The Effect of Chelation on the Selective Transport of Alkaline-Earth Metal Ions in Asymmetric Cellulose Acetate Hyperfiltration Membranes

K. L. LEE, H. B. HOPFENBERG, and V. T. STANNETT, *Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27607*

Synopsis

The rejection of calcium and/or magnesium ion by asymmetric cellulose acetate hyperfiltration membranes is increased significantly by formation of the corresponding alkaline-earth metal chelate. Typically solute fluxes are reduced by a factor of 5 consequent to chelation with ethylenediaminetetraacetic acid (EDTA) at pH 6.0. Selective chelation and, in turn, selective transport of magnesium is observed when equimolar solute mixtures corresponding to 1:1:1 magnesium:calcium:EDTA are hyperfiltered. Under these conditions, calcium successfully competes for the stoichiometrically limiting EDTA, and the rejection of magnesium is lower than the rejection observed for the hyperfiltration of the MgEDTA^{2-} complex in the absence of competitive calcium. Alternatively, the rejection of the CaEDTA^{2-} complex is increased under these identical conditions, presumably as a consequence of specific interactions between the available free magnesium and the cellulose acetate membrane. The effects reported here all seem to be related to reductions in solute diffusivity associated with the increased size of the alkaline-earth metal ion complex.

INTRODUCTION

Work is in progress to study the effect of selective chelation on the hyperfiltration of feed solutions containing mixtures of magnesium and calcium ions. The selectivity normally achieved in hyperfiltration of aqueous solutions of mixed salts is generally related explicitly to cation size, valence, solubility in the membranes, membrane structure, and the complex colloid and electrochemical effects which maintain at the interface between the feed solution and the membrane surface.[1-4]

The study reported here was motivated by the notion that the rejection of cations could be increased significantly consequent to chelation; and moreover, under specified conditions of ionic strength and pH, selective chelation and, in turn, selective ion transport could be effected. Presumably, the major effect resulting from chelation is dramatic alteration of the size and shape of the ionic diffusant. Alternatively, significant alteration in the effective solubility of the complexed metal ion may also contribute to the observed transport behavior. In most cases, charge reversal from cationic to anionic functionality is an additional and significant effect of chelation.

EXPERIMENTAL

Asymmetric cellulose acetate membranes, designated CA-70, CA-75, and CA-85, were annealed at 70, 75, and 85°C, respectively. These membranes were prepared at and kindly provided by Max Planck Institute for Biophysics in Frankfurt, Germany, using a casting process similar to that described by Manijikian et al.[5]

ACS reagent-grade magnesium chloride hexahydrate and calcium chloride dihydrate of 99.5% minimum purity were supplied by Fisher Scientific Co. and were used without further purification. Ethylenediaminetetraacetic acid (EDTA) and ethylenebis(oxyethylenenitrilo)tetraacetic acid (EGTA) were obtained from Fisher Scientific Co. and J. T. Baker Co., respectively, as free acids. Their purities were determined by titrimetry to be better than 99.9%. These chelating agents were solubilized with two equivalents of sodium hydroxide.

Hyperfiltration experiments were conducted over the pressure range of 0–300 psi in a continuous, recirculating test loop which effectively eliminated concentration polarization. The experimental program reported here consisted of hyperfiltration experiments involving the individual salts in the presence and absence of equivalent concentrations of chelating agent. Alternatively, equimolar mixtures of the alkaline-earth metal salts were hyperfiltered in the presence and absence of chelating agents. Chelating agents were added to the mixed salt feed to provide a Mg:Ca:chelating agent ratio of 1:1:1. This ratio was established to permit selective chelation of the inherently more stable metal chelate. In all cases, the feed concentration of each solute specie was fixed at $10^{-2}M$. Additional sodium hydroxide or hydrochloric acid was used to adjust the feed solution to pH 6.0. No buffering materials were used since they might act as auxiliary complexing agents for the metal ions. The concentration of calcium and magnesium ions was monitored by atomic absorption spectrometry,[6] and the concentration of chelating agents was determined by complexometric titration.[7] All hyperfiltration experiments were performed at 25°C.

RESULTS AND DISCUSSION

For a given set of membranes with otherwise identical casting histories, the rejection of solute species typically increases monotonically with the degree of annealing. The set of membranes studied here exhibited this expected behavior, and, for the sake of brevity, attention will be focused on the experiments with the CA-75 membrane which has experienced an intermediate degree of annealing. Presentation of quantitative results will also be confined to experiments using EDTA as the chelating agent. The effects observed with CA-70 and CA-85 membranes as well as EGTA will be reported when the experimental program is completed. The early results suggest, however, that the complete set of data involving all membranes and chelating agents will be consistent with the overall effects discussed here for the CA-75 membrane and EDTA.

