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

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Synopsis

The effects of chelation on the transport of calcium and magnesium, both separately and in a variety of admixtures, in a controlled series of asymmetric cellulose acetate membranes were characterized.   Ethylenediaminetetraacetic acid (EDTA) and ethylenebis(oxyethylenenitrilo)tetraacetic acid (EGTA) were used as chelating agents for the alkaline earth metal ions.   Asymmetric cellulose acetate membranes annealed at 70°, 75°, and 85°C were studied.   Chelation of each of these alkaline earth metals ions in aqueous solutions at pH 6, by either EDTA or EGTA, significantly increased the overall hyperfiltration rejections of these metals by all the membranes studied.   The increase in rejection varied montonically with the fraction of metal ion complexed.   The higher rejection of metal chelates, compared to the rejection of unbound metal ions, was considered to be the result of the significantly larger size of the chelated species.   Calculations suggested that selective (or competitive) chelation took place at pH 6 in a mixture of calcium and magnesium ions in the presence of a stoichiometrically limiting amount of chelating agent.   Calcium successfully competed for most of the available chelating agent in equimolar aqueous solutions of chelating agent, calcium, and magnesium.   The calcium rejection was explained primarily in terms of the effects of chelation *per se* on the effective size of the formed complex even in feeds comprised of these ternary solute mixtures. The complexation reaction between magnesium and EGTA is, however, so unfavorable at pH 6 that the Mg^{2+} ion remains uncomplexed even in the presence of an equivalent amount of EGTA.   The observed increased rejection of magnesium ions, therefore, in ternary systems was explained by electroneutrality criteria and by solute–membrane interactions involving the various calcium species and the membranes.

INTRODUCTION

Asymmetric cellulose acetate membranes have been used in the past two decades mainly for the pressure-driven separation of solutes from their aqueous solutions.   Typically, for electrolyte feed mixtures involving cations that are members of a common group in the periodic table, such as magnesium and calcium or cobalt and nickel, the individual metal ions are rejected about equally.[1,2]

The present work is motivated by the possibility of improving the hyperfiltration rejection of alkaline earth cations by chelation.   The significantly increased size of the metal chelate compared to the unbound metal ion should result in a lower diffusivity of the metal chelate.   Furthermore, by selectively chelating only one of the metal ion species present in a two-metal ion mixture, the accompanying charge reversal and size increase becomes specific only to the chelated metal.   Selective transport across the membrane is, therefore, expected to be based upon the artificially imposed change in the physicochemical properties of the metal ion that competes successfully for the available chelating agent.

Alternatively, complexation with suitable organic chelating agents may increase the apparent solubility of the metal ion in the membrane to the extent that facilitated transport or even selective facilitated transport of one or more metal species could be achieved.
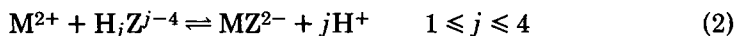
These suggested solute flux changes, induced by specific solute–solute interactions (chelation), form an interesting extension to some previous research work in this area where it was demonstrated that the water fluxes in reverse osmosis/hyperfiltration experiments could be markedly influenced by well-characterized interactions between solute species in the feed solution.[3,4] Since the present solute systems involve rather complex chelation equilibria, which are sensitive functions of solution acidity, it is likely that the observed rejection phenomena might involve the combined effects of solute–solute as well as solute–membrane interactions.[5-7]

The formation of a 1:1 metal–chelate complex MZ^{2-} from a tetrabasic chelating agent Z^{4-} and a divalent metal cation M^{2+} is characterized by the equilibrium constant K_{MZ}:

$$K_{MZ} = \frac{[MZ^{2-}]}{[M^{2+}][Z^{4-}]}$$ (1)

Molar concentrations instead of activities are used in the expression since activity coefficients are rarely known precisely.

Except under strongly alkaline conditions, the dissolved chelating agent is present in a variety of protonated forms depending upon the solution pH. Each of these protonated species is capable of undergoing independent complexation with the metal ions to form anionic 1:1 complexes by the general reaction

$$M^{2+} + H_j Z^{j-4} \rightleftharpoons MZ^{2-} + jH^+ \qquad 1 \leqslant j \leqslant 4$$ (2)

The formation of uncharged M_2Z complexes by alkaline earth metals has been shown to be negligible.[24]

