Rev.Téc.Ing., Univ.Zulia Vol.3 , N°2 , 1980

THE EFFECTS OF SELF-INDUCED ELECTRIC FIELD ON THE CALCULATIONS OF MOVING-BED ION-EXCHANGE UNITS

C, García Escuela de Ingeniería Química Facultad de Ingeniería, Universidad del Zulia Maracaibo, Venezuela

M. David Departamento de Ingeniería Química Universidad de Washington Seattle, Washington

ABSTRACT

The effects on bed size, for steady-state moving-bed ion-exchange processes, of ionic migration resulting from self induced electric fields were studied using the film model of mass transfer. The ratio H/He provides a quantitative indication of the relative importance of the ionic-migration inclusion on design calculations. A large deviation from unit indicates a significant over-prediction or under-prediction of the bed length by neglecting the ionic-migration effects. In general, H/He increases with increasing diffusivity ratio. However, the relative importance of ionic migration on H/He depends on the selectivity of the ion exchanger for the entering ion (α), degree of removal of the ion from solution, and percentage of exchanger capacity used.

The electric-field effects are more important for linear and slightly-favorable equilibrium systems ($\alpha < 10$), where H/He varies between 1.40 and 4.75 for the range of diffusivity ratios analyzed

1

(up to 15). For unfavorable equilibrium systems, the effects are significant, even for slightly unfavorable equilibrium systems, for which H/He varies between about 0.80 and 0.40. For very unfavorable equilibrium systems ($\alpha < 0.10$), H/He can approach a limiting value determined by the ionic self-diffusivity ratio only. The results indicate that a constant mass-transfer coefficient can not be used for an ion-exchange process over a wide range of degree of removal or saturation of the resin.

RESUMEN

Los efectos de migración iónica resultante del campo eléctrico auto-inducido son analizados en diseño de lechos móviles de intercambio iónico en régimen estacionario usando el modelo de transferencia de masa de película. En general, *H/He*, definido como la relación entre la altura total de la columna basada en la difusividad del catión entrante y la altura total de la columna incluyendo mi gración iónica, aumenta con aumento de relación de difusividades. No obstante, la importancia relativa de migración iónica sobre *H/He* depende de la selectividad de la resina por el ión entrante, grado de eliminación del ión de solución y porcentaje de la capacidad de la resina.

Para sistemas de equilibrio favorable, *H/He* varía entre 1.40 y 4.75 para un rango de relación de difusividad máxima hasta 15. Esto significa que cualquier diseño, despreciando los efectos de migración iónica, puede resultar en un sobre-diseño de columnas, particularmente para sistemas iónicos con equilibrio lineal y ligeramente favorable para el ión entrante de la solución.

INTRODUCTION

The rate of ion exchange is controlled by diffusional processes. The mass-transfer rate may be controlled by diffusion between the bulk solution and the surface of the exchanger, by diffusion within the resin itself or by a combination of both resistances. Diffusion within the particle will be the rate-determining process when the transfer of ions to the surface of the particle takes place more readily than their transfer into the solid phase.

However, the interdiffusion of two charged species, generated from a concentration gradient, tends to produce an electric field which couples the fluxes of the exchanging ions. As the faster ions tends to migrate at a higher rate, the accumulation of the charges very rapidly generates an electrical-potential gradient which retards the faster ion and acelerates the slower one. In this manner, the unbalance of the purely diffusional fluxes $\left(J_{diff} = -D_i \nabla C_i\right)$ of the two exchanging ions is automatically corrected by a self-induced electric field (so-called ionic migration $J_{elec} = -D_i Z_i C_i \frac{F \nabla \Phi}{RT}$) upon the transport processes, thereby enforcing the proper equivalence of the ionic fluxes required to preserve electroneutrality [5,6,9,10, 11]. Attempts at correlating such effects, for instance, by calculating the Schmidt number with an effective diffusivity , have been presented by several investigators. Kataoka et. al [7] applying the hydraulic-radius model to the flow in a packed bed, analysed ion-exchange liquid-phase mass-transfer and liquid-phase diffusivity. Van Brocklin [13] studied the effects of ionic migration on mass trans fer rates in terms of an R_{i} factor, which is the ratio of the mass transfer rate with ionic migration of a given set of a conditions to the mass transfer rate at the same set of conditions without ionic migration.

