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Parametric Studies on the Performance of Mixed-Bed Ion Exchange at Ultralow Concentrations
–1. Multicomponent System–

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Abstract–We experimentally evaluated the effects of multicomponent systems of divalent cations on the performance of mixed-bed ion exchange in the concentration range used for ultrapure water processing. Data were collected in the batch and continuous column systems with Dowex Monosphere resins used commercially for ultrapure water applications. The presence of divalent cations in the systems affects significantly the capacity of the units to remove a univalent cation. However, the anion exchange rate increases slightly in the multicomponent systems. The equilibrium and the breakthrough curves of ions, plotted as the ratio of the effluent to influent concentration versus run time or solution volume passed through the experimental column, give detailed results about the effects of the existence of other ionic species on the fate of each ion in MBIE units. The results of the present study are expected to be used to develop and simulate mathematical models and to understand the performance of mixed-bed ion exchange at ultralow concentrations.

Key words: (Mixed-Bed) Ion Exchange, Water Purification, Ultralow Concentrations, Separation Technology, Multivalent Ions

INTRODUCTION

Ion exchange is the reversible stoichiometric exchange of ions between a resin particle and surrounding liquid, without substantial change in the particle structure. It has been used frequently as an economical and convenient separation method for producing high purity water. Stimulated by the appearance of high-capacity and durable ion exchange resins, the industrial applications of ion exchange are widespread, ranging from water purification and bioseparation to treatment of valuable metals such as gold and uranium. However, the most common and largest application of ion exchange is water purification for producing high purity water in diverse industrial fields such as microchip production, ammonia and hydrogen production, steam reformation, condensate polishing and makeup water purification, and closed-loop water reclamation for space missions [Foutch, 1991]. Although ion exchange was developed eighty years ago, improvements in products, techniques, economics and new applications are still continuing.

A typical mixed-bed ion exchange (MBIE) unit is prepared by intimate mixing of strong-acid cation resins and strong-base anion resins in the same column [Helfferich, 1965]. MBIE is particularly used to produce ultrapure water, of which conductance is less than 0.055 μS/cm (18.2 MΩ-cm) at 25 °C [Grammont et al., 1965]. There is more than one cyclic operational choice for MBIE units. The hydrogen cycle (HOH cycle) uses the cationic resin in hydrogen form and the anionic resin in hydroxide form. These ions exchange cations and anions in the liquid phase, and the excess hydrogen and hydroxide ions are consumed to produce water by neutralization reaction. This water equilibrium reaction makes the exchange process fast and irreversible [Kunin and McGarvey, 1951]. Another choice is the ammonia (or amine) cycle, which involves the addition of ammonia (or amine) as pH additives to the feed water to increase pH of the water for corrosion control. Sometimes the ammonia cycle can be operated with cationic resin in the ammonia form. Both of the HOH and the ammonia cycles are used industrially. The purest form of water is produced in the HOH cycle. However, in some cases amine cycles are economical to operate and the pH additives are recycled rather than wastefully removed. Presently, use of the MBIE for the treatment of low level solids water requires realistic estimates of mixed-bed performance. However, the fundamental theories and detailed modeling of the ion exchange process are far behind the current technical applications.

Haub and Foutch [1986a, b] were the first to develop a mathematical model which can predict the MBIE performance operating at ultralow concentrations. Their model was for the hydrogen cycle MBIE with only two ions, Na^+ and Cl^-, considered for exchange with H^+ and OH^-, respectively. They were also the first to accommodate water dissociation at ultralow concentrations, which allows water equilibrium rather than assuming an irreversible reaction. A major improvement of their model is

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the separate material balance considerations for each resin. Divekar et al. [1987] added temperature effects to Haub and Foutch's model. This required expressions as the functions of temperature for all of the physical properties in the model.

Zecchini [1990, 1991] extended the above model for the ternary ionic systems with univalence. His model was also suitable for amine form operation, and was further extended to incorporate divalent ions by Pondugula [1994]. This model could predict the column effluent concentrations for a variety of such industrial cases as bed heels and bed cleaning. Bulusu [1994] extended the model to handle the multicomponent system of the ions with arbitrary valences. These mathematical models still have room to improve the accuracy through experimental data obtained under various industrial conditions.

To evaluate and improve the accuracies of the developed mathematical models, much experimental work has been performed. Yoon et al. [1994, 1995] studied the effect of the ratio of cation resin to anion resin on the MBIE performance at ultralow concentrations. Noh et al. [1995, 1996] obtained experimental data to evaluate the MBIE performance for the variable feed concentration and for the incomplete mixing of anion and cation resins. Yoon et al. [1999] investigated the effect of temperature on the MBIE performance and reported that the exchange rates of cation and anion increased with temperature. Even though those experimental studies have contributed to trim the models, they have been restricted to NaCl feed solution, that is, binary ion exchange system with univalence.