The true thermodynamic equilibrium constant, including the reactions between the metal and all chelating agent species at a specified pH, would be quite cumbersome in its explicit form. It has become customary in chelate chemistry, therefore, to define a "conditional stability constant" $K_{MZ'}$ as follows:

$$K_{MZ'} = \frac{[MZ^{2-}]}{[M^{2+}][Z]'}$$ (3)

in which the combined yield of metal chelate MZ^{2-} from the variously protonated chelating agent anions are expressed in terms of $[Z]'$, the total quantity of chelating agent not yet complexed with the metal ions. Specifically,

$$[Z]' = [Z^{4-}] + [HZ^{3-}] + [H_2Z^{2-}] + [H_3Z^-] + [H_4Z]$$ (4)

The ratio $[Z]'/[Z^{4-}]$ is generally denoted by $\alpha_{Z(H)}$ to indicate the extent of stepwise protonation imposed on the chelating agent at a particular solution acidity. The conditional stability constant written as

$$K_{MZ'} = \frac{K_{MZ}}{\alpha_{Z(H)}}$$ (5)

incorporates the competitive effect of protonation on the main chelation reaction and is invariably used to calculate the extent of complexation and the concen-

tration of all free and chelated species in a system containing one metal and one chelating agent. Simple mass action considerations dictate that, in the absence of interfering reactions such as hydrolysis of the metal ion or complexation between metal ions and any added buffering agent, the conditional stability constant of a metal chelate increases with increasing pH. Ringbom[22] calculated the pH dependence of $K_{MZ'}$ for the single metal–chelate systems containing magnesium or calcium (as M^{2+}) and EDTA or EGTA (as Z^{4-}). His results are shown in Figure 1. The hydrolysis of magnesium and calcium has not been taken into account because the formation of $Mg(OH)_2$ and $Ca(OH)_2$ is insignificantly small below pH 11. Notably, whereas EDTA forms stable equimolar complexes with either calcium or magnesium at pH 6, the EGTA complex of calcium is markedly more stable than the corresponding complex of magnesium, illustrating the chelation selectivity of EGTA for calcium.

Predicting the chelation selectivity in a mixed solution of two metal ions, M_1^{2+} and M_2^{2+}, requires some modification of the conditional stability constant shown in eq. (5). As a result of the mutual interference between the two metal ions, the stability of each metal chelate is lower than its equivalent single metal stability. The competitive effect of M_2^{2+} can be considered a side reaction with
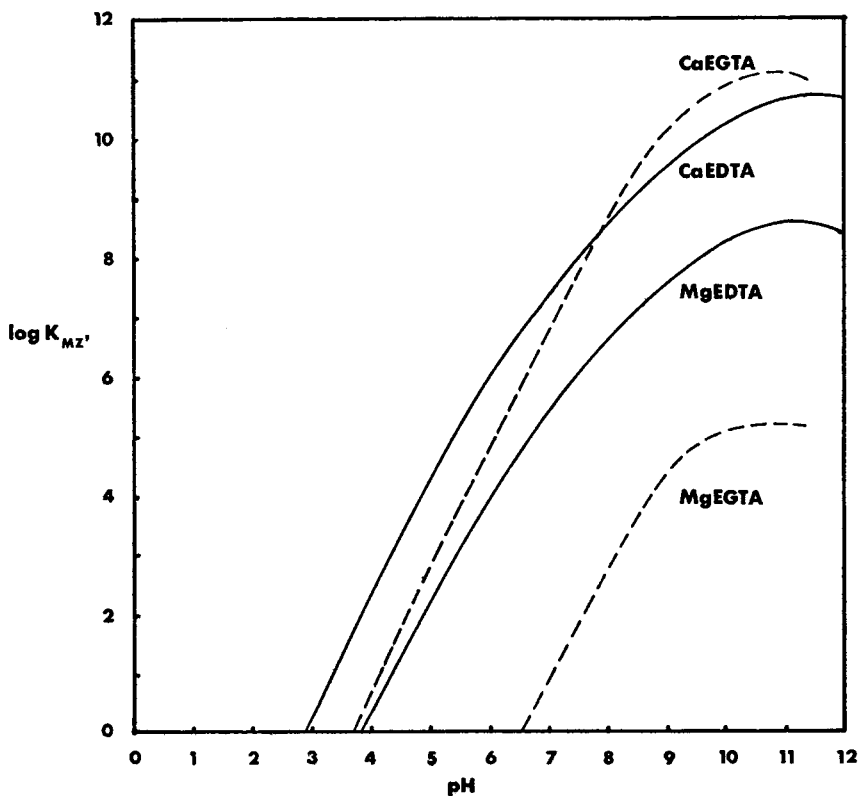

