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Removal of Divalent Metal Cations and Their Mixtures from Aqueous Streams Using Micellar-Enhanced Ultrafiltration

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ABSTRACT

Micellar-enhanced ultrafiltration (MEUF) is a novel membrane-based separation technique that can be used to remove multivalent metal cations from aqueous streams. In this technique an anionic surfactant is added to the aqueous stream containing the metal cations to be removed. The surfactant forms highly charged aggregates called micelles onto which the metal cations adsorb or bind. The aqueous stream is then passed through an ultrafiltration membrane with pores small enough to block the passage of the micelles and adsorbed metal cations. In this study, MEUF has been shown to remove divalent cadmium, zinc, copper, and calcium ions and their mixtures with rejections of at least 96%. A previously developed equilibrium binding model describes the results successfully. Under reasonable conditions the flux rates are not substantially below that of pure water, indicating the feasibility of MEUF for industrial application.

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INTRODUCTION

Industrial wastewater streams frequently contain high concentrations of dissolved toxic metal cations (often called heavy metals) that constitute a major environmental hazard. Sources of such wastewaters include metal plating industries, semiconductor manufacturers, mining operations, and chemical processes, among many others. Improved methods of removing these heavy metals from water would be of great value.

Surfactant-based separation techniques are becoming increasingly important for purposes of industrial application (1, 2). These techniques generally require much less energy than traditional methods and have the added advantage that many of the surfactants used are environmentally innocuous and of low toxicity.

Micellar-enhanced ultrafiltration (MEUF) is a recently developed technique that has shown to be effective in removing multivalent metal ions from aqueous streams (3–6). A schematic diagram of the use of MEUF to remove multivalent metal cations is presented in Fig. 1. An anionic surfactant is injected into the aqueous stream coming from an industrial process. The final surfactant concentration in the stream should be well above the critical micelle concentration (CMC) of the surfactant, so that micelles (aggregates of 20–200 surfactant molecules in size) form in solution. The micelle (see Fig. 1) will form with the hydrophobic tail groups

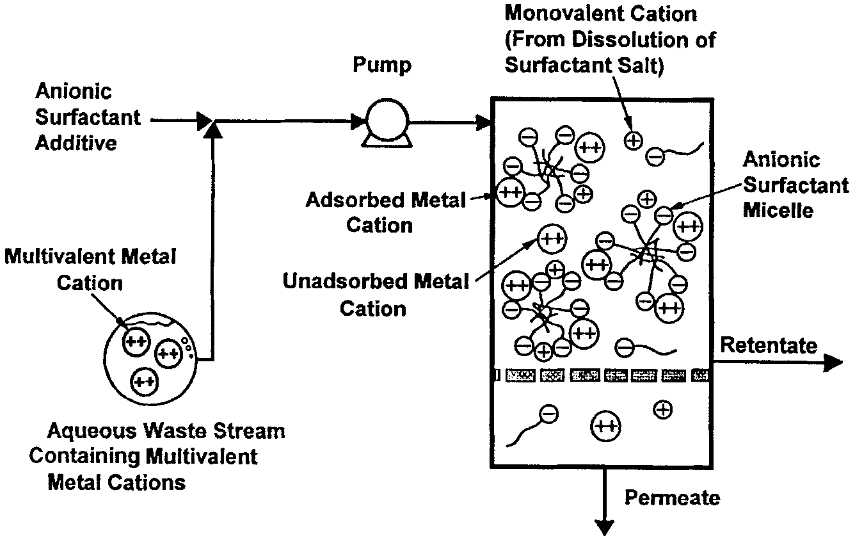

FIG. 1 Schematic of MEUF. Removal of multivalent metal cations.

(of the surfactant molecules) intertwined together in the "core," while the hydrophilic, anionic headgroups are packed on the surface toward the aqueous solution (7). The micellar surface has a high charge density and a high absolute electrical potential (8); therefore, the multivalent metal cations electrostatically adsorb or bind onto the micellar surface. The stream is subsequently forced through an ultrafiltration membrane with pore sizes small enough to almost completely reject the micelles and associated metal cations. As a result, the permeate stream which passes through the membrane will have very low concentrations of both the multivalent metal cation and the surfactant. The retentate stream (which does not pass through the membrane) will have very high concentrations of both the multivalent metal cation and the surfactant, and will be much lower in volume (or flow rate) than the initial feed stream. Therefore, downstream treatment or disposal of this retentate can be performed more economically than treatment or disposal of the original feed stream.

The divalent metal cations selected for this study were cadmium, zinc, cupric, and calcium ions (Cd^{2+}, Zn^{2+}, Cu^{2+}, and Ca^{2+}) representing heavy metals (cadmium), transition metals (zinc and copper), and alkaline earth metals (calcium). The use of MEUF to remove each of these cations from a single metal stream was investigated in this study. The model anionic surfactant used was sodium dodecyl sulfate (SDS). Metal chloride salts were used as a source of the metal ions in order to have the same co-ion (chloride) in the four systems studied.

EXPERIMENTAL

The surfactant used in this study, sodium dodecyl sulfate (SDS), was purified by recrystallization from reagent-grade ethanol (plus about 50 mL distilled water per 600 mL solution), followed by freeze-vacuum drying. Analytical reagent-grade cadmium chloride ($CdCl_2$), zinc chloride ($ZnCl_2$), cupric chloride dihydrate ($CuCl_2 \cdot 2H_2O$), and calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) were used as received. All the materials were obtained from Fisher Scientific Company except the calcium chloride dihydrate which was supplied by J. T. Baker Chemical Company. Water used in all experiments was distilled and deionized.

The ultrafiltration experiments were carried out in 400 mL batch, stirred cells manufactured by Spectrum Medical Industries, Inc. The temperature of the solution inside the cell was maintained constant at 30°C by wrapping the Plexiglas sleeve with a plastic tubing containing circulating water. The pressure drop across the membrane (ΔP) was maintained at 414 kPa gauge using nitrogen gas. The agitation speed was approximately 845 rpm for all runs, as measured by a strobe light. Ultrafiltration membranes used were 76 mm in diameter, anisotropic cellulose acetate, with an effective area of 38.5 cm^2, supplied by Spectrum Medical Industries, Inc. Molecular weight cut-offs (MWCO) of 1000 and 5000 were used in this study. The membranes were equilibrated overnight in a solution containing SDS at a concentration near its cmc, and the metal ion at a concentration approximating that expected in the permeate. The cell was initially charged with 300 mL of feed solution, and the permeate solution was collected until approximately 100 mL of the retentate solution remained. As samples were collected throughout a run, fluxes were measured. The permeate samples were analyzed for SDS using high performance liquid chromatography with a conductivity detector. The permeate was analyzed for the metal ion using an atomic absorption spectrophotometer. The ultrafiltration data reported in this study were calculated at midpoint of each run, at which point 150 mL of permeate had been collected.

