Micellar-Enhanced Ultrafiltration of Chromate Anion from Aqueous Streams

Micellar-enhanced ultrafiltration can be used to remove multivalent anions or cations from aqueous streams. In the removal of chromate ions (CrO_4^{2-}), the cationic surfactant hexadecylpyridinium chloride is added to the solution, and the chromate ions preferentially adsorb at the surface of the highly charged surfactant micelles. The solution is processed by ultrafiltration, using a membrane with pore sizes small enough to block the passage of the micelles and adsorbed ions. The permeate solution has a chromate concentration less than 0.1% that in the original stream. A new equilibrium model, combining the simple two-phase polyelectrolyte theory of Oosawa with thermodynamic activity, material-balance, and charge-balance equations, successfully correlates ultrafiltration and equilibrium dialysis results for chromate solutions.

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Introduction

Micellar-enhanced ultrafiltration (MEUF) has been shown to be an effective method for removing water-soluble organic compounds from aqueous streams (Dunn et al., 1985, 1987; Gibbs et al., 1987; Smith et al., 1987; Bhat et al., 1987; Scamehorn and Christian, in press; Scamehorn and Harwell, 1987a; Scamehorn and Harwell, 1987b). There have also been a few examples of the use of MEUF in separating divalent metal cations from aqueous solutions containing both monovalent and divalent ions (Scamehorn et al., 1986; Scamehorn et al., in press). In removing either metal cations or small neutral molecules from aqueous streams, advantage is taken of the fact that these species are preferentially solubilized by or bound to the surface of micelles. Micelles are spherical or spheroidal aggregates that typically contain 50 to 100 surfactant molecules. Nonpolar organic molecules tend to solubilize in the hydrocarbon interior of micelles, whereas polar solutes solubilize preferentially near the polar/ionic micellar surface. Ions having charges opposite those of ionic micelles tend to bind near the micellar surface; multivalent counterions are particularly strongly adsorbed by the intensely charged micelles.

In an MEUF separation, the pores of the ultrafilter are small enough to block the passage of the micelles and associated ions or small molecules, with the result that these species become highly concentrated in the solution that does not pass through the membrane (the retentate). Under ideal operating conditions, the solution passing through the membrane (the permeate) is practically pure water, containing only small concentrations of the free surfactant, the unbound metal ions, and the unsolubilized organic solutes.

There have been no previous reports of the use of MEUF to remove polyvalent anions from aqueous solutions. However, many metals (e.g., chromium, iron, and cadmium) can exist in divalent or trivalent anionic forms—for example, as complexes with halide or cyanide ions, or as oxy-acid anions. Therefore, we thought it would be useful to study the removal of chromate (CrO_4^{2-}), which exists as a stable anionic species throughout relatively wide pH ranges. MEUF results show that the process is highly efficient in removing CrO_4^{2-}, even in the presence of moderate concentrations of added sodium chloride.

Most of the present experimental study of the transfer of aqueous chromate solutions through membranes has involved the use of semiequilibrium dialysis (SED) (Christian et al., 1985; Smith et al., 1986; Smith, 1986). In SED experiments, concentrations of the low molecular weight electrolytes are determined on both sides of the dialysis membrane, after sufficient time has elapsed so that equilibrium is reached with respect to these solutes. However, equilibrium is not reached by the surfactant, which continues to have a much greater concentration and a slightly greater thermodynamic activity in the retentate solution than in the permeate. It is possible to interpret the SED results to infer the concentrations of chromate ions that are adsorbed on the micelles and those that remain unassociated in the aqueous retentate solution.

In previous studies, we have been able to show that the concentrations of unassociated neutral solutes or ionic electrolytes in the permeate in SED experiments are practically the same as the permeate concentrations of these species in the analogous MEUF experiments, even when substantial concentration polar-

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ization occurs. Our MEUF results are in satisfactory agreement with the extensive SED data. Therefore, it is reasonable to suggest that the performance of actual MEUF separations can be predicted from the somewhat simpler semiequilibrium dialysis measurements, under at least some conditions. In this paper, the SED and MEUF results for multivalent ion removal can be correlated with a new equilibrium model, incorporating the simple theory of Oosawa (1971) to explain the binding of metals to polyelectrolytes.

