Mixed Beds for Selective Removal of Ammonium Carbonate in Dialysate

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ABSTRACT

We have studied experimentally and theoretically the exchange of NH_4^+, Na^+, K^+, Ca^{++}, Mg^{++}, and H^+ ions in zeolite beds, weakly-acidic resin beds, and mixed beds of the zeolite and the resin. The zeolite is highly selective for NH_4^+ and K^+, whereas the resin with carboxyl functional groups is highly selective for Ca^{++} and Mg^{++}. The effluent histories of single exchanger beds can be well predicted by the Multicomponent Chromatography Theory developed by Helfferich and Klein (1970). These histories are mainly the result of ion competition for ion exchanger sites; they can not be adjusted to meet the goal that NH_4^+ ions are removed and simultaneously the pH and concentrations of all the major physiological cations are maintained at normal values. The effluent histories of mixed beds, on the other hand, can be adjusted. We have designed a mixed bed which can meet the goal except that for each equivalent of NH_4^+ removed, 0.3 equivalents of Na^+ are returned. The effluent histories of K^+ and NH_4^+ for the mixed beds are similar to those of the zeolite beds, whereas the Ca^{++} and Mg^{++} histories are similar to those of the resin beds.
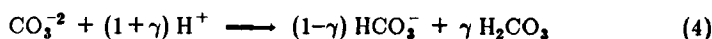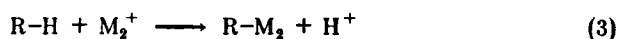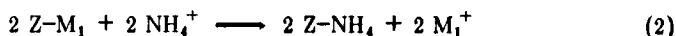
INTRODUCTION

Mixed beds of a cation resin in H^+-form and an anion in OH^--form have been used in water treatment for removing salts.[1,2] The reaction of H^+ and OH^-, which are displaced from the resins by the salts, drives the ion exchange process to completion. For this reason, mixed beds can produce water of higher quality than two single resin beds in series. The purpose of this paper is to show a different advantage of mixed beds, which has not been explored in the literature. We describe here mixed beds of two cation exchangers. By appropriate combination, such mixed beds can achieve unique separations which can not be achieved by single exchanger systems.

In general, for multicomponent ion exchange in single exchanger beds, the effluent behavior is mainly determined by the separation factors of the ions and their interference. By varying preloading conditions, one can change the effluent histories to some extent, but the flexibility is quite limited.[3,4] Effluent behaviors of mixed beds, however, are much more flexible. They can be changed over a wide range by different combinations and different volume ratios. Such a flexibility in effluent histories is crucial for applications which require specific effluent histories. For example, in dialysate regeneration, urea is first hydrolyzed enzymatically into ammonium carbonate.

$$CO(NH_2)_2 + 2\,H_2O \xrightarrow{\text{urease}} 2\,NH_4^+ + CO_3^{--} \tag{1}$$

Ideally, the ammonium carbonate should be removed via ion exchange processes which do not disturb the balance of pH and all the major physiological cations.[5-7] No single exchanger, however, can achieve this goal. Zirconium phosphate has been used in a dialysate regeneration system which is commercially available, the Sorbsystem (the former REDY system).[5,6] It is loaded with H^+ and Na^+ ions, which exchange for NH_4^+ ions. The released H^+ ions then combine with CO_3^{--} ions to lower the pH in the dialysate. This system has two major problems. First, if a large fraction of the ion exchange sites are loaded with H^+, the pH of the treated dialysate becomes too low (less than 7).[8,9] Secondly, the zirconium phosphate prefers Ca^{++}, Mg^{++}, and K^+ to NH_4^+ and removes all these ions in the dialysate.[8,9] Consequently, this system requires separate reinfusion devices to replenish these ions in the dialysate.

The approach of this paper is to use a mixture of two cation exchangers in a fixed bed, a zeolite for removing NH_4^+ ions and a weakly acidic resin for providing H^+ ions to control the pH. The exchange can be written as follows.

$$2 \text{ Z-}M_1 + 2 \text{ } NH_4^+ \longrightarrow 2 \text{ Z-}NH_4 + 2 \text{ } M_1^+ \tag{2}$$

$$R\text{-}H + M_2^+ \longrightarrow R\text{-}M_2 + H^+ \tag{3}$$

$$CO_3^{-2} + (1+\gamma) H^+ \longrightarrow (1-\gamma) HCO_3^- + \gamma H_2CO_3 \tag{4}$$

where Z and R stand for the zeolite and the resin respectively. Because of the nature of multicomponent exchange, M_1^+ and M_2^+ can be combinations of dialysate cations as discussed below. A fraction of CO_3^{--} is converted to H_2CO_3. As expected from the Henderson-Hasselbalch equation, the fraction γ is determined by the solution pH.[10] Our results presented below show that mixed beds can remove NH_4^+ ions and maintain balances of pH, K^+, Ca^{++}, and Mg^{++} ions.

THEORETICAL ANALYSIS

For stoichiometric exchange in single exchanger beds, the Multicomponent Chromatography Theory developed by Helfferich and Klein can be applied to predict the transient column profiles and effluent histories of all the ions.[3,4,11] Major assumptions of this theory are local equilibrium (no mass transfer effects) and constant separation factors. The advantage of this theory is that once the separation factors are known, the column profiles and effluent histories can be easily calculated for given presaturation and influent conditions, whereas other methods would require solution of coupled partial differential equations of transport.[12] This theory, however, does not consider mass transfer effects. As a result, the details of the breakthrough curves can not be accurately predicted. Summary of the theory and calculation procedures have been reported elsewhere.[3,4] Computer programs for calculating the effluent histories and column profiles for a multicomponent system are given elsewhere.[3]

Modification of the Theory for a Weakly Acidic Resin with
Neutralization Reaction (Shrinking Reservoir Model)

