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Ion exchange accompanied by neutralization in an anion bed

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Abstract

The performance of the anion bed in a two-bed deionization process was investigated. Experiments and simulation were carried out with a feed solution concentration of about 0.005N. The prepared solutions were dilute acid of HCl, H_2SO_4 and a mixture of the two. The bed height was about 40 cm and the flow rate in the range of 75–150 ml/min. Both the binary and ternary models were used to predict the column performance. In both models, it was found that the equilibrium parameters do not affect significantly the breakthrough behavior. This is due to the accompanied neutralization reaction which results in the irreversible form of the rate equation. The experimental and theoretical breakthrough curves show very good agreement especially for the early part of the data. Results of this study suggest that a pseudo-binary or pseudo-ternary model can be used to model the fixed bed deionization process by ion exchange.

Keywords: Anion exchange; Resin bed; Neutralization

1. Introduction

The demand for deionized water is increasing due to the rapid expansion of the electronic and microelectronic industries. Recent studies have been focused on the production of ultrapure water by ion exchange process [1,2]. Deionized water is produced using either a mixed-bed or a two-bed ion exchange system [3–10]. In the later configuration, the effluent from the cation bed is essentially a mixture of dilute acids. This effluent, when passed through the anion bed of OH^- form, yields water with very low ionic content. The reaction that takes place in the anion bed not only deals with ordinary ion exchange, but also involves neutralization. Although a mixed bed has much higher treatment efficiency than a two-bed system, there are instances when a two-bed unit can be used in series with a mixed bed. When the feed water ionic concentration is high, the two-bed system can be used as a pre-treatment unit. In this case, the mixed bed unit that treats effluent from the two-bed system can produce water of utmost purity. The performance of the cation bed in the two-bed system is dictated by the same basic principles for any ion exchange column operation. However, for the anion bed, the assumption of a constant ionic concentration in the solution phase is no longer valid. This is because of the neutralization that takes place as the anion resin bed treats the effluent discharged from the cation bed. The total ionic concentration of the solution from an anion bed will be reduced as exchange proceeds. In this work, we present both experimental data and a simple and practical quantitative model for investigating column dynamics of anion exchange accompanied by neutralization. Simulation results were used to compare with the experimental data obtained in this study.

2. Theoretical

It is assumed that the feed to an anion bed is a mixture of dilute strong acids consisting of HCl and H_2SO_4. The continuity equations for anionic species Cl^- and $SO_4{}^{2-}$, after neglecting axial dispersion terms, are

$$u\frac{\partial C_i}{\partial z} + \beta\frac{\partial C_i}{\partial t} + \frac{\partial q_i}{\partial t} = 0, \quad i = 1, 2 \tag{1}$$

where C and q denote the concentration of chloride or sulfate ion in the solution and resin, respectively, z the axial bed distance from solution inlet, u the superficial linear flow rate, β the void fraction of the bed and t the absolute time.

Since the feed is dilute, a rough estimate using the Helfferich number criterion [11] indicates that film diffusion is likely the rate-controlling step. The linear driving force rate equations based on film diffusion rate control are

$$\frac{\partial q_i}{\partial t} = K_f a_p (C_i - C_i^*), \quad i = 1, 2 \tag{2}$$

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Nomenclature

a_p	mass transfer surface area per unit volume of contacting volume (m^2/m^3)
C	concentration of counter ions in the solution (meq./l)
C^*	equilibrium liquid phase concentration with respect to resin phase (meq./l)
D	self-diffusion coefficient in solution (cm^2/s)
D_{eff}	effective diffusivity (cm^2/s)
K_f	rate parameter for film diffusion rate equation (s^{-1})
L	resin bed height (cm)
q	concentration of one species of counter ions in the resin (meq./ml)
Q_c	exchange capacity of the resin (meq./ml)
r_0	resin bead radius (cm)
t	absolute time (s)
T	throughput parameter
u	linear flow rate (cm/s)
y	normalized resin concentration of one of the species of counter ions
z	axial distance from the inlet of the resin bed (cm)

Greek symbols

α	separation factor
β	void fraction of resin bed
δ	liquid film thickness (cm)
κ	selectivity coefficient