Experimental Procedures

Sodium chromate tetrahydrate (Fisher Scientific, certified grade) and high-quality cetylpyridinium chloride (CPC) monohydrate (Hexcel Corp.) were used as received. Distilled, deionized water was used for preparing all solutions.

Semiequilibrium dialysis

The semiequilibrium dialysis experiments were performed as described previously (Christian et al., 1985) using equilibrium dialysis cells from Fisher Scientific, with membranes presoaked in distilled water for at least 30 min and thoroughly washed before use. An aqueous CPC solution containing a known concentration of sodium chromate (and in some cases added NaCl) was added to one compartment of the dialysis cell and pure water or an aqueous solution containing the same concentration of NaCl was placed in the other compartment. Cells were thermostatted at 25°C for approximately 20 h. The permeate solutions (and in certain cases the retentate solutions) were analyzed for total chromate.

Chromate concentrations were determined by direct spectrophotometric measurement of CrO_4^{2-}. At the slightly alkaline pH values of the solutions (approximately 8.3), a small but nearly constant fraction of the Cr exists as $HCrO_4^-$. Corrections were made to account for the fraction of Cr present as $HCrO_4^-$ in both the retentate and the permeate solutions. However, considering the fact that the monovalent bichromate ion will be only very weakly adsorbed by the cationic micelles, we felt justified in ignoring the concentration of this species in the mass action equations of the model developed to correlate the SED and MEUF results.

During the time period of the SED experiments, very little micellar surfactant forms in the permeate compartment. Although the total concentration of CPC in the permeate does continue to increase with time, analysis of the permeate at approximately 20 h avoids the necessity of correcting for the adsorption of anions on the positively charged CPC micelles in these dilute solutions. That is, at times less than 24 h, the permeate consists of a very dilute solution of CPC and sodium chromate, containing unbound sodium and chromate ions as well as free surfactant at a concentration well below the critical micelle concentration (CMC). The duration of the SED experiments is long enough so that, except for the surfactant itself, the individual electrolytes (specifically, NaCl and Na_2CrO_4) reach thermodynamic equilibrium with both the permeate and the retentate solutions.

Micellar-enhanced ultrafiltration

The ultrafiltration experiments were carried out in 400 dm^3 stirred cells (Nuclepore), wrapped in flexible tubing containing circulating water for isothermal operation at 30°C. The pressure drop across the membrane was maintained at 414 kPa and the stirrer speed was set at 845 rpm during a run. The ultrafiltration membranes (Spectrum) were anisotropic cellulose acetate membranes, 76 mm in dia. and having an effective area of 30.2 cm^2. The molecular weight cutoff was 5,000 Daltons. Membranes were preequilibrated overnight in a solution containing CPC and sodium chromate at concentrations approximating the permeate concentrations in actual experiments. The cell was initially filled with 300 dm^3 of the feed solution and the ultrafiltration proceeded until approximately 100 dm^3 remained in the retentate. Permeate samples were collected during the run and fluxes were measured. The permeate samples were analyzed for chromate concentration by using the spectrophotometric method described above.

Results

Table 1 gives results of SED experiments for aqueous solutions of CPC, containing known concentrations of sodium chromate and, in several of the experiments, added sodium chloride. Values of the concentrations of CPC and chromate, in the retentate and permeate solutions after about 20 h, are included in Table 1. The column headed "[CrO_4^{2}] M, per calc." lists values of the chromate concentration calculated by a least-squares method incorporating a model (Oosawa, 1971) for the binding of ions to polyelectrolytes.

The bottom four rows in Table 1 list similar results obtained from MEUF experiments. Concentration data for the permeate and retentate solutions correspond to analyses made at times near the middle of individual ultrafiltration experiments; therefore, only one datum is reported for each batch run. The "[CrO_4^{2}] M, per calc." column pertaining to the four MEUF experiments again lists values of the permeate concentration of chromate ion predicted by the polyelectrolyte ion-binding model. The same optimized values of the variable parameters were used in fitting all of the SED and MEUF data. Although the MEUF results were obtained at 30°C and the SED results at 25°C, little difference is expected (or observed) because of this small temperature difference.

