Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Modeling and Performance Study of MEUF of Divalent Metal Ions in Aqueous Streams

A. J. Chhatre[a]; K. V. Marathe[a]
[a] Department of Chemical Engineering, Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai, India

To cite this Article Chhatre, A. J. and Marathe, K. V.(2008) 'Modeling and Performance Study of MEUF of Divalent Metal Ions in Aqueous Streams', Separation Science and Technology, 43: 11, 3286 — 3304
To link to this Article: DOI: 10.1080/01496390802212641
URL: http://dx.doi.org/10.1080/01496390802212641

Separation Science and Technology, 43: 3286–3304, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802212641

Taylor & Francis
Taylor & Francis Group

Modeling and Performance Study of MEUF of Divalent Metal Ions in Aqueous Streams

A. J. Chhatre and K. V. Marathe
Department of Chemical Engineering, Institute of Chemical Technology,
University of Mumbai, Matunga, Mumbai, India

Abstract: Modeling of micellar enhanced ultrafiltration (MEUF) was studied for the removal of Ni from aqueous phase by using sodium dodecyl sulphate for micellisation. Localized adsorption equilibrium model was used to predict the bound and unbound counter ions. The retentate concentration was predicted using localized adsorption equilibrium and a material balance model, and the experimental values are in close agreement with less than 1% deviations. Experimental values of the permeate flux were in close agreement with the predicted values obtained by resistances in the series model. An algorithm was developed for the prediction of the retentate concentration.

Keywords: Heavy metals, localized adsorption model, micellar-enhanced ultrafiltration, modeling of MEUF, nickel ion removal, sodium dodecyl sulfate, wastewater treatment

INTRODUCTION

Micellar enhanced ultrafiltration (MEUF) is a recent technique being studied for removal of metal ions (1–8) from dilute aqueous streams; originally suggested by Scamehorn et al. (9). This article makes an attempt to model MEUF from process engineering point of view. Phenomena that are modeled in order to predict the performance of MEUF in a dead end ultrafiltration system are:

1. Equilibrium between bound and unbound counterions: In MEUF tendency of ionic surfactant to alter its ionic environment is primarily

Received 12 September 2007; accepted 10 March 2008.

Address correspondence to K. V. Marathe, Department of Chemical Engineering, Institute of Technolocgy, University of Mumbai, Matunga, Mumbai, 400019, India. Email: kvm@udct.org

responsible to induce enhancement in the rejection coefficient of metal ions. Definition of the equilibrium between bound and unbound counterions thus forms a basis in the modeling of MEUF. There have been several attempts for the modeling of counterion binding to the surfactant micelles (12–15); most of which have aimed at solving the Poison- Boltzmann equation for charged micelle and attempted deriving the distribution functions from the first principles. Rathman and Scamehorn (13) have suggested the use of a Langmuir kind of equilibrium relation to define the equilibrium between the bound and the unbound counterions. This article attempts to extend this model to be applicable to the divalent metal ion removal by MEUF.

2. Dynamic material balance for UF: If the concentration of bound counterions in the feed solution is known, dynamic material balance would be able to predict the concentration of Ni(II) in retentate at any given value of V_P/V_F. To achieve this, the model described by Tsapiuk (16) has been used.
3. Permeation rate: Permeate flux is a performance parameter that primarily determines sizing, the initial investment, and the recurring cost of the membrane based separation unit. An attempt is made here to develop resistances in the series model for the prediction of permeate flux in terms of process variables in MEUF.

EXPERIMENTAL WORK

Materials

Sodium dodecyl sulfate (SDS), nickel sulfate ($NiSO_47H_2O$), cetyltrimethylammonium bromide (CTAB), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), carbon tetrachloride (CCl_4) for SDS analysis by two phase titration method, were obtained from Merck and were used as received. Conductivity measurements revealed that the CMC of the obtained SDS was 4.523 mM. Analysis reagent 2-mercapto propionic acid was obtained from Himedia and was used as received. All chemicals were of analytical grade. Stock solutions of $NiSO_4$ and SDS were prepared and were used by diluting appropriately for the MEUF experiments. Distilled water was used throughout for making the solutions.

Ultrafiltration Setup

Ultrafiltration experiments were carried out in a dead end batch filtration cell; 120 cm^3 in capacity; with active membrane area of 15.91 cm^2. The cell was fabricated in-house from stainless steel. Membrane for ultrafiltration was obtained from Permionics and was a flat sheet polysulfone membrane with MWCO of 20 kD. The transmembrane pressure gradient (TMP) was maintained by use of N_2 gas. All experiments were carried out at the temperature of $303 \pm 2\,K$; the agitation speed was held constant in all experiments by use of a magnetic stirrer and was maintained at 350 ± 10 rpm throughout.

Analysis

SDS as single component was analyzed by conductivity measurements with a conductimeter from EQUIPTRONIX EQ 660. In presence of Ni(II) ions SDS was analyzed by 2 phase titration method. Ni(II) ions were analyzed on FP-6200 model of spectroflurometer supplied by JASKO using UV-VIS spectrophotometry at $\lambda_{max} = 408\,nm$ (17).