Since the exchange of anionic species is accompanied by neutralization, the total anion or cation concentration is not constant. The value of C_i^* thus depends on the variation of cation concentration, that is, the change of concentration of hydrogen ion. For the Cl^-–OH^- exchange system, the separation factor is defined by

$$\alpha_3^1 = \frac{[q_1][C_3]}{[q_3][C_1]} \tag{3}$$

where q and C represent the concentration in resin and liquid phases, respectively. Subscript 1 denotes chloride ions and subscript 3 the hydroxide ions. For this binary exchange system, the equilibrium relation can also be expressed by

$$\alpha_3^1 = \frac{y[OH^-]}{(1-y)[Cl^-]} \tag{4}$$

where y is the equivalent fraction of exchanger in the chloride form. Since electroneutrality must be obeyed

$$[Cl^-] = [H^+] - [OH^-] = \frac{y[OH^-]}{(1-y)\alpha_3^1} \tag{5}$$

Assuming that $[OH^-]$ is negligible compared to $[H^+]$ and after substituting the dissociation constant for water, the equilibrium value of $[Cl^-]$ is

$$[Cl^{-*}] = 0.0000001\sqrt{\frac{y}{(1-y)\alpha_3^1}} \tag{6}$$

Similarly, the equilibrium value for $[SO_4{}^{2-}]$ is

$$[SO_4{}^{2-*}] = 2.32\times 10^{-10}\left[\frac{2y}{\kappa_3^2 Q_c(1-y)}\right]^{1/3} \tag{7}$$

where y is the equivalent fraction of exchanger in the sulfate form, κ_3^2 is the selectivity coefficient for the exchange between sulfate and hydroxide ions.

For the ternary $SO_4{}^{2-}$–Cl^-–OH^- exchange system, the equilibrium relations are obtained from the relations defined for binary Cl^-–OH^- and $SO_4{}^{2-}$–OH^-. We have

$$\alpha_3^1 = \frac{y_1[OH^-]}{y_3 C_1^*} \tag{8}$$

$$\kappa_3^2 Q_c = \frac{y_2[OH^-]^2}{y_3^2 C_2^*} \tag{9}$$

Electroneutrality requires that

$$C_1^* + C_2^* + [OH^-] = [H^+] = \frac{K_w}{[OH^-]} \tag{10}$$

Given the resin phase composition y_1 and y_2, the values of C_1^*, C_2^* and $[OH^-]$ can be determined by the above three independent equations.

For a feed solution containing multiple anionic species, a pseudo-ternary model can be used to characterize the exchange of these species with the hydroxide ions. In this case, all the divalent and monovalent species can be lumped together into two single components. An average α and κ can be used for the calculation. The rate parameter (K_f) in the linear driving force film diffusion equation can be estimated by $K_f = 1.5D_{eff}/(r_0\delta)$ [12], where D_{eff} is the effective diffusivity in the liquid phase, r_0 the resin bead radius and δ the liquid film thickness. The liquid film thickness can be calculated from Glueckauf's correlation equation [12]. Helfferich [13,14] showed that for ion exchange process involving neutralization, the rate actually depends on the diffusion of both the counter ions and the co-ions. The effective diffusivity for the Cl^- and OH^- exchange is derived by equating the net flux of H^+ and Cl^- to obtain

$$D_{eff} = \frac{2D_{H^+}D_{Cl^-}}{D_{H^+} + D_{Cl^-}} \tag{11}$$

Similarly, the effective diffusivity for the $SO_4{}^{2-}$–OH^- exchange can be derived in the same manner to obtain

$$D_{eff} = \frac{3D_{H^+}D_{SO_4{}^{2-}}}{D_{H^+} + 2D_{SO_4{}^{2-}}} \tag{12}$$