The importance of the effect of ionic migration on design implication has not been yet established. The general objective of this work is to examine the effects of ionic migration on design of moving bed ion-exchange units, using the Film model of mass transfer proposed by Nernst. This model is simpler for calculational purposes and serves to indicate the maximum effects which can result from ionic migration. The selection of continuous motion of the resin bed countercurrent to the solution allows in almost straight-forward manner to analyze such electrical effects instead of considering the mathematical complexity of the transient behavior of fixed beds.

THEORY

For most ion exchange operations of an industrial scale, which usually treat dilute solutions in the laminar flow region, the liquid-phase mass transfer resistance is the significant rate-controlling factor ion-exchange mass transfer. For dilute solution mass transfer of aqueous electrolyte and film control, the fundamental equations at any point of the column are the conservation and constitutive equations plus the constraints of no electric current and electroneutrality [9]. For the film model, all velocity components in the film are zero, and one dimension, y, in the direction of mass transfer is considered. The equations for the exchange reaction

$$Z_A B_S^{Z_B} + Z_B A_R^{Z_A} = Z_B A_S^{Z_A} + Z_A B_R^{Z_B}$$
 are:

The flux of each disolved species may be expressed as

$$J_{i} = -D_{i} \left| \frac{dC_{i}}{dy} + Z_{i} C_{i} \frac{F}{RT} \frac{d\Phi}{dy} \right|$$
(1)

where i = A, B, and Y (co-ion)

The current density in the solution is

$$I = 0 = F(Z_A J_A + Z_B J_B + Z_y J_y), J_y = 0$$
(2)

The electrolytic solutions are electrically neutral

$$Z_{A}C_{A} + Z_{B}C_{B} + Z_{y}C_{y} = 0$$
 (3)

The boundary conditions are the following:

In the bulk solution, at $y = \delta$ (thickness of the film)

$$C_{y} = C_{y}^{0}$$

$$n_{B}^{0} = -Z_{B} C_{B}^{0} / Z_{y} C_{y}^{0}$$

$$\Phi = \Phi^{0} = 0$$
(4)

At the exchanger - solution interface, at y = 0

 $C_y = C_y^i$

$$n_{B}^{i} = Z_{B} C_{B}^{i} / Z_{Y} C_{Y}^{i} , \quad \Phi = \Phi^{i}$$
(5)

By solving the Nernst-Plank equations with determined constraints and boundary conditions, an expression for B ion flux of the liquid phase may be obtained:

$$J_{B} = \frac{c}{\delta} D_{B} \delta \left(n^{0}, n^{i}, D_{A}, D_{B}, D_{Y}, Z_{A}, Z_{B}, Z_{Y} \right)$$
(6)

Applying the film diffusion theory for the liquid phase mass transfer in ion exchange, the diffusion rate is defined by

$$J_{\mathcal{B}}a_{\mathcal{B}} = \left(K_{\delta}\right)_{e} a_{\mathcal{B}}Z_{\mathcal{B}}\left(C^{\circ} - C^{i}\right) = \frac{\mathcal{D}_{e}}{\delta} a_{\mathcal{B}}C_{o}\left(n^{\circ} - n^{i}\right)$$
(7)

where \mathcal{D}_{e} is the effective liquid phase diffusivity. So, equating Eq. (6) with (7) the following expression is derived

$$\mathcal{D}_{e} = \mathcal{D}_{B} \delta \left(n^{\circ}, n^{i}, \mathcal{D}_{A}, \mathcal{D}_{B}, \mathcal{D}_{Y}, Z_{A}, Z_{B}, Z_{Y} \right) / \left(n^{\circ} - n^{i} \right)$$
(8)

Similarly, a theoretical expression for the liquid-side mass-trans - fer coefficient can be derived

$$\binom{\kappa_{6}}{e} = \mathcal{D}_{e}/\delta = \frac{\mathcal{D}_{B}}{\delta} \frac{\delta(n^{\circ}, n^{\acute{l}}, \mathcal{D}_{A}, \mathcal{D}_{B}, \mathcal{D}_{Y}, \mathcal{Z}_{A}, \mathcal{Z}_{B}, \mathcal{Z}_{Y})}{(n^{\circ} - n^{\acute{l}})}$$
(9)