Fig. 1. Conditional stability constants of the magnesium and calcium complexes of EDTA or EGTA in single metal chelate systems. From Ringbon.[22]

respect to the formation of M_1Z^{2-} in a manner similar to the protonation of the chelating agent anion. It can be shown that the conditional stability constant of M_1Z^{2-} in the presence of M_2^{2+} is described by

$$K_{M_1Z'} = \frac{K_{M_1Z}}{\alpha_{Z(H)} \cdot \alpha_{Z(M_2)}} \qquad (6)$$

where $\alpha_{Z(M_2)}$ is defined analogously as $\alpha_{Z(H)}$. The values of the conditional stability constants for the ternary systems studied have been calculated as functions of pH using eq. (6). The results are shown in Figure 2. Concentrations of the various free and chelated species at a given pH can, in turn, be computed from these K values. These calculations have been used in an attempt to provide a concise and meaningful explanation of the effect of chelation on the observed rejection behavior in this present study.

Many previous studies of chelation-assisted separation involve ion exchange methods. The isolation of a particular metal ion can be facilitated by selective chelation. The metal chelate anions would pass through a cation exchange column relatively fast, while the unbound metal cations would be retained. In a recent application of this technique, magnesium was successfully separated from calcium using EGTA as the selective chelating agent.[8]
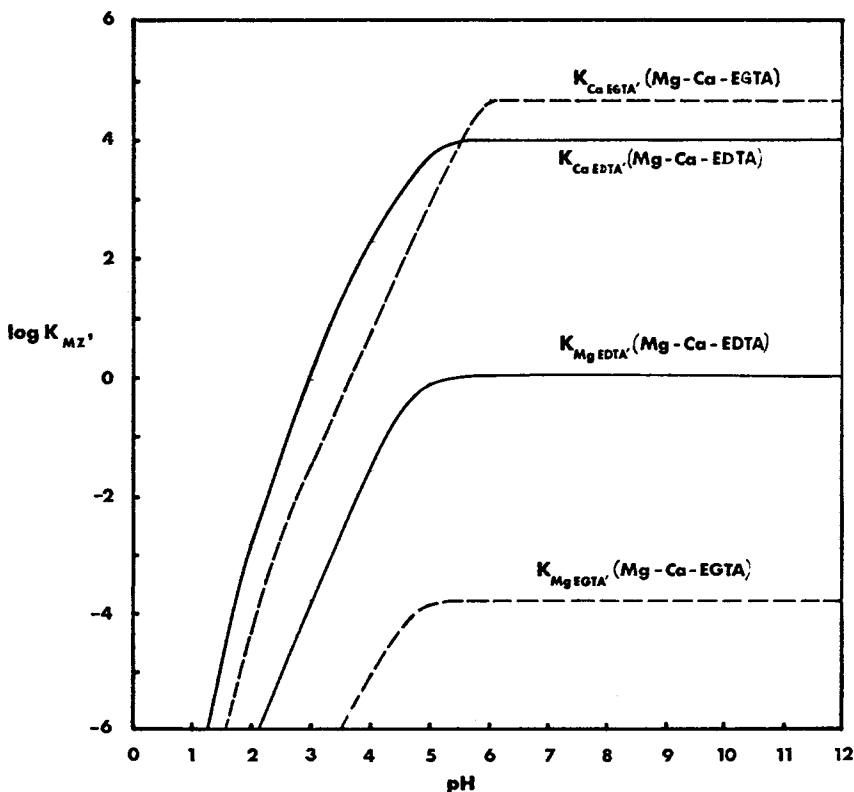

Fig. 2. Conditional stability constants of magnesium and calcium in ternary systems involving EDTA or EGTA.

Electrodialysis has also been used in the separation of cobalt and nickel[2] subsequent to the selective chelation of nickel by EDTA. The uncomplexed cobalt cations and the nickel–EDTA chelate anions would migrate, under an applied electric field, through ion exchange membranes to the cathode and anode, respectively, resulting in a highly efficient separation.

Pressure-driven membrane separation processes have been combined with chelation recently; excess quantities of EDTA were added to hyperfiltration feeds to recover trace concentrations of mercury.[9] The resulting complexation markedly increased the observed hyperfiltration rejection of mercury. The same principle has also been utilized recently in a study of the removal of copper from water.[10] The use of chelating agents to bias solute transport in pressure-driven aqueous membrane separations has not, however, been explored systematically.

The initial phase of this experimental study treats the effect of EDTA chelation of Ca^{2+} and Mg^{2+}.[11] The results reported in this paper extend the earlier experimental program, treating more general cases of chelating agents under stoichiometrically limiting and nonlimiting conditions.

