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Bulk-Phase Criteria for Negative Ion Rejection in Nanofiltration of Multicomponent Salt Solutions

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ABSTRACT

An expression for calculating the change in the rejection of a given ion under nanofiltration conditions when adding other salts to the bulk solution has been derived using the extended Nernst–Planck equations. This expression gives a simple means for calculating in which direction the change of the rejection will go from knowledge of the equivalent conductance and the concentration changes of the ions added to the bulk solution. Using the multisalt system $NaNO_3$–Na_2SO_4–HCl as an example, the nitrate rejection plane was calculated from the derived model. The experimental nitrate rejection data fit very nicely into this plane, showing increasing negative rejections by increasing the Na_2SO_4 concentration which can be reversed by the addition of HCl to the bulk solution.

INTRODUCTION

A problem of considerable importance in reverse osmosis desalination is the prediction of rejection of ionic solutes in mixed systems from experimental data obtained in simplified single-salt solutions.

Many results on single-salt solutions have been published. See, for example, Reference 1. Normally, the salt has been considered as neutral salt molecules per se. By using a mean distribution coefficient, K_s, and a mean diffusion coefficient, D_s, the electrical potential term is neglected.

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Thus, reasonable agreement with theories for uncharged solutes has been found.

Fewer papers have dealt with solute rejection involving mixed solutes in aqueous solutions. These concern the performance of mixed nonelectrolytes (2–5) and of mixed electrolytes (6–15), and they show a variety of theoretical approaches. An important feature of mixed-solute rejection is the solute–solute interaction which may be observed as a change of the single-solute rejection induced by the addition of a second solute.

Only weak interactions have been reported in the case of nonelectrolytes (5). However, due to primary charge effects and to differences in the mobilities of cations and anions, electrolytic interactions can be rather strong. The general trend found is that in a mixture of more and less permeable ions, rejection of the more permeable ions decreases and that of less permeable ions increases (6, 7). A similar situation is seen in the diffusion behavior of ternary systems without a membrane where solute–solute flow interactions are rather large and give rise to particularly large values of the cross-term diffusion coefficients (16).

Heyde and Andersen (17) studied the influence of added electrolytes upon ion sorption by membranes. They found that membrane sorption of permeable ions is substantially increased by the addition of membrane impermeable salts to the bulk solution and vice versa. This change in sorption was explained in terms of constrained phase equilibria, using the ideas developed by Donnan (18).

Lonsdale et al. (8) were able to pass from positive to negative rejection of Cl^- upon addition of membrane-impermeable sodium citrate. The experimental results were explained by a solution-diffusion model coupled to the Donnan equilibrium theory.

Jonsson (10) demonstrated both experimentally and theoretically how the rejection of the separate ions in two-salt solutions was influenced by the induced boundary, diffusion, and streaming potentials under reverse osmosis conditions. The experimental results were explained from a theory developed by using a combined frictional and exclusion model together with the extended Nernst–Planck equations. However, the set of equations had to be solved numerically.

Vonk and Smit (11) presented a thermodynamic description of reverse osmosis applied to two interacting solutes. It provided a generalization of the classical formula of solute rejection as a function of volume flux put forward by Spiegler and Kedem (19). However, coupling between the two solute flows required the introduction of an additional transport parameter.

In another paper (12) the same authors applied the extended Nernst–Planck equation to the separate ions and derived analytically expressions describing the rejection curves in ternary systems valid under the limiting cases of either high volume fluxes or low volume fluxes.

In the present study the extended Nernst–Planck equations have also been used as the starting equations. However, to obtain an analytical solution the integration is restricted to loose RO membranes (nanofiltration) where the rejections of the different ions are not too high. This enables us to derive a "titrator function" from which the change in rejection of a given ion by adding other salts to the solution can be calculated from the change in the bulk solution composition and knowledge of the self-diffusion coefficient of the individual ions in that solution.

THEORY

The theoretical treatment of multicomponent salt solutions outlined below is based on a combined viscous-flow and frictional model with the extension that the individual ion fluxes are coupled with each other by an induced membrane potential. Here the extended Nernst–Planck equation with a convection term included is used to describe the flux of the separate ions "i" per unit pore area:

$$J_{ip} = -D_{ip}\frac{\partial C_{ip}}{\partial x} - D_{ip}z_i C_{ip}\frac{F}{RT}\frac{\partial \Phi}{\partial x} + C_{ip}V \qquad (1)$$

It is supposed that all solute and solvent transport is taking place in the water-filled pore phase of the membrane, and that friction between the ions and the pore surface of the membrane is negligible. Thus, all concentrations and fluxes in Eq. (1) refer to unit pore volume and pore area, respectively. The measured volume flux per unit membrane area is related to the linear velocity in the pore solution by

$$J_v = \epsilon V \qquad (2)$$

where ϵ is the fractional pore area.