Another way is defining the diffusion rate based on the self-diffusivity of the entering ion, thus

$$J'_{B}a_{B} = \frac{v_{B}}{\delta} a_{B} C_{o} \left(n^{o} - n^{i}\right)$$
(10)

where $K_{\delta} = \mathcal{D}_{B}/\delta$ does not take into account the ionic migration. The ratio between Eq. (6) and Eq. (10) provides a measure of the effects of ionic migration, thus

$$R_{B} = \frac{\delta(n^{\circ}, n^{i}, D_{A}, D_{B}, D_{Y}, Z_{A}, Z_{B}, Z_{Y})}{n^{\circ} - n^{i}}$$
(11)

Combining the results Eq.(8) and Eq. (11) one can get,

$$\mathcal{D}_{e} = \mathcal{R}_{B} \mathcal{D}_{B} \tag{12}$$

Combining the definitions Eq. (9) and (10) results in,

$$\frac{(\kappa_{b})_{e}}{\kappa_{b}} = R_{B}$$
(13)

The integration of the flux equations with the constraints (2) and (3), and the boundary conditions (4) and (5) is analogous to the analytical procedure used by Schlogl and Hellfferich [10]. Thus Van Brocklin [12] derived an expression for the R-factor:

$$R_{B} = \frac{P}{\left(n^{0} - n^{\acute{\ell}}\right)} \left\{ \left[\left(1 - \frac{Z_{B}}{Z_{A}}\right) n^{0} + T \right] - \left[\left(1 - \frac{Z_{B}}{Z_{A}}\right) n^{\acute{\ell}} + T \right] \right] \left[\frac{S - Q n^{0} \left(-\frac{Z_{Y}}{Z_{B}}\right)}{\frac{S - Q n^{\acute{\ell}} \left(-\frac{Z_{Y}}{Z_{B}}\right)} \right]^{M}} \right\}$$
(14)

where

$$P = \frac{Z_A \mathcal{D}_A}{Z_A \mathcal{D}_A - Z_B \mathcal{D}_B} \quad Q = \left[1 - P\left(1 - \frac{Z_B}{Z_A}\right)\right]$$
$$M = \frac{-Z_y}{\left(\frac{Z_B}{Q} - Z_y\right)} \quad S = \frac{\left(1 - \frac{Z_y}{Z_A}\right)\left(-Z_y\right)}{\left(\frac{Z_B}{Q} - Z_y\right)} P$$
$$T = \left(1 - \frac{Z_y}{Z_A}\right)\left(-\frac{Z_B}{Z_y}\right)$$

Consider a countercurrent ion-exchange column with a constant cross section (S), a finite length (Z), and filled with spherical ion-exchanger beads of identical radius (r_p) . At any point of the column, if plug flow of solution with negligible diffusion of solute ions in the axial direction is assumed, the material balance equation for a given ion is

-132-

$$u \frac{dn^{0}}{dz} - v \frac{dN^{0}}{dz} = 0$$
(15)

where $u = L^*C_0$, and $V = R^*a$, C_0 is the total concentration of the ion to be separated in solution - meq/lt, a the total capacity of the exchanger - meq./g, L^* solution flow rate - lt/hr - sq.cm., R^* resin flow rate - g/hr - sq.cm.

The transport rate of the diffusing ion is

$$u \frac{d n^{\circ}}{d z} = K_{\delta} a_{B} R_{B} C_{\circ} \left(n^{\circ} - n^{\acute{L}} \right)$$
(16)

where K_0 is the mass-transfer coefficient for non-electrolytes which can be calculated by a *J*-factor baseline such as Carberry's correlation, Dryden et. al. curve, McCune and Wilhelm correlation.