Experimental Procedure

In each experimental run $100\,cm^3$ of distilled water was charged in UF cell to measure pure water flux. The membrane was then equilibrated with a very dilute solution of SDS ($\sim 1\,mM$) for half an hour and fitted in the UF cell. The cell was then charged with $50\,cm^3$ of feed solution. p^H of feed solution was adjusted (if required) between 7 and 7.5 by adding small quantities of 0.01 N NaOH or 0.01 N H_2SO_4. The cell was then pressurized to 4×10^5 Pag. The samples collected were analyzed for Ni(II) content. After completion of each run the membranes were rinsed thoroughly with distilled water and flux of distilled water was measured. If this flux was found $<95\%$ of the distilled water flux measured before run the membrane was replaced by new piece. Rejection of Ni(II) was calculated as per following formula (18).

$$R = 1 - ([Ni(II)]_P/[Ni(II)]_R) \tag{1}$$

The membrane being non uniform in its pore distribution, the flux data obtained from a single piece of membrane was utilized for parameter estimation in the resistances in series model for flux; determined as:

$$\text{Flux } J_p = \left(\frac{V_p}{A \times t}\right) = \left(\frac{\text{Permeate volume (Mass/density)}}{\text{Time} \times \text{Active membrane area}}\right) \tag{2}$$

MODEL DEVELOPMENT AND RESULTS

Localized Adsorption Equilibrium Model for Counterion Binding

The most commonly accepted model of a micelle is a sphere with a uniform surface charge surrounded by electric double layer divided into diffuse layer outside and stern layer inside the shear surface (19). The dimensions of counterions may or may not be taken into account. On the basis of the above idea it has been proposed to consider the counterions in a stern layer as counterions adsorbed over the micelle and localized in the stern layer while the ions in the diffuse double layer to be free counterions (20). The key assumptions in this treatment could be stated as:

- Counterions around the charged micelle are considered to be distributed in two regions: the stern layer and the diffuse double layer.
- Counterions in the stern layer are considered as adsorbed on the micelle surface and will be referred to as bound counterions.
- The adsorbed counterions are assumed to be localized to a specific surfactant head group which hereafter will be referred to as the binding site and is represented schematically in Fig. 1.
- The distribution of counterions in the diffuse double layer can be described by the Poisson Boltzmann equation.
- The net charge in the diffuse double layer is equal and opposite to the net charge on the micelle (including the stern layer) for the electroneutrality of the solution (10,14).
- The surface curvature of the micelles is assumed to be negligibly small.
- Intermicellar interactions are assumed to be insignificant.
- Micelles are considered as separate phase (called as pseudo phase) but considered to have point masses i.e. they are assumed to occupy an insignificant fraction of the solution volume.

Rathman and Scamehorn, (1984) have presented the solution of the Poisson-Boltzmann equation (under above stated assumptions), and arrived at the localized adsorption model, which takes the final form as

$$\beta = \text{degree of counterion binding} = \frac{K_B C_C \exp\left(\frac{-Z_C e\psi_0}{kT}\right)}{\left[1 + K_B C_C \exp\left(\frac{-Z_C e\psi_0}{kT}\right)\right]} \tag{3}$$

Where β is the degree of counterion binding, K_B is the binding constant and C_C is average unbound counterion concentration, and the term ψ_0 represents the stern layer potential of surfactant micelle-metal ion system.

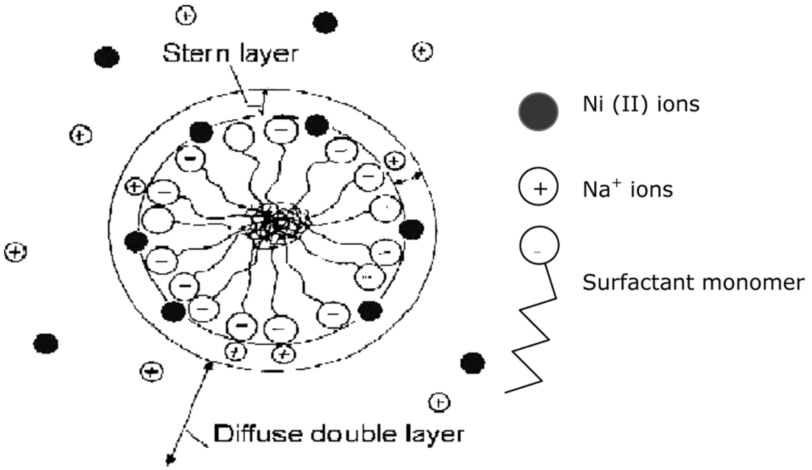

Figure 1. Counterion binding on SDS micelle.

Equation 3 defines the equilibrium between the bound and unbound counterions. The term beta, the degree of counter ion binding could be defined in terms of process variables as

$$\beta = \frac{Z_C \times C_B}{S_T - CMC} \tag{4}$$

i.e. the fraction of micellized surfactant that is neutralized because of adsorption of counterion on micelle.

Where C_B is the concentration of the bound counterions and S_T is the total concentration of the surfactant in the system. From eq. 4 and eq. 3 it can be easily observed that the Langmuir adsorption isotherm explains the adsorption of counterions on micelle.