THEORY

Flux

When a solute is rejected at an ultrafiltration membrane, the concentration of the solute becomes higher in the region of the retentate solution adjacent to the membrane surface than in the bulk retentate solution (that is, a hydrodynamic boundary layer develops). This phenomenon is defined as concentration polarization. The development of concentration polarization in the retentate solution reduces the flux through the membrane due to the increase in resistance to flow caused by the highly viscous solution in the boundary layer (called the gel layer) through which the permeate must pass to reach the membrane. Concentration polarization can be described by the gel polarization theory (9–15), which assumes that the concentration of solute at or near the membrane surface under these conditions of gel polarization is Cg, and the flux (J_w) varies with the bulk concentration of solute (C_b) as follows:

$$J_W = K_T \ln\left(\frac{C_g}{C_b}\right) \tag{1}$$

were K_T is the mass transfer coefficient for backdiffusion from the membrane surface. This expression indicates that the bulk concentration is equal to the gel concentration (C_g) when the corresponding flux is zero and that flux is linear with log(retentate solute concentration) in the concentration polarization region. We have shown that C_g is independent of membrane pore size and applied pressure for MEUF in removal of nonionic organic pollutants using a cationic surfactant (15).

Single Component Systems

In previous applications of MEUF to treat aqueous streams, we have shown that the multivalent ion concentration in the permeate is equal to that expected if the permeate and retentate solutions are at equilibrium and that micelles are totally rejected under normal MEUF conditions (6). Therefore, a thermodynamic model describing the activity of the unassociated metal ion in the retentate solution should predict the permeate metal ion concentration in this study. The model used here has been described previously (4, 6).

For an aqueous stream containing only SDS and metal chloride, the conditions of electroneutrality and equality of thermodynamic activities lead to the equations

$$2[\mathrm{Me}^{2+}]_{\mathrm{ret}} + [\mathrm{Na}^{+}]_{\mathrm{ret}} = [\mathrm{DS}^{-}]_{\mathrm{ret}} + [\mathrm{Cl}^{-}]_{\mathrm{ret}} \tag{2}$$

$$2[\mathrm{Me}^{2+}]_{\mathrm{per}} + [\mathrm{Na}^{+}]_{\mathrm{per}} = [\mathrm{DS}^{-}]_{\mathrm{per}} + [\mathrm{Cl}^{-}]_{\mathrm{per}} \tag{3}$$

$$a_{\mathrm{Me(DS)2ret}} = a_{\mathrm{Me(DS)2per}} \tag{4}$$

$$a_{\mathrm{NaDSret}} = a_{\mathrm{NaDSper}} \tag{5}$$

$$a_{\mathrm{NaClret}} = a_{\mathrm{NaClper}} \tag{6}$$

where subscripts ret and per denote the retentate and permeate solutions, Me^{2+} denotes the divalent metal cation, DS^{-} represents the dodecyl sulfate anion, and $a_{\mathrm{Me(DS)2}}$, a_{NaDS}, and a_{NaCl} are the 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 assume that activity coefficients are equal in permeate and retentate and rewrite Eqs. (4)–(6) in the following approximate forms:

$$[\mathrm{Me}^{2+}]_{\mathrm{ret}}\,[\mathrm{DS}^{-}]^{2}_{\mathrm{ret}} = [\mathrm{Me}^{2+}]_{\mathrm{per}}\,[\mathrm{DS}^{-}]^{2}_{\mathrm{per}} \tag{7}$$

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

$$[\mathrm{Na}^{+}]_{\mathrm{ret}}\,[\mathrm{Cl}^{-}]_{\mathrm{ret}} = [\mathrm{Na}^{+}]_{\mathrm{per}}\,[\mathrm{Cl}^{-}]_{\mathrm{per}} \tag{9}$$

In order to predict the concentrations of electrolytes passing through the membrane, the counterion binding model developed by Oosawa was applied (16). 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. The basic equations of the Oosawa model for spherical electrolytes (in this case, micelles) and two binding counterion species of different valence are

$$\ln\{(1 - \beta)/\beta\} = \ln\{\Phi/(1 - \Phi)\} + (\beta q + \beta' q')zP(1 + \Phi^{1/3}) \quad (10)$$

$$\ln\{(1 - \beta')/\beta'\} = \ln\{\Phi/(1 - \Phi)\} + (\beta q + \beta' q')z'P(1 - \Phi^{1/3}) \quad (11)$$

where β and β' are the degrees of dissociation of the two counterions (Na^+ and Me^{2+}), Φ is the fraction of the total volume in which the bound counterions are located; 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 sodium and 2 for divalent metal ions); and P is a dimensionless potential parameter. The parameter P is related to the intensity of electrical potential of the macroion, and it accounts for the binding between counterions of all valences and the micelles.

It has been shown (6) that the analysis is not sensitive to the choice of the variable Φ, so this variable may be set equal to the product of the molar concentration of the surfactant in micellar form and the partial molar volume of the surfactant, assumed to be 0.25 $L \cdot mol^{-1}$ for SDS.

Another equation is introduced to account for the equilibrium between monomeric and micellar SDS in the retentate solution (6). Assuming no micelles are forming in the permeate stream, the following equation is used to relate the concentration of the free ions in the retentate solution to the critical micelle concentration (cmc):

$$(1 + \beta^*) \ln\{[Na^+]_{per} + 2[Me^{2+}]_{per}\} + \ln[DS^-]_{per} = (2 - \beta^*) \ln(\text{cmc}) \quad (12)$$

where $(1 - \beta^*)$ is the fraction of the micellar charge that is neutralized by the bound sodium and metal ions. A similar expression has been used by Elworthy and Mysels (17). Although this equation may be only approximately correct at large concentrations of multivalent counterions, the exact form does not greatly influence the modeling results (6).

For solutions containing added salt, the use of the model with the P value obtained from data in the absence of salt yields much lower permeate Me^{2+} concentrations than those actually determined in MEUF experiments. The following empirical relation has been proposed to relate P to the concentration of added salt (6):

$$P = P^0/\{1 + \alpha\sqrt{[NaCl]_{per}}\} \quad (13)$$

where P^0 is the potential parameter calculated in absence of added salt, α is a second adjustable parameter, and [NaCl] is the concentration of added NaCl in the retentate solution.