In addition to Eq. (1), we have the condition of electroneutrality in the pore solution:

$$\sum z_i C_{ip} = 0 \qquad (3)$$

together with the restraint of zero electrical current:

$$\sum z_i J_{ip} = 0 \qquad (4)$$

By combining Eqs. (3) and (4) with Eq. (1) a set of coupled differential equations can be derived which might be solved numerically (10). However, to derive an analytical solution, we now introduce the function α_{ip}, defined as

$$J_{ip} = \alpha_{ip} C_{ip} V \Rightarrow \alpha_{ip} = v_{ip}/V \tag{5}$$

Inserting Eq. (5) in Eq. (1) gives

$$(1 - \alpha_{ip}) V \frac{C_{ip}}{D_{ip}} = \frac{\partial C_{ip}}{\partial x} + z_i C_{ip} \frac{F}{RT} \frac{\partial \Phi}{\partial x} \tag{6}$$

By multiplying Eq. (6) by z_i and summarizing over all the ions "i," it follows that

$$V \sum \frac{(1 - \alpha_{ip})}{D_{ip}} z_i C_{ip} = \sum z_i \frac{\partial C_{ip}}{\partial x} + \frac{F}{RT} \frac{\partial \Phi}{\partial x} \sum z_i^2 C_{ip} \tag{7}$$

Here the first term on the right-hand side must be zero according to Eq. (3), so the potential gradient in the pore solution is given as

$$\frac{\partial \Phi}{\partial x} = V \frac{RT}{F} \frac{\sum \frac{(1 - \alpha_{ip})}{D_{ip}} z_i C_{ip}}{\sum z_i^2 C_{ip}} \tag{8}$$

Inserting Eq. (8) in Eq. (6) and rearranging gives the following relation for the concentration gradient of the individual ion "j" as a function of all ions "i":

$$\frac{\partial C_{jp}}{\partial x} = V C_{jp} \left(\frac{(1 - \alpha_{jp})}{D_{jp}} - z_j \frac{\sum \frac{(1 - \alpha_{ip})}{D_{ip}} z_i C_{ip}}{\sum z_i^2 C_{ip}} \right) \tag{9}$$

Equation (9) is now integrated over the total pore length with the boundary conditions as shown, with the assumption that the rejection should be very close to zero. Although this is not normally the case in reverse osmosis, the relations which will be derived can nevertheless be used to deduce some general conclusions about ionic interactions under nanofiltration conditions, as will be demonstrated.

$$\int_{C'_{jp}}^{C''_{jp}} \frac{dC_{jp}}{C_{jp}} = V \left[\frac{(1 - \alpha_{jp})}{D_{jp}} - z_j \frac{\sum \frac{(1 - \alpha_{ip})}{D_{ip}} z_i C_{ip}}{\sum z_i^2 C_{ip}} \right] \int_0^{t\lambda} dx \tag{10}$$

Introducing the solute rejection for the ion "j" as

$$R_j = 1 - \frac{C''_j}{C'_j} = 1 - \frac{C''_{jp}}{C'_{jp}} \tag{11}$$

where the second equality comes from the reasonable assumption that the pore distribution coefficient, K_{jp}, is constant:

$$K_{jp} = \frac{C'_{jp}}{C'_j} = \frac{C''_{jp}}{C''_j} \tag{12}$$

Combining Eq. (11) with the integrated Eq. (10) gives

$$R_j = 1 - \exp\left[J_v \frac{t\lambda}{\epsilon}\left(\frac{(1-\alpha'_{jp})}{D'_{jp}} - z_j \frac{\sum \frac{(1-\alpha'_{ip})}{D'_{ip}} z_i C'_{ip}}{\sum z_i^2 C'_{ip}}\right)\right] \tag{13}$$

with the limit for the boundary conditions

$$\lim_{x \to t\lambda} (C''_{ip}, \alpha''_{ip}, D''_{ip}) = (C_i^{\mathrm{P}}, \alpha_i^{\mathrm{P}}, D_i^{\mathrm{P}})$$

and

$$\lim_{x \to 0} (C'_{ip}, \alpha'_{ip}, D'_{ip}) = (C_i^{\mathrm{B}}, \alpha_i^{\mathrm{B}}, D_i^{\mathrm{B}})$$

Equation (13) can be rewritten as

$$R_j = 1 - \exp\left[J_v \frac{t\lambda}{\epsilon}\left(\frac{(1-\alpha_j^{\mathrm{B}})}{D_j^{\mathrm{B}}} - z_j \frac{\sum \frac{(1-\alpha_i^{\mathrm{B}})}{D_i^{\mathrm{B}}} z_i C_i^{\mathrm{B}}}{\sum z_i^2 C_i^{\mathrm{B}}}\right)\right] \tag{14}$$

From Eq. (14) it can be seen that the criteria for having either positive or negative rejection of the ion "j" depends on the sign of the function Π_j, defined as

$$\Pi_j \equiv \frac{(1-\alpha_j^{\mathrm{B}})}{D_j^{\mathrm{B}}} - z_j \frac{\sum \frac{(1-\alpha_i^{\mathrm{B}})}{D_i^{\mathrm{B}}} z_i C_i^{\mathrm{B}}}{\sum z_i^2 C_i^{\mathrm{B}}} \tag{15}$$

since the term $J_v(t\lambda/\epsilon)$ is always positive. It is also seen that, when the rejection of the ion "j" is close to zero, the sign is determined to the composition of the bulk solution.