The composition of both phases at the interface are equilibrium concentration and for liquid-phase controlled ion-exchange

$$N^{\acute{l}} = N^{0}, \quad n^{\acute{l}} = N^{\acute{l}} / |\alpha - (\alpha - 1) N^{\acute{l}}|$$
 (17)

Integrating Eq. (16)

$$\int_{0}^{H} dZ = \int_{n_{t}^{0}}^{n_{t}^{0}} \frac{dn^{0}}{K_{\delta} a_{B} R_{B} (n^{0} - n^{i})}$$
(18)

where n_b^0 is the composition of the bulk solution at the bottom of

the column and n_{t}^{0} is the composition of the bulk solution at the top. The integrand can be separated in two parts: one representing the height of a transfer unit (no electrical effects taken into account) and the other representing the number of transfer units for the liquid-phase (including electric effects). Thus

$$HTU_{L} = \frac{u}{K_{6} a_{B}}$$
(19)

and

$$NTU_{L} = \int_{n_{b}^{0}}^{n_{t}^{0}} \frac{d n^{0}}{R_{B} (n^{0} - n^{\ell})}$$
(20)

The average *R*-factor over the entire column can then be defined in the following manner:

$$(R_{B})_{avg} = \frac{\int_{n_{b}^{0}}^{n_{t}^{0}} \frac{d n^{0}}{(n^{0} - n^{\ell})}}{\int_{n_{b}^{0}}^{n_{t}^{0}} \frac{d n^{0}}{R_{B}(n^{0} - n^{\ell})}}$$
(21)

By using this result, one can show that:

$$H/He = (R_B)_{avg}$$
(22)

This equation measures the importance of ionic migration on the size

of the column.

RESULTS AND DISCUSSION

For liquid-phase ion exchange, a computer program was set up for steady-state moving bed processes, and integral results of the effects of the electric field on bed size are presented in this section for a range of pertinent parameters covering the usual ionexchange systems. Every ionic systems is identified by the ionic valences, (Z_1, Z_2, Z_3) , ionic self diffusivity ratio ($\lambda = \mathcal{P}_A/\mathcal{P}_B$), and selectivity of the resin for the entering ion (α). For every ionic system, the results are expressed by H/He, the ratio of the total height of the column based on the entering ion diffusivity without including ionic migration effects to the total height calculated including ionic migration, as given by Eq. (22). Four different cases were studied, dictated by the preference of the resin (α) and by the entering ion being either the faster or slower ion (λ). Thus: (1) $\alpha \ge 1$ and $\lambda > 1$; (2) $\alpha \ge 1$ and $\lambda < 1$; (3) $\alpha \le 1$ and $\lambda < 1$; or (4) $\alpha \le 1$ and $\lambda > 1$.

1. Favorable equilibrium ($\alpha \ge 1$) and the ionic self-diffusivity ratio greater than unity, $\lambda = D_A/D_B > 1$.

This case corresponds to the ion-exchanger initially containing the faster ion, but the resin prefers the ion initially in the solution. A practical case can be Cu^{++} ion replacing H^{+} ion in the resin. Figure 1 shows the effects of the selectivity of the resin (α) on H/He as a function of the ratio of the flow rates (u/v) and λ . Figure 2 shows the effects of ionic self-diffusivity ratio (λ) on H/He as a function of u/v for a fixed value of selectivity. The preceding figures indicate that the overall effects of ionic migration on H/He, as the ionic self-diffusivity ratio of the exchanging ions varies from 2.00 to 15 (these values of λ cover the range of ion-exchange systems usually encountered in industrial separation processes), are quite significant and different from unity. For not very favorable equilibrium systems ($\alpha = 1-10$), H/He varies between 1.40 and 4.75 while for very favorable equilibrium systems between 1.20 and 1.60. This means that any design neglecting the effects of ionic migration can lead to an over-size of columns, particularly for linear and slightly favorable equilibrium systems. For instance, at $\alpha = 1$ and $\lambda = 5.0$, H/He varies between 1.60 and 3.40. This indicates that the real height of the column can be 37.5% to 67.75% smaller than the height of the column calculated based on non - electrolyte data where the prediction of the mass transfer coefficient of the liquid phase $K_{\dot{0}}$ by a *j*-factor contains the ionic self-diffusivity of the entering ion.