However, this equilibrium relation cannot be directly applied to the MEUF of the divalent metal ions because in the system, for which the equilibrium relation was developed, only pure SDS micelles were present and the counterion was the Na^+ ion dissociated from SDS. In the present system Ni^{2+} is the main counter ion that is of concern rather than the Na^+ ion. The Ni^{2+} ion binds with two DS^- ions as against a single DS^- ion in case of the Na^+ ion. So the Langmuir equation for adsorption over a single site needs to be modified. The Ni^{2+} ion need two DS^- ions to be in the vicinity of each other to be able to bind or unbind from the micelle; and hence the equation needs to be modified to the Langmuir equation for the duel site adsorption. The equation therefore takes the form

$$\beta = \frac{2 \times [Ni(II)]_B}{([SDS]_R - CMC)} = \frac{\sqrt{K_B[Ni(II)]_{UB} \times \exp\left(\frac{-2e\psi_0}{kT}\right)}}{1 + \sqrt{K_B[Ni(II)]_{UB} \times \exp\left(\frac{-2e\psi_0}{kT}\right)}} \tag{5}$$

This equation can be used to define the equilibrium relation between the bound and unbound Ni(II) ions.

In order to find the parameters in equation (5) MEUF experiments were carried out at 3 different temperatures i.e. at 303 K, 313 K, and at 323 K. The following simplifying assumptions were made to render the system solvable with gathered experimental data

- Only bound counterions get rejected while the unbound ions can easily cross the membrane and are not rejected at all. This assumption states that $[Ni(II)]_{UB} = [Ni(II)]_P$ and facilitates calculation of bound counterion concentration as $[Ni(II)]_B = [Ni(II)]_R - [Ni(II)]_p$.
- The concentration of SDS in the permeate will be considered as the CMC of the SDS under the respective experimental conditions. This assumption was found to be valid under the considered experimental conditions; as the surfactant concentration in the permeate rarely exceeded CMC; unless at very high concentrations or at very high ratios of V_P/V_F.
- The co-ions SO_4^{2-} coming from dissociation of $NiSO_4$ do not get rejected and hence the concentration of SO_4^{2-} in the retentate and the permeate remains the same as the feed concentration.
- Conditions of electroneutrality are strictly satisfied which take the form as:

$$2[Ni(II)]_R + [Na^+]_R = 2[SO_4^{2-}]_R + [DS^-]_R \tag{6}$$

$$2[Ni(II)]_P + [Na^+]_P = 2[SO_4^{2-}]_P + [DS^-]_P \tag{7}$$

- Experimental studies show that Ni(II) ions bind to micelles selectively and hence the binding of Na^+ ions will be neglected in this attempt (19).

The binding constant (product of K_B and temperature dependant term) was found at each temperature by using least square regression methods and the values of ψ_0 and K_B (Table 1) were determined by plotting ln(K) vs. 1/T (Fig. 2). The slope corresponds to the value of $(-2e\psi_0/k)$ while the intercept corresponds to the value of $\ln(K_B)$.

The value of ψ_0 obtained in these experiments is 38.06 mV; whereas the value of the stern layer potential reported by Hafiane et. al. (1991) is 45 mV for the MEUF of Cu^{2+}. This indicates that the values obtained

Table 1. Values of K at different temperatures

Temperature (K)	K ($dm^3 \cdot mol^{-1}$)	1/T (K^{-1})	Ln (K)	Average error in fitting (%)
303	7.32×10^4	3.30×10^{-3}	11.20	9.18
313	6.67×10^4	3.19×10^{-3}	11.11	10.59
323	6.11×10^4	3.10×10^{-3}	11.02	5.41

are well in the range of the reported values. The model fitting in this work has an absolute relative error of 9.8% between the regressed and experimental values. Table 2 enlists values of K_B and ψ_0; while Table 3 provides experimental as well as predicted values of the counterion binding at various temperatures.

Material Balance Model for Predicting Retentate Concentration

$$C_R = C_F\left[(1-\phi)^{\frac{C_F - C_R}{\phi \times C_R}}\right] \tag{8}$$

Equation 8 facilitates the calculation of retentate concentration at any given volume reduction ϕ. If the C_F is known the equation can be solved

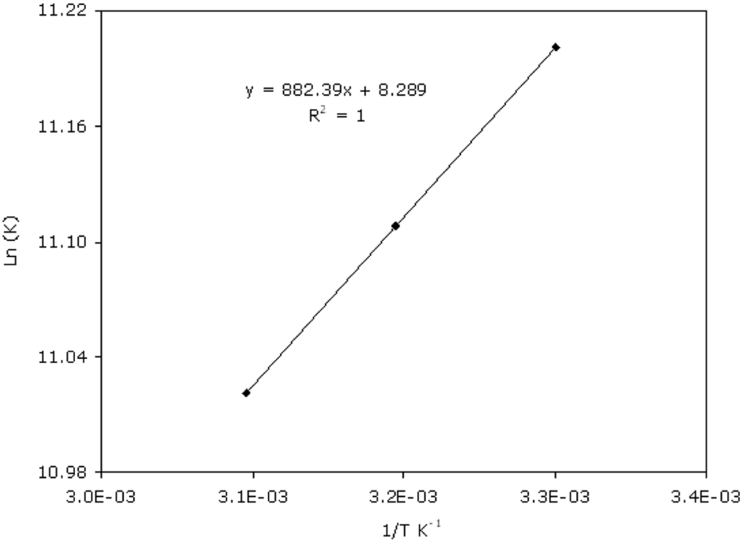

Figure 2. Determination of K_B and ψ_0.