Mixtures of Metals

In order to predict the total divalent metal concentration in the permeate for a mixture of two or more metal ions, it is possible to use the same equations developed to model the one-component metal MEUF results. However, the values of P^0 and α to be used for mixtures are taken to be the *mole weighted* averages of parameter values derived from the single-component results. Thus, it is assumed that

$$P^0 = \sum_i X_i P_i^0 \tag{14}$$

$$\alpha = \sum_i X_i \alpha_i \tag{15}$$

where X_i is the mole fraction of metal ion i in the retentate (as a fraction of total divalent metal ions present), P_i^0 is P^0 for the single component metal i, and α_i is α for the single component i. These values of P^0 and α yield the value of P at a given salinity from Eq. (13).

In modeling results for the individual metal ions in a mixture of divalent cations, it is observed that the permeate concentration of a given cation varies nearly inversely with the value of P_i^0 for that species. Thus it is reasonable to predict that the relative permeate concentrations of two different cations, i and j, will be given by

$$[M_i]_{per}/[M_j]_{per} = (X_i P_j^0)/(X_j P_i^0) \tag{16}$$

where $[M_i]_{per}$ and $[M_j]_{per}$ are the permeate concentrations of the individual ions and X_i and X_j are the mole fractions of ions i and j, respectively, in the retentate solution. When the method of the previous paragraph has been applied to calculate the total concentration of M^{2+} in the permeate, Eq. (16) can be used to calculate the distribution of the various divalent cations in the permeate solution. In this way, Eqs. (14) to (16) are used to make a priori predictions of the permeate concentrations of all of the component metal ions.

RESULTS

Single Component Systems

Table 1 presents the permeate and retentate concentrations obtained for the single metal systems studied under a variety of conditions. Each row in this table presents the data for the SDS/Me^{2+} systems under the same conditions in the retentate solution. The symbol Me^{2+} refers generally to any of the four investigated metal ions. The corresponding rejec-

TABLE 1
Results of MEUF Runs

Retentate concentration				Permeate concentration					Rejection (%)			
SDS (mM)	Me^{2+} (mM)	NaCl (mM)	Membrane pore size MWCO	SDS (mM)	Cd^{2+} (mM)	Zn^{2+} (mM)	Cu^{2+} (mM)	Ca^{2+} (mM)	Cd^{2+} (mM)	Zn^{2+} (mM)	Cu^{2+} (mM)	Ca^{2+} (mM)
100	20	0	5000	3.4386	0.7420	0.4920	0.3915		96.28	97.57	98.08	
100	10	0	5000	4.8341	0.0854	0.0614	0.0429	0.0383	99.18	99.41	99.59	99.63
100	4	0	5000	7.1682	0.0096	0.0102	0.0089	0.0121	99.78	99.77	99.80	99.73
100	4	50	5000	3.3471	0.5083	0.2112	0.2231	0.1156	85.87	94.63	94.35	97.14
200	4	0	5000	6.8540	0.0098	0.0158	0.0150	0.0123	99.75	99.60	99.62	99.72
400	4	0	5000	14.1212	0.0314	0.0835	0.0523	0.0488	99.19	98.17	98.75	98.82
200	4	0	1000		0.0048	0.0070	0.0019	0.0071	99.88	99.83	99.95	99.82
400	4	0	1000		0.0102	0.0089	0.0117	0.0149	99.75	99.78	99.71	99.63

tions are also given in this table. Rejection is defined as

$$\text{Rejection (\%)} = 100[1 - [Me^{2+}]_{per}/[Me^{2+}]_{ret})] \qquad (17)$$

Table 2 presents the values of the equilibrium model parameters P^0 and α inferred for each system, utilizing only data for systems containing 0.100 M surfactant. The root-mean-square deviation (RMSD) is the average relative difference in the predicted permeate Me^{2+} concentrations compared to the experimental permeate Me^{2+} concentrations obtained.

The effect of the Me^{2+} concentration in the retentate solution on the experimental and theoretical permeate Me^{2+} concentration is shown in Fig. 2 for the four metal ion systems. The effect of added salt on experimental and theoretical permeate Me^{2+} concentration is shown in Fig. 3. The effect of the surfactant concentration in the retentate solution on measured and predicted permeate Me^{2+} concentration is shown in Fig. 4.

Figure 5 shows the fluxes for the four metal ion systems during the MEUF runs using 1000 and 5000 MWCO membranes versus the retentate

TABLE 2
Values of Equilibrium Model Parameters

System	P^0	α ($M^{-0.5}$)	Root-mean-square deviation (RMSD)
SDS/Cd^{2+}	25	17	0.12
SDS/Zn^{2+}	33	10	0.19
SDS/Cu^{2+}	52	19	0.29
SDS/Ca^{2+}	55	8	0.60

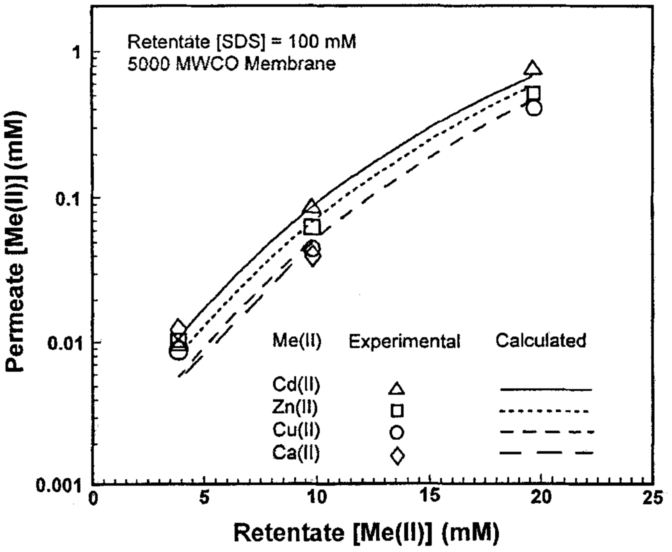

FIG. 2 Effect of retentate [Me^{2+}] on permeate [Me^{2+}] for single metal ions.