Garcia et al. [1992] made a theoretical analysis of multicomponent ion exchange in fixed beds. The concentration profiles and the number of transitions between plateau zones were obtained for the systems with an arbitrary number of exchanging species. Lopez et al. [1992] examined modeling and experimental behavior of multicomponent anion exchange with Amberlite IRA-410. The equilibrium theory developed by Helfferich [1967] was used to predict the effluent concentration profiles. de Lucas et al. [1992] studied the cation-exchange equilibria between Amberlite IR-120 resin and aqueous solution of calcium, magnesium, potassium, and sodium chlorides and hydrochloric acid. They reported the experimental data for ion-exchange equilibria of the ternary and quaternary systems, and also developed a model which allows the prediction of multicomponent ion-exchange equilibria from the binary data. They concluded that the predictions of ternary and quaternary systems based solely on the binary data are in good agreement with the experimental results. However, most of the experimental work was performed at relatively high concentration, and few systematic studies have been done on multicomponent ion exchange at ultralow concentrations because of the complexity of experimental multi-ionic systems.

Feed solution of the industrial MBIE units usually contains more than one ionic species of arbitrary valences. These other ionic species have different properties and the ability to predict their fate within the units is essential for an industrially useful model. The extension of the previous binary exchange work to consider the multicomponent systems should address these needs. The objective of the present study is to experimentally evaluate the effects of the multicomponent systems of divalent cations on the performance of the MBIE at ultralow ionic concentrations of part per billion levels. The data obtained in this study will provide a basic data for understanding the performance of the MBIE operating under various conditions observed in full-scale industrial units and give a good design tool for an ion exchange process.

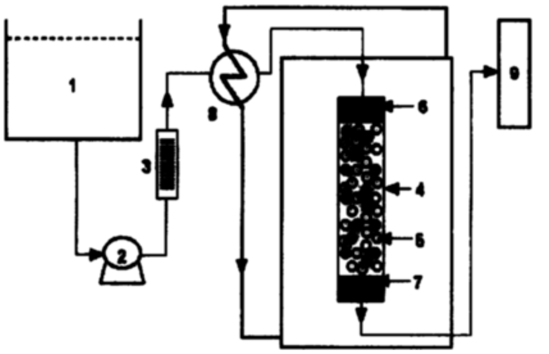

Fig. 1. Schematic diagram of the continuous MBIE experimental system.

1. Feed storage
2. Pump
3. Flow meter
4. Glass column
5. Ion exchange resin
6. Silicone stopper
7. Glass wool
8. Heat exchanger
9. Ion chromatography

EXPERIMENTAL

The experiments for the present study were performed using both batch and continuous operation systems. The batch system was used for the equilibrium data of each cation, and the continuous system for the breakthrough data of each ion in the multicomponent systems. Fig. 1 shows the schematic diagram of the continuous MBIE experimental system, utilized for most of experimental runs in this study.

The batch system simply consists of a flask, a magnetic stirrer and bar, and a thermometer. A temperature controller and a glass wool board were used to maintain the least variation of temperature. The experimental runs were performed with a stirrer velocity of more than 1,000 rpm for complete mixing of resin and solution. The volume of the solution taken periodically as samples was so small that the change of the total volume of the solution could be negligible.

Table 1 shows the experimental conditions used for the batch system. All the experiments were carried out under the same

Table 1. Experimental conditions for the batch system

Parameter	Value
Reactor size	1.0 *l*
Cation resin wt.	0.01 g
Feed volume	500 mL
Feed concentration	NaCl 1.0×10^{-4} M $CaCl_2$ 1.0×10^{-4} M $MgSO_4$ 1.0×10^{-4} M
Temperature	20 °C
Stirrer velocity	1,000 rpm

conditions except the feed solution. The specified weight of cation resin was mixed with the feed solution and then introduced into the flask. Water samples were collected every hour by hand using sample bottles. The bottles were rinsed at least three times with ultrapure water before sampling and filled fully to remove air in the bottles. To avoid any leaching from the bottle itself, the samples were analyzed within at most 6 hours using off-line IC procedure. The results of the sample analysis were described as the concentration ratio (C/C_o) vs. run time.

The continuous operation system is composed mainly of an experimental column, its accessories for feeding, heating, and measuring the experimental parameters such as volumetric flow rate, temperature and pH, and an ion chromatograph (IC) for measuring effluent concentration. A Dionex IC (model DX-300) was used for this work. The experimental column was made from transparent Pyrex glass to see the resins loaded inside the column. Glass wool with stainless steel screens was used to support the mixed-bed resins and to ensure uniform flow distribution.

