

Criterion of Ion Separation by Reverse Osmosis

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Synopsis

The order of ion separation by the NS-100 membrane differed slightly from that of the cellulose acetate membrane. The separation of an ion by the NS-100 membrane increased with increase in the valence of the ion, but decreased with the increase in the ionic radius. The sole criterion determining this separation order for the NS-100 membrane was the enthalpy of hydration. An ion having a higher enthalpy of hydration is bulkier in the hydrated form and is, therefore, separated more effectively by the NS-100 membrane, according to the diffusional model of solute separation. The permeability of an ion through the membrane material can be related to its enthalpy of hydration. By using this relationship, the separation of individual ions in aqueous solution with a given NS-100 membrane can be predicted from a test with a sodium chloride solution.

INTRODUCTION

Reverse osmosis has gradually become one of the major separation processes. Although the physicochemical criteria of organic removal by reverse osmosis have been studied extensively,¹⁻⁷ there is only limited theoretical work being done regarding the separation of inorganic salts.⁸

Glueckauf⁹ has analyzed the repulsive forces between ions and a porous membrane material using the reverse osmosis operating conditions. Bean,¹⁰ on the other hand, has analyzed the diffusion of ions through pores and the electrostatic force which causes ions to avoid a region of low dielectric constant. Solute separation conducted in these studies was expressed as a function of molecular parameters, such as pore size, dielectric constant, ionic radius, ionic charge, etc. Although both of these analyses were based on sound physical parameters of the membrane material and the ions under study and even though both studies generally agreed qualitatively in their experimental results, their final equations were too complicated to have much practical use.

Sourirajan⁸ has also shown that separation of inorganic ions by cellulose acetate membrane is in the order of the lyotropic series of ions. However, this criterion of separation has a few exceptions. In addition, the lyotropic number cannot be used as a parameter to predict quantitatively the ion separation with cellulose acetate membranes.

A crosslinked polyethylenimine membrane, commonly known as NS-100, was employed in this study. The NS-100 membrane was first developed by Cadotte and Rozelle¹¹ and subsequently studied extensively by Chian and Fang.^{1-3,12,13} This is a composite membrane consisting of a microporous

polysulfone support coated with an ultrathin layer of polyethylenimine. The latter is further crosslinked with *m*-tolylene 2,4-diisocyanate. This membrane gives an excellent separation of salts as well as low molecular weight polar organic compounds, and has a good stability over a wide range of pH (2–12).

The objective of this work was to study the criterion for the separation of inorganic ions with the NS-100 membrane. Hopefully, it can be used to predict the separation of other salts from data obtained with a reference salt solution of sodium chloride.

EXPERIMENTAL

Three NS-100 membranes were fabricated and tested with a number of inorganic salts. The procedures of NS-100 fabrication were discussed in detail elsewhere.^{11,13} The stainless steel test cells based upon Manjikian's design¹⁴ were used for this study. The effective area of each membrane was 3.14 in.²

Each test solution was prepared by dissolving the specific inorganic salt of interest in deionized water at a concentration of 0.1 mole/l. The testing conditions for each solution were 600 psig and 25°C at a feed flow rate of 0.3 gal/min. The membranes were first tested with a sodium chloride solution followed by eight different salts of chloride and three additional sodium halides. Finally, each membrane was tested another time with the sodium chloride solution in order to examine the reproducibility of the solute separation and any possible deterioration of the membrane material.

The concentration of individual salt in an aqueous solution containing a single solute was measured with a Yellow Spring Conductivity Bridge, Model 1485 (Cole-Parmer, Chicago, Ill.). The concentrations of individual cations in an aqueous solution containing multiple solutes were measured by a Beckman atomic absorption unit, Model 485 (Fullerton, Calif.)

RESULTS AND DISCUSSION

All of the membranes tested gave satisfactory reproducibility and showed no sign of deterioration, according to both the initial and the final tests with the sodium chloride solution.