The pressure dependence of the rejection of magnesium ion, calcium ion, and the EDTA complexes is presented in Figures 1 and 2. The increase in rejection with increasing transmembrane pressure drop, observed in all cases, is consistent with the solution-diffusion mechanism for solute transport.[8] The rejection of the metal chelates of calcium and magnesium was much higher than the rejection
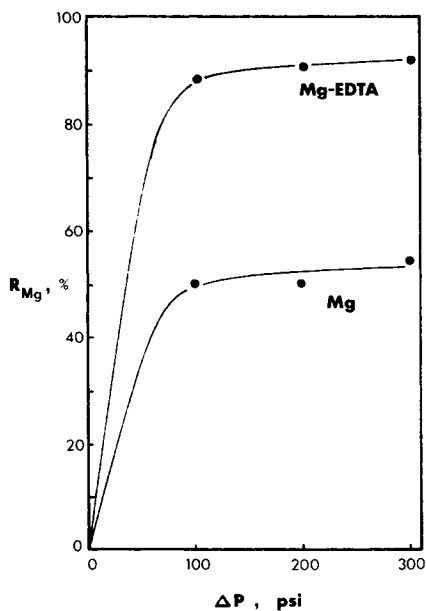
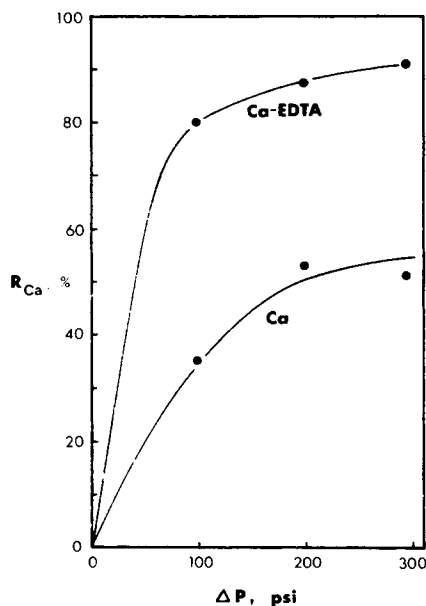Fig. 1. Pressure dependence of the magnesium rejection by a CA-75 membrane in the presence and absence of EDTA.

Fig. 2. Pressure dependence of the calcium rejection by a CA-75 membrane in the presence and absence of EDTA

of the unbound cations. The analysis of the permeate involved independent determination of the concentrations of metal ion and EDTA. In most cases, equimolar ratios of metal ion to chelating agent were observed in the permeate, confirming the somewhat obvious hypotheses that virtually all of the metal ions are bound and that virtually all of the metal ions that are transported are

transported as complexed species. EDTA forms a 1:1 equimolar complex with the alkaline-earth ions.[13] The stable complex carries a double negative charge. In a solution of $CaCl_2$ and EDTA at pH 6, for example, the $CaEDTA^{2-}$ complex exists to the virtual exclusion of all other complexed species. In the 1:1:1 ternary system containing both metal ions and EDTA, calculations based upon the equilibrium or stability constants reported by Schwarzenbach and Ackermann[13] suggest that about 98% of the calcium and only 0.4% of the magnesium is in the form of $CaEDTA^{2-}$ and $MgEDTA^{2-}$, respectively. The remainder of the metal exists as unbound ions, although they are most likely present in a variety of hydrated forms.

In terms of solute fluxes, the free cations permeated about five times as rapidly as the respective metal chelates. Chelation by EDTA apparently increased magnesium and calcium rejections about equally, and these increases are most likely a consequence of the increased size of the resulting metal complex compared with the size of the unbound, albeit hydrated, metal ion. The rejection of unbound EDTA, at the same pH, was only slightly lower than the rejections reported here for the metal complexes, confirming the notion that, for these specific cases, the observed solute transport is largely controlled by the size and shape of the diffusing solute.

Alternatively, in related cases, complexation with an organic sequestering agent may increase the apparent solubility of the metal ion in the essentially nonpolar membrane. Determinations of the distribution coefficient of EDTA and magnesium ion indicate that EDTA is indeed approximately 400 times more soluble in cellulose acetate than is magnesium ion. This increase may be sufficient to overcome the competitive effect of decreased diffusivity related to size and shape per se. The overall result, for these limiting cases, could actually be augmented transport of the solute species consequent to chelation. Specifically, it is anticipated that, in certain limiting cases, chelation with relatively small sequestering agents will result in higher solute transport and, therefore, lower solute rejection. Clearly, however, the results described here seem to be controlled by kinetic effects related to the size and shape of the complexed metal ion.