Table 2. Model parameters for localized adsorption equilibrium model

K_{B0}	3.98×10^3 ($dm^3 \cdot mol^{-1}$)
Ψ_0	38.06 (mV)

by any root finding method like the Newton Raphson method. This material balance model can be used to predict the concentration of retentate in MEUF along with the equilibrium relation between bound and unbound Ni(II) ions. The algorithm is shown schematically in Fig. 3. Table 4 gives the experimental and the predicted values of $Ni(II)_R$ (predicted values are calculated by using the algorithm illustrated in Fig. 3). Figure 4 shows the parity plot for this model. The experimental and predicted values fit very well with less than 1% deviations.

Resistance in Series Model for Flux in MEUF

UF flux shows distinct regimes namely pressure controlled at low pressures and the pressure independent at high pressures. Flux in the pressure controlled regime is usually modeled by using the Hagen-Poiseuille equation while in the pressure independent regime it is modeled by applying the film theory approach. However, neither of the two models describes the entire pressure flux behavior observed during typical UF so the resistances in the series model is used as a better approach (21). The concept is similar to the heat transfer. It is developed as follows:

$$J = \frac{\Delta P_T - \Delta\pi}{R_M + R_F + R_G} \tag{9}$$

Where R_M is the intrinsic membrane resistance calculated from the pressure flux behavior of pure water. This term includes the viscosity of water and thus is dependent on the temperature only. This term can be used as an indicator of the cleanness of the membrane obtained after the cleaning process. The term $\Delta\pi$ signifies the osmotic pressure gradient across the membrane which is usually neglected in the ultrafiltration of macromolecules.

Under the actual operating conditions the resistance of membrane changes because of specific membrane solute interaction. This is accounted for by adding a new resistance in the denominator as R_F and is called fouling resistance. The major phenomena that is responsible for the decline in the flux during MEUF is the pore blocking by micelles and hence we assume this resistance to vary linearly with respect to the fraction the of surfactant present in the micellar form; thus this resistance

Table 3. Experimental Data for beta prediction

T (K)	$[Ni]_F$ (mM)	$[Ni]_R$ (mM)	$[Ni]_P$ (mM)	$[Ni]_B$ (mM)	$[Ni]_{UB}$ (mM)	$[SDS]_F$ (mM)	$[SDS]_R$ (mM)	[SDS] misR (mM)	β Exp.	β Pred.	% abs. error
303	1	1.974	0.026	1.949	0.026	8	11.47	6.954	0.5605	0.6596	17.69
303	1.5	2.977	0.023	2.954	0.023	10	15.45	10.9	0.5421	0.6462	19.2
303	1.75	3.474	0.026	3.447	0.026	10	15.46	10.918	0.6314	0.6633	5.04
303	2	3.969	0.031	3.938	0.031	10	15.46	10.92	0.7213	0.6799	5.73
303	2.25	4.464	0.036	4.428	0.036	10	16.36	12.72	0.6963	0.6962	0.02
303	2.5	4.958	0.042	4.917	0.042	10	16.6	13.2	0.7449	0.7119	4.43
303	3	5.948	0.052	5.897	0.052	10	17.06	14.12	0.8352	0.7335	12.17
313	1.5	2.977	0.023	2.955	0.023	10	15.45	10.9	0.5422	0.6344	17.01
313	2	3.97	0.03	3.94	0.03	10	15.46	10.92	0.7216	0.6667	7.6
313	2.5	4.962	0.038	4.924	0.038	10	16.6	13.2	0.7461	0.6925	7.6
323	1.5	2.983	0.017	2.967	0.017	10	15.47	10.954	0.5443	0.5875	7.93
323	2	3.965	0.035	3.93	0.035	10	15.46	10.92	0.7199	0.6735	6.44
323	2.5	4.927	0.073	4.854	0.073	10	16.6	13.2	0.7355	0.7492	1.86