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 the Max Planck Institute for Biophysics in Frankfurt, Germany.[11]

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 equimolar (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 and 1:1:2. In all cases, the unit feed concentration of each solute species 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, and the concentration of chelating agents was determined by complexometric titration.[11] All hyperfiltration experiments were performed at 25°C.

RESULTS AND DISCUSSION

One-Metal Chelate Systems

The effects of chelation on the rejection of magnesium and calcium ions are shown respectively in Figures 3 and 4 as functions of hyperfiltration pressure. The rejection characteristics of CA-70, CA-75 and CA-85 are included.   In all cases, the overall metal rejection increases monotonically with pressure.   The results are consistent with a solution–diffusion type mechanism[12] since the permeation of water is directly proportional to the transmembrane pressure drop whereas the solute flow is largely pressure independent.   A monotonic rela-
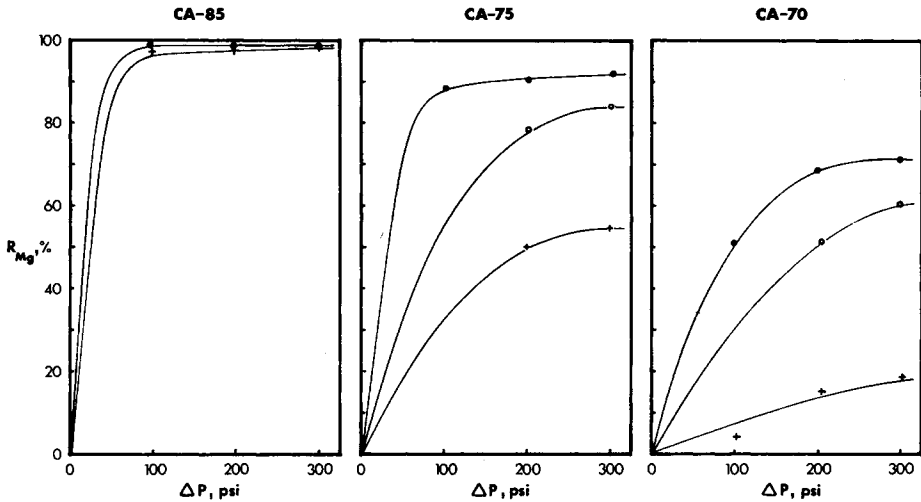

Fig. 3. Pressure dependence of the magnesium rejections by three membranes in the presence *and* absence of EDTA or EGTA: (+) Mg; (●) Mg–EDTA; (○) Mg–EGTA.
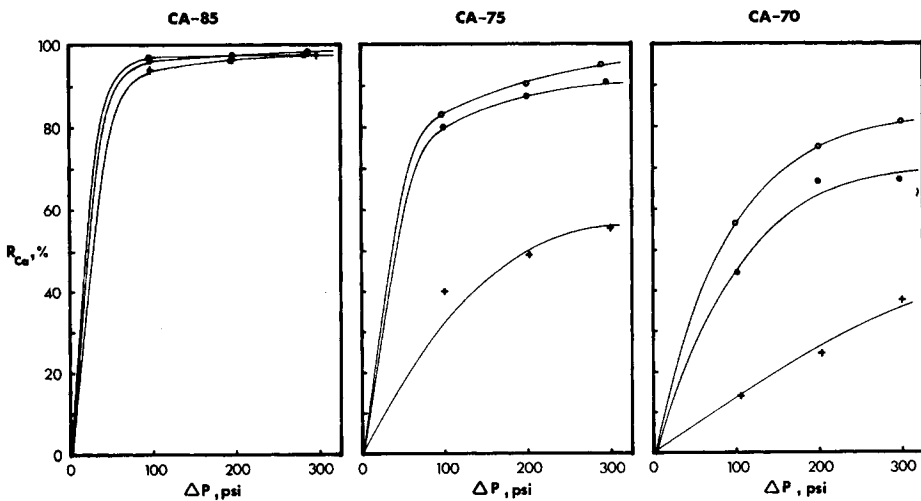

Fig. 4. Pressure dependence of the calcium rejections by three membranes in the presence and absence of EDTA or EGTA: (+) Ca; (●) Ca–EDTA; (○) Ca–EGTA.

tionship between rejection and pressure drop has also been explained by the so-called finely porous membrane model.[13,14] The rejections also increase with increasing membrane annealing temperature since the decrease in solute flux with increasing membrane consolidation is not accompanied by a correspondingly large decrease in water flux.