The good agreement between MEUF and SED results, observed under the conditions of the present experiments, was also found in previous studies of the removal of neutral organic molecules (Dunn et al., 1985, 1987; Gibbs et al., 1987), even when concentration polarization occurred. Because shear is not uniform across the membrane in a stirred cell, it is difficult unambiguously to elucidate concentration polarization effects in such experiments. Current research includes a study of this phenomenon in a spiral-wound unit. However, under the conditions of the present study, concentration polarization has little apparent effect on the mean permeate concentration.

Ion-binding Model

Several equilibria need to be considered in modeling the properties of the aqueous stream that passes through the ultrafilter in an MEUF separation. First of all, the condition of electrical neutrality applied to the permeate stream requires that the sum of the products of ion concentration and electrical charge for the individual species must equal zero. Another assumption, justified in part by the results of previous MEUF studies, is also applied. We equate the thermodynamic activity of each electrolyte in the permeate stream at the moment the solution passes through the membrane to the activity of the same electrolyte in the retentate solution. An analogous assumption has been invoked previously and tested in analyzing equilibrium dialysis and ultrafiltration data for neutral molecules: that the activity of the organic solute species is the same on both sides of the membrane, in either SED or MEUF experiments. (It must be remembered that the thermodynamic activities of individual ions—e.g., the chromate ion—cannot be equated in the two solutions.)

Table 1. Semiequilibrium Dialysis and Micellar-Enhanced Ultrafiltration Results

$[CrO_4^{2-}]$ M, *ret*	[NaCl] M, *ret*	[CPC] M, *ret*	$[CrO_4^{2-}]$ M, *per* Exp.	$[CrO_4^{2-}]$ M, *per* Calc.**	Rejection*
Semiequilibrium Dialysis Runs, 25°C Data Sets 1–48					
0.00401	0.000	0.104	0.0000055	0.0000041	0.9986
0.00793	0.000	0.104	0.0000236	0.0000247	0.9970
0.00783	0.000	0.104	0.0000269	0.0000238	0.9966
0.01027	0.000	0.104	0.0000547	0.0000526	0.9947
0.01032	0.000	0.104	0.0000617	0.0000534	0.9940
0.00460	0.000	0.054	0.0000102	0.0000096	0.9978
0.00470	0.000	0.054	0.0000100	0.0000101	0.9978
0.00475	0.000	0.025	0.0000231	0.0000318	0.9951
0.00420	0.000	0.0099	0.000336	0.000421	0.920
0.00430	0.000	0.0099	0.000354	0.000472	0.918
0.00417	0.000	0.0143	0.0001056	0.0000824	0.9746
0.00410	0.000	0.0143	0.0000954	0.0000745	0.9767
0.00472	0.000	0.052	0.0000095	0.0000107	0.9980
0.00468	0.000	0.052	0.0000110	0.0000104	0.9976
0.00472	0.000	0.026	0.0000312	0.0000298	0.9934
0.00477	0.000	0.026	0.0000284	0.0000313	0.9940
0.00425	0.000	0.0105	0.000312	0.000342	0.920
0.00423	0.000	0.0105	0.000323	0.000331	0.924
0.00486	0.000	0.110	0.0000079	0.0000065	0.9984
0.00493	0.000	0.110	0.0000090	0.0000067	0.9982
0.00451	0.050	0.100	0.000351	0.000381	0.922
0.00447	0.050	0.100	0.000345	0.000377	0.923
0.00471	0.025	0.100	0.000145	0.000155	0.969
0.00471	0.025	0.100	0.000149	0.000155	0.968
0.00470	0.0125	0.100	0.000053	0.000064	0.989
0.00466	0.0125	0.100	0.000054	0.000062	0.988
0.00421	0.025	0.100	0.000133	0.000126	0.973
0.00415	0.025	0.100	0.000110	0.000122	0.973
0.00312	0.049	0.0143	0.00188	0.00117	0.622
0.00319	0.049	0.0143	0.00131	0.00120	0.589
0.00441	0.025	0.099	0.000112	0.000138	0.975
0.00435	0.025	0.099	0.000118	0.000135	0.973
0.00213	0.026	0.102	0.000042	0.000051	0.980
0.00219	0.026	0.102	0.000054	0.000053	0.979
0.00177	0.025	0.098	0.000023	0.000024	0.980
0.00108	0.025	0.098	0.000023	0.000022	0.979
0.00463	0.025	0.100	0.000168	0.000146	0.964
0.00460	0.025	0.100	0.000159	0.000144	0.965
0.00225	0.025	0.100	0.000067	0.000052	0.970
0.00244	0.025	0.100	0.000065	0.000053	0.971
0.00078	0.025	0.100	0.000020	0.000015	0.974
0.00077	0.025	0.100	0.000019	0.000015	0.975
0.00405	0.025	0.100	0.000141	0.000122	0.965
0.00408	0.025	0.100	0.000143	0.000124	0.965
0.00418	0.025	0.050	0.000280	0.000229	0.933
0.00422	0.025	0.050	0.000293	0.000233	0.931
0.00394	0.025	0.024	0.000562	0.000484	0.857
0.00393	0.025	0.024	0.000571	0.000481	0.855
Micellar-Enhanced Ultrafiltration Runs, 30°C Data Sets 49–52					
0.0239	0.000	0.119	0.00046	0.00074	0.981
0.0120	0.000	0.120	0.000062	0.000073	0.995
0.0048	0.000	0.119	0.0000058	0.0000059	0.999
0.0049	0.050	0.122	0.000280	0.000368	0.943