To evaluate the effect of the multicomponent systems with divalent ions on the MBIE performance for the removal of Na^+ and Cl^- at ultralow concentrations, the specified concentrations of $CaCl_2$ and $MgSO_4$ solution were added to the same concentration of NaCl solution and then introduced into the continuous experimental column. The sample was taken every hour and analyzed by using the on-line IC procedure. Table 2 shows the continuous column experimental conditions. The experimental conditions were decided to be close to the industrial conditions and to perform an experimental run within a day. The detailed industrial conditions have been described in previous papers [Noh et al., 1996; Yoon et al., 1995, 1999].

The experiments were conducted with more cation resin than the anion resin for conditions close to industrial practice. The weight of each resin was decided to have a reasonable experimental period so that it is possible to conduct an experimental run within a day.

Because the feed concentrations for these experiments were very low, special attention was given to prevent water contamination. Ultrapure water was prepared by passing either distilled water or the effluent from the experimental column through high capacity MBIE columns in series. Resistivity greater than 18.2 MΩ-cm at room temperature was checked to ensure water quality. Water produced from the purification column was collected in a carboy and used to prepare either the feed solution or the chemicals for the IC. A leaching problem from the carboy became significant after about 48 hours, so water stored in the carboy for more than 12 hours was fed into the purification columns again to ensure water quality.

Table 2. Experimental conditions for the continuous column system

Parameter	Value
Column diameter	12 mm
Resin wt.	cation 2 g, anion 1 g
Flow rate	10.8 L/hr
Feed concentration	NaCl 1.0×10^{-4} M $CaCl_2$ 1.0×10^{-4} M $MgSO_4$ 1.0×10^{-4} M
Temperature	20 °C

Table 3. Physical properties of Dowex resins*

Parameter	Cation resin	Anion resin
Name	Monosphere 650C	Monosphere 550A
Capacity (meq/ml)	1.90	1.10
Selectivity** Coefficient	Na^+-H^+ 1.13 Mg^{2+}-H^+ 16.6 Ca^{2+}-H^+ 27.5	Cl^--OH^- 22.0
Water retention capacity (%)	46-51	44-50
Density (lb/ft^3)	50.0	40.0
Diameter (cm)	0.065	0.059
Appearance	hard, black, spherical beads	hard, white, spherical beads

*From the vendor

**At 20 °C

The feed solution was prepared by diluting the concentrated solution with pure water, and the concentrated solution was obtained by dissolving the calculated weights of salts in a 100 ml flask with pure water. After pippetting 10 ml of the concentrated solution into a 10 liter carboy and adding pure water, we used vigorous agitation and checked complete mixing by conductivity measurement. Only a specified carboy was used for a certain duty. If necessary, the makeup feed water was made and added to the feed carboys.

Dowex Monosphere resins provided by the Dow Chemical Company were used for the study, and the physical properties are shown in Table 3. These resins were rinsed with pure water from the purification columns and stored in plastic containers. For the experiments, specific wet volumes of the cation and anion resins were taken from the resin containers and mixed. Then, the resins were placed in the experimental column carefully followed by being checked to ensure complete mixing and uniform packing throughout the column cross section. The column was fully filled with pure water, while being tipped to remove any air bubbles between the resin particles and to promote uniform packing. The air bubbles might be the source of carbonate or bicarbonate which affect the breakthrough curve of chloride strongly. After the system was assembled, pure water was fed into the column and flowed downward until the desired experimental conditions were reached. To maintain a constant temperature, a constant-temperature reservoir and a heat exchanger were used. After the system was stabilized at the experimental conditions, the feed solution was introduced into the system.

When the feed solution reached the top portion of the column, the resistivity of the entrance portion would decrease. This point was considered as the starting point of the experimental run. Periodically, on-line resistivity and pH data were collected during the run and recorded on computer output files by Labtech software. For the continuous column experiments, an on-line IC procedure was utilized for the accurate sampling procedure. The IC was connected directly to the flow system and the effluent samples were periodically collected and analyzed with the results recorded on computer files. All the sampling and analyzing procedures were controlled by the AI-450 program. The post run processing of the chromatography data was performed by using utilities in the AI-450 program and a spreadsheet.

RESULTS AND DISCUSSION

The results obtained by analyzing the effluent samples were given in terms of the ratio of the feed concentration (C_o) to the effluent concentration (C) as a function of run time or solution volume passed through the experimental column. When plotted, the data showed smooth curves, even though they tended to scatter at the early stage of each run. To evaluate the effect of the multicomponent cationic systems, the experimental results of the binary systems (H^++Na^+, H^++Mg^{2+}, and H^++Ca^{2+}) were compared to those of the ternary (H^++Na^++Mg^{2+} and H^++Na^++Ca^{2+}) and the quaternary system (H^++Na^++Mg^{2+}+Ca^{2+}). Six different feed solutions for both the batch and the continuous systems were prepared according to the experimental conditions: NaCl, $MgSO_4$, $CaCl_2$, NaCl+$MgSO_4$, NaCl+$CaCl_2$, and NaCl+$MgSO_4$+$CaCl_2$. The present work was carried out with only the multicomponent cationic systems because it is possible to roughly imagine the effects of the multicomponent anionic systems with divalences on the performance of MBIE, based on the results of the present work.