Chelation of magnesium or calcium by either EDTA or EGTA markedly increases the overall rejection of these alkaline earth metals by the various membranes. EDTA is approximately 400 times more soluble than the magnesium in cellulose acetate membranes at pH 6.[11] This comparison relates equilibrium sorption of EDTA in cellulose acetate determined[23] to be 1.64 (g EDTA/cm^3 polymer) (g EDTA/ml solution)$^{-1}$ in the presence of sodium hydroxide for pH control, with a magnesium partion coefficient of about 0.004, based on an extrapolation of data reported by Heyde et al.[15] The solubility of the MgEDTA^{2-} anion in cellulose acetate membranes may be regarded to have the same magnitude as those of other EDTA anions because the chelate structure effectively shields the center metal ion from the surrounding medium such that the organic nature of the chelate anion is largely preserved. Despite their higher solubilities, both EDTA and EGTA are more highly rejected than either magnesium or calcium. The higher rejections of the metal chelates are presumably a consequence of the significantly larger size of these complexes compared with the unbound though most likely hydrated[16] metal ions. Apparently, the kinetic considerations related to the decreased diffusivity of the metal ion consequent to chelation more than compensated for the increased solubility of the metal chelate. The decreased diffusivity of solute results in an overall observed increase in the metal ion rejection consequent to complexation.

The overall rejection of calcium is higher in the presence of EGTA than in the presence of EDTA. These rejection changes are most noticeable in the CA-75 and CA-70 membranes. CA-85 highly rejects both the unbound metal and the metal chelate and therefore shows a less marked difference in metal rejection in the presence or absence of the chelating agent.

Complete complexation occurs between calcium ions and either EDTA or EGTA at pH 6 in a solution containing equimolar quantities of calcium and the chelating agent. The observed overall calcium rejection is therefore equal to the rejection of the calcium chelate. Measurement of molecular scale models suggests that the characteristic dimension of EDTA and EGTA chelate anions are approximately 11 Å and 15 Å, respectively. The presumably larger CaEG-TA^{2-} chelate anion would then be expected to permeate somewhat more slowly than the CaEDTA^{2-} chelate anion. The data of Figure 4 show that the rejection of CaEGTA^{2-} is indeed higher than the rejection of CaEDTA^{2-} by membranes annealed at 70° and 75°C, apparently supporting a sieve-filtration mechanism since asymmetric cellulose acetate membranes annealed at 60–75°C have been estimated to have mean surface micropore diameters of 10–20 Å.[7,17]

In contrast, magnesium is more highly rejected in the presence of EDTA than in the presence of EGTA. Magnesium chelates almost completely with EDTA at pH 6 but only partially with EGTA under the same conditions. The observed lower overall magnesium rejection is, therefore, due to the presence of a large fraction of unchelated magnesium in the feed solution. The magnesium ions permeate the membranes more rapidly than the MgEGTA^{2-} chelates, which increases the overall magnesium concentration in the permeate and results in reduced overall magnesium rejection.

The effect of the degree of complexation on the overall metal rejection is demonstrated by hyperfiltering feed solutions of various known ratios of free to complexed magnesium ion. The difference in conditional stability constants of the MgEDTA^{2-} and MgEGTA^{2-} chelates is exploited to generate a series of feed compositions with varying ratios of free to complexed magnesium. The solute compositions employed, and the respective calculated fraction of magnesium chelated, are listed in Table I. The overall magnesium rejections from these feed systems are shown in Figure 5 as functions of the calculated fractional chelation. Significantly, the magnesium rejection seems to increase monotonically with the fraction of magnesium chelated, regardless of the type of chelating agent present.

Two-Metal Chelate Systems

Four ternary solute systems are studied in the present work: two feed systems contain magnesium and calcium ions in equimolar quantities plus a stoichiometrically limiting amount of either EDTA or EGTA (e.g., Mg–Ca–Z 1:1:1); and in the other two feed solutions, a concentration of the chelating agent equal to the total metal concentration (e.g., Mg–Ca–Z 1:1:2). The overall rejections of magnesium and calcium in the various ternary systems are shown in Figures 6–9 as functions of transmembrane pressure drop.

Computations using literature values of the stability constants of magnesium and calcium chelates suggest that selective or competitive chelation takes place in a solution of the two metals and either EDTA or EGTA. Specifically, almost no magnesium chelates are formed in the Mg–Ca–Z 1:1:1 systems since calcium successfully competes for all the available chelating agent. By increasing the supply of EDTA to equal the total ion concentration of both metals, about one sixth of the magnesium does, however, become complexed. In the case of the Mg–Ca–EGTA 1:1:2 ternary system, however, the reaction between the magnesium and the available chelating agent remains so unfavorable compared to the protonation reaction that EGTA is protonated rather than forming the MgEGTA^{2-} complexes.

