Salt Rejection by a Porous Glass

Abstract. *Porous glass partly filters dissolved salt from aqueous solutions passed through it under pressure. Rejection of salt can be increased by increase in the* pH *of the solution or by addition of Th(IV). The filtration seems to accord with a mechanism of salt exclusion characteristic of ion exchangers.*

Ion-exchange membranes of the type used in electrodialysis reject salt from NaCl solutions passed through the membranes under pressure (*1*). Such rejection is expected in view of the salt exclusion typically shown by ion-exchange materials in contact with dilute salt solutions. In the familiar Donnan theory the salt exclusion derives from the requirement that the ion products (or more correctly the activities) in the two phases are equal at equilibrium. Because of the high counter-ion concentration of the exchanger, the co-ion concentration, which measures salt invasion, must necessarily be lower than the feed concentration; concentration of the permeating solution also will be lower if permeation is fast enough. The permeation rates of commercial electrodialysis membranes are too slow to be practical for the hyperfiltration, or reverse-osmosis, method of desalination; other membranes of the ion-exchange type (*2, 3*) also are too impermeable or reject too little solute.

Dresner and Kraus (*4, 5*) have suggested that membranes with pores as large as 100-Å diameter, having charged (ion-exchange) walls, would reject sufficient salt to be interesting and would be relatively permeable. Unfired Vycor glasses (*6*) have remarkably uniform pores about 40 Å in diameter; other sizes are apparently obtainable by appropriate preparative procedures. We now present a preliminary report on hyperfiltration properties of such Vycor frits. Although in configurations now available the material is of little practical interest for desalination, it should enable testing of predictions concerning transport behavior of membranes.

The starting material was Vycor No. 7930 glass (*7*) in flat squares that had been withdrawn from production before final firing. Gas adsorption and desorption techniques (*8*) confirmed that the variation in pore diameter was narrow; diameters peaked at 53 Å (133 m^2 g^{-1}) and 95 percent of the pores had diameters between 36 and 56 Å. From this stock, disks were cut, about 2 cm in diameter and 0.5 or 1 mm thick; they were baked for several hours at temperatures up to 550°C or treated with boiling concentrated HNO_3 (with or without baking) to remove organic matter (*6*). The disks were placed in certain hyperfiltration cells (*3*) (about 1.6 cm^2 exposed to feed) in which the Vycor glass is supported by porous metal frits. Feed solutions were circulated under pressure past the membranes, either in the apparatus described in (*3*) or in another system in which a large volume of feed is kept under pressure and circulated much more rapidly in order to assure that the molality (m_α) at the feed interface is essentially the molality of the bulk of feed solution (m_f). Samples of the product (m_ω) that passed through the membrane were compared with the feed by analysis to determine rejection: $\mathbf{R} = (m_f - m_\omega)/m_f$.

Although results with various individual frits and with the same frit over a period of time are not completely reproducible, the broad outline of the hyperfiltration behavior of this material is established by the results in Table 1. Vycor glass rejected NaCl and Na_2SO_4 to a small but appreciable extent from neutral solutions (air equilibrated, *p*H about 6; the entry in the table for 0.03*M* NaCl summarizes experiments with a number of different frits). Since the isoelectric point of silica is stated to be about 2 (*9*), one would expect cation-exchange properties in solutions of neutral *p*H (*10*). The slight rejection observed is consistent with a low ion-exchange capacity. The fact that the salt containing the divalent co-ion, sulfate, is rejected more strongly than the 1,1 salt, NaCl, at the same sodium concentration, is also consistent qualitatively with an ion-exchange mechanism if the activity-coefficient ratios $\Gamma = \gamma^*_\pm/\gamma_\pm$ of the solutes, between membrane and aqueous phases, are unity. (Here the standard states for the two phases are taken to be the same, and the membrane-activity coefficient $\gamma^*_\pm$ is defined as being consistent with concentration expressed as moles of salt per kilogram of water in the membrane phase.) With magnesium chloride, however, the solution passing through the frit was more concentrated than the feed. Similar surprising enrichment occurred with $La(NO_3)_3$; it appears that with multivalent counterions Γ is less than unity, and there must be other interactions which overshadow simple "ion-exclusion" or "Donnan"-type rejection, at least at the low surface-charge densities on silica in contact with approximately neutral solutions.

We have investigated two methods (*10*) of modifying pore-surface charge and therefore rejection properties. In one, the *p*H is changed. In the other, polyvalent ions or polyelectrolytes of opposite charge sign to the silica are adsorbed; under favorable conditions, these may increase the pore-charge density and reverse the charge sign (that is, convert the frit to an anion exchanger).

Column experiments with crushed Vycor glass indicated that its cation-exchange capacity increased as expected with increase in *p*H of the feed. Re-

Table 1. Hyperfiltration properties of Vycor glass frits, 0.5 to 1 mm thick, at 25°C.

Feed (*M*)	Additive*	Feed pressure (atm)	Permeation rate (cm $hour^{-1}$ atm^{-1})	Salt rejection (%)
0.03 NaCl		25 to 55	0.003 to 0.01	5 to 10
.03 NaCl	*p*H 10, silicate	120	.009	35
.01 NaCl	*p*H 9.4	80	.008	35
.01 NaCl	*p*H 10.2	100	.009	55
.03 NaCl	Th(IV)	50	.003	55
.10 NaCl	Th(IV)	50	.003	30
.015 Na_2SO_4		50	.009	20
.005 Na_2SO_4	*p*H 10, silicate	100	.004	70†
.015 $MgCl_2$		50	.01	−10
.02 $MgCl_2$	Th(IV)	40	.005	45
.015 $MgSO_4$		55	.008	5
.015 $CaCl_2$		50	.01	−5
.03 $CaCl_2$	Th(IV)	35	.006	40

* Where mentioned, *p*H was adjusted with $NaHCO_3$ or Na_2CO_3; Th(IV) concentration, $10^{-3}M$; silicate concentration, 0.007*M*. † Based on analysis with ^{24}Na.

jection was correspondingly increased for a given NaCl concentration when the pH was raised (Table 1); with $0.03M$ NaCl, rejection increased from about 10 to 35 percent with increase in pH from 6 to 10; with $0.01M$ NaCl, from 35 to 55 percent between pH 9.4 and 10.2. The greater rejection observed with $0.01M$ than with $0.03M$ NaCl at pH about 10 is in the direction expected for an ion-exchange mechanism.