3. Simulation of column performance

Numerical algorithms were developed for the simulation of deanionization of the systems based on both binary and ternary models. The equations employed in the simulation were Eqs. (1) and (2), and the appropriate equilibrium relationships given in Eqs. (3)–(10). Simple boundary conditions of constant feed concentration and zero pre-saturation in the bed are also incorporated in the simulation. If needed, the numerical algorithms can be modified to take account of variable feed and non-uniform pre-saturation which are likely to occur in a cyclic process. The present experimental work covered Cl^-–OH^-, $SO_4{}^{2-}$–OH^- and $SO_4{}^{2-}$–Cl^-–OH^- exchange. The ion exchange in these three systems is accompanied by a neutralization reaction. The basic equations for computing column dynamics, which include continuity, rate and equilibrium relationship, are the same as those formulated for the ordinary exchange system. However, because of the neutralization, the total electrolyte concentration in the solution is not constant as in the case for the ordinary exchange system. Thus, the charge balance and the dissociation expression for water are also incorporated in the simulation calculation. The computations for the binary system of Cl^-–OH^- and $SO_4{}^{2-}$–OH^- are easier to perform compared to the simulation for the ternary system. In the simulation for the ternary system, it is assumed that feed contains chloride and sulfate ions while the resin bed is initially in OH^- form. The exchange and reaction between these three counter ions and the hydrogen co-ion proceed in two stages. In the first stage, all the OH^- ions in the resin are being replaced by the incoming Cl^- and $SO_4{}^{2-}$ ions in the solution. The OH^- ions released from the resin is further neutralized by H^+ co-ion present in the solution. The second stage commences when all OH^- ions in the resin are consumed and further treatment of feed solution will result in a redistribution of chloride and sulfate composition in the resin phase. For the binary and ternary system simulation, the self-diffusivities of $SO_4{}^{2-}$, Cl^-, OH^- and H^+ are taken from [15]. For binary system the effective diffusivity for Cl^-–OH^- and $SO_4{}^{2-}$–OH^- exchange are calculated from Eqs. (11) and (12), respectively. For the ternary system simulation, the rate parameters in the two rate equations are assumed to be equal in the first stage of exchange. That is, assuming the effective diffusivity involving exchange between Cl^- and OH^- is the same as that of exchange between $SO_4{}^{2-}$ and OH^-. The value of this effective diffusivity was obtained from the average value of $D_{Cl^-–OH^-}$ and $D_{SO_4{}^{2-}–OH^-}$. In the second stage of exchange, which involves only Cl^- and $SO_4{}^{2-}$, the effective diffusivity is calculated from the Nernst–Planck equation [16]. By assuming an equal equivalent fraction of sulfate and chloride ions in the resin phase, that is, $y_{Cl^-} = y_{SO_4{}^{2-}} = 0.5$, the average effective diffusivity is

$$D_{SO_4{}^{2-}–Cl^-} = \frac{5D_{Cl^-}D_{SO_4{}^{2-}}}{D_{Cl^-} + 4D_{SO_4{}^{2-}}}$$

The values of equilibrium parameters of $\alpha_{OH^-}^{Cl^-}$ and $\kappa_{OH^-}^{SO_4{}^{2-}}$ used for the simulation study were taken from the published data of Anderson [17].

4. Experimental

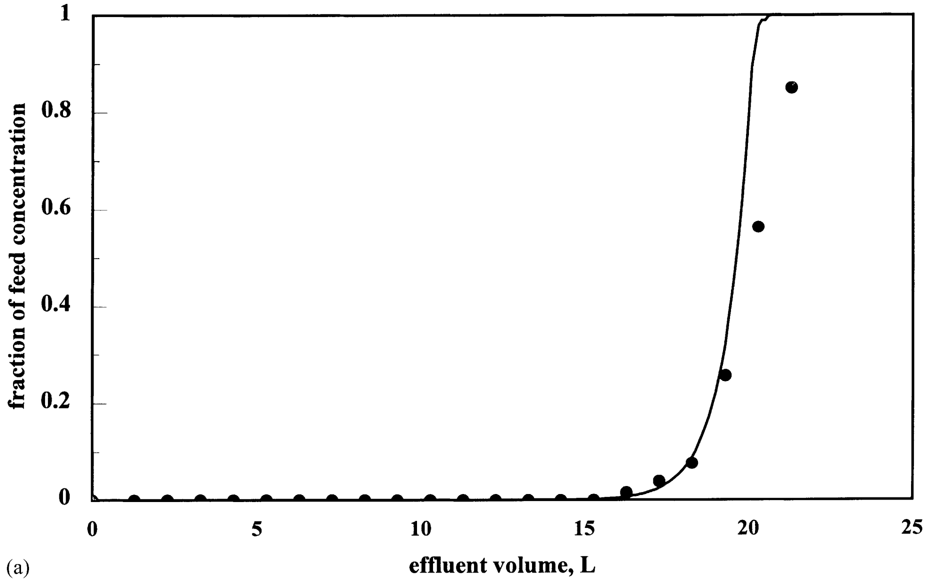
In each run, fresh Dowex 1 (20–50 mesh) resins in chloride form were weighted and dried in an oven. The weight of the dry resins was recorded. The resins were placed in a beaker containing distilled water. The resin solutions were then slowly introduced to a 1.5 cm i.d. glass column for the preparation of a resin bed. Two liters of 0.5N NaOH solution was passed through the bed at a flow rate of 25 ml/h. After the elution, the bed was washed with 2 l of distilled water. The eluted solution, which contained chloride ions, together with the discharged wash water was collected. Samples of the collected solutions were analyzed for total chloride content. From the results of the analysis, the bed capacity was calculated. To start a run, the prepared resin bed in OH^- form was first rinsed with distilled water before feed solutions of either pure HCl, pure H_2SO_4 or mixed feed of HCl and H_2SO_4 were introduced to the top of the resin bed. The flow rate was pre-adjusted with proper settings in a MasterFlex pump. The flow rates employed in the study were 75, 100 and 150 ml/min. In the process of treating the feed solution, samples of effluent from the bed were collected at regular interval (either 10 or 20 min). The volume of samples collected was about 100–200 ml. The experimental run was conducted until the measurement of effluent pH and anion concentration measurements were almost identical to those of the feed solution. The collected samples were analyzed for their pH value and the Cl^- and $SO_4{}^{2-}$ concentration. The analysis of Cl^- and $SO_4{}^{2-}$ was conducted using a HACH DR 2000 spectrophotometer.