The abundance of unchelated magnesium ions in the Mg–Ca–EDTA 1:1:1 system results in a lower overall magnesium rejection compared to the Mg–EDTA single-metal system where complexation is practically complete. The observed magnesium rejection in the 1:1:1 ternary EDTA system is, however, about the same as the magnesium rejection observed in the presence of a 1:1 binary Mg–EGTA at pH 6.

The excess chelating agent present in the Mg–Ca–EDTA 1:1:2 system reduces

TABLE I
Calculated Fraction of Magnesium Chelated in Various Solute System Stoichiometries

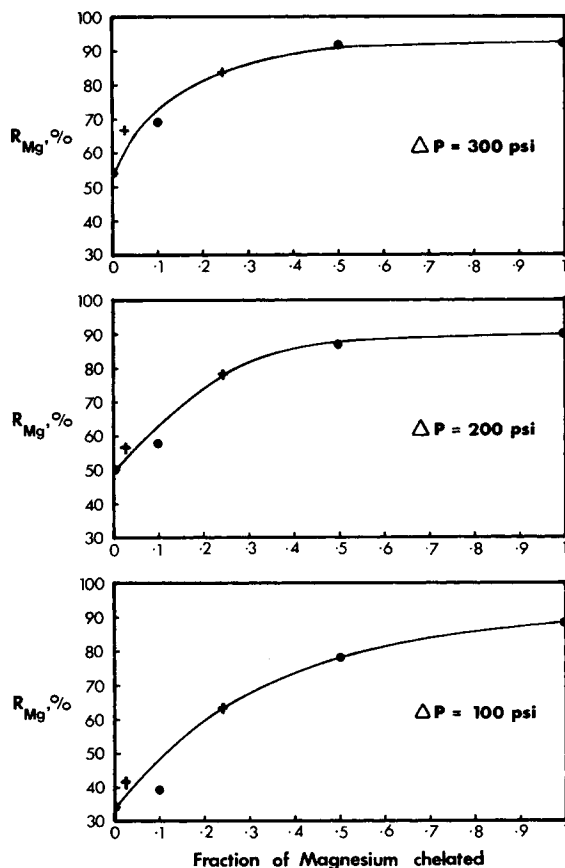| Solute(s)	Stoichiometric ratio $(1 = 10^{-2}M)$	Calculated fraction of magnesium chelated
MgCl$_2$	—	0
MgCl$_2$–EGTA	1:0.1	0.024
MgCl$_2$–EDTA	1:0.1	0.1
MgCl$_2$–EGTA	1:1	0.24
MgCl$_2$–EDTA	1:0.5	0.5
MgCl$_2$–EDTA	1:1	1.0

Fig. 5. Effects of the fraction of magnesium chelated by EDTA or EGTA on the overall magnesium rejection by CA-75 membranes: (●) Mg–EDTA; (+) Mg–EGTA.

the quantity of unchelated magnesium, which tends to increase the overall rejection of magnesium as discussed earlier.   Moreover, the increase in the amount of relatively impermeable, uncomplexed chelating agent anions in addition to the well-rejected metal chelate anions present in the feed solution may favor ion pair formation with the remaining unbound magnesium cations, further lowering the mobility of these metal ions.   From an electrostatic viewpoint, the high concentration of partially impermeable anionic species in the hyperfiltration feed requires a corresponding decrease in the number of cations which may be transferred across the membrane in order that electroneutrality in the feed solution be maintained.   The combined effect of these processes is considered to lead to the observed high overall magnesium rejection.