1. Batch System

Fig. 2 shows the concentration profiles of cations in each binary system (H^++Na^+, H^++Mg^{2+}, and H^++Ca^{2+}). As is shown in this figure, the concentrations of cations decrease with the increase of time until they reach the equilibrium concentrations. However, the slope of the breakthrough curve of the Ca^{2+} is the biggest and that of the Na^+ is the smallest. The equilibrium concentration of the Ca^{2+} is the lowest and that of the Mg^{2+} is between the Na^+ and Ca^{2+}. This means that the order of the selectivity coefficient is (H^+<)Na^+<Mg^{2+}<Ca^{2+}. Selectivity of a resin is defined as the degree of preference for one ion with respect to another, even if the ions are present in equivalent quantities. In theoretical studies, it is usually defined in terms of the selectivity coefficient, which is the mass action relationship between the interfacial and resin phase concentrations as:

$$K_B^A = \frac{C_B^* \overline{C_A}}{\overline{C_B} C_A^*} \tag{1}$$

where the bar denotes the resin phase and the * denotes the interfacial concentration. Selectivity depends on the nature of the counterions, the nature of the fixed charges in the resin matrix, the degree of resin saturation, the total solution concentration, and external factors such as temperature and pressure. According to the experimental results by Helfferich [1962] and Triay and Rundberg [1987], the ion exchange resin prefers counterions that have the higher valence, smaller equivalent volume, greater polarity, and stronger association with fixed ionic groups in the matrix. Kunin [1960] reported that the selectivity coefficient increases with increasing atomic number of the exchanging ionic species at low concentrations, ordinary temperatures, and constant valence. The results of the present study confirm the observations of these researchers.

It can be also observed in Fig. 2 that the difference in the equilibrium concentrations of ions is small, contrary to expectation. Eq. (1) means the selectivity coefficient directly relates to the ability of the ion exchange unit to remove an ion over another. Considering the selectivity coefficients shown in Table 3, significant differences in the equilibrium concentrations of ions could be expected. This conflict might be due to the relatively small amount of the resin and the reaction mechanism of ion exchange. In the exchange reaction, one divalent ion is exchanged with two H^+ and one univalent ion with one H^+. This results in faster exhaustion of the resin operation capacity for the divalent ions than for the univalents. The operation (breakthrough) capacity of the resin is defined as the net number of ionic sites utilized in a given volume of the resin in a given cycle. While the total capacity of the resin is constant and the characteristics of the resin, the operation capacity depends on several operation factors such as resin volume, flow rate, feed concentration, resin particle size, temperature, and pH of the aque-

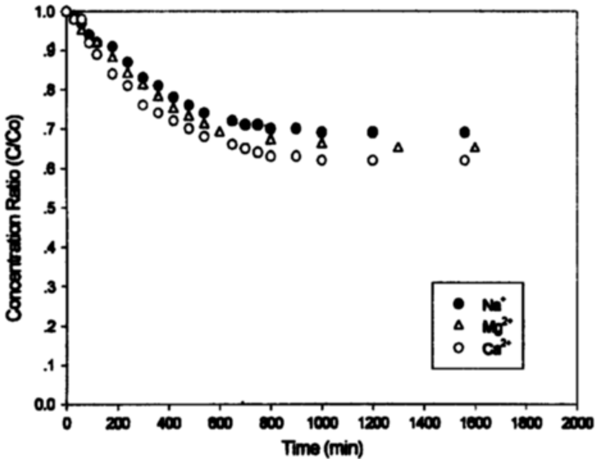

Fig. 2. The concentration profiles of cations for the two-component batch systems.

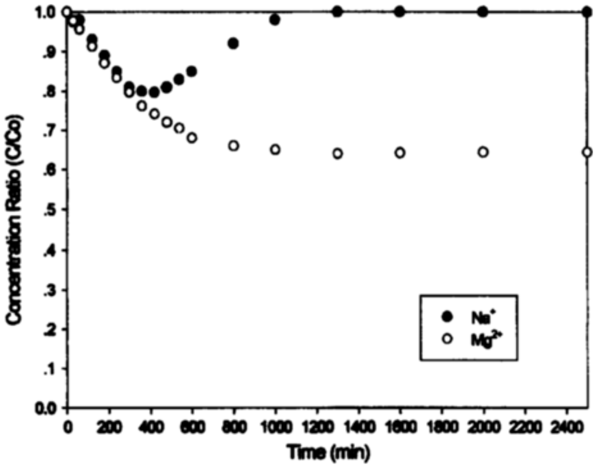

Fig. 3. The concentration profiles of cations for the H^++Na^+ Mg^{2+} system.