The pressure dependence of the rejection of magnesium and calcium in an equimolar admixture of the two salts is presented in the lower curves in Figures 3 and 4, respectively. Comparison of the lower curves of Figures 1 and 2 with the lower curves of Figures 3 and 4 suggests that the rejection of each ion is virtually unaffected by the presence of a stoichiometric equivalent of the other free alkaline-earth ion. For example, the corresponding curves in Figure 2 and 4, depicting the calcium rejection in the presence and absence of magnesium ion respectively, essentially superimpose.

The pressure dependence of the rejection of the various free and complexed ions, in ternary solute systems, is presented in Figures 3 and 4 for magnesium and calcium, respectively. The magnesium rejection was significantly lower in the presence of calcium and EDTA than in the presence of EDTA alone. This is most likely a consequence of the successful competition by calcium ion for the stoichiometrically limited amount of EDTA present.

In marked contrast, the calcium rejection observed during the hyperfiltration of these ternary solute feeds was, in fact, measurably *higher* than the calcium rejection observed during hyperfiltration of feeds containing only calcium and EDTA. The selective chelation, predicted from reported literature values of the stability constants of the magnesium and calcium chelates,[9] are consistent
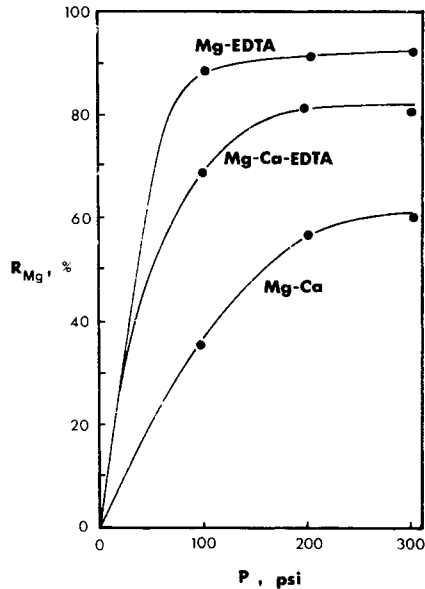
Fig. 3. Pressure dependence of the magnesium rejection by a CA-75 membrane, including the effects of added calcium, added EDTA, and added mixtures of calcium and EDTA on the magnesium rejection.
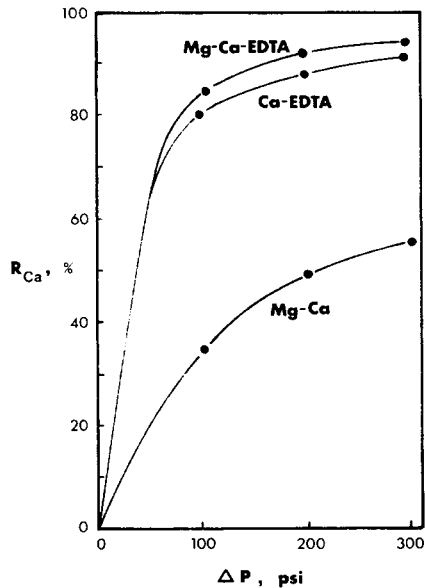

Fig. 4. Pressure dependence of the calcium rejection by a CA-75 membrane, including the effects of added magnesium, added EDTA, and added mixtures of magnesium and EDTA on the calcium rejection.

with the notion that calcium is bound as strongly to the EDTA in the presence of magnesium as it is when calcium and EDTA are simply admixed.

The provocative increase in the rejection of the $CaEDTA^{2-}$ complex in the presence of magnesium is quite consistent with results recently reported by Drioli et al.[10] where quite similar effects have been noted for hydrated aluminum ion

interactions with the CA-75 membrane. Although the calcium competes effectively for the available EDTA, the hydrated magnesium ion may interact with the microporous structure of the asymmetric cellulose acetate membrane essentially "plugging" the membrane and, thereby, increasing the inherent rejection to the calcium complex. Alternatively, the presence of the more permeable magnesium chloride may actually decrease the sorption of the relatively impermeable calcium chelate salts, resulting in a still higher rejection of the $CaEDTA^{2-}$. This effect has been described in detail recently by Heyde and Anderson[14] and has been explained in the context of those various independent ionic exclusion phenomena which are all commonly presented as "Donnan" effects.

These early results are completely consistent with the hypothesis that metal ion transport can be significantly affected by the presence of chelating agents, and are gratifyingly consistent with the recently reported complex phenomena observed by other investigators with these identical membranes.[10] The complete scope of the investigation in progress will include study of several of the Group II and Group III metal ions in the presence of a variety of chelating agents chosen to afford selective chelation at pH values consistent with the requirements for stable membrane performance. The seeming anomalies, clearly related to solute–solute and solute–membrane interactions,[4,11,12,14] have been, heretofore, reported as isolated special cases. These observations may be related, however, to a more general set of complex solute–membrane interactions which affect significantly hyperfiltration and dialytic aqueous separations.

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