In the weakly acidic resin, the exchange of H^+ ions in general is determined by the ionization constant of the carboxyl groups and pH.[13] For urea hydrolysis, the CO_3^{--} ions which are produced from the hydrolysis tend to raise the solution pH to above 8.5. Therefore according to the equilibrium titration curve of the resin, H^+ ions should be released to react with the CO_3^{--} ions and lower the pH to the equilibrium value.[3]

The resin can act not only as a pH buffer but also as a reservoir for Ca^{++} and Mg^{++} ions, provided the resin is partly preloaded with these ions. When the resin is presaturated with dialysate, which contains only 3% Ca^{++} and 1% Mg^{++}, about 57% and 16% of the non-H^+ sites are loaded with Ca^{++} and Mg^{++} respectively.[3,4] If an influent to the resin bed does not contain Ca^{++} and Mg^{++} ions, the preloaded ions are released to maintain the effluent concentrations at the presaturant levels (the Ca^{++}–Mg^{++} plateau zone) until the reservoir is depleted.[3,4] This behavior is theoretically predicted. The observed plateau zone is shorter than the predicted because the theory assumes no mass transfer resistances.[3,4]

We now consider the case that an influent containing CO_3^{--} ions is fed into the resin bed which is presaturated with dialysate and partly loaded with H^+. Upon H^+ release, the sites previously occupied by H^+ remove all the Ca^{++} and Mg^{++} from the mobile phase. Since there are not enough Ca^{++} and Mg^{++} ions in the mobile phase, the rest of the sites are temporarily loaded with Na^+. These Na^+ sites then continue to exchange for Ca^{++} and Mg^{++} in the mobile phase. Consequently, the portion of bed upstream from the H^+ front acts as a Ca^{++} and Mg^{++} sink, whereas the portion downstream from the H^+ front acts as a Ca^{++} and Mg^{++} source. As the H^+ front advances through the bed, the effective reservoir shrinks. Overall, the effluent histories of Ca^{++} and Mg^{++} for this case are qualitatively similar to those without Ca^{++} and Mg^{++} in the influent except that the effective reservoir portion is smaller and consequently the Ca^{++}–Mg^{++} plateau zone is shorter.[3,4] The steps of calculation for the Shrinking Reservoir Model are summarized as follows:

(1) The number of bed volumes of effluent BV_{H^+} at which the H^+ capacity of the bed is exhausted (or the time that the H^+-front appears in the effluent) can be calculated from the H^+ capacity of the bed and γ, which is the fractional conversion from CO_3^- to H_2CO_3 (Eq. (4)).

$$BV_{H^+} = \frac{2\overline{C}_H}{[CO_3^{-}](1 + \gamma)} \qquad (5)$$

where $\overline{C}_H$ is the H^+ capacity of the bed (it equals 2590 meq/L multiplied by the fraction loaded with H^+) and $[CO_3^-]$ is the concentration of CO_3^{--} ions in mN.

(2) Assuming the influent contains no Ca^{++} and Mg^{++} ions, one can find from the Multicomponent Chromatography Theory the bed volumes of effluent at which the Ca^{++}–Mg^{++} plateau zone ends.

(3) The estimated plateau zone calculated in Step (2) is multiplied by an experimentally determined mass transfer efficiency; in our results this efficiency is 0.40.[3]

(4) The average fraction of bed which can act as a Ca^{++}–Mg^{++} reservoir is

$$1 - 0.5 \, [BV_{(3)}/BV_{H^+}]$$

where $BV_{(3)}$ is the bed volumes calculated in Step (3).[3] If BV_{H^+} is less than $BV_{(3)}$, the Ca^{++}–Mg^{++} plateau zone ends when the H^+ front appears in the effluent.

(5) The estimated Ca^{++}–Mg^{++} plateau zone is therefore the plateau zone obtained in Step (3) multiplied by the effective bed fraction obtained in Step (4).

Separation Factors of a Mixed Bed

If the average separation factors of a mixed bed are constant, the Multicomponent Chromatography Theory can be directly applied to predict the behavior of

the mixed bed. Nevertheless, the separation factors for mixed beds in general vary with the composition and the extent of exchange. Let α_{ij} and β_{ij} be the separation factors of the i-j ion pair in the zeolite and in the resin respectively. For a mixed bed in which the volume ratio of the resin to the zeolite is r, the volume average separation factor $\bar{\alpha}_{ij}$ in a mixed bed is

$$\bar{\alpha}_{ij} = \frac{\alpha_{ij} \, y_j + r\beta_{ij} \, z_j}{y_j + rz_j} \tag{6}$$

Here y_j and z_j are the mole fractions of j in the stationary phase of the zeolite and the resin respectively. Hence for a given volume ratio r the average separation factor $\bar{\alpha}_{ij}$ can vary with y_j and z_j and only for special cases it can be constant. For example, if α_{ij} is much larger than β_{ij} and rz_j is much smaller than y_j, $\bar{\alpha}_{ij}$ would approach α_{ij}. Similarly, if β_{ij} is much larger than α_{ij} and y_j is small, $\bar{\alpha}_{ij}$ would approach β_{ij}. In this paper, we examine the case that the zeolite prefers K^+ and NH_4^+ ions to Na^+ ions, whereas the resin prefers Ca^{++} and Mg^{++} ions to Na^+ ions. Under certain conditions, the effluent histories of K^+ and NH_4^+ of the mixed beds are similar to those for zeolite beds, whereas the effluent histories of Ca^{++} and Mg^{++} ions are similar to those of the resin beds.