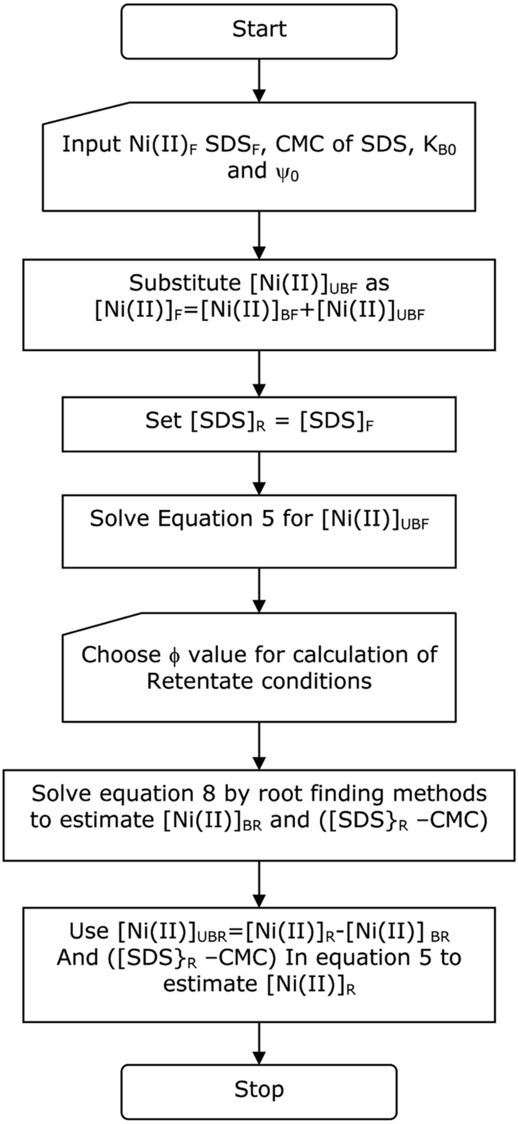

Figure 3. Algorithm to predict $NI(II)_R$ from $Ni(II)_F$.

can be defined as:

$$R_F = \alpha \times \left(\frac{C_R - CMC}{C_R} \right) \tag{10}$$

Table 4. Experimental and predicted values of $[Ni]_R$

$[Ni]_F$ (mM)	$[Ni]_P$ (mM)	$[Ni]_R$ Experimental (mM)	$[SDS]_F$ (mM)	$[SDS]_R$ (mM)	$[SDS]_{misR}$ (mM)	$[Ni]_R$ predicted. (mM)	% abs. error
1.0	0.0172	1.9828	10	15.477	10.955	1.990	0.26
1.25	0.0196	2.4808	10	15.468	10.936	2.4881	0.19
1.5	0.0228	2.9772	10	15.45	10.900	2.9786	0.10
1.75	0.0265	23.4735	10	15.459	10.918	3.4707	0.26
2	0.0308	3.9692	10	15.46	10.920	3.9579	0.52
2.25	0.0358	4.4642	10	16.36	12.720	4.4605	0.27
2.5	0.0417	4.9583	10	16.60	13.200	4.9520	0.34
3.0	0.0517	5.9483	10	17.06	14.120	5.9179	0.80
3.5	0.0763	6.9237	10	17.25	14.500	6.8151	2.17
1.0	0.0258	1.9744	8	11.477	6.954	1.9750	0.2

Where C_R is the retentate concentration of SDS at the volume fraction at which we want to calculate the flux value.

The gel layer resistance R_G is the function of permeability of gel and its thickness which are related to the pressure drop by eq. 9 (18).

$$R_G = \phi \times P_T \tag{11}$$

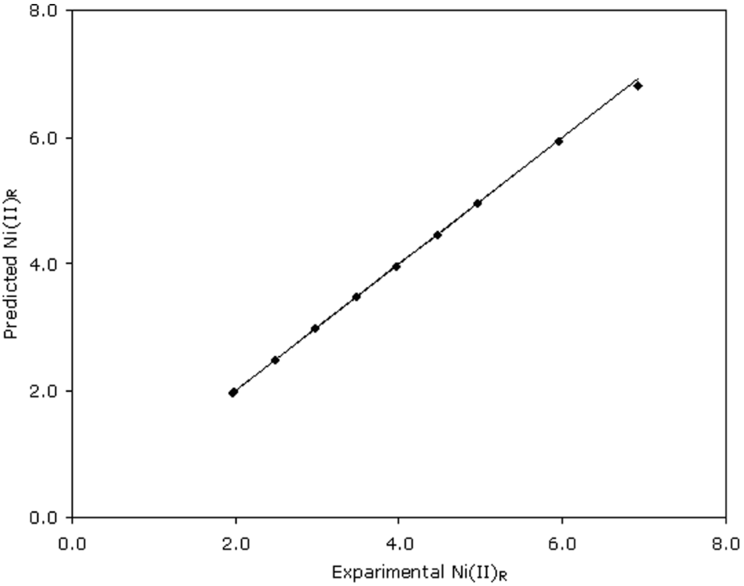

Figure 4. Parity plot for material balance model.

Where ϕ is the gel coefficient which is assumed to vary in the exponential manner w.r.t retentate concentration of SDS as shown in the following eq.

$$R_G = a \times e^{(b \times C_R)} \times P_T \tag{12}$$

Combining all the above discussed points we get the final form of the equation as:

$$J = \frac{P_T}{R_M + \alpha \times \left(\frac{C_R - CMC}{C_R}\right) + \left(a \times e^{b \times C_R}\right) \times P_T} \tag{13}$$

For determining the parameters of the above equations experiments were carried out in $[\mathrm{SDS}]_F$ range of 5 mM to 20 mM at S/M ratio of 5 and TMP range of 2×10^5 to 6×10^5 Pa. Maximum pressure was limited by the membrane's operating pressure limit of 7×10^5 Pa.