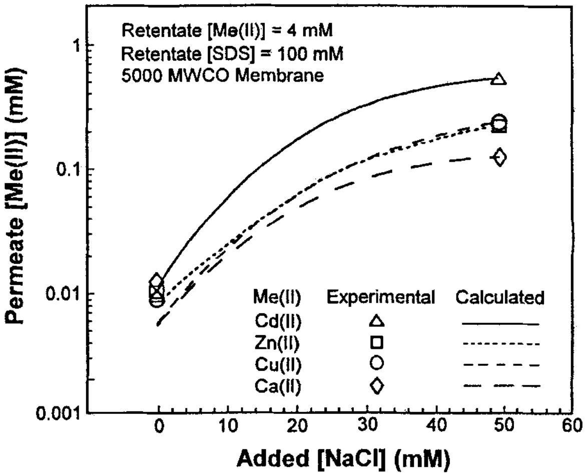

FIG. 3 Effect of added [NaCl] on permeate [Me^{2+}] for single metal ions.

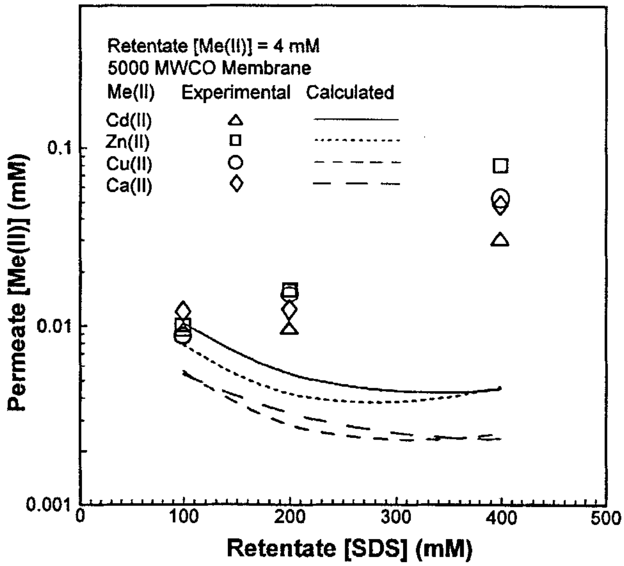

FIG. 4 Effect of retentate [SDS] on permeate [Me^{2+}] for single metal ions.

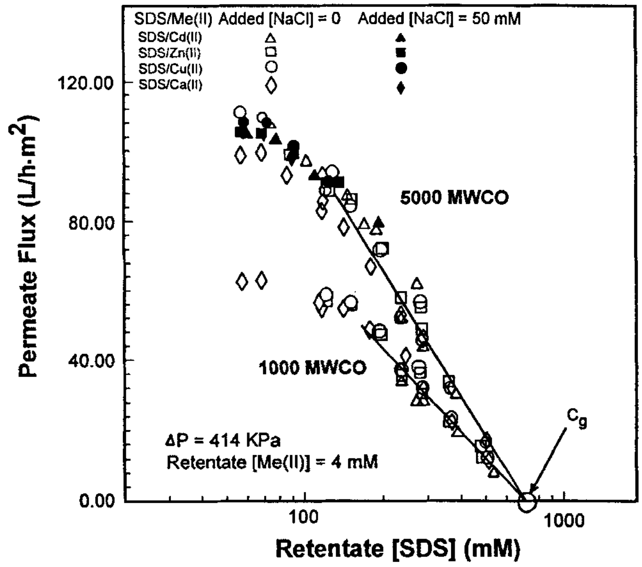

FIG. 5 Permeate flux as a function of retentate [SDS] for single metal ions.

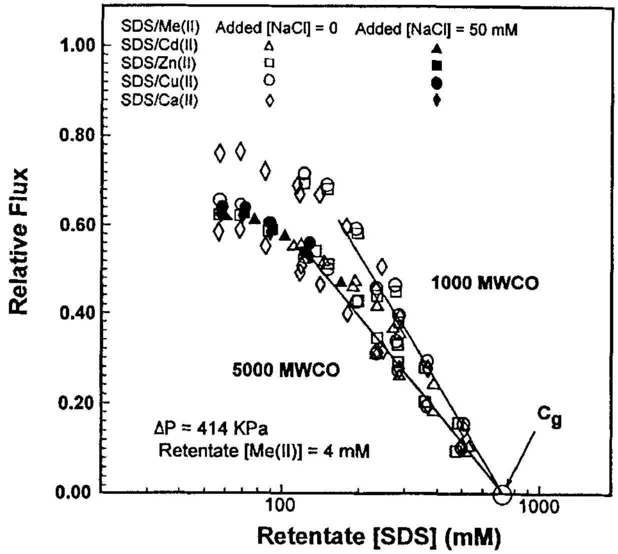

FIG. 6 Permeate relative flux as a function of retentate [SDS] for single metal ions.

TABLE 3
MEUF Results for the Binary Zn^{2+}/Cu^{2+} Mixture[a]

Retentate concentrations (mM)			Premeate concentrations						Rejection (%)		
			Experiment (mM)			Calculated (mM)					
Zn^{2+}	Cu^{2+}	NaCl	Zn^{2+}	Cu^{2+}	Total	Zn^{2+}	Cu^{2+}	Total	Zn^{2+}	Cu^{2+}	Total
4	0	0	0.0102	0	0.0102	0.0080	0	0.0080	99.75	0	99.75
0	4	0	0	0.0089	0.0089	0	0.0057	0.0057	0	99.78	99.78
2	2	0	0.0033	0.0025	0.0058	0.0039	0.0027	0.0067	99.84	99.88	99.86
4	4	0	0.0170	0.0138	0.0308	0.0160	0.0102	0.0262	99.58	99.66	99.62
5	5	0	0.0271	0.0168	0.0439	0.0294	0.0187	0.0481	99.46	99.66	99.56
10	10	0	0.2180	0.1693	0.3873	0.2770	0.1764	0.4534	97.82	98.31	98.06
3	1	0	0.0059	0.0023	0.0082	0.0059	0.0014	0.0073	99.8	99.77	99.79
1	3	0	0.0025	0.0050	0.0075	0.0020	0.0042	0.0062	99.75	99.83	99.81
3.6	0.4	0	0.0060	0.0012	0.0072	0.0072	0.0006	0.0077	99.83	99.7	99.82
0.4	3.6	0	0.0015	0.0054	0.0069	0.0008	0.0051	0.0059	99.63	99.85	99.83
4	0	50	0.2112	0	0.2112	0.2112	0	0.2112	94.72	0	94.72
0	4	50	0	0.2231	0.2231	0	0.2231	0.2231	0	94.42	94.42
2	2	50	0.1068	0.0603	0.1671	0.1363	0.0865	0.2228	94.66	96.99	95.82
4	4	50	0.2273	0.1892	0.4165	0.3786	0.2403	0.6189	94.32	95.27	94.79
3	1	50	0.1528	0.0337	0.1865	0.1814	0.0384	0.2198	94.91	96.63	95.34
1	3	50	0.0531	0.1367	0.1898	0.0775	0.1475	0.2250	94.64	95.44	95.26

[a] Retentate [SDS] = 100 mM.