CPC: hexadecylpyridinium chloride; *ret:* retentate solution; *per:* permeate solution

*Rejection = $1 - [CrO_4^{2-}]_{per}/[CrO_4^{2-}]_{ret}$

**Calculated by text model

Analysis of SED and MEUF results in the absence of added NaCl

With only CPC and sodium chromate present, the conditions of charge balance and the equality of thermodynamic activities lead to the equations:

$$2[CrO_4^{2-}]_{ret} + [Cl^-]_{ret} = [CP^+]_{ret} + [Na^+]_{ret} \tag{1}$$

$$2[CrO_4^{2-}]_{per} + [Cl^-]_{per} = [CP^+]_{per} + [Na^+]_{per} \tag{2}$$

$$a_{Na_2CrO_4,ret} = a_{Na_2CrO_4,per} \tag{3}$$

$$a_{CPC,ret} = a_{CPC,per} \tag{4}$$

$$a_{NaCl,ret} = a_{NaCl,per} \tag{5}$$

where subscripts *ret* and *per* denote the retentate and permeate solutions, CP^+ denotes the hexadecylpyridinium cation, and $a_{Na_2CrO_4}$, a_{CPC}, and a_{NaCl} denote thermodynamic activities of these salts.

In the absence of added electrolyte, the ionic strength is quite small on both sides of the membrane; therefore, it may be reasonable to neglect activity coefficient effects and rewrite Eqs. 3–5 in the approximate forms

$$[Na^+]^2_{ret}[CrO_4^{2-}]_{ret} = [Na^+]^2_{per}[CrO_4^{2-}]_{per} \tag{6}$$

$$[CP^+]_{ret}[Cl^-]_{ret} = [CP^+]_{per}[Cl^-]_{per} \tag{7}$$

$$[Na^+]_{ret}[Cl^-]_{ret} = [Na^+]_{per}[Cl^-]_{per} \tag{8}$$

In attempting to predict the concentrations of electrolytes passing through the ultrafiltration membrane, it is necessary to account for the concentrations of ionic species that are adsorbed on the surface of the ionic micelles. Commonly, the adsorption of individual ions has been assumed—and in certain systems, shown—to occur with a nearly constant "binding fraction," throughout relatively wide ranges of concentrations of micelles and added electrolyte. Typically, monovalent anions or cations, binding to ionic micelles with aggregation numbers between 50 and 150, have been found (Rathman and Scamehorn, 1984, 1987) to have binding fractions in the range 0.5 to 0.9.

An equivalent problem, that of determining the fractions of counterions that are bound to a macroion, arises in research on polyelectrolyte solutions (Oosawa, 1957, 1971; Manning, 1972). Although aqueous polyelectrolyte solutions are very complex, it seemed reasonable to try to apply the counterion binding model developed by Oosawa (1971) to correlate the MEUF and SED results. Oosawa relates the extent of counterion binding to the intensity of the surface potential of the macroion, adopting a two-phase approximation in which a given counterion must either be bound to the polyelectrolyte or free in the bulk aqueous solution. While recognizing the limitations of Oosawa's treatment (Manning, 1972), we have used the model to account for the binding of Cl^- and CrO_4^{2-} ions to the surface of CPC micelles. The approach is successful in fitting the SED and MEUF results and it avoids the necessity of making any assumption about the value or constancy of the counterion binding fraction. A dimensionless parameter P, relating to the intensity of the potential of the macroion, must be inferred from the analysis. However, this single parameter accounts for the binding of both monovalent and divalent anions to the micelles, making it unnecessary to introduce specific counterion binding fractions for these species.