The term "α" is an expression of interaction between surfactant micelles and membrane. The term "b" represents gelling tendency of surfactant and accounts for the increase in the resistance to flow because of increase in micellar concentration in the region near membrane. This term is expected to be a characteristic for a given surfactant. While the term "a" is an expression of all turbulence related terms, which is the

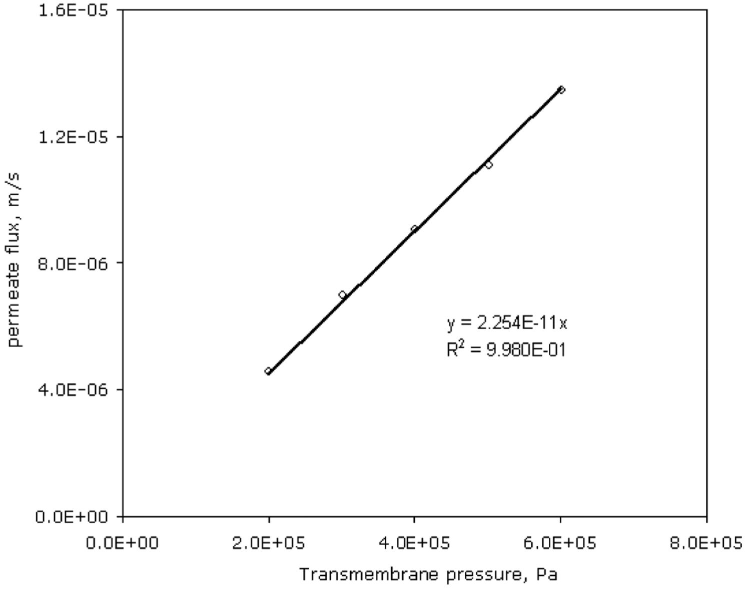

Figure 5. Calculation of intrinsic membrane resistance.

function of the geometry and operational parameters like rpm, back current velocity etc.

In order to determine the value of R_M distilled water fluxes were measured at different pressures and were plotted against the corresponding TMP. The slope of the line that was obtained gives the value of $1/R_M$ as shown in Fig. 5. The remaining parameters were found by the least square method of nonlinear regression. Optimization was done by utilizing Newton's algorithm. Table 5 gives the experimental as well as the predicted values of flux while Fig. 6 shows the plot of the predicted permeate flux versus the experimentally measured values of the permeate flux. Experimental data used in the model fitting are presented in the Table 5, and the model parameters obtained are enlisted in Table 6.

While defining the above discussed model it was assumed that the total resistance to the permeation was only because of the presence of the SDS micelles in the system and it was considered that the resistance offered by Ni(II) ions as well as the surfactant monomer was negligible. Also, no attempt was made to separate the viscosity terms from the individual resistances.

SUMMARY OF MODEL EQUATIONS AND DISCUSSION

The overall model equations for MEUF of Nickel ions in the dead end ultrafiltration system could be summarized as:

The localized adsorption equilibrium model

$$\beta = \frac{2 \times [Ni(II)]_B}{([SDS]_R - CMC)} = \frac{\sqrt{K_B[Ni(II)]_{UB} \times \exp\left(\frac{-2e\psi_0}{kT}\right)}}{1 + \sqrt{K_B[Ni(II)]_{UB} \times \exp\left(\frac{-2e\psi_0}{kT}\right)}} \tag{5}$$

Material balance model

$$C_R = C_F\left[(1-\phi)^{\frac{C_F - C_R}{\phi \times C_R}}\right] \tag{8}$$

Resistances in series model for permeate flux prediction

$$J = \frac{P_T}{R_M + \alpha \times \left(\frac{C_R - CMC}{C_R}\right) + (a \times e^{b \times C_R}) \times P_T} \tag{13}$$

These equations when solved by using the algorithm presented in Fig. 3 can predict the performance of MEUF of the divalent metal ion removal system in the dead end mode i.e. the prediction of flux and rejection ratio as a function of V_P/V_F. The same equations could be extended to

Table 5. Experimental and predicted values of flux

$[SDS]_F$ (mM)	P_T (Kpa)	Volume collected (ml)	Time (hr)	$[SDS]_R$ (mM)	Micellized fraction in Retentate	Experimental flux (Lit/hr·m^2)	flux predicted (Lit/hr·m^2)	Relative error in fitting (%)
5	400	45	1.2992	44.3112	0.8979	21.7710	22.0436	1.24
	500	45	0.9439	44.2287	0.8977	29.9655	27.5559	8.74
	600	45	0.8453	44.2954	0.8979	33.4613	33.0647	1.20
10	200	45	2.3681	90.4643	0.9500	11.9440	10.8117	10.47
	300	45	1.6356	89.2571	0.9493	17.2933	16.2198	6.62
	400	45	1.3397	89.7172	0.9496	21.1119	21.6216	2.36
15	200	45	2.4650	133.8848	0.9662	11.4743	10.7330	6.91
	300	10	0.3707	134.8674	0.9665	16.9569	16.0827	5.44
	400	45	1.3425	134.8030	0.9664	21.0682	21.4251	1.67
	500	45	0.9778	134.4504	0.9664	28.9269	26.7605	8.10
	600	45	0.8544	134.7467	0.9664	33.1023	32.0819	3.18
20	400	45	1.3436	181.8902	0.9751	21.0508	20.8494	0.97
	500	45	1.0533	181.9320	0.9751	26.8520	25.8837	3.74
	600	45	0.8917	182.0163	0.9752	31.7205	30.8465	2.83