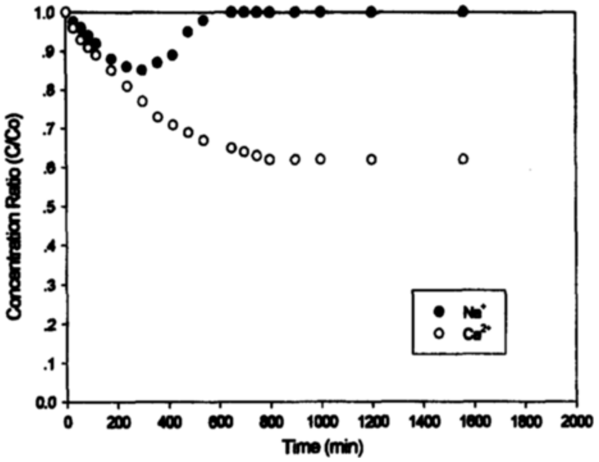

Fig. 4. The concentration profiles of cations for the H^{+}+Na^{+}+ Ca^{2+} system.

ous solution [Hsu and Pigford, 1991]. In the figure, the operation capacity of the resins appears to increase with the selectivity of ion and be exhausted after 700 min for all ions.

Figs. 3 and 4 show the concentration profiles of cations in the H^{+}+Na^{+}+Mg^{2+} and H^{+}+Na^{+}+Ca^{2+} systems, respectively. In these figures, the concentrations of the Mg^{2+} and Ca^{2+} decrease continuously at the early stage and reach the equilibrium state at about 700 min. However, that of the Na^{+} decreases during the early stage of about 350-400 min, and then increases to the equilibrium concentration after that stage. This phenomenon means that the Na^{+} exchanged with the H^{+} on resin phase at the early stage are exchanged again with the Mg^{2+} or Ca^{2+} present in the solution. In particular, all the Na^{+} exchanged is re-exchanged, and after all, the equilibrium concentration becomes equal to the initial concentration. These might be due to the large difference between the selectivity coefficients of the Na^{+} and that of the Mg^{2+} or Ca^{2+}. Comparing each curve of the Na^{+} in Figs. 3 and 4 to that in Fig. 2, it can be said that the amount of the Na^{+} exchangeable with the H^{+} is much affected by the presence of the divalent ions in the system.

The lowest point of the concentration profile of the Na^{+} in Fig. 3 is 0.78 and that in Fig. 4 is 0.84. This phenomenon indicates that a lesser amount of the Na^{+} at the early stage of the reaction is removed in the H^{+}+Na^{+}+Ca^{2+} system than in the H^{+}+Na^{+}+Mg^{2+} system. This is because the selectivity of the Ca^{2+} is greater than that of the Mg^{2+} and therefore, the competition for the Na^{+} to exchange the H^{+} in the system with the Ca^{2+} becomes more severe. In order to remove the Na^{+} from the multicomponent systems with higher valent ions before the breakthrough time, it is obvious more cation resin is needed. The equilibrium curves of the Ca^{2+} and Mg^{2+} do not appear to be changed by the Na^{+} significantly, except the slope at the early stage.

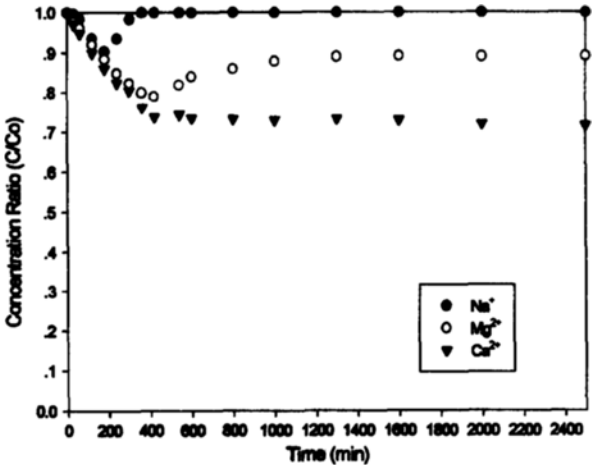

Fig. 5. The concentration profiles of cations for the H^{+}+Na^{+}+ Mg^{2+}+Ca^{2+} system.