2. Favorable equilibrium ($\alpha \ge 1$) and the ionic self-diffusivity ratio less than unity, $\lambda = D_A/D_B < 1$.

This case states that the faster ion is in the solution and the ion exchanger prefers the ion in the solution at the beginning of the exchange. A practical case can be when resin is in the NH_{μ}^{\dagger} form. The overall result of the ionic migration effects on H/He are determined by the general trend of $R_{\rm B}$ factors which can be grater or smaller than unity depending if the ionic self-diffusivity ratio is greater or smaller than unity respectively. All factors which tend to increase or decrease the $R_{\rm B}$ - factors affect H/He in the same way. When the solution contains the faster ion, the rate of exchange increases from the bottom to the top of the counter current column. At the region near the bottom, the driving forces produces the lowest values of $R_{\rm B}$, approaching the value $\lambda = \mathcal{D}_{\rm A}/\mathcal{D}_{\rm B}$, which increases up the column to $R_{\rm B} \rightarrow 1$. Figure 3 shows the effects of the ionic self-diffusivity ratio on H/He as a function of u/v and for a determined value of selectivity. As λ decreases, H/He decreases approaching to

a limiting value as u/v increases. The overall effects on H/He as λ varies from 1/15 to 1 are quite significant for every value of selectivity. For linear equilibrium systems, H/He varies between 0.55 and 0.08. This means that any design neglecting the ionic-migration effects can lead to a smaller column than is required in order to ac complish the proper levels of removal of the ion from the solution, since the real height of the column can be 1.8 to 12.5 times the height of the column based on non-electrolyte data. The effects of ionic migration are smaller for very favorable equilibrium systems but always significant. For instance, for $\alpha = 25$, H/He varies between about 0.25 and 0.80, therefore the real height can be 1.25 to 4 times bigger. Two concluding remarks can be derived from those results: (i) As the ion initially in the ion exchanger is slower, the required column is higher; (ii) As the faster ion initially in the solution is less preferred by the resin, the effects of ionic migration on column height are larger.

3. Unfavorable equilibrium ($\alpha \le 1$) and the ionic self-diffusivity ratio less than unity, $\lambda = \mathcal{D}_A/\mathcal{D}_B < 1$.

This situation corresponds to the faster ion initially in the solution and the resin preferring the slower ion. A practical case can be H^{\dagger} ions replacing $Cu^{\dagger\dagger}$ ions in the exchanger. The numerical calculations were based on the following assumptions: (i) The feed contains 100% of the ion to be separated from the solution; (ii) 99% of the capacity of the resin available; (iii) Percentage of re - moval of the ion in the resin = 50, 75, 95 and 99%; (iv) The ion-exchange isotherm is characterized by the separation factor, α , for $\alpha = 1, 1/2, 1/5, 1/10, 1/25, 1/50, 1/75, 1/100$.

The range of operation for the flow rates (u/v) is limited by the concavity of the ion-exchange isotherm. As the ion exchanger has lower preference for the ion initially in the solution, for the exiting resin to have a high percentage of this ion requires a high ratio of the flow rates. For every different equilibrium curve, in order to have the same exit exchanger composition, the relative flow rates are different. For a given selectivity, as the percentage of removal (from the exchanger) is increased, the range of variation of the bulk composition in the solution is smaller, and n° lies much closer to $n^{\circ} = 1.0$. Since the ion exchanger prefers the slow ion initially present on it, the $R_{\rm B}$ -factors increase from the bottom to the top of the counter-current column, with a maximum range from λ to 1. As the entering cation is less preferred by the ion exchanger,

the concentration at the solution side of the interface (concentration at equilibrium, n*) is larger, n* is closer to n° and thus the concentration difference across the film is smaller. For $n^* \rightarrow n^o$, $R_{\rm R}$ values are closer to the limiting curve . Since $R_{\rm R}$ is smallest at the region near the bottom of the column, the closer the pinch point is to the bottom, the greater the effects on column height. The integral effects of ionic migration on H/He as a function of relative flow rates, selectivity, and ionic self-diffusivity ratio are shown in Figure 4. As the ratio of flow rates increases, H/He decreases, deviating from unity because as u/v increases, the pinch point is closer to the bottom of the column. For very unfavorable equilibrium systems, that figure shows that H/He approaches a limiting value determined by the ionic self-diffusivity ratio $(\lambda = D_A/D_R)$ only . As the selectivity decreases H/He decreases for the same levels of regeneration. However, as λ increases, H/He increases and this increment is greater as λ increases. The general shapes of H/He plots for various separation factors and diffusivity ratio are similar. The effects of ionic migration on H/He show more dependence of the percentage of regeneration (or u/v) for less unfavorable equilibrium system, such as $\alpha = 1$, 1/2, 1/5, and 1/10. In general H/He decreases smoothly as u/v increases but then levels out for very unfavorable equilibrium systems ($\alpha < 0.10$). The overall effects, on H/He for the range of λ analyzed are quite significant even for slightly unfavorable equilibrium systems, H/He varies roughly between 0.80 and 0.10. Again, this implies that any design based on non-electrolyte data can lead to a smaller column if the effects of ionic migration