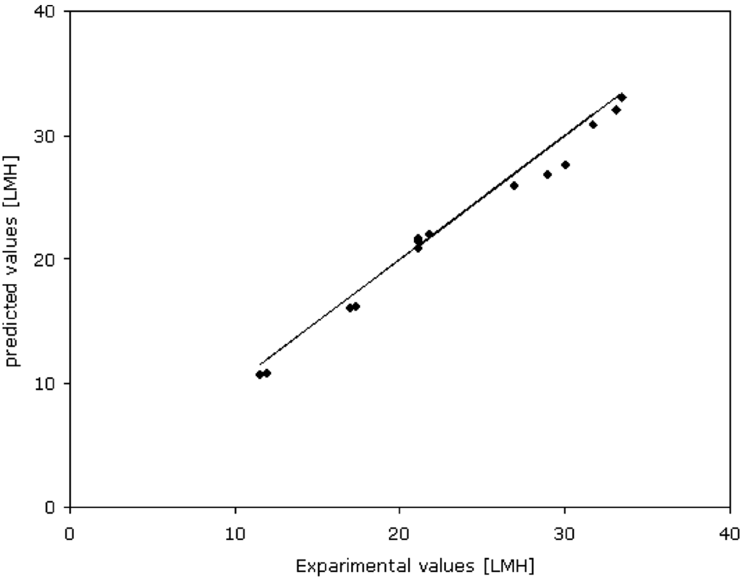

Figure 6. Parity plot for permeate flux at $[SDS]_F = 15\,(mM)$.

continuous MEUF by changing the ratio of V_P/V_F, ratio of the permeate volume collected to the volume of feed, to the ratio of the permeate flow to the feed flow.

The error in fitting may be attributed to a large number of assumptions made in developing and solving the model; and may be stated as

- The variations in the CMC and the monomer micelle equilibrium of the surfactant are not accounted for,
- The effect of the ionic strength of the solution on the CMC of the surfactant is not accounted for,
- The presence of the Na^+ ions is neglected.

Table 6. Parameters of resistances in series model for predicting flux in MEUF

No.	Parameter	Value	Unit	Average relative error in fitting
1	R_M	4.37×10^{10}	$Pa \cdot s \cdot m^{-1}$	4.67%
2	α	2.41×10^{10}	$Pa \cdot s \cdot m^{-1}$	
3	a	1.55	$s \cdot m^{-1}$	
4	b	44.10	$dm^3 \cdot mol^{-1}$	

The model also has a major shortcoming that is only capable of handling +2 oxidation state of metal ions and is expected to fail to predict the behavior of other oxidation states like +3 or +6 as in the case with Cr; and thus also is unable to predict the ionic selectivity of MEUF in solution containing a mixture of ions with different charges. Even the parameters in equation 13 for predicting fluxes are of a semi-empirical nature and their exact dependencies are yet undetermined.

CONCLUSION

Model equations presented in this article are focused at quantifying the three major phenomena, namely the equilibrium relation between bound and unbound counterions, the material balance of the bound metal ions, and the permeate flux in the MEUF. The localized adsorption equilibrium model was fitted to the experimental data with an average relative deviation of 8.23% between the predicted and the experimental values. The same data when used and the predictions of the retentate concentration were made by use of the material balance equation resulted into average deviations of less than 1% between the predicted and the calculated values of the retentate concentrations. It signifies that the values of K_B and stern layer potential obtained by fitting experimental data in equation 5 may be used in solving the material balance eq. 8 without significant deviations in the final results.

Although models presented here are preliminary and applicable to only limited cases; the equations and algorithm may be used for predictions of MEUF of ions with +2 oxidation state in a semi-empirical way; with a fairly narrow deviation range of ± 10%.

NOMENCLATURE

ε	Dielectric constant
β	Degree of counterion binding
ϕ	Fraction of permeate taken as permeate (eq. 6–14)
ϕ	Gel coefficient $s{\cdot}m^{-1}$
ψ_∞	Potential at infinite distance from stern layer V
ψ_0	Potential of stern layer V
$[DS^-]$	Dodecyl sulfate ion concentration mM
$[Na^+]$	Concentration of sodium ions mM
[NaBr]	Concentration of NaBr mM
[NaCl]	Concentration of NaCl mM
[NaI]	Concentration of NaI mM
[Ni(II)]	Concentration of Ni(II) ions mM

[SDS]	Concentration of SDS mM
$[SO_4^{2-}]$	Concentration of sulfate ions mM
A_m	Active membrane area m^2
C_C	Concentration of counterion mM
C_F	Feed concentration mM
C_M	Concentration of surfactant monomers mM
CMC	Critical micellar concentration mM
C_P	Permeate concentration mM
C_R	Retentate concentration mM
e	Charge on electron C
J_N	Normalized flux
J_P	Permeate flux $m \cdot s^{-1}$
J_W	Water flux $m \cdot s^{-1}$
K	Boltzmann constant $J \cdot K^{-1}$
K_B	Binding constant $Dm^3 \cdot mol^{-1}$
MEUF	Micellar enhanced ultrafiltration
MF	Microfiltration
MWCO	Molecular weight cut off Da
n	No. of moles Mol
N_A	Avogadro's number
NF	Nanofiltration
PS	Polysulfone membrane
P_T	Transmembrane pressure Pa
R	Rejection coefficient
R_F	Resistance of fouling layer $Pa \cdot s \cdot m^{-1}$
R_M	Intrinsic membrane resistance $Pa \cdot s \cdot m^{-1}$
RO	Reverse osmosis
S/M	Surfactant to metal ion ratio
SDS	Sodium dodecylsulfate
t	Time s
T	Absolute temperature K
TMP	Transmembrane pressure Pa
UF	Ultrafiltration
V_F	Volume of feed cm^3
V_P	Volume of permeate cm^3
V_R	Volume of retentate cm^3
y	Distance from stern layer-diffuse double layer interface M
Z	Valancy