Fig. 5 shows the equilibrium curves of cations in the quaternary system of H^{+}+Na^{+}+Mg^{2+}+Ca^{2+}. The concentration profile of the Na^{+} decreases until about 200 min, and then increases to reach the equilibrium. The lowest concentration ratio is 0.9. Therefore, as expected, much less Na^{+} seems to be removed in the quaternary system than in the binary or ternary system. This figure also indicates that the Ca^{2+} affects the shape of the equilibrium curve of the Mg^{2+}. The concentration of the Mg^{2+} decreases until C/C_o is 0.78 and then increases to the equilibrium concentration of 0.9, which means that a part of the Mg^{2+} adsorbed on the resin phase at the early stage is exchanged with the Ca^{2+} in the solution. The equilibrium concentration of the Mg^{2+} in the binary or ternary system is 0.65. This comparison leads to the conclusion that less Mg^{2+} is removed in the quaternary system. The concentration profile of the Ca^{2+} is also different from other systems. That is, the curve reaches the equilibrium state faster in the quaternary system than in the other systems, and the equilibrium concentration of 0.71 is higher than that in the binary or ternary system of 0.62. From these facts, it can be said that most of the ionic sites available for ion exchange on the resin are occupied by the Ca^{2+} and the rest by the Mg^{2+} at the equilibrium state.

2. Continuous Column System

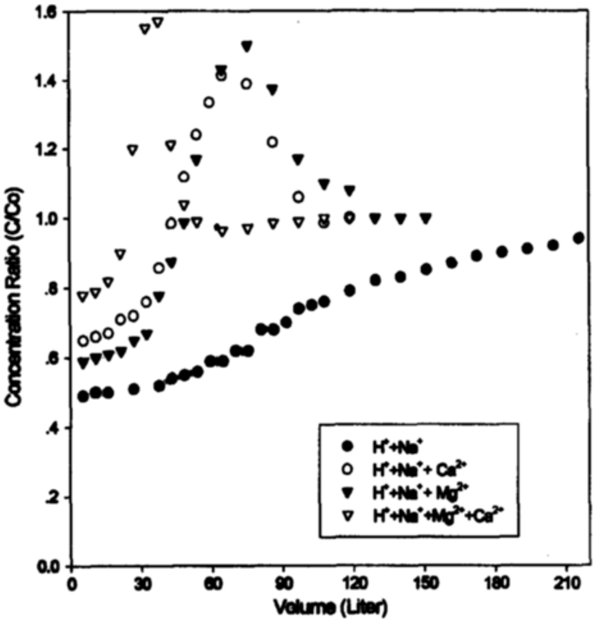

Fig. 6. The breakthrough curves of Na^{+} ion for the four different systems.

The results of the continuous column experiments are given in Figs. 6-10, from which one can see that different levels of initial leakage of each ion appear in the effluent of the exchange process. These leakages might be due to the insufficient contact time between the solution and the resins, which results from the high flow rate and the relatively short bed depth. These conditions were selected for the reasonable duration of the experimental runs.

Fig. 6 shows the effluent profiles of the Na^+ for the four different systems; H^++Na^+, H^++Na^++Mg^{2+}, H^++Na^++Ca^{2+}, and H^++Na^++Mg^{2+}+Ca^{2+}. It is observed from the figure that the existence of divalent ions affect the curve shape significantly. As the number of divalent ions increases, the breakthrough curve becomes steeper and the equilibrium is more favorable. With the divalences, C/C_o increases beyond unity, which means the effluent concentration is higher than the influent concentration. This is due to re-exchange of the Na^+ in the resin phase with divalent ions in the solution which have the greater selectivity coefficients than the Na^+. In the figure, the amount of the Na^+ exchanged with the H^+ at the early stage appears to be close to the amount of the Na^+ re-exchanged with the Ca^{2+} or/and Mg^{2+}. Therefore, it can be expected that the least competitive ion, Na^+, in the solution is not likely to exist on the resin phase after it reaches the equilibrium state. The Ca^{2+} and Mg^{2+} seem to have a similar effect on the breakthrough curve of Na^+ ion, even though the breakthrough of the Na^+ with the Ca^{2+} shows a slightly higher concentration at the early stage. As a result, the capacity of the MBIE column for the removal of a univalent ion decreases significantly by the presence of divalent ions.

Figs. 7 and 8 show the effluent concentration profiles of the Mg^{2+} and the Ca^{2+} in the three different systems, respectively. The Na^+ itself does not affect the breakthrough curves of the two divalent ions significantly. However, it shows that the Na^+ is more effective on the initial leakage and the slope of the breakthrough curve of the Mg^{2+} than on those of the Ca^{2+}. The effluent concentration of the Mg^{2+} in the presence of the Na^+ in Fig. 7 shows higher initial leakage and the wider slope of the breakthrough curve than that without the Na^+. While, the concentration profile of the Ca^{2+} in the presence of the Na^+ in Fig. 8 shows a slightly higher initial leakage and a similar slope. These facts indicate that the Na^+ affects the breakthrough curve of an ion with a smaller selectivity coefficient more than that of an ion with a larger selectivity coefficient. These figures also indicate that the total amounts of the Mg^{2+} and Ca^{2+} removed in the ternary systems are independent of the presence of the Na^+.