Similar to the cellulose acetate membranes, the NS-100 gave better separation of the bivalent ions than the univalent ions. Nevertheless, for ions having the same valence, the separation with the NS-100 membrane increased with the decrease of ionic radius,¹⁵ i.e., $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{NH}_4^+$; $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$; $\text{Mg}^{2+} = \text{Co}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$. This general rule, however, was not followed with the cellulose acetate membrane, which showed that the order of separation for the bivalent cations was $\text{Mg}^{2+} = \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+}$.¹⁰ The discrepancy in the separation order of ions between these two membranes may be due to the weak anion exchange properties of the NS-100 membrane.

A single ionic parameter which can be used to show these orders of separation for the NS-100 membrane is the enthalpy of hydration. Figure 1 illustrates a plot of the relative permeability of cations against the enthalpy of hydration of these ions. The relative permeability P of an ion is defined as

$$P = \frac{C_p}{C_f} \times 100\%$$

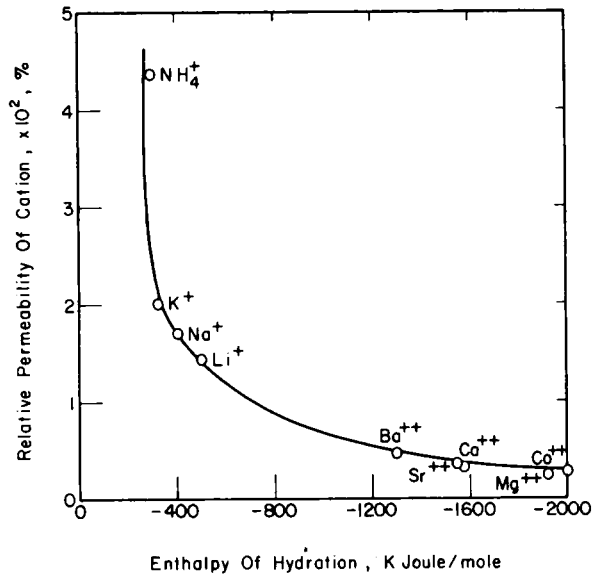


Fig. 1. Relative permeabilities of cations.

where C represents molar concentration of an ion, and subscripts p and f represent permeate and feed solutions, respectively. The separation S is hence defined as

$$S = 100\% - P \tag{1}$$

The data of relative permeability for the nine cations tested, including both uni- and bivalent ions, fall nicely on a smooth curve. A similar plot for the four anions tested is illustrated in Figure 2.

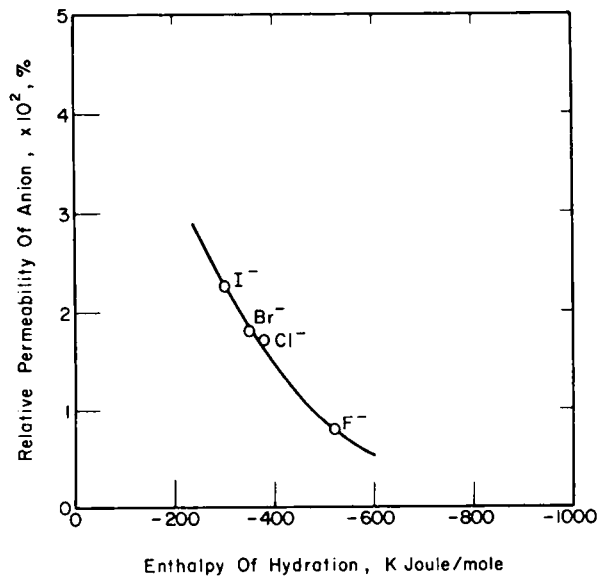
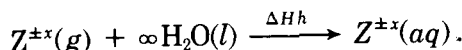


Fig. 2. Relative permeabilities of anions.