Permeation rates increased with time, the increase being much more rapid at high pH; this we attribute to dissolution of the glass, and this explanation is supported by surface-area measurements (*8*). These changes in permeability could be minimized by addition of sodium silicate to the feed.

As to the other technique for increasing charge density on the silica, we had little or no success in increasing rejection by treating the glass with several polyvalent cations [for example, Fe(III), Zr(IV), Bi(III), Al(III)], but the conditions tested so far are by no means exhaustive. Rejection was substantially modified by addition of thorium salts to the solution under study. For example, a frit which rejected 6 percent of solute from a $0.03M$ NaCl solution rejected 63 percent of total chloride during pretreatment with a solution $0.03M$ in NaCl and $0.05M$ in $ThCl_4$; it then rejected 55 percent of the salt from a solution $0.03M$ in NaCl and $0.001M$ in $ThCl_4$ and 31 percent from a solution $0.1M$ in NaCl and $0.001M$ in $ThCl_4$. The permeation rate was about 0.0035 cm hour^{-1} atm^{-1} [or (cm^3/cm^2) hour^{-1} atm^{-1}] before addition of thorium and 0.0025 cm hour^{-1} atm^{-1} in the presence of Th(IV). Although this example is typical, reproducibility with Th(IV) added is low (about ± 10 percent); frit behavior is to some extent dependent on past history.

Presumably adsorption of thorium converted the frit to an anion-exchange membrane of higher capacity than the untreated silica, a modification perhaps foreshadowed by earlier work on the properties of silica gel (*11*). With a feed of $0.015M$ $MgCl_2$ or $CaCl_2$ alone, the effluent was 5 to 10 percent more concentrated than the feed. With $ThCl_4$ added to bring the feed to $0.001M$ Th(IV), rejection (based on total chloride) from 0.02 to $0.03M$ $MgCl_2$ or $CaCl_2$ solutions was 40 to 50 percent. The permeation rate of the frit used in these experiments was about 0.01 cm hour^{-1} atm^{-1} in the absence of thorium and fell to about 0.005 cm hour^{-1} atm^{-1} when thorium was added.

From a practical point of view, the rejections are high enough to warrant at least marginal interest. Permeabilities (Table 1) of the frits studied are not striking, but should be quite high if thinner membranes can be prepared on supports having large pores, the glaze then being leached to form a fine-porosity Vycor layer. For a 1-μ layer, transmission is calculated at about 10 cm hr^{-1} atm^{-1}, compared to 0.01 to 0.1 cm hr^{-1} atm^{-1} for cellulose acetate, equivalent to production rates, at 100-atm pressure, of about 60 gal ft^{-2} day^{-1} (2.4 m day^{-1}) for a 100-μ layer and 600 gal ft^{-2} day^{-1} for a 10-μ layer. Over the range of pressure studied by us, permeation per atmosphere and rejection are independent of pressure for a given frit.

Although the rejection properties of Vycor glass can be understood qualitatively in terms of ion-exchange properties of the solid and of their modification, we have not yet progressed to the point of testing to what extent simple theory can adequately explain rejection quantitatively; it appears clear that filtration of polyvalent cations by the glass in cation-exchange form is more complicated than simple ion-exclusion rejection.

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References and Notes

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Lunar Experiments: The Moon as a Site for Certain Physical Measurements

Abstract. *If the lunar surface becomes available for conducting physical experiments, it may be particularly suited to thermal neutron and molecular and atomic beam measurements. The application of these beams for the purpose of communication on the lunar surface appears possible.*

Because of freedom from atmospheric absorption and scattering, the surface of the moon should be an ideal location for conducting certain experiments with elementary particles. Some experiments of this nature are discussed in this report, and a possible application of particle beams on the moon's surface will be suggested.

As a consequence of a gravitational acceleration of 167 cm sec^{-2}, the escape velocity of a particle at the moon's surface is only 2.4×10^5 cm sec^{-1}. However, this limit is still sufficiently high to hold in trajectories those protons and neutrons whose energies are less than approximately 0.03 ev. This energy is slightly above the most probable thermal energy (kt) at 300°K. Thus thermal neutrons, and thermal molecular and atomic beams, should provide suitable particle sources for experiments at the moon's surface.

The velocity of a particle which describes a circular orbit at the moon's surface is 1.7×10^5 cm sec^{-1}. As first pointed out by Aston (*1*), and as subsequently analyzed by Purcell (*2*) and others for electrostatic forces, the force field, described by the inverse-square law, of spherical symmetry has the interesting property that particles of the correct energies, traversing great circle paths, are partially focused after 180°. Such transmissions could be very useful for the purpose of communication on the moon's surface where, because of the absence of an ionospheric layer, radio-wave transmission will not be as straightforward as on the earth's surface (*3*). In order to inspect the feasibility of particle transmissions, the following considerations of beam intensities were made.

According to Ramsey (*4*), beams of neutral Na and K atoms have been detected with intensities as low as 5 to 10 atoms per second. (The maximum sensitivity appears to have been achieved for alkali metal atoms with