The magnesium in the presence of EGTA and Ca^{2+} remains virtually completely unchelated for both ternary stoichiometries studies, but there is a higher concentration of relatively impermeable EGTA anions in the Mg–Ca–EGTA 1:1:2 system.   The electroneutrality effect is therefore more pronounced, and higher overall magnesium rejection is observed in the Mg–Ca–EGTA 1:1:2 system compared to feed streams comprised of 1:1:1 ratios of the same constituents.   Alternatively, solute–membrane interactions involving calcium chelates and cellulose acetate may similarly contribute to the somewhat anomalously high overall rejections of magnesium in the ternary systems.
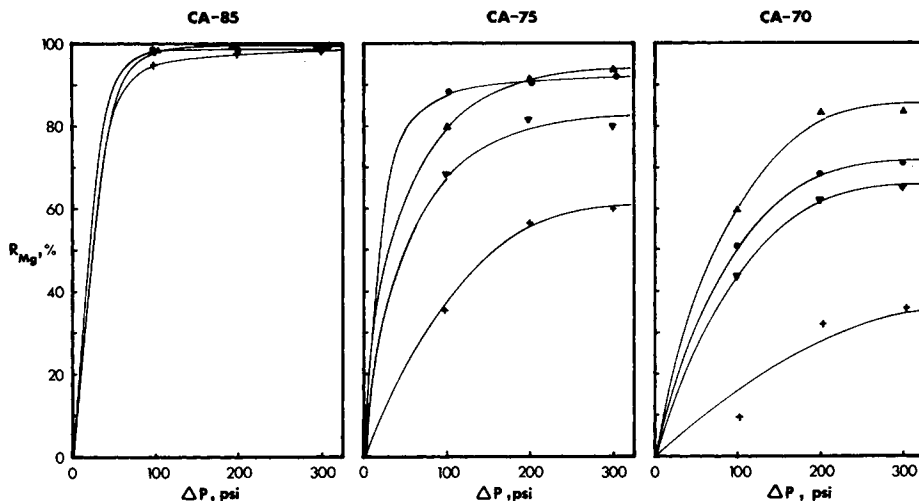
Fig. 6. Pressure dependence of the magnesium rejections by three membranes in the presence of different stoichiometric quantities of EDTA: (●) Mg–EDTA; (+) Mg–Ca; (▼) Mg–Ca–EDTA 1:1:1; (▲) Mg–Ca–EDTA 1:1:2.
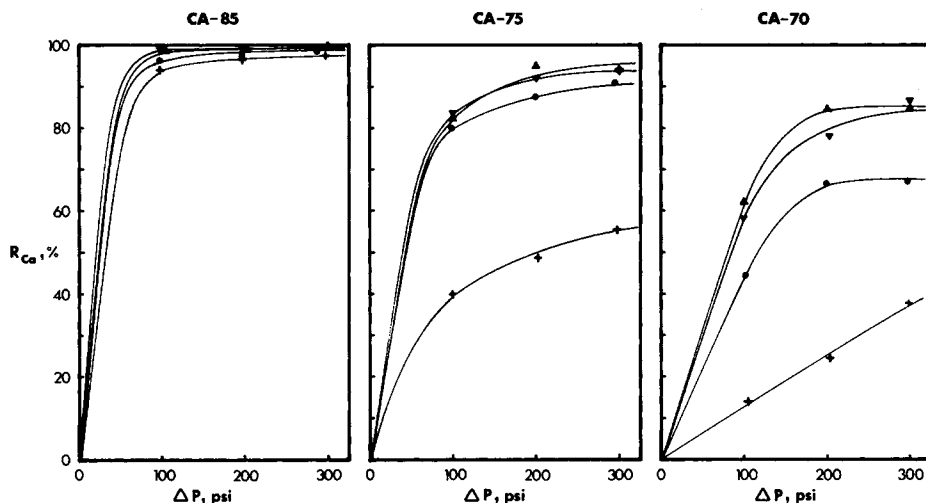

Fig. 7. Pressure dependence of the calcium rejections by three membranes in the presence of different stoichiometric quantities of EDTA: (●) Ca–EDTA; (+) Mg–Ca; (▼) Mg–Ca–EDTA 1:1:1; (▲) Mg–Ca–EDTA 1:1:2.

The calcium chelate rejection in the presence of magnesium is generally higher than the calcium chelate rejection in the single-metal chelate system. This may be attributed to the formation of $Mg(H_2O)_6^{2+}$ from the unchelated magnesium ions in the feed solution. Strong evidence[18] suggests that, under specific conditions of annealing history of the membranes and solute concentrations of the feed, significant pore constriction due to "solute plugging" may result which could lead to anomalously high rejection of microions accompanied by a volumetric flux decline of the permeate solution.