The enthalpy of hydration of an ion¹⁵ is defined as the enthalpy released in the following process:



The higher the enthalpy of hydration of an ion, the more the water molecules will form a hydrated complex with the ion in aqueous solution. Better separation of the ion with the NS-100 membrane is attributable to the bulkiness of the hydrated ion. The smooth curves shown in Figures 1 and 2 indicate that the enthalpy of hydration is the sole criterion determining the order of separation of ions, either uni- or bivalent, with a given NS-100 membrane.

By arbitrarily choosing sodium ion as a cation reference, the reduced permeability \bar{P}_c and the reduced enthalpy of hydration $\overline{\Delta H}_{ch}$ of a cation are defined as follows:

$$\bar{P}_c = P_c / P_c^\circ$$

and

$$\overline{\Delta H}_{ch} = \Delta H_{ch} / \Delta H_{ch}^\circ$$

where the superscript zero represents a property of reference ion; subscripts *c* and *h* represent cation and hydration, respectively. A plot of reciprocal of \bar{P}_c versus $\overline{\Delta H}_{ch}$ for various cations falls on a straight line, as shown in Figure 3. The linear regression equation for the cations can be given as follows:

$$\bar{P}_c^{-1} = 1.44 \overline{\Delta H}_{ch} - 0.44 \quad (2)$$

or

$$P_c = \frac{P_c^\circ}{1.44 \frac{\Delta H_{ch}}{\Delta H_{ch}^\circ} - 0.44} \quad (3)$$

Similarly, by choosing chloride ion as a reference anion, the reduced properties of an anion are defined as

$$\bar{P}_a = P_a / P_a^\circ$$

and

$$\overline{\Delta H}_{ah} = \Delta H_{ah} / \Delta H_{ah}^\circ$$

where subscript *a* represents a property of anion. Figure 4 again illustrates the linear relationship between \bar{P}_a^{-1} and $\overline{\Delta H}_{ah}$ which can be expressed as

$$\bar{P}_a^{-1} = 2.85 \overline{\Delta H}_{ah} - 1.85 \quad (4)$$

or

$$P_a = \frac{P_a^\circ}{2.85 \frac{\Delta H_{ah}}{\Delta H_{ah}^\circ} - 1.85} \quad (5)$$

The simple function as shown in eqs. (3) and (5) provides a basis for predicting the permeability of a salt through a given NS-100 membrane. By testing with a sodium chloride solution, the relative permeabilities of both references, i.e., P_c° and P_a° , can be determined. Therefore, the relative per-

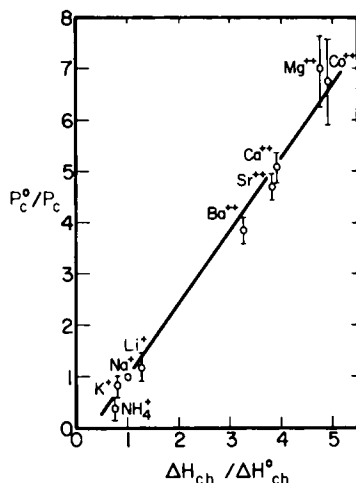


Fig. 3. Reduced permeabilities of cations.

meabilities of both cation and anion of another salt, i.e., P_c and P_a , can be calculated from their respective enthalpies of hydration using eqs. (3) and (5).

In a feed solution containing a mixture of salts, the permeability of an ion depends not only on its concentration in the feed solution but also on the presence of other ions. In a neutral pH solution, in which the concentrations of both hydronium and hydroxide ions are relatively low, the concentration of individual cation and anion in the permeate solution can be estimated by the following equations:

$$C_{pi} = A_{ci} C_{fi} P_{ci} \quad (6)$$

$$C_{pj} = A_{aj} C_{fj} P_{aj} \quad (7)$$

where subscripts i and j represent i th cation and j th anion, respectively. The parameters A_c and A_a in eqs. (6) and (7) are governed by the electroneutrality of the permeate solution as given in the following equation:

$$\sum n_i C_{pi} = \sum n_j C_{pj} \quad (8)$$

where n is the valence of the respective cation or anion.