SDS concentration. The corresponding relative fluxes are presented in Fig. 6. The relative fluxes were calculated as the ratio of the absolute flux to the flux of pure solvent (water) obtained under identical conditions.

Mixtures of Metals

The binary system Zn^{2+}/Cu^{2+} and the ternary system $Cd^{2+}/Zn^{2+}/Cu^{2+}$ were studied under a variety of conditions, and the results are shown in Tables 3 and 4, respectively. Figures 7 and 8 show the total and individual permeate metal concentrations for the Zn^{2+}/Cu^{2+} system as a function of retentate metal composition, respectively. Figure 9 presents the total permeate metal concentrations for an equimolar retentate Zn^{2+}/Cu^{2+} system as a function of total retentate metal concentration. Figures 10–12 are the same as Figs. 7–9 except that the former refer to systems containing 50 mM added NaCl while the latter are for systems with no added salt. Figures 13 and 14 present the individual and total permeate metal concentra-

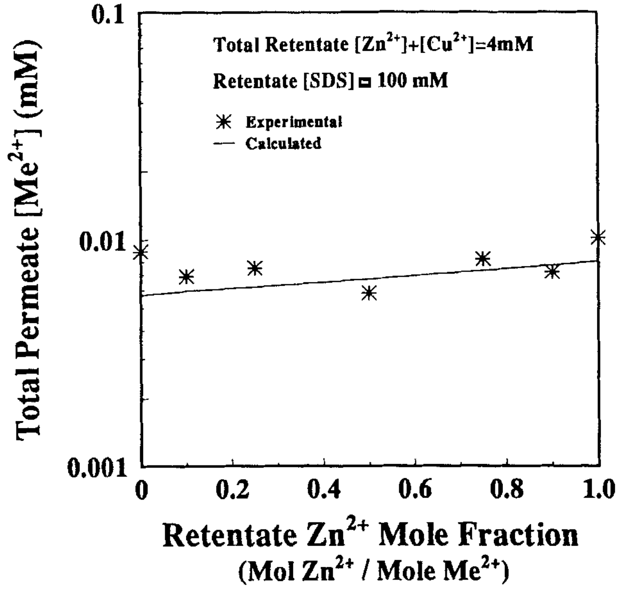

FIG. 7 Effect of retentate Zn^{2+} mole fraction on total permeate $[Me^{2+}]$ for a Zn^{2+}/Cu^{2+} system.

TABLE 4

MEUF Results for the Ternary $Cd^{2+}/Zn^{2+}/Cu^{2+}$ Mixture[a]

Retentate concentrations (mM)				Permeate concentrations								Rejection (%)			
				Experimental (mM)				Calculated (mM)							
Cd^{2+}	Zn^{2+}	Cu^{2+}	NaCl	Cd^{2+}	Zn^{2+}	Cu^{2+}	Total	Cd^{2+}	Zn^{2+}	Cu^{2+}	Total	Cd^{2+}	Zn^{2+}	Cu^{2+}	Total
4	0	0	0	0.0096	0	0	0.0096	0.0106	0	0	0.0106	99.76	0	0	99.76
0	4	0	0	0	0.0102	0	0.0102	0	0.0080	0	0.0080	0	99.75	0	99.75
0	0	4	0	0	0	0.0089	0.0089	0	0	0.0057	0.0057	0	0	99.78	99.78
1.33	1.33	1.33	0	0.0027	0.0027	0.0023	0.0077	0.0026	0.0020	0.0012	0.0058	99.80	99.80	99.83	99.81
2.66	2.66	2.66	0	0.0126	0.0115	0.0050	0.0291	0.0131	0.0099	0.0063	0.0293	99.53	99.57	99.81	99.64
1	1	2	0	0.0036	0.0034	0.0041	0.0111	0.0020	0.0015	0.0019	0.0054	99.64	99.66	99.80	99.72
1	2	1	0	0.0031	0.0044	0.0031	0.0106	0.0020	0.0030	0.0010	0.0060	99.69	99.78	99.69	99.74
2	1	1	0	0.0053	0.0035	0.0032	0.0120	0.0039	0.0015	0.0009	0.0063	99.74	99.65	99.68	99.70
4	0	0	50	0.5083	0	0	0.5083	0.5080	0.0000	0	0.5080	87.29	0	0	87.29
0	4	0	50	0	0.2112	0	0.2112	0	0.2112	0	0.2112	0	94.72	0	94.72
0	0	4	50	0	0	0.2231	0.2231	0	0	0.2231	0.2231	0	0	94.42	94.42
1.33	1.33	1.33	50	0.1640	0.0730	0.0550	0.2920	0.1296	0.0984	0.0624	0.2904	87.67	94.51	95.86	92.70
2.66	2.66	2.66	50	0.4175	0.1826	0.1471	0.7472	0.3516	0.2670	0.1692	0.7878	84.30	93.14	94.47	90.66
1	1	2	50	0.1255	0.0514	0.0840	0.2609	0.1060	0.0531	0.1100	0.2691	87.45	94.86	95.80	93.48
1	2	1	50	0.1325	0.0965	0.0342	0.2632	0.1080	0.1080	0.0560	0.2720	86.75	95.18	96.58	93.42
2	1	1	50	0.2560	0.0539	0.0358	0.3457	0.2237	0.0560	0.0581	0.3378	87.20	94.61	96.42	91.36

[a] Retentate [SDS] = 100 mM.

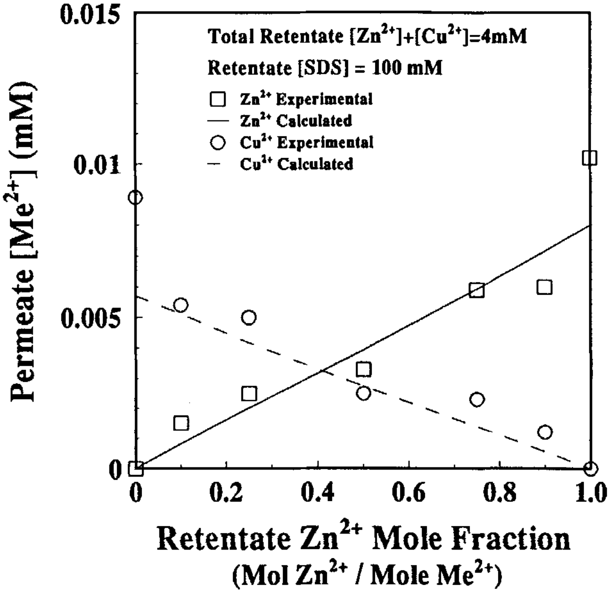

FIG. 8 Effect of retentate Zn^{2+} mole fraction on permeate $[Me^{2+}]$ for a Zn^{2+}/Cu^{2+} system.