If further examination is restricted to the special case where the velocity of the ion "j" is only slightly smaller than the water velocity through the membrane, then

$$1 - \alpha_j > 0 \tag{16}$$

From Eqs. (14)–(16) it clearly follows that

$$R_j > 0 \Rightarrow \Pi_j < 0 \Rightarrow \frac{1-\alpha_j^{\mathrm{B}}}{D_j^{\mathrm{B}}} < z_j \frac{\sum \frac{1-\alpha_i^{\mathrm{B}}}{D_i^{\mathrm{B}}} z_i C_i^{\mathrm{B}}}{\sum z_i^2 C_i^{\mathrm{B}}}$$

$$\Rightarrow \frac{1}{D_j^{\mathrm{B}}} - z_j \frac{\sum \frac{1}{D_i^{\mathrm{B}}} z_i C_i^{\mathrm{B}}}{\sum z_i^2 C_i^{\mathrm{B}}} < \frac{\alpha_j^{\mathrm{B}}}{D_j^{\mathrm{B}}} - z_j \frac{\sum \frac{\alpha_i^{\mathrm{B}}}{D_i^{\mathrm{B}}} z_i C_i^{\mathrm{B}}}{\sum z_i^2 C_i^{\mathrm{B}}} \tag{17}$$

Assuming the validity of Eqs. (3) and (4), then

$$\sum J_i z_i = \sum \alpha_i V C_i z_i = \sum v_i C_i z_i = 0 \tag{18}$$

One solution to this equation is to consider the velocity of the different ions, v_i, as approximately the same constant γ, so that

$$\sum J_i z_i = \gamma \sum C_i z_i = 0 \tag{19}$$

With the assumption of the existence of such a constant mean ion velocity, γ, it clearly follows that

$$\frac{1}{D_j^{\mathrm{B}}} - z_j \frac{\sum \frac{1}{D_i^{\mathrm{B}}} z_i C_i^{\mathrm{B}}}{\sum z_i^2 C_i^{\mathrm{B}}} < \frac{\gamma}{V}\left(\frac{1}{D_j^{\mathrm{B}}} - z_j \frac{\sum \frac{1}{D_i^{\mathrm{B}}} z_i C_i^{\mathrm{B}}}{\sum z_i^2 C_i^{\mathrm{B}}}\right)$$

$$\Rightarrow \frac{V}{\gamma}\left[-\sum\left(\frac{D_j^{\mathrm{B}}}{D_i^{\mathrm{B}}} z_j z_i - z_i^2\right) C_i^{\mathrm{B}}\right] < \left[-\sum\left(\frac{D_j^{\mathrm{B}}}{D_i^{\mathrm{B}}} z_j z_i - z_i^2\right) C_i^{\mathrm{B}}\right] \tag{20}$$

where $V/\gamma > 1$ if $R_j > 0$. Then

$$\sum\left(\frac{D_j^{\mathrm{B}}}{D_i^{\mathrm{B}}} z_j z_i - z_i^2\right) C_i^{\mathrm{B}} > 0$$

If we define the positive number ξ_j as

$$\xi_j \equiv \frac{V}{\gamma} \sum\left(\frac{D_j^{\mathrm{B}}}{D_i^{\mathrm{B}}} z_j z_i - z_i^2\right) C_i^{\mathrm{B}} \tag{21}$$

it is seen, according to Eq. (20), that

$$\xi_j > \sum \left(\frac{D_j^{\mathrm{B}}}{D_i^{\mathrm{B}}} z_j z_i - z_i^2\right) C_i^{\mathrm{B}} > 0$$

$$\Rightarrow \xi_j > \left|\sum \left(\frac{D_j^{\mathrm{B}}}{D_i^{\mathrm{B}}} z_j z_i - z_i^2\right) C_i^{\mathrm{B}}\right| > 0 \tag{22}$$

$$\Rightarrow \xi_j > \sum \left(\frac{D_j^{\mathrm{B}}}{D_i^{\mathrm{B}}} |z_j||z_i| - |z_i|^2\right) C_i^{\mathrm{B}} - e_j$$

$$\Rightarrow \xi_j > \sum \left(\frac{D_j^{\mathrm{B}}}{D_i^{\mathrm{B}}} \frac{|z_j|}{|z_i|} - 1\right) |z_i|^2 C_i^{\mathrm{B}} - e_j$$

where e_j is a limited and positive number.