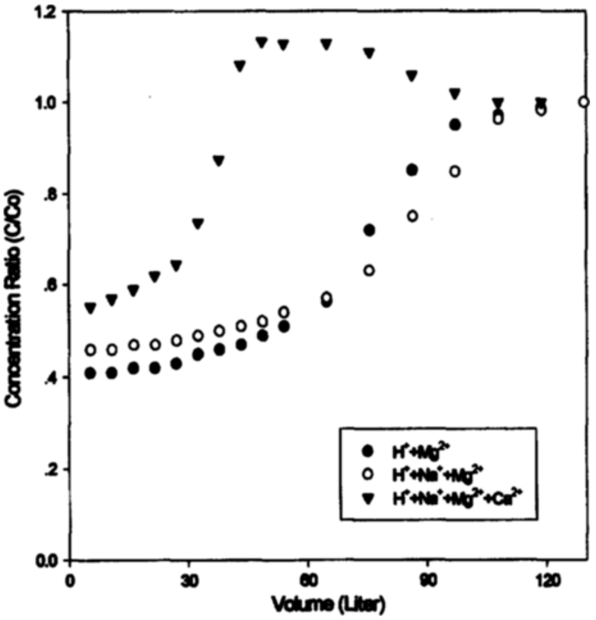

Fig. 7. The breakthrough curves of Mg^{2+} ion for the three different systems.

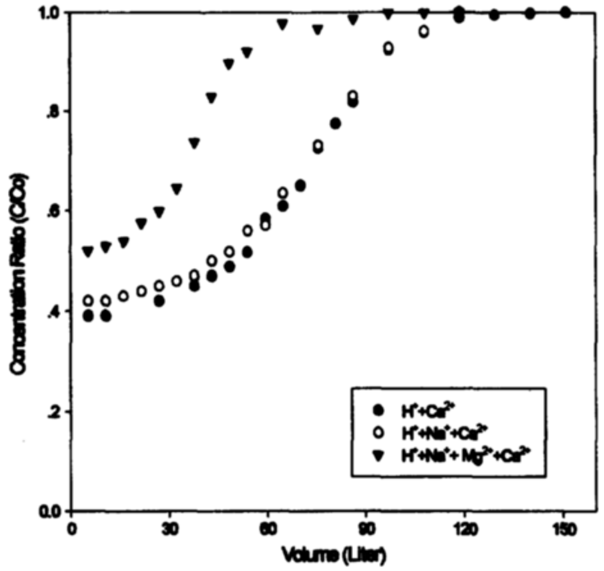

Fig. 8. The breakthrough curves of Ca^{2+} ion for the three different systems.

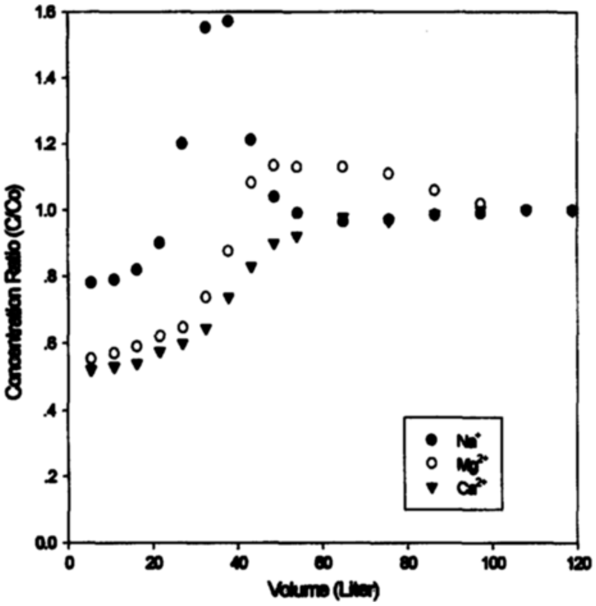

Fig. 9. The breakthrough curves of ions for the four component systems.

It is also observed in both Figs. 7 and 8 that the divalent ions affect significantly the breakthrough curve of each divalent ion in the quaternary system. As can be seen in these figures, the breakthrough curves of the ions in the quaternary system show faster breakthrough times, sharper slopes, and higher initial leakages than in the other systems. These trends are more significant in the Mg^{2+} than in the Ca^{2+}. It is especially observed in Fig. 7 that the breakthrough curve of the Mg^{2+} increases to more than C/C_o=1.0, and then drops to the equilibrium state. This is also because of the re-exchange process of the Mg^{2+} on resin with the Ca^{2+} in solution as in the case of the Na^+, which can be expected by considering that the selectivity coefficient of the Mg^{2+} is smaller than that of the Ca^{2+}. However, the maximum value of the concentration is 1.17, which is much lower than that of the Na^+. From this, it can be said that a part of the Mg^{2+} exchanged with H^+ ion is re-exchanged with the Ca^{2+}. Fig. 9 rearranges the effluent concentration profiles of the ions in the quaternary system to compare with each other.