The basic equations of the Oosawa model, given here for assumed spherical micelles, and two (negative) counterions of different charge are

$$\ln [(1 - \beta)/\beta] = \ln [\varphi/(1 - \varphi)] + (\beta q + \beta' q')zP(1 - \varphi^{1/3}) \quad (9)$$

and

$$\ln [(1 - \beta')/\beta'] = \ln [\varphi/(1 - \varphi)] + (\beta q + \beta' q')z'P(1 - \varphi^{1/3}) \quad (10)$$

where β and β' are the degrees of dissociation of the two types of counterions (e.g., Cl^- and CrO_4^{2-}), P is the dimensionless potential parameter, q and q' are the fractions of the free ion charge carried by the two types of counterions, z and z' are the absolute values of the counterion charges (1 for chloride, 2 for chromate), and φ is the fraction of the total volume in which the bound ions are located. Although there is some uncertainty in choosing φ, we have found that the analysis is not sensitive to the choice of this variable, so we have arbitrarily set it equal to the molar concentration of CPC in micellar form, multiplied by the partial molar volume of CPC, assumed to be $0.38\ L \cdot mol^{-1}$.

Because CPC can exist either as free ions or in micelles, one other relation is needed to account for the equilibrium between monomeric and micellar CPC in the retentate solution. (No account is taken of the presence of very small concentrations of micellar CPC in the permeate.) The equation

$$(1 - \beta^*) \ln \{[Cl^{-1}] + 2[CrO_4^{2-}]\} + \ln [CP^+] = (2 - \beta^*) \ln (\mathrm{CMC}) \quad (11)$$

(where $1 - \beta^*$ is the fraction of the micellar charge that is neutralized by bound chloride and chromate ions) relates the concentrations of the free ions in the retentate solution to the critical micelle concentration (CMC). In the limit as $[CrO_4^{2-}]$ approaches zero, $1 - \beta^*$ becomes equal to $1 - \beta$, and the equation pertains to a mass action equilibrium between n CP^+ ions and $n(1 - \beta)$ Cl^- ions to form the charged micelle. A similar expression has been used previously (Elworthy and Mysels, 1966). Although Eq. 11 may be only approximately correct at large concentrations of chromate or if the micelles are highly polydisperse, the exact form of the equation does not greatly influence the modeling of the present results because almost all of the CPC is in micellar form in the retentate solution.

We have incorporated Eqs. 1, 2, and 6–11 in a nonlinear least-squares model designed to predict values of the chromate concentration in the permeate solution (in either SED or MEUF experiments) from the initial conditions in the retentate compartment. Our goal has been to compare experimental values of the concentration of CrO_4^{2-} in the permeate stream with values predicted from the Oosawa model, using only the single variable parameter, P, of the model. Values of $[CrO_4^{2-}]$ in the "M, per, calc." column of Table 1, for the solutions in which $[NaCl] = 0$, are the end result of this analysis, corresponding to the value of P that leads to a minimum in the sum of squares of the (relative) errors in chromate concentration in the permeate. Also included in Table 1, in the righthand column, are values of the rejection, defined as $1 - [CrO_4^{2-}]_{per}/[CrO_4^{2-}]_{ret}$. This parameter, which is widely used in membrane science to represent the efficiency of membrane separation processes, indicates that MEUF is very effective in removing chromate ion from aqueous streams at the given concentrations of Cr, CPC, and NaCl.