5. Discussion of results

Experimental results were obtained for column runs with feed solution containing only HCl or H_2SO_4. The feed concentrations for these two runs are both about 0.005N. Two other experimental runs were also conducted for a mixed feed solution containing about 0.0025N of HCl and 0.0025N of H_2SO_4. In all these runs, a 1.5 cm i.d. glass column was employed. The resin bed height was 40 cm. The total bed volume with resin in OH^- form is about 70.6 ml. Although the model equations proposed can be used to predict both the solution and resin phase concentration history, only the effluent concentration breakthrough data were determined experimentally. The experimental determination of resin phase concentration profile development was not performed in this study because of the expected tedious laboratory work involved. However, the solid phase composition characteristics were examined through the results obtained from simulation.

5.1. Binary system

Fig. 1a is the experimental data and calculated breakthrough curve for feed solution containing 0.0051N Cl^- with



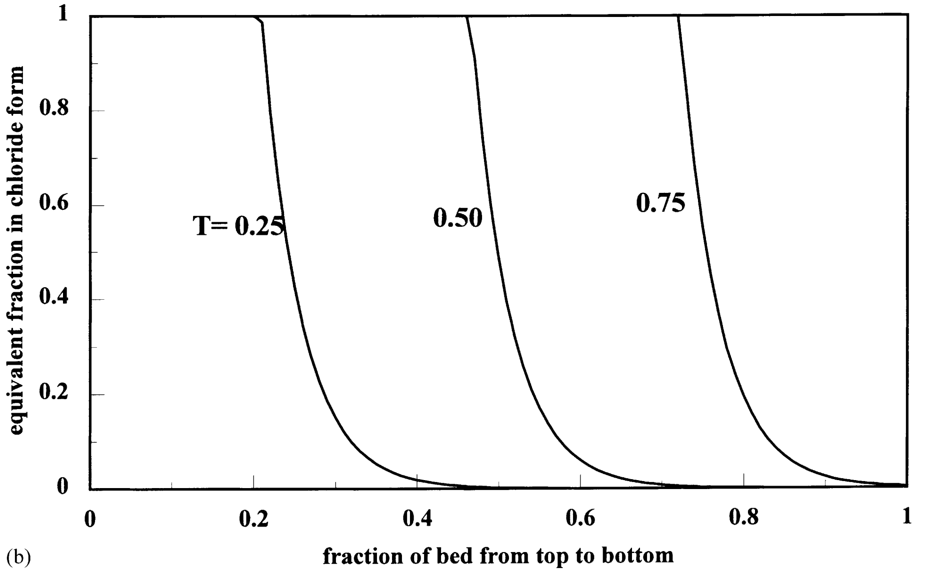
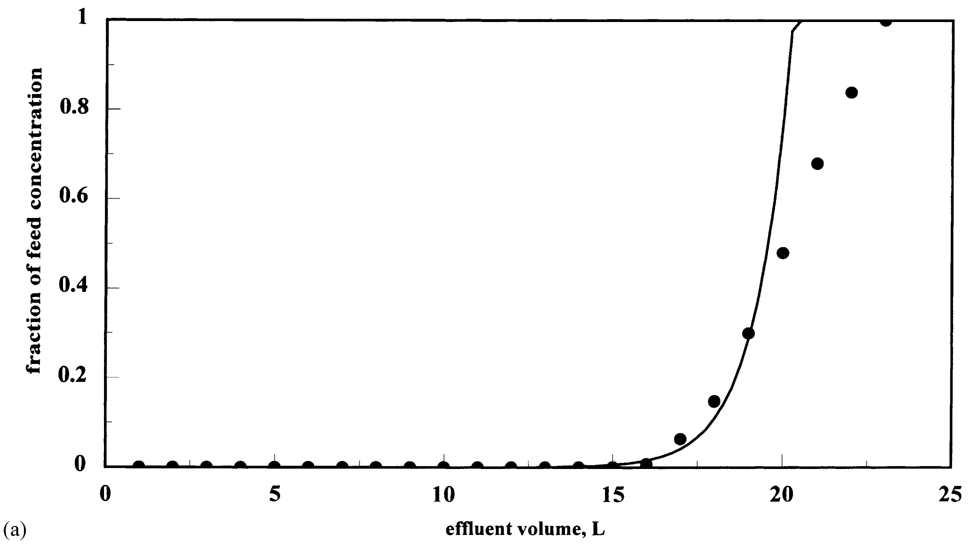