These particular solute–membrane interactions were studied recently by Drioli et al.[7] who suggested that the stable hydroxy complexes of aluminum might be
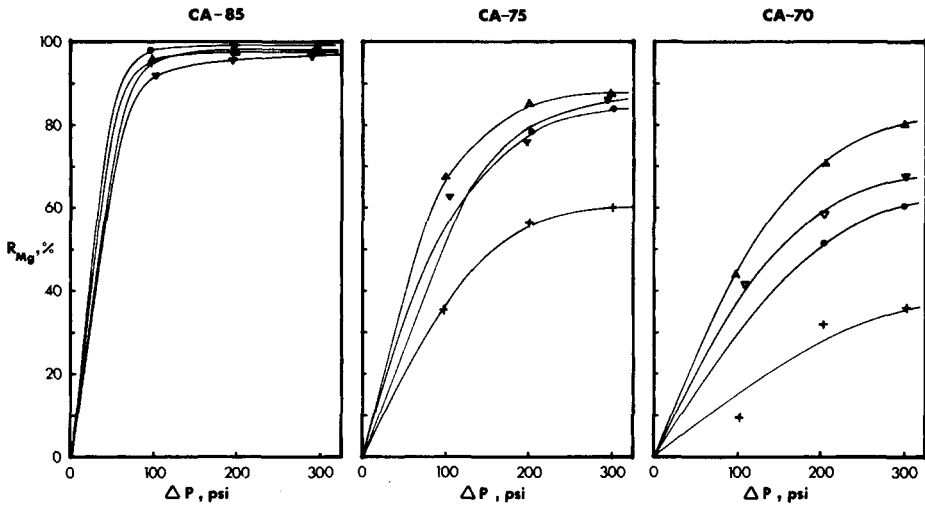
Fig. 8. Pressure dependence of the magnesium rejections by three membranes in the presence of different stoichiometric quantites of EGTA. (O) Mg–EGTA; (+) Mg–Ca; (▽) Mg–Ca–EGTA 1:1:1; (△) Mg–Ca–EGTA 1:1:2.
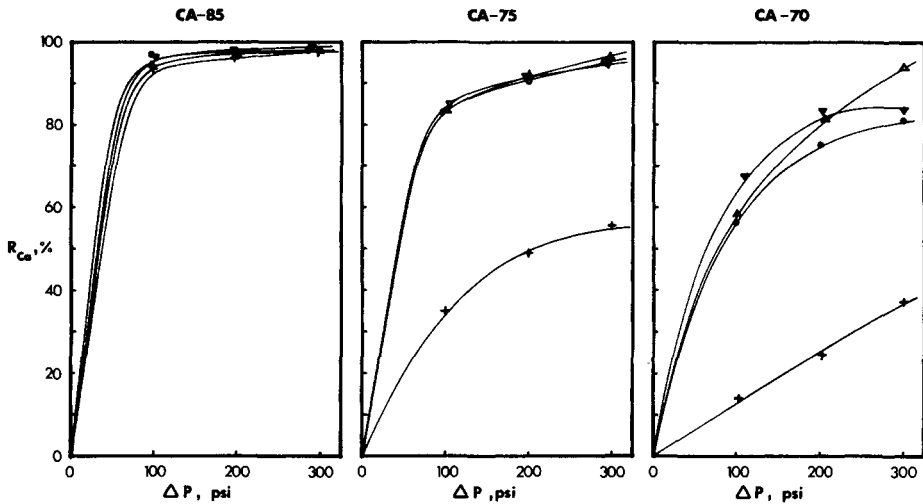

Fig. 9. Pressure dependence of the calcium rejections by three membranes in the presence of different stoichiometric quantities of EGTA: (O) Ca–EGTA; (+) Mg–Ca; (▽) Mg–Ca–EGTA 1:1:1; (△) Mg–Ca–EGTA 1:1:2.

responsible for pore constriction which, in turn, contributes to a high rejection of lithium ions. It is possible that magnesium hexahydrate ions partially constrict the micropores on the surface of the asymmetric cellulose acetate membranes by a similar mechanism, thereby restricting the passage of the $CaEDTA^{2-}$ or $CaEGTA^{2-}$ chelate anions.

The calcium chelate rejections of all four ternary systems are remarkably similar. The differences between rejection levels in the 1:1:1 and 1:1:2 stoichiometries are, for all practical purposes, insignificantly small. This insensitivity toward stoichiometry is to be expected since the addition of excess quantities of a relatively impermeable anion ($EDTA^{2-}$ or $EGTA^{2-}$) is not expected

to affect the sorption, and thus the permeability, of another comparably impermeable anion ($CaEDTA^{2-}$ or $CaEGTA^{2-}$) based upon the principles of electrostatic ionic distribution.[19]

Most inorganic penetrants do not significantly affect the transport properties of cellulose acetate membranes. Organic solutes, on the other hand, usually have much higher solubilities in the essentially nonpolar polymer matrix.[20] Negative rejection may even take place in the limit of very high affinity between the solute and cellulose acetate. For example, Lonsdale et al.[21] observed the negative rejection of phenol which is about four orders of magnitude more soluble in cellulose acetate than most inorganic salts. The continuing research in these laboratories will therefore attempt to demonstrate and characterize decreased solute rejection consequent to solubilizing chelation with relatively small chelating agents. In addition, well-controlled experiments are planned which will separate explicitly electroneutrality effects from effects related to extraneous solute–membrane interactions. These continuing studies should delimit a set of independent physicochemical processes which affect the performance of membrane processes involving mixed solute feeds.

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