are neglected. For these particular ionic systems, the real height of the column can be 1.25 to 10 times the column size calculated without including the electric-field effects. For very unfavorable equilibrium systems, H/He approaches to λ , thus the actual bed size can be almost $1/\lambda$ (i.e. 2.0 to 15) times bigger.

The ratio of the overall mass-transfer coefficient including ionic migration to the overall mass-transfer coefficient without ionic migration under the same set of conditions, $(K_{f})_{e}/K_{f}$, behaves in the same fashion as H/He. $(K_{f})_{e}$ decreases from the top to the bottom of the column, as the ion exchanger becomes saturated with the intering species. If the mass transfer coefficient of the liquid phase for non-electrolyte is given by the Carberry's correlation [2], the $(K_{f})_{e}$ for $\alpha < 0.10$ can be obtained so:

$$(K_{f})_{e} = 1.15 \frac{D_{A}}{D_{B}} u_{f} \qquad Sc_{i}^{-2/3} \quad Re_{e}^{-1/2}$$
(23)

with Re, \leq 1000, Sc_i \geq 1, and $\alpha < 0.10$.

4. Unfavorable equilibrium ($\alpha \le 1$) and the ionic self-diffusivity ratio greater than unity, $\lambda = D_A/D_B > 1$.

This case occurs when the faster ion is in the resin and is also preferred by the resin. A practical case could be when $NH_{\frac{1}{2}}^{\dagger}$ is the entering ion in the resin.

When the faster ion is initially in the ion exchanger, the R_B -factors decreases from the bottom to the top of the column. As a result, H/He versus u/v curves are mirror images for case 3, as shown in Figure 5. At low percentage of the ion removed from the exchanger, the overall effects of ionic migration on H/He are not really important for not too unfavorable equilibrium systems but are al-

ways evident. For instance, at 50% of exchange, H/He varies between 1.10 and 1.30 for $\alpha = 1$; 1.25 and 1.50 for $\alpha = 1/2$; 1.50 and 2.25 for $\alpha = 1/5$; 1.75 to 3.75 for $\alpha = 1/10$ when λ varies from 1.0 to 15. In short, the effects of R_g on H/He become more noticeable as: (i) the degree of exchange increases; (ii) the selectivity decreases; (iii) the ionic mobility ratio increases. The results indicate that any design of counter-current units for ion exchange based on the customary approach for non-electrolytes can lead to an over size of columns. If a high degree of replacement of the ion ini tially on the exchanger is required, H/He approaches to λ for very unfavorable equilibrium systems. So, for this particular case, the real height required can be $1/\lambda$ less than height that could result neglecting the ionic-migration effects.

5. Effects of saturation of the resin.

The effects of ionic migration were studied as function of the degree of saturation of the ion exchanger when the slow ion is extering $(\lambda < 1)$ for favorable equilibrium systems $(\alpha \ge 1)$. The numerical calculations were based for values of $\lambda = 1, 2, 5, 10$ and 15. The results are given for 99, 75, and 50% of saturation of the resin and for 99.5, 99, 85, 75, 60 and 50% of removal of the ion in the solution. Figures 6-7 show, the effects of the degree of saturation of the resin on H/He or (K_{ρ}/K_{χ}) as a function of u/v for determined values of selectivity and ionic self-diffusivity ratio, λ . Several important characteristics of the plots can be noted . First, the effects of ionic migration on H/He tend to increase for decrease of the percentage of removal (or increase of u/v) and increment of the degree of saturation of the resin. Second, as the resin becomes more saturated, the $R_{\rm R}$ -factor is more important, but this effect is noticeable only on linear equilibrium systems or for $\alpha = 5$ or 10. For very favorable equilibrium systems ($\alpha = 25, 50, 75, 100$), the effect of degree of saturation of the resin on H/He does not make too much difference. Third, the variation of H/He depends strongly

