage of the porous glass surface with sulfonic acid groups can be due to several factors. It is not known whether the surface concentration is limited by the extent of the silane reaction or the sulfonation of the phenyl groups. It is also possible that the silicon-carbon bond is being split by exposure to oleum. Further infrared investigations of the surface species are necessary.

The effect of the membrane upon the cation-to-anion mobility ratio is made clear by considering the ratio¹⁶

$$R = (\bar{U}_C/\bar{U}_A)_M / (U_C/U_A)_{aq}$$

where M and aq refer to the membrane phase and the aqueous solution, respectively. If the mobilities of the counterion and co-ion (in this case, cation and anion, respectively) are affected equally by the membrane phase, then R is equal to 1.

The mobilities of both the counterion and co-ion have been found to decrease in the membrane phase.¹⁷ This lowering of the effective ionic mobilities is believed to be the result of the membrane obstruction and not the result of a different kinetic entity, such as an ion with more or less hydration. The membrane obstruction may be divided into two parts:¹⁸ an increase in the effective path length (the tortuosity factor) and

an interaction with the membrane wall (a viscous effect). This analysis is complicated by the dependence of the membrane obstruction upon the concentration ratio \bar{X}/m , where m is the molality of the external solution.

The dependence of the membrane obstruction upon concentration is primarily caused by the fact that the counterion may be present in the membrane under two conditions: as an exchange ion, *i.e.*, in an amount equivalent to the fixed-charge concentration, and together with the co-ion as a sorbed salt. There is evidence from both self-diffusion¹⁹ and conductivity²⁰ studies that the mobility of the counterion is much less in the exchange than in the sorbed state. This has been explained by Richman and Thomas¹⁹ as a result of two mechanisms for counterion transport through the resin: an exchange between fixed-ion sites with an activation energy of about 10 kcal/mol in the absence of a sorbed electrolyte and a diffusion involving free co-ions with an activation energy of about 2 kcal/mol.

The cation-to-anion mobility ratio determined by the MS method used in this report most likely involves the cation in the sorbed state. The ratio R is equal to 1 for the untreated porous glass membranes and indicates that the membrane obstructs the potassium and chloride ions in an equal manner. The increase in R to 1.2 for the sulfonic acid type porous glass is probably related to the increase in fixed-charge concentration and to the geometrical nature of the pores in porous glass. Electron micrographs of code 7930⁸ porous glass indicate that the geometry of the pores is more likely "bottle-neck" than cylindrical. Such pores would have a small mouth and a large body. In that case even the presence of 1 dissociated phenyl sulfonate group/1300 Å² of surface might be able to block effectively some of the more direct paths available to the chloride ion.^{8,21} The tortuosity factor would favor the potassium ion and result in $R > 1$. If this is the case, then an increase in \bar{X} would always result in R being greater than 1, even for anion-selective porous glass membranes. Preliminary results indicate that this is the case and will be reported later.

Acknowledgment. I wish to thank Miss M. C. Trondsen for her able assistance with the potentiometric measurements, and Dr. M. L. Hair for his helpful suggestions.

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