By substituting eqs. (6) and (7) into eq. (8) and assuming the parameters A_c and A_a to be identical respectively for all species of cations and anions, the following equation is obtained:

$$A_c = \left(\frac{\sum n_j C_{fj} P_{aj}}{\sum n_i C_{fi} P_{ci}} \right) A_a \quad (9)$$

The parameter A_a can be estimated from eq. (7) by measuring the concentration of an anion in both the feed and the permeate solutions and its relative permeability, P_a , determined from eq. (5); the parameter A_c is hence calculated from eq. (9). Accordingly, the concentrations of other ions in the permeate solution can be estimated from eqs. (3), (5), (6), and (7) with the known feed concentrations.

The validity of eqs. (6), (7), and (9) was examined by the following experiments. Two NS-100 membranes were first tested with a 0.1M sodium chlo-

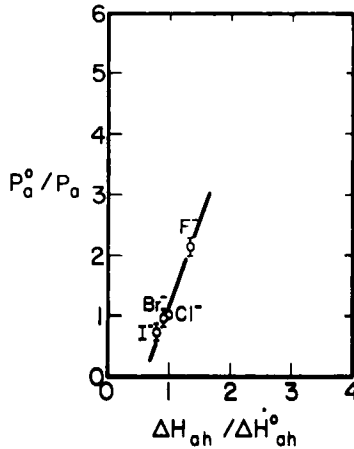


Fig. 4. Reduced permeabilities of anions.

ride solution followed by a solution containing a mixture of salts, including sodium chloride, potassium chloride, barium chloride, and magnesium chloride at a concentration of 0.025M for each salt. Since chloride was the common anion employed in this experiment, the permeability of chloride ion was assumed constant in both the sodium chloride solution and the solution containing a mixture of these salts. As a result, parameter A_a is equal to unity; the separation of individual cations of known concentration in the feed solution can then be estimated from eqs. (3), (6), and (9). The experimental results and the predicted values are given in Table I. It is seen that close agreement is obtainable between the observed and the predicted values at two levels of salt separation under study.

Agrawal and Sourirajan¹⁶ have developed a model for predicting the separation of individual cations in aqueous solution containing two solute systems with the cellulose acetate membrane. They have also successfully extended their model developed for the two solute systems for the prediction of separation of individual cations from an aqueous solution containing four solutes, such as those employed in this study. This study, however, offers another approach in predicting separation of individual ions from a mixture of multiple solutes in aqueous solution with the newly developed NS-100 membrane. Results of this study have shown that the enthalpy of hydration of ions appears to be a simpler criterion for being used to predict the separation of salts in aqueous solution with the NS-100 membrane.

TABLE I
Prediction of Separation of Individual Cations in Aqueous Solution Containing
a Mixture of Metallic Chloride

Cation	Membrane 1		Membrane 2	
	Observed, %	Calculated, %	Observed, %	Calculated, %
Sodium	97.56	97.29	95.25	92.02
Potassium	97.50	96.15	88.67	88.77
Barium	99.18	99.35	98.97	98.09
Magnesium	99.28	99.59	99.10	98.79

CONCLUSIONS

Like the cellulose acetate membrane, the NS-100 membrane separates the bivalent ions more effectively than the univalent ions. However, unlike the cellulose acetate membrane, the separation of ions of the same valence with the NS-100 membrane increases with the decrease of ionic radius. The enthalpy of hydration of an ion can be used as a sole parameter to determine the ionic separation with a given NS-100 membrane. An ion of higher enthalpy of hydration is bulkier in its hydrated form, and hence is separated more effectively.

The simple relation between the relative permeability of an ion and its enthalpy of hydration enables one to predict the separation of an individual ion in aqueous solution based upon a single test with sodium chloride solution.

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