Subscripts

B	Indicates quantity in bound state
F	Corresponding quantity as measured in feed
P	Corresponding quantity as measured in Permeate

R Corresponding quantity as measured in Retentate
UB Indicates quantity in unbound state

REFERENCES

1. Scamehorn, J.F.; Christian, S.D.; El-Sayed, D.A.; Uchiyama, H.; Younis, S.S. (1994) Removal of divalent metal cations and their mixtures in aqueous streams using micellar-enhanced ultrafiltration. *Separation Science and Technology*, *29* (7): 809–830.
2. Sadaoui, Z.; Azoug, C.; Charbit, G.; Charbit, F. (1997) The recovery of hexavalent chromium by micellar-enhanced ultrafiltration: influence of operating conditions. *Journal of Chemical Engineering of Japan*, *30* (5): 799–805.
3. Morel, G.; Ouazzani, N.; Graciaa, A.; Lachaise, J. (1997) Surfactant modified ultrafiltration for nitrate ion removal. *Journal of Membrane Science*, *134*: 47–57.
4. Gzara, L.; Dhahbi, M. (2001) Removal of chromate anions by micellar-enhanced ultrafiltration using cationic surfactants. *Desalination*, *137*: 241–250.
5. Yurlova, L.; Kryvoruchko, A.; Kornilovich, B. (2002) Removal of Ni(II) ions from wastewater by micellar-enhanced ultrafiltration. *Desalination*, *144*: 255–260.
6. Aoudia, M.; Allal, N.; Djennet, A.; Toumi, L. (2003) Dynamic micellar-enhanced ultrafiltration: use of anionic (SDS)-nonionic(NPE) system to remove Cr^{3+} at low surfactant concentration. *Journal of Membrane Science*, *217*: 181–192.
7. Kamble, S.B.; Marathe, K.V.S. (2005) Membrane characteristics and fouling study in MEUF for removal of chromate anions from aqueous streams. *Separation Science and Technology*, *40* (15): 3051–3070.
8. Chhatre, A.J., Marathe, K.V. (2006) Dynamic analysis and optimization of surfactant dosage in micellar enhanced ultrafiltration of nickel from aqueous streams. *Sep Sci Tech.*, *41* (12): 2755–2770.
9. Scamehorn, J.F.; Ellington, R.T.; Christian, S.D.; Penney, B.W.; Dunn, R.O.; Bhat, S.N. (1986) Removal of multivalent metal cations from water using micellar-enhanced ultrafiltration. *AICHE Symposium Series*, *82* (250): 48–58.
10. Stigter, D. (1964) On the adsorption of counterions at the surface of detergent micelles. *Journal of Physical Chemistry*, *68* (12): 3603–3611.
11. Bunton, C.A.; Ohmenzetter, K.; Sepulveda, L. (1977) Binding of hydrogen ions to anionic micelles. *Journal of Physical Chemistry*, *81* (21): 2000–2004.
12. Bartet, D.; Gamboa, C.; Sepulveda, L. (1980) Association of anions to cationic micelles. *Journal of Physical Chemistry*, *84* (3): 272–275.
13. Rathman, J.F.; Scamehorn, J.F. (1984) Counterion binding on mixed micelles. *Journal of Physical Chemistry*, *88* (24): 5807–5816.
14. Stigter D. (1975) Micelle formation by ionic surfactants. III. Model of stern layer, ion distribution, and potential fluctuations. *Journal of Physical Chemistry*, *79* (10): 1008–1014.

15. Evans, D.F.; Ninham, B.W. (1983) Ion binding and the hydrophobic effect. *Journal of Physical Chemistry*, *87* (24): 5025–5032.
16. Tsapiuk, E.A.S. (1997) Calculation of the product composition and the retention coefficient by pressure driven membrane separation of solutions containing one and two solutes. *Journal of Membrane Science*, *124*: 107–117.
17. Lear, J.B.; Mellon, M.G. (1953) Absorptiometric determination of nickel with beta-mecaptopropionic acid. *Analytical Chemistry*, *25* (9): 1411–1412.
18. Cheryan, M. (1998) Process Design. In: *Ultrafiltration and Microfiltration Handbook*, Technomic Publishing co. INC: USA.
19. Hafiane, A.; Issid, I.; Lemordant, D. (1991) Counterion binding on micelles: An ultrafiltration study. *Journal of Colloid and Interface Science*, *142* (1): 167–178.
20. Beunen, J.A.; Ruckenstein, E. (1983) A model for counterion binding to ionic micellar aggregates. *Journal of Colloidal and Interface Science*, *96* (2): 469–487.
21. Purkait, M.K.; Dasgupta, S.; De, S. (2004) Resistance in series model for micellar enhanced ultrafiltration of eosin dye. *Journal of Colloid and Interface Science*, *270*: 496–506.