EXPERIMENTAL

Materials

The ion exchanger for removing NH_4^+ ions was a natural zeolite, Ionsiv IE 95 from Union Carbide. The ion exchanger for pH control was Amberlite IRC 50 from Rohm and Haas; it was a weakly acidic resin with carboxyl functional groups. The solution in most experiments was designed to simulate dialysis fluids commonly used in dialysis treatments. This solution is termed "dialysate". It was normally prepared from chloride salts (AR grade) of the following ions: Na^+(135 mN), Ca^{++}(5.0 mN), K^+(3.5 mN), and Mg^{++}(2.0 mN). Ammonium carbonate at concentrations of 15 and 50 mN was added to the dialysate in certain experiments to simulate spent dialysate.

Apparatus and Procedure

Standard procedures for determining the ion exchange capacities and separation factors were used.[3] All the experiments were carried out at room temperature, $25 \pm 3°C$. For column experiments, a peristaltic pump and glass columns with an inner diameter of 1 cm were used. Exchanger preparation and packing procedure were reported elsewhere.[3] The flow rate was 2.5 ml/min. The ammonium carbonate was added to the influent by mixing a stream containing Na_2CO_3 with another stream containing chloride salts of NH_4^+ and dialysate cations immediately before infusion into the column in order to prevent precipitation of CO_3^- with Ca^{++} and Mg^{++}. The effluent from the column was collected in 20 ml portions and analyzed. The concentrations of Na^+ and K^+ were determined from flame emission and those of Ca^{++} and Mg^{++} were determined from atomic absorption with an atomic absorption-emission spectrophotometer (Perkin Elmer, Model 2380). The NH_4^+ ion concentrations were measured with an ammonia electrode (Orion, Model 95-10) and an Ion analyzer (Orion, Model 901). The pH values of the effluent were measured immediately after collection. Details of the column experiments and the analytical procedures have been reported elsewhere.[3] The major experimental conditions for the column experiments are summarized in TABLE I.

RESULTS AND DISCUSSION

The total ion exchange capacities per unit packed volume for the zeolite and the resin are 1.76 and 2.59 meq/ml respectively. The affinity sequences and separation factors of major ions against Na^+ ions are reported in TABLE II. The zeolite is highly selective for K^+ and NH_4^+ and the resin is highly selective for Ca^{++} and Mg^{++}.

Effluent Histories of Zeolite Beds

The effluent histories of NH_4^+ and dialysate cations in zeolite beds for removing NH_4^+ ions from dialysate are shown in Fig. 1. The influent was 15 mN NH_4Cl in dialysate. Predicted histories are also shown for comparison. Tabulated values of the predicted histories are available elsewhere.[3] Major features of the history such as the sequences of breakthrough and the average times of breakthrough are

TABLE I
Experimental Conditions of Mixed Beds

RUN#	EXCHANGER			PRESATURANT	INFLUENT		
	Zeolite Vol.,ml	Resin Vol.,ml	%H^+ loading		[NH_4^+]	[CO_3^{-2}]	
1a	11.8	0		dialysate	15	0	dialysate$^+$
1b	6.6						
2	0	10.8	15	dialysate but 150mN Na$^+$	0	15	dialysate but 150mN Na$^+$
3a	15.2	14.8	8	dialysate	15	15	dialysate 120mN Na$^+$
3b	10.2	9.9					
4	10.3	9.8	15	dialysate	15	15	dialysate
5*	12.3	17.2	45	dialysate	15	15	dialysate
6a	8.7	8.2	15	dialysate but 120mN Na$^+$	50	50	dialysate but 120mN Na$^+$
6b	9.5	9.6					
7	9.5	10.2	45	dialysate but 120mN Na$^+$	50	50	dialysate but 120mN Na$^+$

+ Composition listed in the materials section.

* Multilayer column in which each layer was about 1 cm in thickness; the bed
   volume of the resin was 1.4 times that of the zeolite.

TABLE II
Cation Affinity Sequences and Average Separation Factors
for the Zeolite and the Resin[+]

Zeolite

Affinity sequence	1	2	3	4	5
Species	K^+	NH_4^+	Ca^{++}	Na^+	Mg^{++}
α_{i-Na}	11.0	5.0	2.5	1.0	0.2

Resin

Affinity sequence	1	2	3	4	5
Species	Ca^{++}	Mg^{++}	NH_4^+	K^+	Na^+
α_{i-Na}	78.2	55.1	2.0*	1.1*	1.0

+ Total concentration of the cations is 167 mN for all the experiments.

* These values were inferred from the effluent histories of column experiments
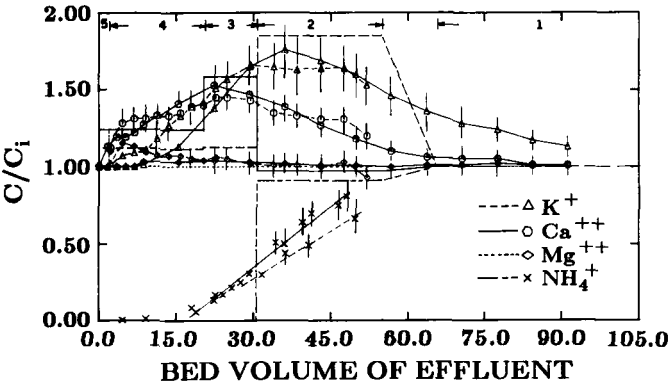   and the Multicomponent Theory; the rest were measured directly.