Although details of the numerical analysis are not given here, it may be appropriate to indicate the steps involved in applying the model to correlate MEUF or SED data. Initially, one assumes a trial value for P and solves Eqs. 1, 2, and 5–9 to infer values of $[CrO_4^{2-}]_{per}$ and the concentrations of other ions in both the permeate and the retentate solutions. Next, P is varied according to a well-known algorithm from nonlinear least-squares analysis (Christian and Tucker, 1982) and all of the calculations are repeated for each modified value of P. Ultimately, the least-squares program finds the optimum value of P leading to an absolute minimum in the sum of squares of relative deviations in the chromate concentration in the permeate. The analysis of the SED results in Table 1, for the solutions containing no added NaCl, leads to a root mean square relative deviation of only 0.19, or to a relative error in the predicted chromate concentration in the permeate of 19%.

The goodness of fit obtained with the one-parameter analysis is considered to be quite satisfactory, given the fact that the permeate contains chromate ion at concentrations at least one or two orders of magnitude smaller than those in the retentate (for all of the solutions without added NaCl). In the case of the three MEUF experiments (in the absence of added NaCl), the predicted values of chromate concentration in the permeate stream differ on average by only 27% from the experimental values. Taken together, the results and the mathematical analysis support the assumption that electrolyte activities are equal on the two sides of the membrane in MEUF separations; they also strengthen our belief in the predictive ability of the model introduced here. The analysis combines straightforward material-balance, charge-balance, and thermodynamic activity relations with the simple Oosawa theory of polyelectrolytes.

Figure 1 illustrates a somewhat surprising result predicted by the polyelectrolyte model: the degree of separation greatly increases as the concentration of chromate in the retentate solution decreases. Values of the retention ratio (defined as the total concentration of chromate in the retentate solution divided by that in the permeate) are plotted against the concentration of chromate in the retentate, for solutions containing 0.102 M CPC. The solid line is calculated from the mathematical model, and the three SED data points (at 10.3, 7.9, and 4.0 mM chromate) lie in a region where the retention ratio increases rapidly as $[CrO_4^{2-}]$ decreases. The predicted retention ratios do not reach a limiting value (1.6×10^5) until chromate concentrations in the retentate are reduced to the 10 μM level. In this limit, which Scamehorn et al. (1986) term the dilute-metal limiting case, the predicted rejection of chromate in MEUF exceeds

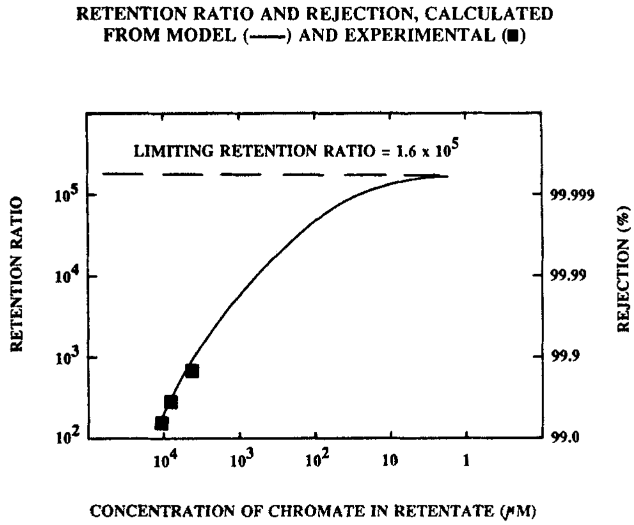

Figure 1. Retention ratio and rejection.
——— calculated from model; ⊠ experiment

0.99999 or 99.999%. Rejection (%) is defined as:

$$\left[1 - \frac{(\text{chromate in permeate})}{(\text{chromate in retentate})}\right](100)$$

[Values of the rejection are indicated near the righthand margin of Figure 1, corresponding to the retention ratios listed along the ordinate.] Although it would require very sensitive analytical methods to verify the correctness of this prediction, it is apparent that the use of MEUF in removing chromate from very dilute chromate solutions will be highly efficient.

Many other separation methods for removing ions from water (for example, precipitation) become less efficient as the concentration of the ion decreases. In contrast, MEUF effects a greater proportional decrease in the concentration of the multivalent ion as the feed concentration decreases. At extremely low concentrations, the proportional decrease becomes constant as the feed concentration decreases still further; the rejection reaches a limiting value of 0.99999. In the future, as pollution control requirements for extremely toxic metals or metal complexes are made more stringent, MEUF should become even more competitive as a separation technique because of this unusual behavior.