Normally it is observed that

$$R_j \to 0+ \qquad \text{for} \qquad V \to 0$$

or

$$R_j \to 0+ \qquad \text{for} \qquad \xi_j \to 0$$

from which it follows that

$$-k_j^{\mathrm{obs}} \equiv \sum \left(\frac{D_j^{\mathrm{B}}}{D_i^{\mathrm{B}}} \frac{|z_j|}{|z_i|} - 1\right) |z_i|^2 C_i^{\mathrm{B}} - e_j \tag{23}$$

where k_j^{obs} clearly is a positive number.

If an extra salt compound is added to the bulk solution of the nanofiltration system, it is seen that the rejection of ion "j" is positive if the following criterion is met:

$$\xi_j + k_j^{\mathrm{obs}} > \Psi_j \tag{24}$$

where the right-hand side is defined as

$$\Psi_j = \Psi_j(\Delta \mathbf{C}^{\mathrm{B}}) \equiv \sum \left(\frac{D_j^{\mathrm{B}}}{D_i^{\mathrm{B}}} \frac{|z_j|}{|z_i|} - 1\right) |z_i|^2 \Delta C_i^{\mathrm{B}} \tag{25}$$

for all the added ions only.

According to Eq. (24), it clearly follows that if the volume flux is fixed, then

$$\frac{\partial \Psi_j}{\partial \Delta C_n} > 0 \Rightarrow \frac{\partial R_j}{\partial \Delta C_n} < 0 \tag{26a}$$

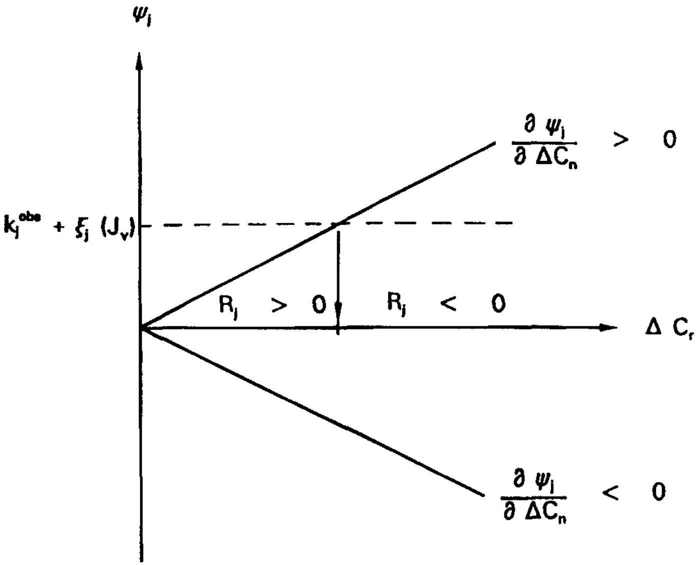

FIG. 1 Outline showing the rejection of the ion "*j*" with respect to the donated "*n*"-ion as indicated from Eq. (25).

and

$$\frac{\partial \Psi_j}{\partial \Delta C_n} < 0 \Rightarrow \frac{\partial R_j}{\partial \Delta C_n} > 0 \qquad (26b)$$

If Eq. (25) has a positive slope with respect to the "*n*"-ion addition, then Ψ_j will have the possibility of passing the number $k_j^{obs} + \xi_j$, and in this case negative "*j*"-ion rejection will occur because of the falsification of Eq. (24).

If Eq. (25) has a negative slope with respect to the "*n*"-ion addition, then Ψ_j can never pass the number $k_j^{obs} + \xi_j$, and therefore Eq. (24) will be confirmed and a greater "*j*"-ion rejection will occur. These tendencies are outlined in Fig. 1.

EXPERIMENTAL

The experiments were performed in the reverse osmosis loop using test cell I without sectioning as described elsewhere (20). The membrane was a commercial nanofiltration membrane from Dow Denmark Separation Systems, HC50. Before use it was pressurized at the maximal pressure (40 bar) for 8 hours to ensure stability during the experiments. The nitrate concentrations of the feed and product were determined by potential measurements with a Radiometer nitrate ion selective electrode, using a standard curve for the potential value and the nitrate concentration.

Rejection of the nitrate ion was investigated for a bulk solution consisting of the following salts:

$$\mathrm{NaNO_3 + Na_2SO_4 + HCl}$$

at a molar ratio of 1:X:Y under nanofiltration conditions, with water as the solvent.

The nitrate concentration in the bulk solution was kept constant (C = 0.01 M) during all the experiments. Hence, the individual ion concentrations in the bulk phase can be represented as:

$$C_{\mathrm{NO_3}} = C$$

$$C_{\mathrm{Cl}} = C\mathrm{Y}$$

$$C_{\mathrm{SO_4}} = C\mathrm{X}$$

$$C_{\mathrm{H}} = C\mathrm{Y}$$

$$C_{\mathrm{Na}} = C(1 + 2\mathrm{X})$$

since all the salts will be completely dissociated.