on the ionic self-diffusivity ratio for linear and slightly favorable equilibrium systems. For instance, for $\alpha = 25$, H/He varies between 1.0 and 1.60 as λ varies from 1.0 to 15.0 while for $\alpha = 1$, the variation of H/He depends on the degree of saturation, mobility ratio, etc., reaching values up to 4.70 for 99%, 2.40 for 75% and 2.0 for 50% of regeneration when $\lambda = 15.0$.

6. Effects of the co-ion.

The discussion of effects of the co-ion, in the case of the film model of mass transfer means effects of the valence of the anion (Z_{2}) since the diffusivity coefficient is eliminated in the derivation of R_B-factor. (However, Van Brocklin [12] and Au Yong [1] also made calculations for the boundary-layer and penetration models, and found that anion diffusivity has no significant effect on the R_{R} values for these models). Figure 8 shows the effects of co-ion valence on H/He as function of u/v, λ , α , for the ionic systems (2,2,-1) and (2,1,-2), several important characteristics of the plots can be noted . First, the increase of the valence of the non-counter ion causes a decrease on the ratio H/He. This difference increases as the percentage of removal decreases. Second, the effects of co-ion valence on H/He increase at large diffusivity ratios of the exchanging ions (λ) . Third, the effects of co-ion show big differences on linear and slightly unfavorable or favorable equilibrium systems. Fourth, the effects on H/He for monovalent - monovalent exchange are less than divalent-monovalent exchange. For practical calculations, the difference on H/He can be ignored for very unfavorable and favorable equilibrium systems.

CONCLUSIONS

When the ionic self-diffusivity ratio of the exchanging ions is

different from unity, the overall effects of ionic migration on H/He can be quite significant and different from unity. However, the role of diffusivity ratio is influenced by selectivity of the resin for the entering cation and by the closeness of approach (and location thereof in the bed) of the liquid composition to equilibrium.

The ratio of the effective liquid - phase diffusivity to the self-diffusivity of the entering ion, $\mathcal{D}_{\varrho}/\mathcal{D}_{\mathcal{B}}$ (Ec.12), can be computed from the plots of H/He. Therefore, a single fixed value of \mathcal{D}_{ϱ} for a given exchange system is not satisfactory yo be used over a wide range of operating conditions. So, any design neglecting the ionic-migration effects can lead to a smaller or bigger column than is really required in order to accomplish the proper levels of removal or saturation. However, those plots of H/He provide a correction factor to be used for column design based on non-electrolyte data.

The results for liquid-phase controlling are independent of Reynolds number but restricted to the limitations of the film model of mass-transfer.

NOMENCLATURE

| a _B | = interfacial area of particles | (cm²/cu.cm) |
|----------------|---|--------------------------------------|
| a | = capacity of the resin | (meq/g) |
| C _i | = concentration of the liquid side | (meq/lt) |
| C | = total concentration of the bulk solu- | |
| | tion | (meq/lt) |
| Di | = 10nic self-diffusivity in solution | (cm ² /sec) |
| De | = effective diffusivity | (cm²/sec) |
| Dp | = diameter of the bead | (cm) |
| F | = Faraday's constant | |
| Н | = Height of the column calculated ne- glecting ionic migration | (cm) |
| He | = height of the column calculated in- cluding ionic migration | (cm) |
| Ji | = ionic flux | (meq/cm ² -hr) |
| k | <pre>= non-electrolyte liquid-phase mass- transfer coeff.</pre> | (cm/sec) |
| (kj)e | = effective mass-transfer coefficient | (cm/sec) |
| L | = flow rate of the solution | (lt/hr-sq.cm) -Z.O. |
| N | = equivalent fraction in the resin | $N_i = \frac{-i}{Z_3} \frac{z_i}{a}$ |
| п | = equivalent fraction in solution | $n_i = \frac{-Z_i C_i}{Z_i C_i}$ |
| 2i | = concentration of the resin side | (meq/g) |
| rp | = radius of the particle | (cm) |
| R | = gas constant | |
| RB | = R_{B} -factor in the liquid phase | |