FIGURE 1

Effluent histories of K^+ (△), Ca^{++} (○), Mg^{++} (◇), and NH_4^+ (x) for zeolite beds
presaturated with dialysate. The influent was 15 mN NH_4 Cl in dialysate. Data
connected by solid lines are from Run 1a and data connected by dashed lines are
from Run 1b. The predicted effluent histories of K^+ (—-), Ca^{++} (—), Mg^{++} (—-
-), and NH_4^+ (—-) are also shown for comparison.

correctly predicted by the theory. The Na^+ (not shown) and Ca^{++} ions, which are less preferred to K^+ and NH_4^+ ions, are eluted before the NH_4^+ breakthrough, whereas the breakthrough of K^+ ions occurs simultaneously with that of NH_4^+ ions. The slopes of the breakthrough curves are not as abrupt as predicted because the theory does not take into account mass transfer resistances. The total amounts of various ions eluted or absorbed can be found from the effluent histories. They agree with the predicted values to within experimental accuracy (about 10%). Before the breakthrough of NH_4^+, mainly Na^+ and Ca^{++} are eluted by NH_4^+. The amounts of K^+ and Mg^{++} eluted are less than 5% of the NH_4^+ absorbed. We can express the equivalent exchange before the NH_4^+ breakthrough as follows:

$$2\ NH_4^+ + 0.24\ Z-(1/2Ca) + 1.76\ Z-Na$$

$$\longrightarrow 2\ Z-NH_4 + 0.24\ (1/2Ca^{++}) + 1.76\ Na^+ \tag{7}$$
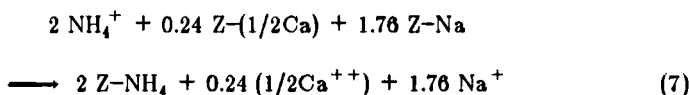
The small amounts of K^+ and Mg^{++} eluted are lumped with Na^+ in the above equation. For each equivalent of NH_4^+ removed, about 0.12 and 0.88 equivalents of Ca^{++} and Na^+ are eluted.

When the influent NH_4Cl concentration is 50 mN, the effluent histories are qualitatively similar to those shown in Fig. 1 except that more Ca^{++} and Na^+ are eluted because of the higher NH_4^+ concentration. For each equivalent of NH_4^+ removed, 0.20 and 0.80 equivalents of Ca^{++} and Na^+ are eluted. Detailed results are given elsewhere.[3]

Effluent Histories of Resin Beds

For a weakly acidic resin, the pH of the solution in equilibrium with the resin is mainly determined by the percentage of H^+ loading in the resin (as shown in the titration curve in Reference 3). When an influent contains $(NH_4)_2CO_3$, the pH is above 8.5. The H^+ ions in the resin are released to lower the solution pH to the equilibrium value. As shown in Fig. 2, the effluent pH values are 7.3 ±0.2 for 15% H^+ preloading in the resin and 6.7 ±0.2 for 45% H^+ preloading. These pH values are in close agreement with the equilibrium pH in the titration curve. As expected from the Henderson-Hasselbalch equation, the value of γ is determined by
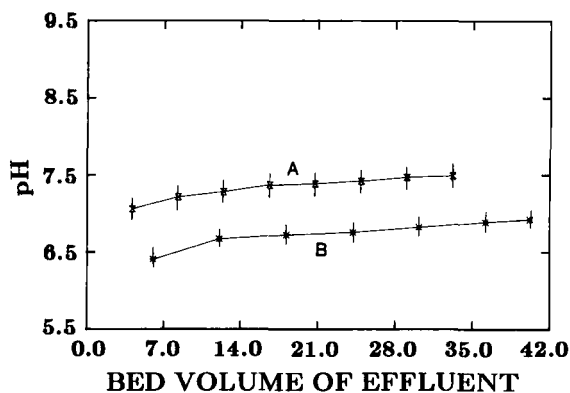
FIGURE 2

Effluent pH histories of resin beds with a H^+-preloading of 15% (Curve A) and 45% (Curve B). The influent was 15 mN Na_2CO_3 in dialysate.
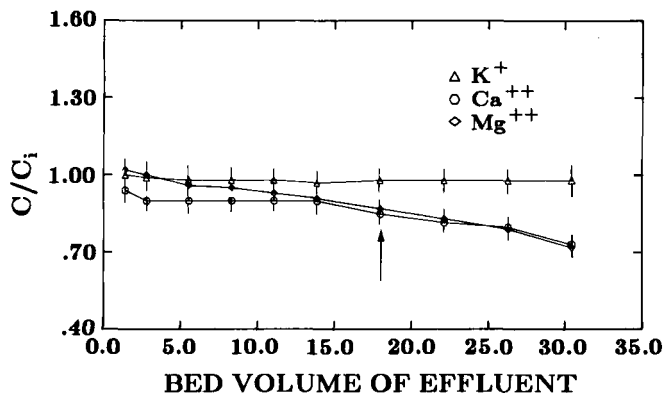

FIGURE 3

Effluent histories of K^+, Ca^{++}, and Mg^{++} for a resin bed presaturated with dialysate (Run 2). The influent was 15 mN Na_2CO_3 in dialysate (150 mN Na^+). The arrow indicates the end of the Ca^{++}–Mg^{++} plateau zone as predicted from the Shrinking Reservoir Model.

the solution pH.[10] The γ value for the former is about 0.1 and the γ value for the latter is about 0.3 (see TABLE III).

TABLE III

Estimated Ca^{++} and Mg^{++} Plateau Zones

| Run	$\%H^{+}$ (%)	CO_3^{-2} conc. (mN)	γ	$Ca^{++}-Mg^{++}$ plateau* (B.V.)	H^{+} front (B.V.)	effective fraction	due to resin (B.V.)	due to zeolite (B.V.)	estimated plateau (B.V.)
2	15	15	0.1	24	48	0.75	18	0	18
3	8	15	0.0	26	28	0.53	14	10	24
4	15	15	0.1	24	48	0.75	18	10	28
5	45	15	0.3	16	122	0.93	$15\times1.4^{+}$	10	31
6	15	50	0.1	24	14				14**
7	45	50	0.3	16	37	0.79	13	38	37**

* 0.4 (mass transfer efficiency) x $Ca^{++}-Mg^{++}$ plateau zone predicted for a resin bed without Ca^{++} and Mg^{++} in the influent.