If it is assumed that the diffusion coefficients can be represented by the self-diffusion coefficients at low total ionic strength, the Nernst relation gives

$$D_n^{\mathrm{B}} \approx D_n^{\circ} = \frac{RT}{F^2}\frac{\lambda_n^{\circ}}{|z_n|} \tag{27}$$

Thus the "titrator" function according to Eq. (25) is expressed as

$$\begin{aligned}\psi_{\mathrm{NO_3}} &= \sum\left(\frac{\lambda_{\mathrm{NO_3}}^{\circ}}{\lambda_i^{\circ}} - 1\right)\Delta C_i^{\mathrm{B}} z_i^2 \\ &= \left(\frac{\lambda_{\mathrm{NO_3}}^{\circ}}{\lambda_{\mathrm{Cl}}^{\circ}} - 1\right)\mathrm{Y}C(-1)^2 + \left(\frac{\lambda_{\mathrm{NO_3}}^{\circ}}{\lambda_{\mathrm{SO_4}}^{\circ}} - 1\right)\mathrm{X}C(-2)^2 \\ &\quad + \left(\frac{\lambda_{\mathrm{NO_3}}^{\circ}}{\lambda_{\mathrm{H}}^{\circ}} - 1\right)\mathrm{Y}C(+1)^2 + \left(\frac{\lambda_{\mathrm{NO_3}}^{\circ}}{\lambda_{\mathrm{Na}}^{\circ}} - 1\right)2\mathrm{X}C(+1)^2\end{aligned} \tag{28}$$

Using the values for the equivalent conductance, λ_i°, for the individual ions taken from the literature (21):

$$\lambda^\circ_{NO_3} = 7.144 \times 10^{-3}\ \text{m}^2/\text{ohm/eq.}$$

$$\lambda^\circ_{Cl} = 7.64 \times 10^{-3}\ \text{m}^2/\text{ohm/eq.}$$

$$\lambda^\circ_{SO_4} = 8.00 \times 10^{-3}\ \text{m}^2/\text{ohm/eq.}$$

$$\lambda^\circ_{H} = 34.98 \times 10^{-3}\ \text{m}^2/\text{ohm/eq.}$$

$$\lambda^\circ_{Na} = 5.011 \times 10^{-3}\ \text{m}^2/\text{ohm/eq.}$$

the "titrator" function can be reduced to

$$\psi_{NO_3} = (0.42\text{X} - 0.86\text{Y})C \qquad (29)$$

According to Eq. (24), the criteria for positive nitrate rejection is given by

$$k^{obs}_{NO_3} + \xi_{NO_3} > \psi_{NO_3} \Rightarrow \text{Y} > 0.49\text{X} - 1.16\left(\frac{k^{obs}_{NO_3} + \xi_{NO_3}}{C}\right) \qquad (30)$$

A qualitative graphical representation of Eq. (30) is shown as "rejection areas" for the nitrate ion in Fig. 2.

As both the constants C and $k^{obs}_{NO_3}$ are positive, the line l_x in Fig. 2 will displace parallel to lower Y-values with increasing permeate flux. This behavior is determined by the parameter ξ_{NO_3} which is an increasing func-

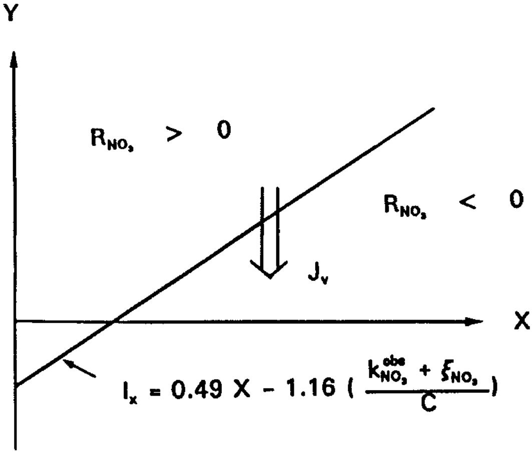

FIG. 2 Outline showing that negative nitrate rejections can be inverted to positive rejections with increasing volume flux as indicated from Eq. (30).

TABLE 1

Specification of the Seven Experimental Bulk Solution Compositions with Predictions from Eq. (31) for the Sign of the Nitrate Rejection

Test number	X	Y	Eq. (31)	Prediction of the sign of R_{NO_3}
1	0	0	—	—
2	1	0	False	Negative
3	5	0	False	Negative
4	10	0	False	Negative
5	1	1	True	Positive
6	5	3	True	Positive
7	10	5	True	Positive

tion of $J_v[(\partial/\partial J_v)\xi_{NO_3} > 0]$. This dependency of J_v might therefore result in a change from negative to positive rejections by increasing the pressure of the feed solution.

Since the parameter $[(k^{obs}_{NO_3} + \xi_{NO_3})/C]$ is unknown, it is not possible to calculate a given bulk composition which makes $R_{NO_3} = 0$. However, if Eq. (31) is fulfilled, then Eq. (30) will also be true:

$$Y > 0.49X \tag{31}$$

The reduction of Eq. (30) to Eq. (31) causes a loss of information. It is now only possible to predict a bulk composition, which gives a positive nitrate rejection (true), whereas the nitrate rejection might still be positive if Eq. (31) is false.