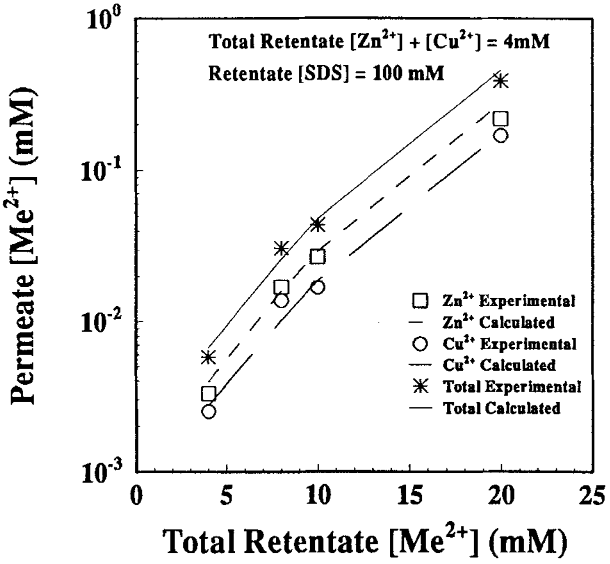

FIG. 9 Effect of total retentate $[Me^{2+}]$ on permeate $[Me^{2+}]$ for equimolar Zn^{2+}/Cu^{2+} system.

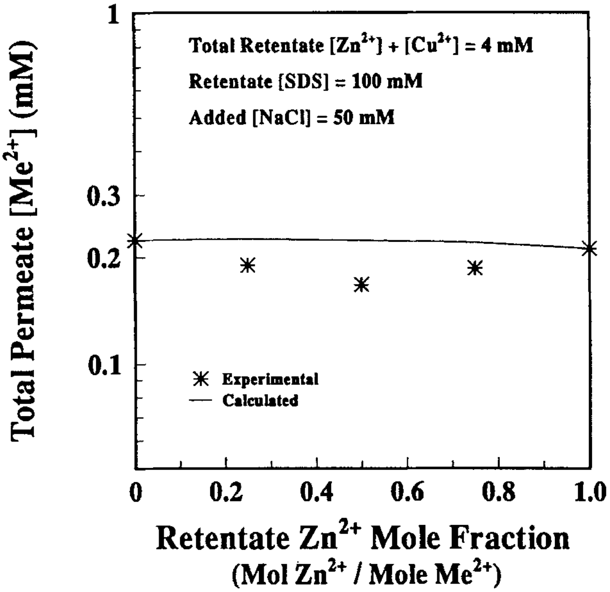

FIG. 10 Effect of retentate Zn^{2+} mole fraction on total permeate $[Me^{2+}]$ in the presence of added salt for a Zn^{2+}/Cu^{2+} system.

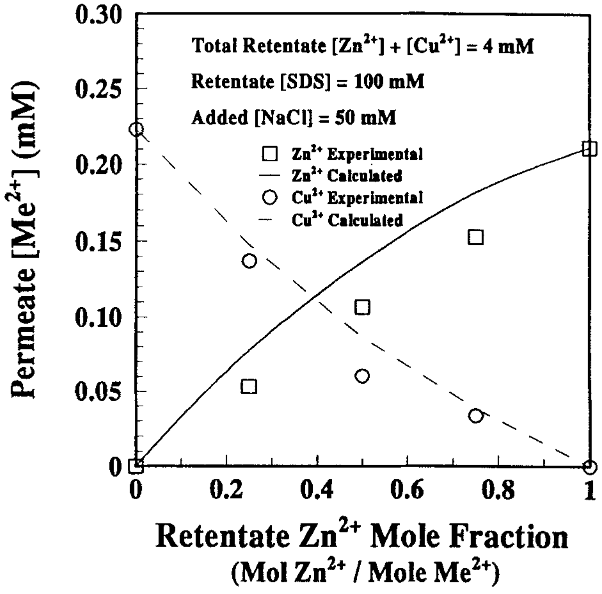

FIG. 11 Effect of retentate Zn^{2+} mole fraction on permeate $[Me^{2+}]$ in the presence of added salt for a Zn^{2+}/Cu^{2+} system.

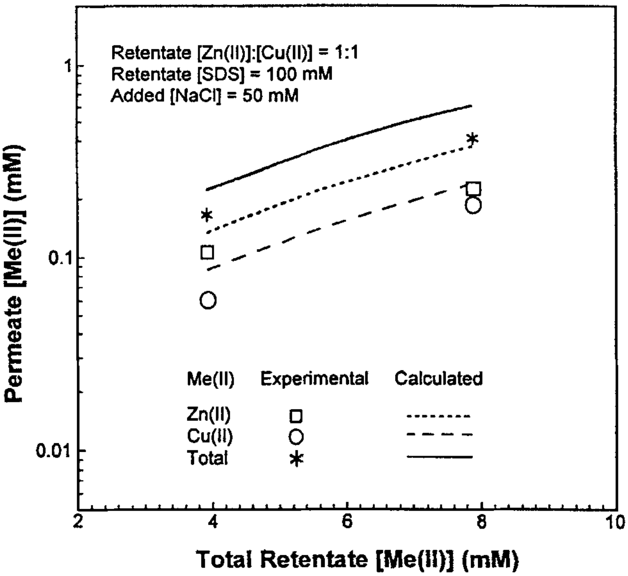

FIG. 12 Effect of total retentate [Me^{2+}] on permeate [Me^{2+}] in the presence of added salt for equimolar Zn^{2+}/Cu^{2+} systems.