** The H^{+} front is controlling.

+ The volume ratio of resin to zeolite is 1.4.

The effluent histories of K^+, Ca^{++}, and Mg^{++} are shown in Fig. 3. As predicted from the Shrinking Reservoir Model, the resin presaturated with dialysate can maintain the effluent Ca^{++} and Mg^{++} concentrations at normal dialysate values until the preloaded ions are depleted. The effluent Ca^{++} and Mg^{++} histories are similar to those without Ca^{++} and Mg^{++} ions in the influent.[3] The only difference is that the Ca^{++}–Mg^{++} plateau zone is shorter; it lasts 18 instead of 24 bed volumes of effluent (see TABLE III).

The equivalent exchange in the resin bed before the Ca^{++}–Mg^{++} depletion can be found similarly as that in the zeolite bed as follows:

$$(1+\gamma)\, Na^+ + (1+\gamma)\, R\text{–}H \longrightarrow (1+\gamma)\, R\text{–}Na + (1+\gamma)\, H^+ \qquad (8)$$
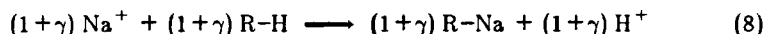
The uptake of Na^+ by the resin is therefore related to the pH in the resin bed, which in turn is determined by the $\%\, H^+$ preloading.

Effluent Histories of Mixed Beds

The effluent histories of mixed beds which consisted of equal volumes of the zeolite and the resin (Runs 3a and 3b) are shown in Figs. 4a and 4b. The influent was 15 mN $(NH_4)_2CO_3$ in dialysate. The effluent history is expressed in terms of the bed volumes of zeolite. The effluent histories of K^+ and NH_4^+ are qualitatively similar to those of the zeolite beds (compare Fig. 4a with Fig. 1). The breakthroughs of K^+ and NH_4^+ occur simultaneously. The effluent histories of Ca^{++} and Mg^{++} are qualitatively similar to those of the resin beds (compare Fig. 4a with Fig. 2). The concentrations of Ca^{++} and Mg^{++} are maintained at the presaturant levels until the reservoir is depleted.

The breakthrough of K^+ is delayed in mixed beds for about 5 bed volumes of effluent. This delay is expected because the resin has some capacity for K^+. Our theoretical calculation shows that when the resin is in equilibrium with a dialysate containing 15 mN NH_4Cl, about 0.6% of the non-H^+ sites are occupied by K^+.[3] According to standard chromatography theory, the retention volume should be $V_m(1 + k')$, where V_m is the volume of mobile phase in the resin bed and k' is the capacity factor which is the ratio of total moles of a solute in the stationary phase
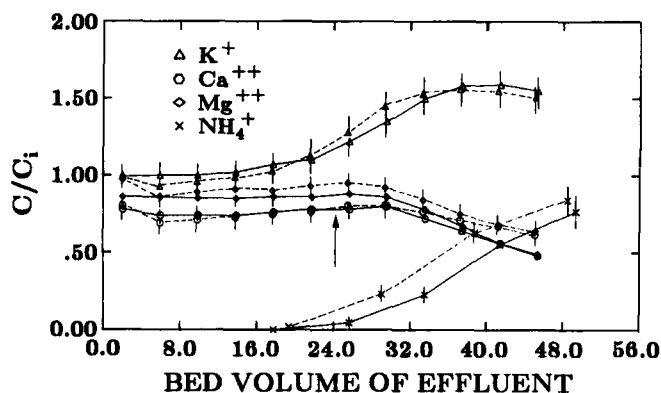
FIGURE 4a

Effluent histories of K^+, Ca^{++}, Mg^{++}, and NH_4^+ for mixed beds presaturated with dialysate. The influent was 15 mN $(NH_4)_2CO_3$ in dialysate. The resin was preloaded with 8% H^+. The data connected by solid lines are from Run 3a and the data connected by dashed lines are from Run 3b. The bed volume refers to that of the zeolite. The arrow indicates the end of the Ca^{++}–Mg^{++} plateau zone as estimated from the Shrinking Reservoir Model.
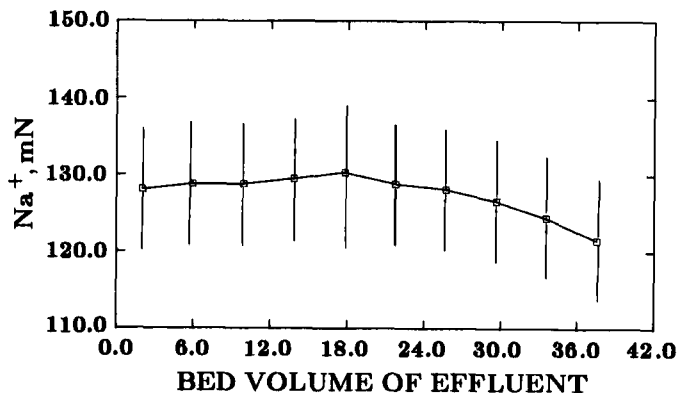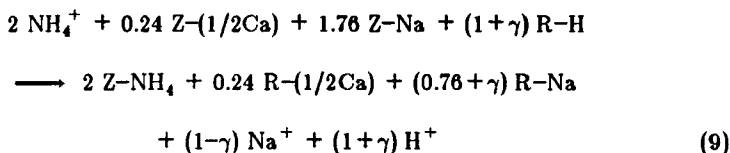

FIGURE 4b

Effluent history of Na^+ for Run 3a.

to that in the mobile phase.[14] The estimated delay of the K^+ peak is about 5 bed volumes of effluent, which agree closely with the results in Fig. 4. The break-through of NH_4^+ is also delayed for the same reason. About 4% of the non-H^+ sites are occupied by NH_4^+ at equilibrium. According to the above equation, the NH_4^+ breakthrough in the mixed beds should be delayed about 7 bed volumes of effluent, which are in agreement with the results in Fig. 4a.