Fig. 1. (a) Experimental data and calculated breakthrough curve for Cl^-–OH^-exchange; (b) simulated resin phase concentration profile development for Cl^-–OH^- exchange.

a flow rate of 100 ml/min. As mentioned before, Glueckauf [12] recommended the expression of $K_f = 1.5D_{eff}/(r_0\delta)$ to calculate the rate parameter for film diffusion. The film thickness (δ) can be calculated from the correlation proposed by Glueckauf [12], in which $\delta = 0.2r_0/(1+70ur_0)$, where u is the linear flow rate in cm/s, r_0 the resin bead radius in cm. For this run, the calculated effective diffusivity is 3.33×10^{-5} cm^2/s. By assuming an average value of r_0 of 0.035 cm for the 20–50 mesh resin used, the calculated film thickness from Glueckauf's correlation is 0.0021 cm. Helfferich [18] stated that film thickness estimated from hydrodynamics consideration or kinetics measurements is about 0.001–0.01 cm. The value of film thickness calculated is within this range. The calculated rate parameter (K_f) for the film diffusion rate equation is 0.68 s^{-1}. The agreement between experimental and calculated breakthrough curve is satisfactory except for the later portion of the curve. The deviation is due to the contribution of particle diffusion that is expected when the bed is almost saturated with chloride ions. Fig. 1b shows the simulated bed composition profile development for this run. The parameter (T) employed in the figure is defined as the throughput ratio by Hiester and Vermeulen [19]. T is a loading factor which represents the amount of ionic species loaded to the bed relative to the total resin bed capacity. It is seen that the bed profile is very sharp and that the reaction zone is very narrow. Fig. 2a is the experimental data and calculated breakthrough curve for a feed solution of 0.0052N H_2SO_4. Like the run for Cl^-–OH^-



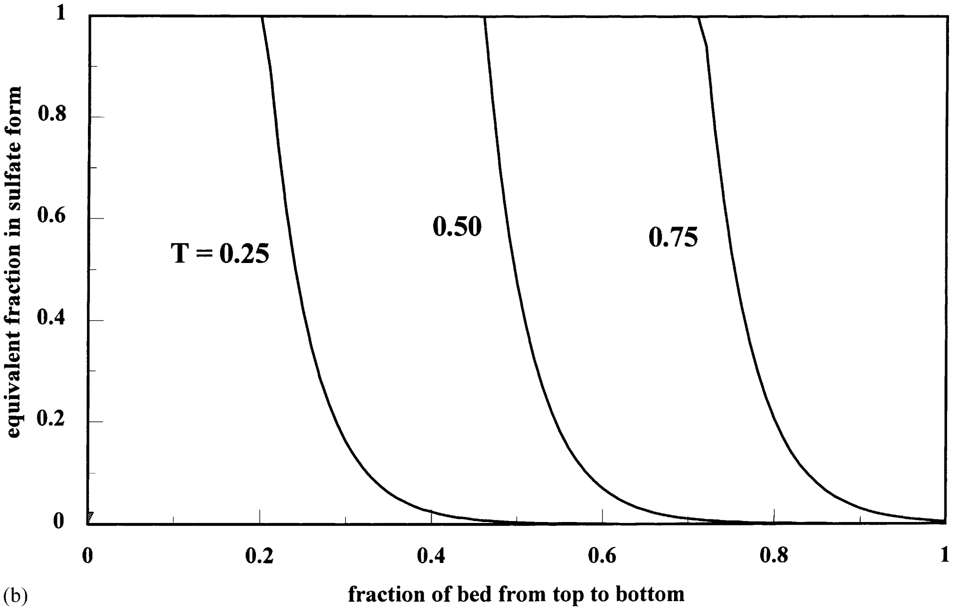


Fig. 2. (a) Experimental data and calculated breakthrough curve for SO_4^{2-}–OH^- exchange; (b) simulated resin phase concentration profile development for SO_4^{2-}–OH^- exchange.