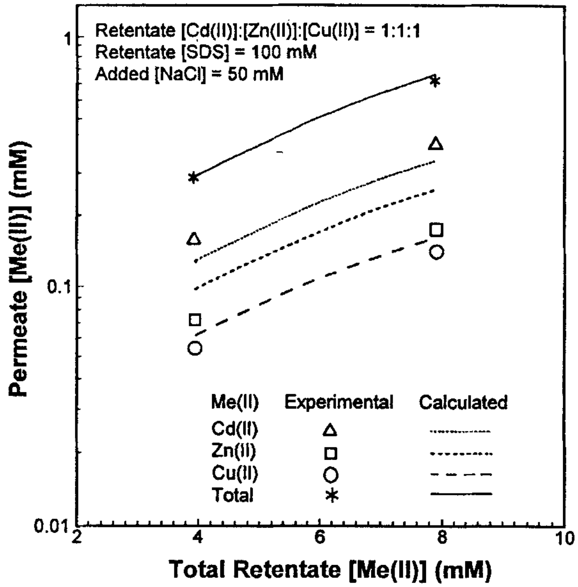

FIG. 13 Effect of total retentate [Me^{2+}] on permeate [Me^{2+}] for equimolar $Cd^{2+}/Zn^{2+}/Cu^{2+}$ systems.

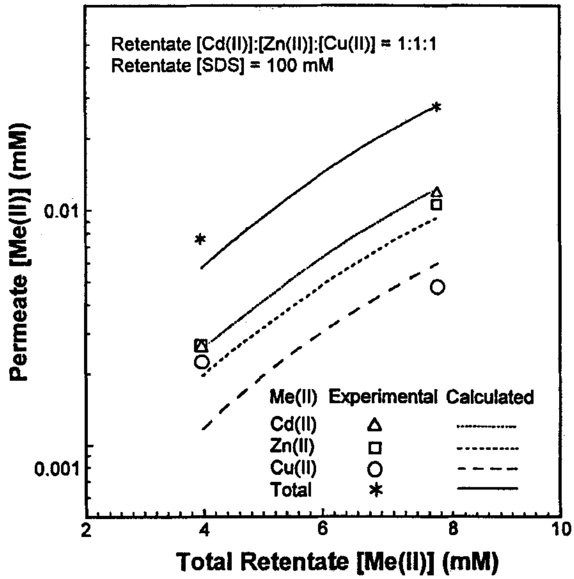

FIG. 14 Effect of total retentate [Me^{2+}] on permeate [Me^{2+}] in the presence of added salt for equimolar $Cd^{2+}/Zn^{2+}/Cu^{2+}$ systems.

tions as a function of total retentate concentration for the ternary $Cd^{2+}/Zn^{2+}/Cu^{2+}$ system.

DISCUSSION

Single Component Systems

The data presented in Table 1 for the studied metal ions in the absence of added salt show that rejections of 96.28 to 98.08% are obtained at 20 mM Me^{2+}, indicating the MEUF has the potential to greatly reduce the concentration of multivalent metal ions in one pass.

The experimental data shown in Fig. 2 indicate that the permeate Me^{2+} concentration increases with an increase in the retentate Me^{2+} concentration. Since the surfactant concentration is constant (100 mM) as the retentate Me^{2+} concentration is further increased, a point should be reached where almost all of the bound counterions are Me^{2+} instead of sodium and no incremental separation capacity will remain. However, even at concentrations of Me^{2+} that are relatively large compared to the SDS concentration (20 or 40 mM compared with 100 mM surfactant), the rejection is greater than 96% for all the examined metal ions. Precipitation occurs in the feed solution of the SDS/Ca^{2+} system at concentrations of 50 mM SDS and 10 mM Ca^{2+}; hence, there is no point at 20 mM retentate concentration of Ca^{2+} in Fig. 2.

The data presented in Fig. 2 and Table 1 indicate only small differences in the permeate Me^{2+} concentration obtained for the four metal ions under the same conditions in the retentate solution. Therefore, the valence (cation charge) is the dominant characteristic determining the separation efficiency of MEUF in removal of multivalent inorganic metal ions from water. From Fig. 2, as the retentate Me^{2+} concentration increases, the permeate Me^{2+} concentration decreases in the order $Cd^{2+} > Zn^{2+} > Cu^{2+} > Ca^{2+}$. This variation can be related to the relative tendency of the metal ions to form complexes with the chloride ion, Cl^-, which is present in solution from the dissociation of the added metal chloride salt. The higher the stability of the metal ion–chloride complexes, the lower the concentrations of the free divalent metal cation which binds most strongly to the micelles. Literature values of the critical stability constant, K, of the monovalent metal chloride complex, $MeCl^+$, vary for the metal ions studied in the order $Cd^{2+} > Zn^{2+} > Cu^{2+} > Ca^{2+}$ under the conditions examined in the retentate solution (18), consistent with this explanation. However, even at 20 mM retentate Me^{2+} concentration, the rejections of the metal ions vary only from 96.28 to 98.08%, reinforcing the conclusion that ion charge is the main factor in separation efficiency using MEUF, and that the metal species type and complexing characteristics are secondary effects.

From Table 1, at a constant retentate SDS concentration of 100 mM, the permeate SDS concentration shows a gradual decrease from 7.17 to 3.44 mM with an increase of the retentate Me^{2+} concentration from 4 to 20 mM. This reflects the increase in counterion concentration, which may be expected to increase the surfactant aggregation number and decrease the concentration of monomeric SDS in the retentate (7).

The experimental data presented in Table 1 and Fig. 3 show the effect of added NaCl. The addition of 0.05 M NaCl causes an increase in the permeate Me^{2+} concentration for the four metal ions. This effect may be attributed to the increase in ionic strength in solution, which may be expected to decrease the absolute magnitude of electrical potential at the micellar surface (6, 8). However, the rejections obtained vary from 85.87% for Cd^{2+} to 97.14% for Ca^{2+}, indicating that excellent separations can still be attained by MEUF at 0.05 M NaCl. The permeate concentrations decrease in the order $Cd^{2+} > Cu^{2+} > Zn^{2+} > Ca^{2+}$, although approximately the same concentrations are obtained for both Zn^{2+} and Cu^{2+}. With added salt, the variation in rejection becomes more pronounced

(85.87 to 97.14%). This may be attributed to the formation of higher concentrations of chlorine-complexed metal ions at the larger NaCl concentrations. The data presented in Table 1 indicate that the addition of 0.05 M NaCl results in a decrease in the permeate SDS concentration, from 7.17 to 3.35 mM, under the same conditions in the retentate solution.