The Ca^{++} peak in the effluent histories of the zeolite beds is missing in those of the mixed beds (Fig. 4a). The eluted Ca^{++} ions apparently are absorbed by the resin and contribute to the extension of the Ca^{++}–Mg^{++} plateau zone. The con-tribution can be estimated from the total amounts of Ca^{++} eluted before the NH_4^+ breakthrough. The estimated contribution from the Ca^{++} ions eluted from the zeolite for Run 3 is about 10 bed volumes of effluent (TABLE III). The pla-teau attributed to the resin is estimated to be 14 bed volumes of effluent. In total, the Ca^{++}–Mg^{++} plateau zone is estimated to be 24 bed volumes of effluent. The Ca^{++}–Mg^{++} plateau zone shown in Fig. 4a agrees closely with this prediction.

The effluent Na^+ history for the mixed bed (Run 3a) is shown in Fig. 4b. The amount of Na^+ eluted from the mixed bed in the Ca^{++}–Mg^{++} plateau zone is affected by γ, or the pH in the mixed bed, as shown in the following equivalent exchange equation:

$$2\ NH_4^+ + 0.24\ Z-(1/2Ca) + 1.76\ Z-Na + (1+\gamma)\ R-H$$

$$\longrightarrow 2\ Z-NH_4 + 0.24\ R-(1/2Ca) + (0.76+\gamma)\ R-Na$$

$$+ (1-\gamma)\ Na^+ + (1+\gamma)\ H^+ \qquad (9)$$

The above equation is derived from the following consideration. For 2 equivalents of NH_4^+ removed, $(1+\gamma)$ equivalents of H^+ are released by the resin; the γ value is determined by the pH or the % H^+ preloading on the resin. For 2 equivalents of NH_4^+ absorbed by the zeolite, 0.24 equivalents of Ca^{++} are eluted from the zeolite (Fig. 1); the eluted Ca^{++} are completely absorbed by the resin (Fig. 4a). There-fore, $(0.76+\gamma)$ equivalents of the resin sites previously occupied by H^+ are now occupied by Na^+. There are in total 1.76 equivalents of Na^+ eluted from the zeol-ite for 2 equivalents of NH_4^+ absorbed. Hence, $(1-\gamma)$ equivalents of Na^+ are eluted from the mixed bed.
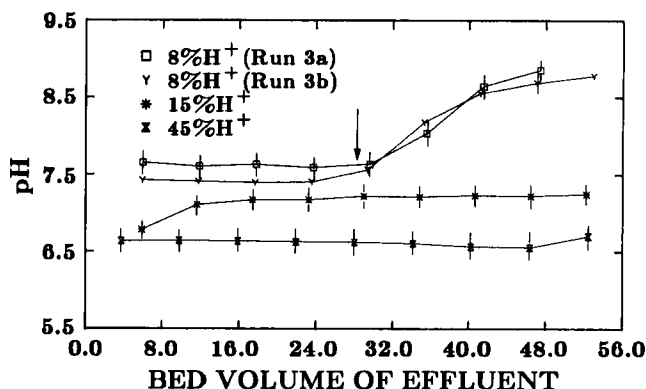
FIGURE 5

Effluent pH histories of mixed beds with 8% (Run 3a and 3b), 15% (Run 4), and 45% (Run 5) H^+ preloadings in the resin. The influent was 15 mN $(NH_4)_2CO_3$ in dialysate. The arrow indicates when the H^+ capacities are exhausted.
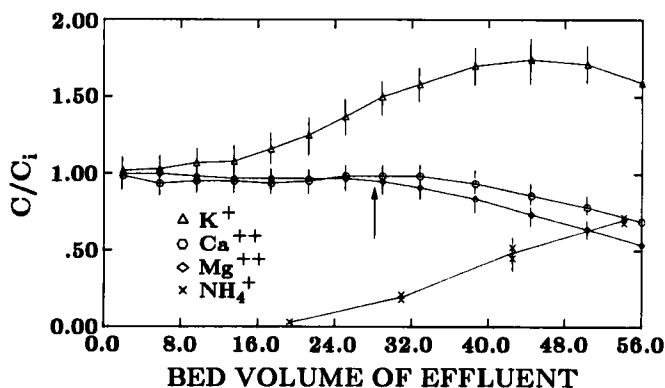
FIGURE 6

Effluent histories of K^+, Ca^{++}, Mg^{++}, and NH_4^+ for a mixed bed presaturated with dialysate. The influent was 15 mN $(NH_4)_2CO_3$ in dialysate (Run 4). The resin was preloaded with 15% H^+. The arrow indicates the end of the estimated Ca^{++}-Mg^{++} plateau.

Because the pH value is about 7.5 (see Fig. 5), the γ value for 8% H^+ preloading is approximately zero. From Eq. (9), the effluent Na^+ in the Ca^{++}–Mg^{++} plateau zone for Run 3a should be 128 mN. As shown in Fig. 4b, the effluent Na^+ concentration in the Ca^{++}–Mg^{++} plateau zone (up to 24 bed volumes of effluent) is close to the predicted value.