exchange, the agreement between calculated and experimental breakthrough curve is also very good except for the later part of the data. For this run, the flow rate was also maintained at 100 ml/min. Fig. 2b shows simulated bed composition profile development for this particular run. Again, like Fig. 1b, a constant pattern [20] is also observed for the simulated results. The diffusivity used for the simulation of this run is $D_{\mathrm{eff}} = 2.56 \times 10^{-5}\,\mathrm{cm^2/s}$ and the calculated K_{f} is $0.53\,\mathrm{s^{-1}}$. Results of a graphical integration, over the entire breakthrough data shown in both Figs. 1a and 2a, agree with total bed capacity to within 3%. This means that the mass balance for the counter ion is accurate within the range of the experimental error. The results of the two breakthroughs show that the curves are very sharp due to the irreversible exchange nature of Cl^- and SO_4^{2-} ions with OH^- ions as a result of the neutralization reaction. The slight variation of K_{f} values used in the calculations does not result in any significant difference in the shape of breakthrough curves. It is expected that the breakthrough curves will be more diffuse if only ordinary exchanges are involved. Because of the very high rate of conversion of OH^- form of resin to chloride or sulfate form, the degree of utilization is also very high. As revealed in Figs. 1a and 2a, at a breakthrough of 1%, the degree of resin utilization is about 90%. The bed profiles demonstrate the development of a constant pattern behavior, indicating a constant pattern model solution is applicable for simplifying quantitative study if desired.

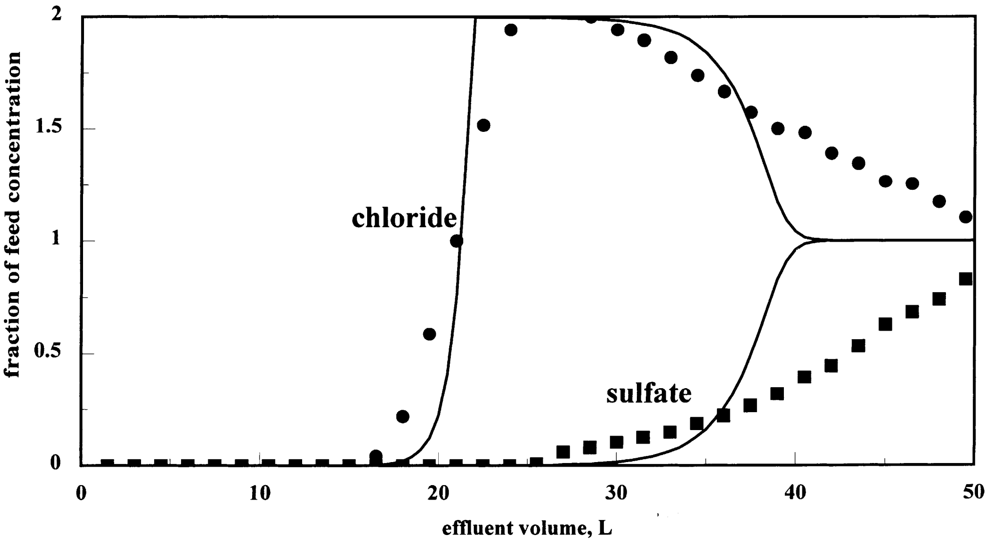


Fig. 3. Experimental data and calculated breakthrough curves for SO_4^{2-}–Cl^-–OH^- exchange, at flow rate of 75 ml/min.