To evaluate the effect of the divalent cation on the anion breakthrough curve, 2.5×10^{-5} M of $CaCl_2$ and 5.0×10^{-5} M of NaCl solutions were mixed, and then introduced into the experimental column. By doing this, the concentration of the Cl^- in the solution is 1.0×10^{-4} M. The result of this experiment was compared to that of the experiment conducted with 1.0×10^{-4} M of NaCl solution. This comparison is shown in Fig. 10. As is shown in this figure, the comparison does not give as much difference as expected. However, it can be observed through a close investigation of this figure that the exchange rate of anion is slightly higher in the ternary system than in the binary system. These experimental results agree well with previous studies of Harries [1988] and Yoon et al. [1995]. They reported that the anion exchange was more favorable in an acidic medium than in an alkaline or a neutral medium because the mass transfer coefficient of the Cl^- is higher in low pH, while that of the Na^+ is higher in high pH. In the ternary system, pH might be lower than in the binary system because the exchange rate of the Ca^{2+} with the H^+ is higher than that of the Na^+ with the H^+. As the cation exchange rate increases, the solution becomes more acidic, and then the anion exchange rate increases.

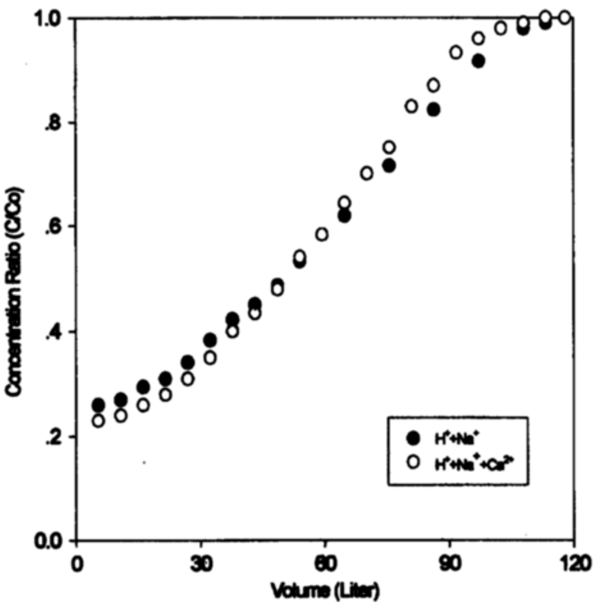

Fig. 10. The breakthrough curves of Cl^- ion for the three different systems.

CONCLUSIONS

The effect of multicomponent cationic systems on the performance of the MBIE at ultralow ionic concentrations of ppb level was experimentally evaluated. The concentration variations of the cations in the H^++Na^+, $H^++Na^++Mg^{2+}(Ca^{2+})$, and $H^++Na^++Mg^{2+}+Ca^{2+}$ systems were compared with each other. Through both batch and continuous column experiments, the following conclusions are drawn:

1. The shape of the equilibrium curves of ions depends on the selectivity coefficients of the ions. The selectivity coefficient increases with the higher valence and the increasing atomic number of the exchanging ions at the experimental conditions. As the selectivity coefficient increases, the ion exchange rate and the operation capacity of resins increase, while the equilibrium concentration decreases.
2. The equilibrium curve of a univalent ion is much affected by the presence of divalent ions, but not vice versa. Divalent ions affect significantly the equilibrium curves of other divalent ions. However, the equilibrium of the ion of a smaller selectivity coefficient is affected much more than that of the ion of a larger selectivity coefficient.
3. There is a re-exchange process between the ions exchanged with the H^+ in resin phase at the early stage of the exchange reaction and other ions of larger selectivity coefficients existing in solution. This results in increases of the equilibrium curves after the re-exchange process takes place.
4. The breakthrough curve of an ion with univalence is affected significantly by the presence of divalent ions. The breakthrough curve becomes steeper and the equilibrium is more favorable as the number of the divalent ions increases. There is also the re-exchange process for the univalent ion in the systems of divalent ions. Thus, the capacity of the MBIE units for the removal of a univalent ion decreases significantly by the presence of divalent ions. The univalent ion affects slightly the shapes of the breakthrough curves of the divalent ions. However, this effect becomes small as the selectivity coefficients of the divalent ions increase. The divalent ions affect significantly the breakthrough curve of each divalent ion. The breakthrough curve of the divalent ion with a smaller selectivity coefficient increases beyond C/C_o=1.0, resulting from the re-exchange process, and then decreases to equilibrium.
5. The effect of the multicomponent systems of cations on the anion breakthrough curve is insignificant. However, the exchange rate of the anion is slightly faster in the multicomponent system which contains a divalent ion than in the univalent cationic system. This is because the solution becomes more acidic as the cation exchange rate increases and the anion exchange is more favorable in an acidic solution than in neutral or alkaline medium.

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