Our results show that the resin can control the pH in mixed beds and by varying the percentage of H^+ preloading the pH can be controlled at different values (Fig. 5). At 8% H^+ preloading, the H^+ front appears at 28 bed volumes of effluent as predicted from Eq. (5). Before the breakthrough of the H^+-front, the effluent pH is controlled at 7.5$\pm$0.2, which is close to the equilibrium pH expected from the titration curve. The effluent pH values for 15% and 45% H^+ preloadings are similar to those for the resin beds shown in Fig. 2. As expected, the effluent histories of K^+, Ca^{++}, and Mg^{++} for the mixed bed with 15% H^+ preloading are similar to those with 8% H^+ preloading (compare Fig. 6 with Fig. 4a). The Na^+ return at 15% H^+ preloading is expected to be 9% lower than that at 8% H^+-preloading (Eq. (9)). The effluent Na^+ concentration is expected to be 127 mN instead of 128 mN. The difference, is, however, too small to be measured.

The effects of changing the volume ratio of the two exchangers are shown in Fig. 7. In Run 5, the volume ratio of the resin to the zeolite was 1.4. The resin was loaded with 45% H^+. As expected, the Ca^{++}–Mg^{++} plateau zone is extended because the higher resin ratio. The predicted Ca^{++}–Mg^{++} plateau zone is 31 bed volumes of effluent (TABLE III), which are in close agreement with the plateau zone shown in Fig. 7. The K^+ breakthrough is not significantly different from that in Fig. 4a. Because of the higher percentage of H^+ loading, the capacity factor k' becomes smaller. This counter balances the effects of a higher resin to zeolite ratio. The NH_4^+ breakthrough is expected to be delayed 11 bed volumes of effluent, when compared with that of the single resin bed (Fig. 1). The results in Fig. 7 are in agreement with this prediction. Although the column in Run 5 consisted of alternating layers (about 1 cm in thickness) of the resin and the zeolite, the effluent histories of K^+, Ca^{++}, and Mg^{++} are not significantly different from those of the mixed beds.

When the influent $(NH_4)_2CO_3$ concentration increases to 50 mN, the effluent histories of mixed beds are shown in Figs. 8 through 11. The effluent histories are similar to those with 15 mN $(NH_4)_2CO_3$ in the influent. The effluent pH and the concentrations of K^+, Ca^{++}, and Mg^{++} are kept constant during the NH_4^+ removal (Figs. 8, 9 and 11). The estimated Ca^{++}–Mg^{++} plateau zones for these runs
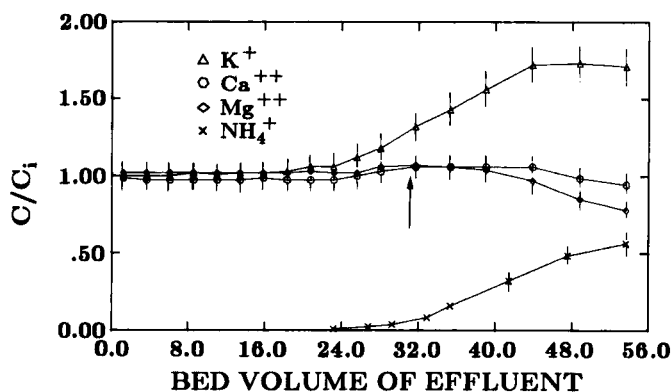
FIGURE 7

Effluent histories of K^+, Ca^{++}, Mg^{++}, and NH_4^+ for a multi-layer bed presaturated with dialysate. The influent was 15 mN $(NH_4)_2CO_3$ in dialysate (Run 5). The bed volume of resin was 1.4 times that of zeolite. Each layer was about 1 cm in thickness. The arrow indicates the end of the estimated Ca^{++}–Mg^{++} plateau zone.
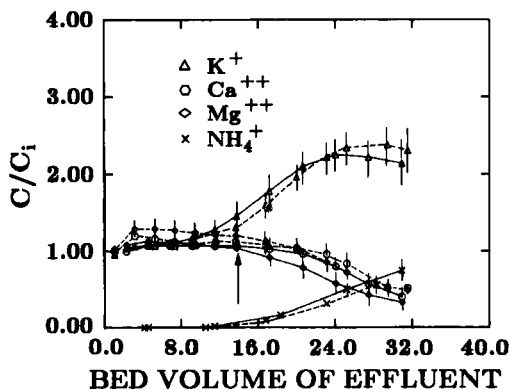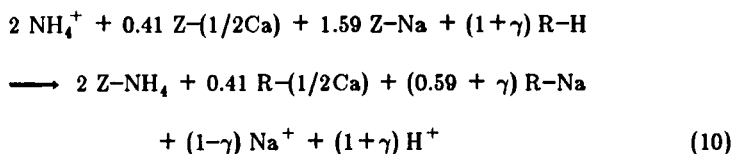

FIGURE 8

Effluent histories of K^+, Ca^{++}, Mg^{++}, and NH_4^+ for mixed beds presaturated with dialysate (Run 6). The influent was 50 mN $(NH_4)_2CO_3$ in dialysate. The resin was preloaded with 15% H^+. The data connected by solid lines are from Run 6a, and those connected by dashed lines are from Run 6b. The arrow indicates the end of the estimated Ca^{++}–Mg^{++} plateau zone.

are reported in TABLE III. For Runs 6a and 6b, as expected the H^+ fronts appear at about 14 bed volumes of effluent (TABLE III and Fig. 11). As explained in the Shrinking Reservoir Model, as soon as the H^+ front appears in the effluent, the whole column acts as a Ca^{++}–Mg^{++} sink and the Ca^{++}–Mg^{++} plateau zone would end. This prediction is confirmed by the results in Fig. 8. For Run 7, both the Ca^{++} preloaded in the resin and the Ca^{++} eluted from the zeolite contribute to the plateau zone (TABLE III). However, the plateau zone should end when the H^+ front appears in the effluent. The observed effluent histories are in agreement with this prediction (TABLE III and Fig. 9).