| Re, E | = Reynolds number, $d_p u_p p/\mu$ | |
|----------------|---|-----------------|
| R* | = flow rate of the resin | (g/hr-sq.cm) |
| Sc | = Schmidt number, $\mu/\rho \mathcal{D}_B$ | |
| Т | = absolute temperatura | (°K) |
| us | = superficial velocity of the solution | (cm/sec) |
| uf | = velocity of the liquid phase, us/ϵ | (cm/sec) |
| u | = liquid rate, L* . Co | (meq./hr-cu-cm) |
| ν | = resin rate, R* a | (meq./hr-cu-cm) |
| Z _i | = ionic valence | |
| Z | = column height | (cm) |
| α | = separation factor | |
| λ | = ionic self-diffusivity ratio | |
| μ | = viscosity of the solution | (g/cm-sec) |
| ε | = porosity | |
| ρ | = density of the solution | (g/cu.cm) |
| Φ | = electrostatic potential | (volt) |
| Superscript | S | |
| 0 | = bulk phase | |
| * | = equilibrium | |
| i | = interface | |
| Subscripts | | |
| В | = cation entering | |
| A | = cation exiting | |
| У | = anion | |
| Ь | <pre>= at entry to bed (solution), bottom of the column</pre> | |
| t | <pre>= at exit from bed (solution), top of the column</pre> | |

T

-144-

REFERENCES

- AU YONG, K.S.: M.S. Thesis, University of Washington, Seattle. Was. (1969).
- [2] CARBERRY, J.J.: A.I.Ch.E. Journal, 6, 460 (1960).
- [3] COPELAND, J.C., HENDERSON, C.L. and MACHELLO, J.M.: A.I.Ch.E.J. 13,449 (1967).
- [4] DRYDEN, C.A., STRONG, D.A. and WINTHROW, A.E.: Chem.Eng.Prog., 49, 191 (1953).
- [5] HELFFERICH, F.: "Ion Exchange", New York, McGraw Hill Book Co., 1962.
- [6] HERING, B. and BLISS, H.: A.I.Ch.E.J., 9, 495 (1963).
- [7] KATAOKA, T., YOSHIDA, H. and YAMADA, T.: J.Chem.Eng.Jap., 6, 172 (1973).
- [8] McCUNE, L.K. and WILHELM R.H.: Ind.Eng.Chem., 41, 1124 (1949).
- [9] NEWMAN, J.: Ind.Eng.Chem.Fundam., 2, 525 (1966).
- [10] SCHLOGL, R. and HELFFERICH, F.: J.Chem. Phys. 26, 5 (1957).
- [11] TURNER, J.C.R. and SNOWDON, C.: Chem. Eng. Sci., 23, 221 (1968).
- [12] VAN BROCKLIN, L.P.: Ph.D. Thesis, University of Washington, Seattle, Was. (1968).
- [13] VAN BROCKLIN, L.P. and DAVID, M.M.: Ind.Eng.Chem.Fund., 11, 91 (1972).



FIG. 1- RATIO OF THE TOTAL HEIGHTS VS. RATIO OF THE FLOW RATES

RELACION DE LAS ALTURAS TOTALES VS. RELACION DE TASAS DE FLUJO.





î.

-147-



Fig.3 . Ratio of the total heights Vs. Ratio of the flow rates RELACION DE LAS ALTURAS TOTALES Vs. RELACION DE TASAS DE FLUJO.

I.

-148-



RELACION DE LAS ALTURAS TOTALES VS. RELACION DE TASAS DE FLUJO





Fig.6. Ratio of the total heights Vs Ratio of the flow rates RELACION DE LAS ALTURAS TOTALES Vs. RELACION DE TASAS DE FLUJO.



-152-

RELACION DE LAS ALTURAS TOTALES Vs. RELACION DE TASAS DE FLUJO.



RELACION DE LAS ALTURAS TOTALES VS. RELACION DE TASAS DE FLUJO.

-153-