Seven different bulk compositions were investigated with respect to nitrate rejection. The compositions are specified in Table 1 together with the eventual fulfillment of Eq. (31).

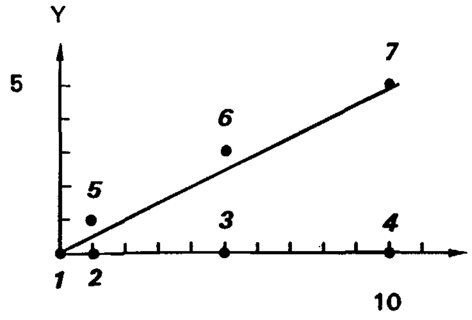

FIG. 3 Nitrate rejection areas for the seven bulk solutions consisting of $NaNO_3$ + Na_2SO_4 + HCl in the molar ratio 1:X:Y.

In Fig. 3 the seven points (X, Y in the nitrate rejection plane) are plotted based on Eq. (31).

RESULTS AND DISCUSSION

Figure 4 shows the measured rejections versus the permeate flux for the single salt solutions $NaNO_3$, Na_2SO_4, and HCl. As expected, there are positive rejections for the single-salt solutions with HCl showing the lowest rejection, $NaNO_3$ an intermediate rejection, whereas Na_2SO_4

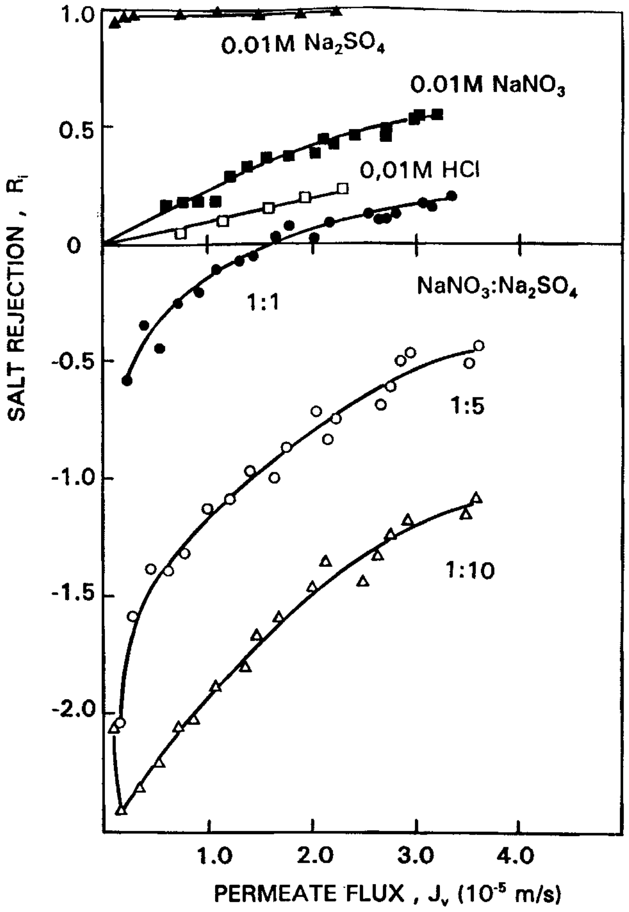

FIG. 4 Salt rejection versus permeate flux for the three single-salt solutions and for the nitrate rejection with increasing Na_2SO_4 in the two-salt solutions.

shows the highest rejection by far because of the divalent sulfate ion. For all three salts there is increased rejection with increasing permeate flux, which is also as expected and found by other authors (4, 19).

In Fig. 4 also shows data for the two-salt solutions $NaNO_3$ + Na_2SO_4. As indicated in Fig. 3, increasing the concentration of Na_2SO_4 should result in a greater distance from the positive nitrate rejection plane and therefore more negative rejections for the nitrate ions. Further, it can be seen that data point 2 (1 : 1 : 0) is situated so close to the zero rejection line, l_x, that it is likely the line will pass this point at higher J_v values, as indicated in Fig. 2. That this is really true is quite nicely demonstrated in Fig. 4.

With increasing addition of Na_2SO_4 the positions of the data points in Fig. 3 move away from the zero rejection line, indicating a more negative rejection of the nitrate ions. With increasing permeate flux the distance to the zero rejection line will decrease, but it is not likely that it will pass the data points. The experimental results shown in Fig. 4 are again in good agreement with these indications.