The equivalent exchange during the NH_4^+ removal for Runs 6 and 7 can be obtained in a similar manner as Eq. (9).

$$2\ NH_4^+ + 0.41\ Z\text{–}(1/2Ca) + 1.59\ Z\text{–}Na + (1+\gamma)\ R\text{–}H$$

$$\longrightarrow\ 2\ Z\text{–}NH_4 + 0.41\ R\text{–}(1/2Ca) + (0.59 + \gamma)\ R\text{–}Na$$

$$+\ (1\text{–}\gamma)\ Na^+ + (1+\gamma)\ H^+ \tag{10}$$

According to Eq. (10), for each equivalent of NH_4^+ removed, 0.45 and 0.35 equivalents of Na^+ should be eluted from the mixed beds with 15% ($\gamma = 0.1$) and 45% ($\gamma = 0.3$) H^+ preloadings. The Na^+ effluent histories for these cases, however, indicate that the amounts of Na^+ eluted are about 70% of the predicted values (Fig. 10). This can be explained by the uptake of NH_4^+ ions by the resin. It is assumed in deriving Eq. (10) that only zeolite can remove NH_4^+ ions. This assumption is valid only when the influent NH_4^+ concentration is 15 mN or less, when the influent NH_4^+ concentration is 50 mN or more, the capacity of the resin for NH_4^+ ions is no longer negligible. Comparing the NH_4^+ breakthrough curves of Figs. 8 and 9 with that for single zeolite beds, we find that about 30% of the NH_4^+ capacity of the mixed beds can be attributed to the resin.[3,4] Since the NH_4^+ ions exchange mainly for H^+ ions in the resin, about 30% of the NH_4^+ ions were removed without any Na^+ elution. Therefore, the amounts of Na^+ eluted are about 70% of the values predicted from Eq. (10).

It is expected from Eq. (10) that if $\gamma = 1$, there would be no Na^+ eluted from the mixed bed. Nevertheless, this would require the pH in the effluent to be about 4, which is unacceptable for dialysis treatments.[9]
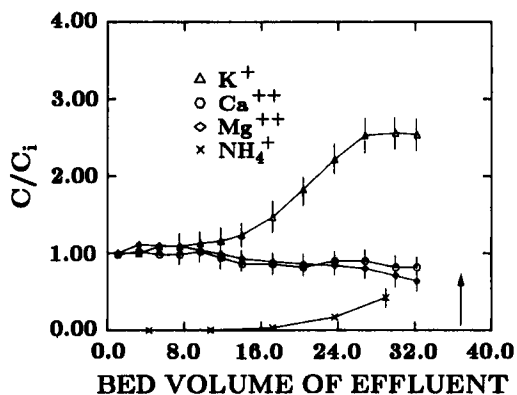
FIGURE 9

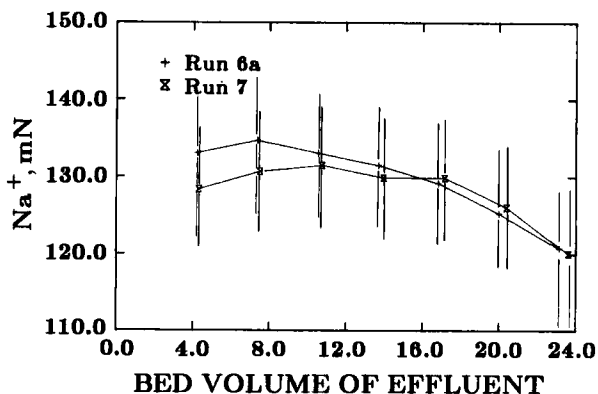Same as Fig. 8 but for 45% H$^+$-preloading (Run 7).

FIGURE 10

Effluent histories of Na$^+$ for mixed beds with 15% (Run 6a) and 45% H$^+$ (Run 7) preloadings in the resin.
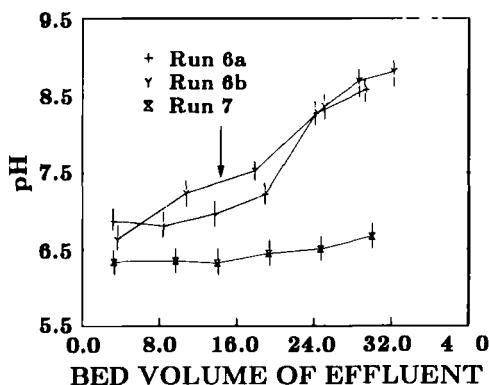
FIGURE 11

Effluent pH histories for mixed beds with 15% (Runs 6a and 6b) and 45% H$^+$ (Run 7) preloadings in the resin. The arrow indicates when the H$^+$ capacity is exhausted for Run 6a and 6b, (TABLE III).

CONCLUSIONS

1. For stoichiometric exchange in single exchanger beds, the Multicomponent Chromatography Theory developed by Helfferich and Klein can be applied to predict the effluent histories. The sequence of breakthroughs, the average times of breakthrough of various ions, and the total amounts of ions eluted or absorbed can be accurately predicted by the Theory.

2. The prediction of the Multicomponent Theory can be modified to estimate the $Ca^{++}-Mg^{++}$ plateau zone in resin beds and mixed beds with neutralization of CO_3^{--}.

3. Mixed beds can achieve unique separations which cannot be achieved by single exchanger systems. For mixed beds of a zeolite which is highly selective for K^+ and NH_4^+ and a resin which is highly selective for Ca^{++} and Mg^{++}, the effluent histories of K^+ and NH_4^+ are similar to those of the zeolite beds, whereas the effluent histories of Ca^{++} and Mg^{++} are similar to those of the resin beds.

4. For the mixed bed of the zeolite and the resin, NH_4^+ can be removed, while the effluent pH and effluent concentrations of Ca^{++}, Mg^{++}, and K^+ can be

controlled at the normal physiological values. For each equivalent of NH_4^+ removed, about 0.3 equivalents of Na^+ are returned to the dialysate.

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