5.2. Ternary system

Two experimental column runs were performed with feed solutions containing a mixture of HCl and H_2SO_4. The total concentration in the feed was about 0.005N. The equivalent fractions of HCl and H_2SO_4 in the mixture were approximately equal to each other. The results of these two runs are shown in Figs. 3 and 4. The corresponding flow rates for these two runs are 75 and 150 ml/min. In the simulation using ternary model, it is assumed that only SO_4^{2-}, Cl^- and OH^- are involved in the anion exchange. The presence of HSO_4^- is expected to be negligible owing to neutralization and the high preference of resins for divalent SO_4^{2-}. For the experimental runs with mixed HCl and H_2SO_4 solution, the total resin bed capacity is determined to be about 104 meq. Figs. 3 and 4 show that the breakthrough of Cl^- ion raises to a maximum value, which exceeds its feed concentration, before falling back to the feed condition. This rollback behavior is typical in a multi-component ion exchange system in which the less preferred ions are being eluted out by the more preferred ionic species. When the total effluent concentration is plotted versus effluent volume, the breakthrough curve is also very sharp as in the case of treating either HCl or H_2SO_4 feed. The column behavior of this two-component feed system, with the bed initially saturated with the third component, can best be explained in terms of a two stages of exchange. In the first stage, the OH^- in the resin has no selectivity with respect to the incoming anions in the solution. All the Cl^- and SO_4^{2-} ions are rapidly captured to the resin bed and OH^- ions expelled from resin phase. The released OH^- ions are subsequently being neutralized by hydrogen ions in the solution. When

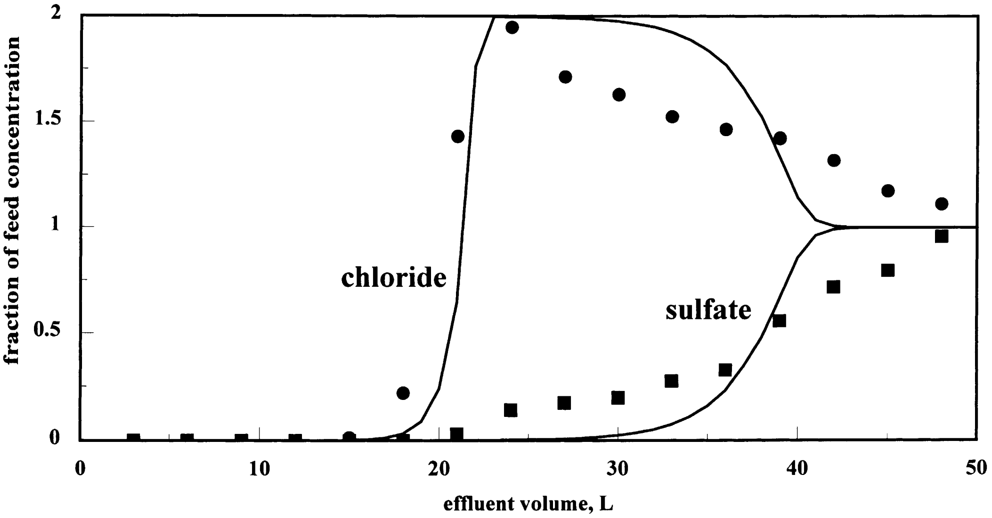


Fig. 4. Experimental data and calculated breakthrough curves for SO_4^{2-}–Cl^-–OH^- exchange, at flow rate of 150 ml/min.