Figure 5 shows the measured nitrate rejections versus the permeate flux for the system $NaNO_3$:Na_2SO_4:HCl equal to 1 : 1 : 1 compared to the system 1 : 1 : 0. Further, data for the single-salt system 1 : 0 : 0 are shown

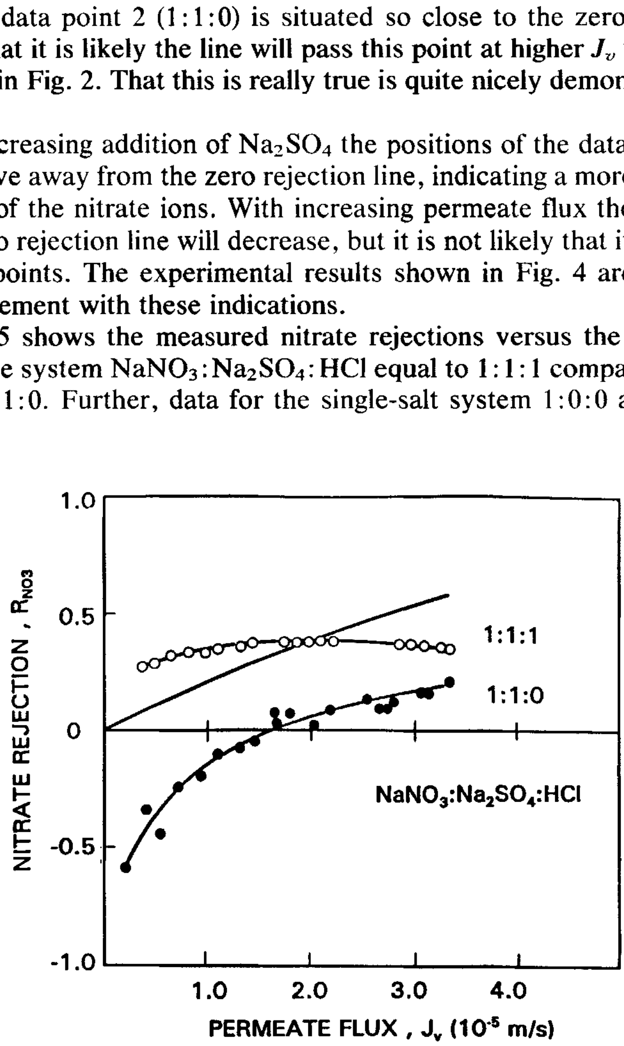

FIG. 5 Comparison of the nitrate rejection versus permeate flux for the single-, two-, and three-salt solutions in the concentration ratio as indicated.

as a curve taken from Fig. 4. As can be seen, the titration of the system by the addition of HCl increases the rejection of the nitrate ion to a positive value which is close to the average value for the single-salt solution. However, the curvature is somewhat changed because the rejection is now much more independent of the permeate flux than for the single-salt solution. As expected from the derived model, Eq. (31), the titration of the bulk solution by HCl addition should result in a shift in the nitrate ion rejection to higher values. As further indicated in Fig. 3, it is likely that

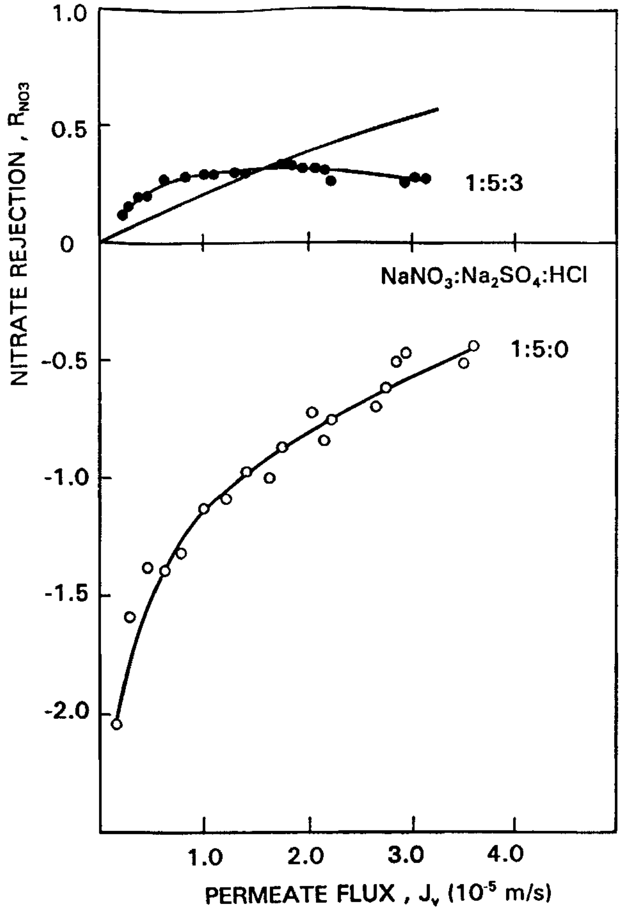

FIG. 6 Comparison of the nitrate rejection versus permeate flux for the single-, two-, and three-salt solutions in the concentration ratio as indicated.

rejection of the nitrate ion should shift to positive values after HCl addition.

