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NOTE

Mechanism of Separation of Metal Ions by Reverse Osmosis*

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Abstract

Reverse osmosis separation data of metal ions using cellulose acetate membranes have been correlated with the water exchange rate constants of the aquo metal ions. This correlation has been found useful in predicting solute separation of the metal ions and also in explaining the mechanism of solute separation by reverse osmosis.

INTRODUCTION

The reverse osmosis separation of metal ions in aqueous solutions using porous cellulose acetate membranes has been discussed in the literature from several points of view. The solution-diffusion mechanism of Lonsdale et al. (*1*) requires that the solute and solvent dissolve in the membrane material and permeate through the membrane by diffusion through the homogeneous nonporous surface layer. Anderson and Heyde (*2*) have proposed a mechanism based on experimental partition coefficients of ionic solutes between water and cellulose acetate membrane material. The selectivity of membranes for different ions has been explained in terms of the relative free energy of interaction of ions between water and membrane material (*3–6*).

The analyses of Glueckauf (*7*), Bean (*8*), and Dytnerskii (*9*) explicitly recognize that the surface layer (skin) of the membrane is microporous and heterogeneous. According to Dytnerskii (*9*), the relative strength of

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the hydration envelope of ions governs solute separation and liquid permeation rate for a given membrane. According to the preferential sorption-capillary flow mechanism of Sourirajan (*10, 11*), the reverse osmosis separation is governed by the relative magnitude of net repulsion of the solute molecules at the membrane solution interface and the porous structure of the membrane surface.

The reverse osmosis process has been used in the treatment of metal-bearing effluents encountered in mining and metallurgical fields (*12–16*). Although reverse osmosis has been applied with success in the treatment of waste solutions and in producing product water of reasonable purity, the actual mechanism of separation of metal ions has not been established with certainty. Hence the work presented in this paper was undertaken to throw some light on the mechanism of separation of metal ions by reverse osmosis.

EXPERIMENTAL

The flow-type cell and the schematic diagram of the flow-type experimental set-up were the same as reported earlier (*13*). Cellulose acetate membranes were prepared under film casting conditions reported in earlier studies (*13*). The membranes, preshrunk under water at different temperatures (72 to 82°C), were initially subjected to a pure water pressure of 350 psig for 1 to 2 hr before subsequent use in reverse osmosis experiments at an operating pressure of 250 psig. In each experiment the pure water permeation rate, the membrane-permeated product rate per given area of film surface, and the solute separation were determined at preset operating conditions. Aqueous feed solutions containing 3500 mg/l of sodium chloride were used to obtain membrane specification data. The concentrations of sodium chloride in the feed and the product solutions were determined by specific resistance measurements. The feed and the product solutions containing Cu, Zn, Mn, Fe, Co, Al, and Cr were analyzed by atmoic absorption spectrophotometry. The specifications of membranes and the feed flow conditions were the same as reported in earlier studies (*13, 14*).

RESULTS AND DISCUSSION

The data on the reverse osmosis separation of various metal ions using six cellulose acetate membranes of different porosities together with the rate constants for water exchange are given in Table 1. The values

TABLE 1

Data on the Reverse Osmosis Separation of Metal Ions

	Metal ion				
	Cu^{2+}	Zn^{2+}, Mn^{2+} Fe^{2+}, Co^{2+}	Ni^{2+}	Al^{3+}	Cr^{3+}
Rate constant for water exchange k (sec^{-1})	8×10^9	2×10^7	3×10^4	6.3×10^{-1}	3.5×10^{-6}
Solute separation (%)					
Film 1	94.31	95.60	97.54	98.29	99.02
Film 2	90.92	91.60	97.29	96.57	97.50
Film 3	86.08	89.70	95.94	95.29	97.05
Film 4	81.85	85.50	89.33	93.04	97.05
Film 5	73.92	82.23	82.22	90.69	95.96
Film 6	67.08	77.78	75.90	88.87	94.98

of the rate constants for water exchange were taken from the literature (*17*, *18*). Before discussing these results, it is useful to digress for a moment and introduce some concepts which are helpful in discussing the mechanism of separation of metal ions by reverse osmosis. It is necessary to consider thermodynamic properties of salt solutions, their structures, and steric factors to explain the variations in permeability and selectivity of membranes for various salt solutions. Based on modern concepts of the structure of electrolyte solutions, it is reasonable to state that the selectivity and permeability of membranes are influenced by the degree of hydration or, in general, solvation of ions. The hydration phenomenon is due to the fact that ions in solution are surrounded by and move together with a certain number of bound solvent molecules. The two types of hydration are primary (proximate) and secondary (or remote) hydration. Primary hydration consists of a strong bonding between the ion and water molecules, while secondary hydration involves an electrostatic type of bonding between the ion of primary hydration and the solvent water molecules. Chemical bonding becomes prominent when the central ion, with an incomplete electron shell, forms stable complexes. In the case of ions with a completely filled electron shell, coulomb forces of attraction, which depend on the charge and crystallographic radius of the ion, are predominant.

Keeping in mind the above concepts, the process of selective permeability of membranes can be viewed as follows. An equilibrium film of bound water exists both on the surface and inside the capillaries of lyophilic membranes submerged in an aqueous solution of an electrolyte. The membranes contain capillaries of various dimensions including large ones containing free water. Initially the flow of liquid under pressure leads to a disturbance of this equilibrium and results in a decrease in the thickness of the film of bound water on the surface of the membrane. The equilibrium is restored as the membrane interacts with the water molecules coordinated to the ions and removes the water molecules. As a result the sizes of the hydrated ions are reduced and they can pass through the capillaries containing free water. The degree of removal of water attached to various ions depends on the forces of interaction between the ion and the solvent, and the membrane and the solvent. This leads to the fact that a metal ion can exchange the coordinated water with water molecules on the membrane surface thus:

$$M(H_2O)_n{}^{m+} + H_2O_{(M)} \overset{k}{\rightleftarrows} M(H_2O)_{(n-1)}(H_2O)_M{}^{m+} + H_2O$$

Thus a metal ion which can exchange its coordinated water with water molecules on the membranes with facility is likely to permeate through the membrane with ease, resulting in low separation. On the other hand, a metal ion which exchanges its coordinated water slowly should result in high separation. The data given in Table 1 show that the rate constants for water exchange process follow the order $Cu^{2+} > Zn^{2+}$, Mn^{2+}, Fe^{2+}, $Co^{2+} > Ni^{2+} > Al^{3+} > Cr^{3+}$. In general the solute separation follows the order $Cu^{2+} < Zn^{2+}$, Mn^{2+}, Fe^{2+}, $Co^{2+} < Ni^{2+} < Al^{3+} < Cr^{3+}$. Thus there is a correlation between the solute separation and the rate constants for the water exchange process. This correlation allows one to predict from the rate constants for the water exchange process whether the solute separation will be low or high in the case of the metal ions in question.

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