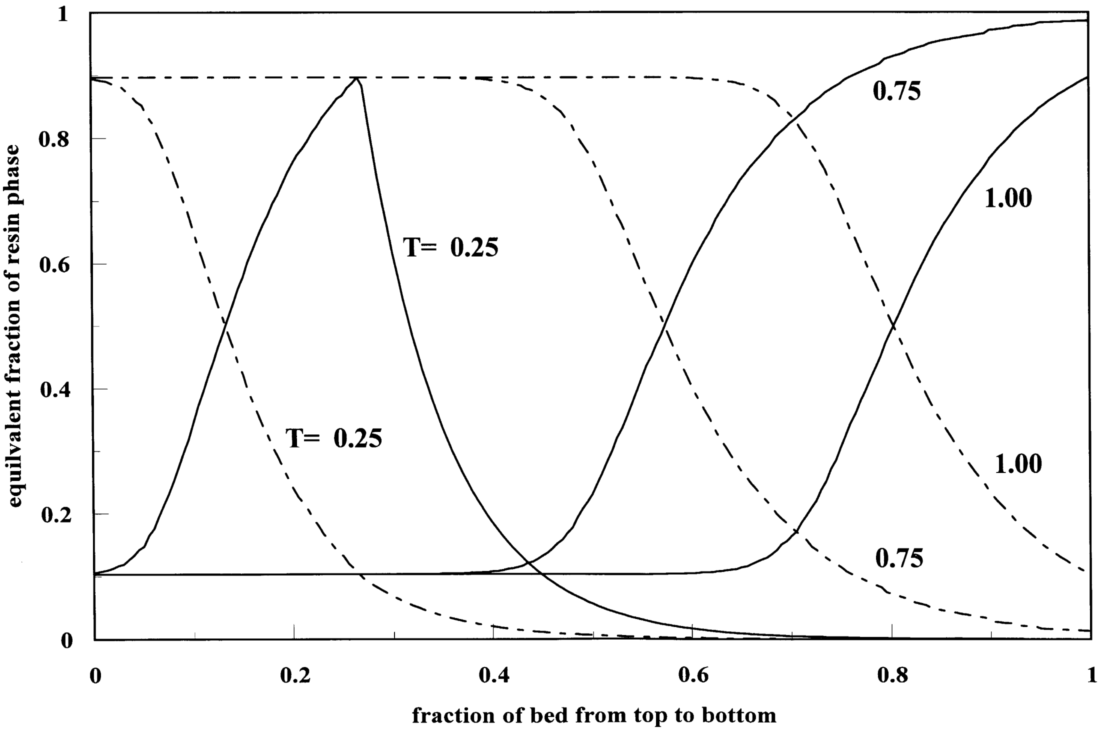


Fig. 5. Simulated resin phase concentration profile development for SO_4^{2-}–Cl^-–OH^- exchange (solid lines for chloride ion; dashed lines for sulfate ion).

the OH^- ions in the resin phase are exhausted, an ordinary exchange of a binary system of Cl^- and SO_4^{2-} takes place. The bed composition is then readjusted and redistributed according to the Cl^- and SO_4^{2-} equilibrium relationship. The results show that the flow rate variation does not affect the time of breakthrough very significantly for chloride. However, the breakthrough for sulfate does come much earlier if a higher flow rate of 150 ml/min is used. The simulated results for these two runs are also shown in Figs. 3 and 4. Like the runs with a single type of acid. The agreement between experimental and simulated results are very satisfactory except for the later part of breakthrough curve. The reason for the discrepancy in the last part of breakthrough curve is likely due to the use of a constant value of effective diffusivity and in neglecting the effect of diffusion in the resin phase. To perform the simulation for the ternary system, the rate parameters must be defined or estimated. In this study, the physical properties and kinetic parameters for the rate equations are estimated from data available in literature or from published empirical correlation. The mass transfer coefficient in the film diffusion rate equation depends on the effective diffusivity, film thickness and resin beads radius. The values of film thickness were also calculated from Glueckauf's correlation. For flow rates of 75 and 150 ml/min, the corresponding calculated values of δ/r_0 were 0.073 and 0.0447, respectively. The effective diffusivity for the first stage of exchange is assumed to be the same for the two runs with a value of 2.9×10^{-5} cm^2/s. For the second stage of exchange involving only the exchange between chloride and sulfate ions, the effective diffusivity was calculated to be 1.72×10^{-5} cm^2/s. For the first stage of exchange, the calculated values of K_f for the two experimental runs were 0.486 and 0.794 s^{-1}. The normalized bed height parameter, which is defined by $K_f L/u$, where L is the bed height, is calculated to be 27.5 and 22.4. Fig. 5 is the simulated results of a typical bed profile development in which the displacement effect of the divalent ion on monovalent ion is clearly shown. It should be emphasized that the rate parameters used in the simulation were estimated independently from resin bed experimental data. This is in contrast with many theoretical studies in which the rate parameters were obtained by fitting experimental breakthrough curves. Since the purpose of the deionization is the removal of all the ions present, a simplified model that can predict the breakthrough of any ion is very useful. The use of a pseudo-ternary model can facilitate the design calculation of the anion bed performance in a two-bed deionization process.

6. Summary and conclusions

Experiments and simulations were performed for deionization of dilute HCl and H_2SO_4 by ion exchange with OH^- form resin in an anion resin bed. The experimental results indicate that OH^- in the resin has no selectivity toward chloride or sulfate ion in the solution. The exchange with the OH^- ion is irreversible and is not significantly affected by the equilibrium relationships with the counter ions. When only HCl or H_2SO_4 is treated in the resin bed, the breakthrough curves for Cl^- or ${SO_4}^{2-}$ are steep and sharp, which leads to very high degree of resin utilization. Results of simulation study also indicated a constant pattern for the bed composition profile development. The ternary model developed for simulation can be extended to a multiple species system in which various monovalent and divalent species are present.

Acknowledgements

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