Figures 6 and 7 show in a similar way the measured nitrate ion rejections versus the permeate flux for the two other systems $NaNO_3$:Na_2SO_4:HCl equal to 1:5:3 and 1:10:5, respectively, and again compared with the two-salt solutions without HCl addition, 1:5:0 and 1:10:0. By comparing Figs. 6 and 7 with Fig. 5, the same general trend can be observed. Further, by comparison with the calculated bulk phase compositions shown in Fig. 3, it can be seen that the amount of HCl addition to each ratio of $NaNO_3$:-

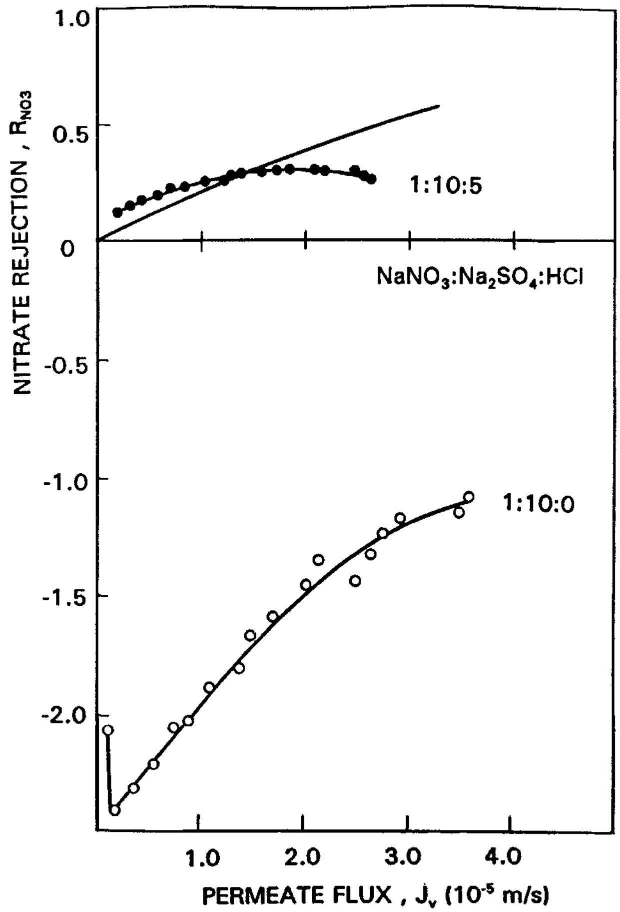

FIG. 7 Comparison of the nitrate rejection versus permeate flux for the single-, two-, and three-salt solutions in the concentration ratio as indicated.

Na_2SO_4 has been chosen so that the data points just pass the zero rejection line, indicating that the rejections of nitrate ion should all be slightly positive. As the distance to the zero rejection line is almost the same for all three ratios, nitrate rejection should be very close for these three sets of data. By comparing the experimental results given in Figs. 5–7, it can be seen that this is very nicely the case, thus confirming the correctness of the derived model, Eq. (31).

CONCLUSION

Using the multisalt system $NaNO_3$–Na_2SO_4–HCl as an example, the nitrate rejection plane was calculated from the derived "titration function." Thus, Fig. 3 shows the line for the concentration ratios of Na_2SO_4:HCl, where the sign of the nitrate rejection changes from positive to negative values. The experimental nitrate rejection data fit very nicely into this plane, showing increased negative rejections with increasing Na_2SO_4 concentration, which can be reversed by the addition of HCl to the bulk solution. The model further predicts that the three different concentration ratios chosen for the three-salt solutions should have almost the same small positive rejection, and this has been experimentally verified.

SYMBOLS

C_{ip}, C_i	ion concentration (mol·m^{-3})
D_{ip}, D_i	ion diffusion coefficient (m^2·s^{-1})
F	Faraday constant (9.64846 × 10^4 C·mol^{-1})
J_{ip}, J_i	ion flux (mol·m^{-2}·s^{-1})
J_v	volume flux (m·s^{-1})
k_i^{obs}	a small positive number which is independent of J_v (mol·m^{-3})
K_{ip}	membrane distribution coefficient (—)
R	gas constant (8.31441 J·K^{-1}·mol^{-1})
R_{ip}, R_i	ion rejection (—)
t	time (s)
t	tortuosity factor for the membrane (—)
T	absolute temperature (K)
V	volume velocity in the pore phase (m·s^{-1})
v_{ip}, v_i	ion velocity (m·s^{-1})
x	argument for the position in the pore phase (m)
z_i	ion valence (—)
α_{ip}, α_i	normalized ion velocity with respect to V (—)
ϵ	fractional pore area (—)

ξ_i	a small positive number which depends on J_v ($\mathrm{mol{\cdot}m^{-3}}$)
Φ	membrane potential (V)
λ	membrane thickness (m)
λ°_{ip}, λ°_{i}	limiting ion conductance ($\mathrm{m^2{\cdot}ohm^{-1}{\cdot}eqv^{-1}}$)
γ	average ion velocity ($\mathrm{m{\cdot}s^{-1}}$)

Subscripts

i, j	ith or jth ion
p	pore phase
v	volume

Superscripts

P	permeate phase
B	bulk phase
$'$	pore phase close to the high pressure side
$''$	pore phase close to the low pressure side
obs	label for a positive number based on the rejection of the ion
$\circ$	limiting value

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