Effects of added NaCl

In principle, one should be able to use the model described above to predict the results of MEUF and SED experiments for solutions containing added salt. Unfortunately, use of the model with the original value of the fitting parameter ($P = 55$) yields predicted chromate concentrations in the permeate that are much smaller than those actually determined in MEUF and SED experiments. In other words, added NaCl considerably reduces the value of P required to force agreement with the model predicted here. This result is not surprising, because NaCl may be expected to compress the double layer and reduce the potential of the charged micelle at any given distance from the surface. In applying the polyelectrolyte model to systems containing added electrolyte, it will be necessary to be able to predict the variation of P with the concentration of NaCl. Rather than approach this problem theoretically, we have developed a simple method for predicting P from knowledge of the concentration of added NaCl.

After experimenting with several equations to relate P to [NaCl], we found that the empirical relation

$$P = P^\circ/\{1 + \alpha[\text{NaCl}]^{1/2}\} \qquad (12)$$

where α is an adjustable parameter, can be used to correlate all of the SED and MEUF results, either in the presence or in the absence of added NaCl. The optimum value of α is found to be $23.8 \pm 2.1\ M^{-1/2}$, and $P^\circ = 55.1 \pm 3.5$. Least-squares results for the systems containing added salt, as well as for the systems without added NaCl, are given in Table 1. In the case of the SED data, all of the results are correlated to a root mean square deviation in relative concentration of 16.6%. The MEUF results are predicted with an average deviation of 28%.

Conclusions

The experimental MEUF and SED results show that very large separation factors can be obtained for the chromate ion in aqueous solutions at low concentration. Thus, in the dilute-metal limiting case, where the concentration of surfactant greatly exceeds that of the multivalent ion, virtually all of the chromate ion will be removed from the stream forced through the ultrafilter in an MEUF separation. Even in the presence of 0.05 or 0.10 M NaCl, the separation is quite good, Table 1.

By combining the polyelectrolyte ion-binding model of Oosawa with material- and charge-balance equations and by invoking the assumption that the electrolytes pass through the membrane at their equilibrium thermodynamic activities, we have been able to develop a two-parameter model that appears to be useful in predicting MEUF results. The model is simple to apply in calculating the degree of separation of multivalent ions from aqueous streams that can be achieved with micellar-enhanced ultrafiltration, either in streams containing added NaCl or without added electrolyte. The parameter P° of the model is directly related to the intensity of the electric potential at the surface of the charged surfactant micelle; an additional parameter, α, is required to attenuate the value of P for micelles existing in the presence of added electrolyte.

Previously Oosawa (1971, ch. 7) was successful in applying an additivity rule to predict thermodynamic and transference properties of salt-containing polyelectrolytes; his method involved a simple superposition of the properties of the individual electrolyte solutes. Our use of Eq. 12, which empirically relates P to the concentration of added NaCl, appears to be consistent with Oosawa's superposition assumption. However, Manning (1972) has criticized both the two-phase model and the additivity law, arguing that proper use of thermodynamic and electrostatic theory will lead to detailed predictions of the distribution of counterions around polyelectrolyte ions, either in the presence or in the absence of added electrolytes. Nonetheless, the model developed here is very simple to apply, and it has been shown to be valuable in making predictions of the separations that can be attained with micellar-enhanced ultrafiltration under the conditions used here. We are at present studying the separation of a number of polyvalent ions from aqueous streams, both to extend the range of utility of MEUF and to provide additional tests of the simple theory presented here.

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Notation

CPC = hexadecylpyridinium chloride or cetylpyridinium chloride
CP = hexadecylpyridinium cation
MEUF = micellar-enhanced ultrafiltration
P = dimensionless potential parameter of Oosawa (1971) model
P^o = parameter P in absence of added NaCl
q = fraction of free anion charge carried by chloride ion
q' = fraction of free anion charge carried by chromate ion
SED = semiequilibrium dialysis
z = absolute value of charge of chloride ion
z' = absolute value of charge of chromate ion

Greek letters

α = parameter accounting for effect of [NaCl] on P
β = fraction of chloride ions not attached to micellar species
β' = fraction of chromate ions not attached to micellar species
β^* = fraction of micellar charge not neutralized by attached negative ions
φ = volume fraction of solution containing bound counterions

Subscripts

per = permeate solution
ret = retentate solution

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