Figure 4 shows the effect of increasing the retentate surfactant concentration at constant Me^{2+} concentration. As the retentate SDS concentration increases from 100 to 200 mM, the permeate Me^{2+} concentration remains approximately the same for the four metal ions. The further increase in the retentate SDS concentration to 400 mM results in an increase in the permeate Me^{2+} concentration. On the other hand, the permeate SDS concentration data presented in Table 1 indicate a slight decrease from 7.17 to 6.85 mM with increasing retentate SDS concentration from 100 to 200 mM, followed by an increase to 14.12 mM at 400 mM retentate SDS concentration. This has been attributed to the formation of smaller surfactant aggregates (dimers, trimers, *n*-mers, etc.) at high surfactant concentrations (19). These smaller aggregates may bind metal cations and transport them through the membrane into the permeate stream. The increase in the permeate SDS concentration beyond its critical micellar concentration (8.2 mM) also supports the previous explanation of the formation of smaller *n*-mers. However, even at 400 mM SDS in the retentate solution, the rejections are still excellent (98.17 to 99.19%), which is in marked contrast to many conventional applications of ultrafiltration.

The same effect was observed when using the 1000 MWCO membrane, as is indicated in Table 1. As the retentate SDS concentration is increased from 200 to 400 mM, the permeate Me^{2+} concentration increases slightly for the four metals studied. However, the rejections obtained at 200 and 400 mM SDS are slightly greater than those obtained using 5000 MWCO membranes under identical conditions.

Equation (1) predicts that the flux will vary linearly with the logarithm of the retentate concentration as the gel concentration is approached. Figure 5 shows that this relationship is valid at high retentate surfactant concentrations for both the 1000 and the 5000 MWCO membranes. The gel concentration (C_g) was found to be 737 and 708 mM for the 1000 and 5000 MWCO membranes, respectively. In a previous study of MEUF (15) with a cationic surfactant (hexadecylpyridinium chloride), C_g was found to be independent of membrane pore size, consistent with the results observed here. The value of C_g for the cationic surfactant was found to be 530 mM, which is somewhat lower than that found for the anionic surfactant in this work.

The results shown in Figs. 5 and 6 indicate that the flux is independent of the metal species type. The decrease in flux with increasing retentate SDS concentration indicates that concentration polarization is present under the conditions studied. However, the relative fluxes plotted in Fig. 6 indicate that as long as the retentate SDS concentration does not exceed 200 to 300 mM, the flux through the two membranes is not substantially below that of water (particularly considering that the overall flux is calculated as the integrated average between the initial and final surfactant concentrations). Therefore, concentration polarization should not greatly decrease MEUF performance under normal operating conditions.

The data presented in Fig. 5 indicate that the absolute flux increases with an increase in membrane pore size from 1000 to 5000 MWCO. From Fig. 6 it can be seen that the 5000 MWCO membrane exhibits a lower relative flux than the 1000 MWCO membrane. This is because the increased absolute flux through the 5000 MWCO membrane increases the amount of surfactant rejected at the membrane surface per unit time per unit area. Consequently, there is a higher concentration of surfactant in the gel layer and the effect of concentration polarization is more severe, as has been observed for a cationic surfactant (15). In other words, the gel layer contributes a higher fraction of the total resistance to flux (compared to the resistance contributed from the membrane itself) for the 5000 MWCO membrane than for the 1000 MWCO membrane.

Values of the parameters α and P^0 [derived by fitting Eqs. (2), (3), and (7)–(13) to the MEUF data] are listed in Table 2, and the resultant predicted permeate concentrations are plotted in Figs. 2–4. The data at 4, 10, and 20 mM metal ion and 100 mM SDS retentate concentrations were used to obtain the parameters P^0 and α used for each component. The experimental results at 4 mM are somewhat poorer than expected (i.e., somewhat more metal escapes into the permeate than the model predicts). By inclusion of the parameter α, the model can predict the dependence of the permeate metal concentration on the NaCl concentration, as is shown in Fig. 3. Although the model implies that an increase in the surfactant concentration in the retentate should cause a decrease in the permeate metal concentration, the experimental results show the opposite effect. This same trend has been observed in removing organics using MEUF at high retentate surfactant concentration—both the organic solute and the surfactant escape into the permeate at higher concentrations when the surfactant concentration in the retentate is increased (19). To explain this effect, it has been proposed that there is some leakage through the membrane of dimers, trimers, and other small surfactant aggregates at the higher surfactant concentrations, and that these aggregates transport small concentrations of solubilized organics and bound counterions. Thus, from a practical point of view, there is an optimum surfactant concentration for minimizing permeate metal concentration.

Mixtures of Metals

For the binary Zn^{2+}/Cu^{2+} mixture, the results in Figs. 7 and 10 show that varying the Zn^{2+} mole fraction, at a total retentate Me^{2+} concentration of 4 mM, causes almost no change in the permeate Me^{2+} concentration. This indicates that at relatively low total retentate metal concentrations, metal ions of the same charge are removed with quite similar efficiencies. An analogous effect is also observed in Figs. 8 and 11; the permeate concentration of Zn^{2+} at a given mole fraction in the retentate is nearly the same as that of Cu^{2+} at that same mole fraction. For equimolar Zn^{2+}/Cu^{2+} mixtures, Figs. 9 and 12 show that as the total retentate metal concentration increases from 4 to 20 mM, the permeate concentration of both the Zn^{2+} and Cu^{2+} increases, although the permeate Zn^{2+} concentration is slightly greater than that of Cu^{2+}, consistent with the behavior of the two species when removed as single components (see Fig. 2). These comparisons for the binary systems hold both in the presence and in the absence of added NaCl.

It may be noted that the calculated permeate metal ion concentrations for the binary mixtures of Cu^{2+} and Zn^{2+}, based on Eqs. (14)–(16) and indicated by the curves in Figs. 7 and 8, are in reasonable agreement with observed concentrations. However, the concentrations predicted for pure Cu^{2+} and pure Zn^{2+} are significantly smaller than the experimental values. [Recall that the experimental values of permeate metal ion concentrations, for the systems containing 4 mM of the individual metal ions and 100 mM SDS, were somewhat larger than predicted from a global fit of results at 4, 10, and 20 mM (see Fig. 2).] But the MEUF separation results for mixtures—specifically, the permeate concentrations of the individual cations and the total metal ion concentrations in mixtures—are well represented by the model.

For the equimolar ternary $Cd^{2+}/Zn^{2+}/Cu^{2+}$ mixture, Figs. 13 and 14 show that the metal component permeate concentrations vary in the order $Cd^{2+} > Zn^{2+} > Cu^{2+}$, an order anticipated qualitatively from single component metal results. As seen in Figs. 7–14, the predictions of the model fit the data quite well over a wide composition range in the presence and absence of added salt. It is encouraging that the simple mixing rules employed in fitting the data for multiple-metal systems [Eqs. (13)–(16)] can be used to predict the results for several +2 metal ions, without requiring the introduction of additional parameters.

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