Module : 6

Surfactant based separation processes:

Liquid membranes: fundamentals and modeling
Micellar enhanced separation processes
Cloud point extraction

Dr. Sirshendu De
Professor, Department of Chemical Engineering
Indian Institute of Technology, Kharagpur
e-mail: sde@che.iitkgp.ernet.in

Keywords:

Separation processes, membranes, electric field assisted separation, liquid membrane, cloud point extraction, electrophoretic separation, supercritical fluid extraction

Surfactant based Separation Processes

6.1 Cloud Point Extraction

Cloud Point:

When temperature is increased in aqueous solution of a non-ionic surfactant, solution separates into two phases, beyond a particular temperature. This temperature is defined as cloud point (CPT). The surfactant rich small phase is known as coacervate phase and the bulk aqueous phase is known as lean or dilute phase.

Critical micellar concentration:

Any surfactant molecule has hydrophilic head and hydrophobic tail. Thus, at lower concentration, they are aligned across the water-air interface, where, the hydrophobic tail points towards the air. When the concentration of surfactant increases further, the surfactants molecules come to the bulk to attain the minimum volume to surface ratio (which is thermodynamically more stable) and they form the spherical globules, known as micelles. In these micelles, the surfactant molecules are aligned such that the hydrophilic heads point towards the aqueous solution and the hydrophobic tails form the core. Therefore, the micelles have polar (hydrophilic) characters on its outer surface and the core is hydrophobic. The concentration of surfactant at which this happens is known as critical micellar concentration (CMC). Therefore, in the dilute phase during cloud point extraction, surfactant concentration is about the critical micellar concentration (CMC).

Mechanism of Phase separation:

Phase change about CPT is reversible. The possible mechanisms of phase separation are as follows:

(i) For non-ionic surfactant, dielectric constant of water decreases as temperature increases. This reduces interaction between hydrophilic part of surfactant and water. Thus, above CPT, dehydration occurs in the external layer of micelle of non-ionic surfactants.

(ii) At lower temperature, intermicellar repulsive force is dominant and beyond CPT, it becomes attractive.

Mechanism of solubilization of solutes in coacervate phase:

For non ionic surfactants, the hydrophilic core is surrounded by a mantle of aqueous hydrophilic chain. Non polar solutes are solubilized within hydrophobic core. Hydrophobicity increases beyond CPT as extensive dehydration of polyoxyethylene chains occurs. Thus, the organic solutes are solubilized within micelles core to a large extent beyond CPT.

Applications:

Removal of polycyclic aromatic hydrocarbon, polychlorinated compounds, vitamins dyes, concentration of dilute solutions of heavy metals, etc. In fact, this method is utilized quite frequently for analysing extremely dilute solutions by concentration them.

Typical non-ionic surfactants:

Triton X-100 (Iso octyl phenoxy polyethoxy ethanol): molecular weight (M_w): 628; CMC= $2.8*10^{-4}$ (M); CPT= 64^0C.

Triton X-114(Octyl phenol poly ethylene glycol ether): Molecular weight: 537; CMC= $2.1*10^{-4}$ (M); CPT= 37^0C.

A case study of removal of dye from aqueous solution using cloud point extraction is presented .

Case Study: Removal of chrysoidine dye.

Extraction:

A typical concentration of 100 ppm of the dye is selected. Both, TX-114 and TX-100 are employed for removal of dye. Depending on their cloud point temperature, the operating temperature for TX-114 is selected as 40^0C and that for TX-100 is 70^0C. Thus, the operating temperature of the former surfactant is lower. It is observed that surfactant concentration about 0.25 (M) is able to remove more than 95% of dye. In fact, the dye extraction is about 95% for TX-100 and that for TX-114 is about 100%. This trend is shown in Fig.6.1. The extraction of dye is defined as,

Extraction of dye, $$E = 1 - \frac{c_d}{c_f} \qquad (6.1)$$

where, c_d is concentration in dilute aqueous phase and c_f is concentration of dye in feed.

The volume reduction factor is denoted as,

$$F_c = \frac{\text{Volume of coacervate phase}}{\text{Total volume of solution}} \qquad (6.2)$$

The value of F_c lies in between 0.04-0.23 for various operating conditions.

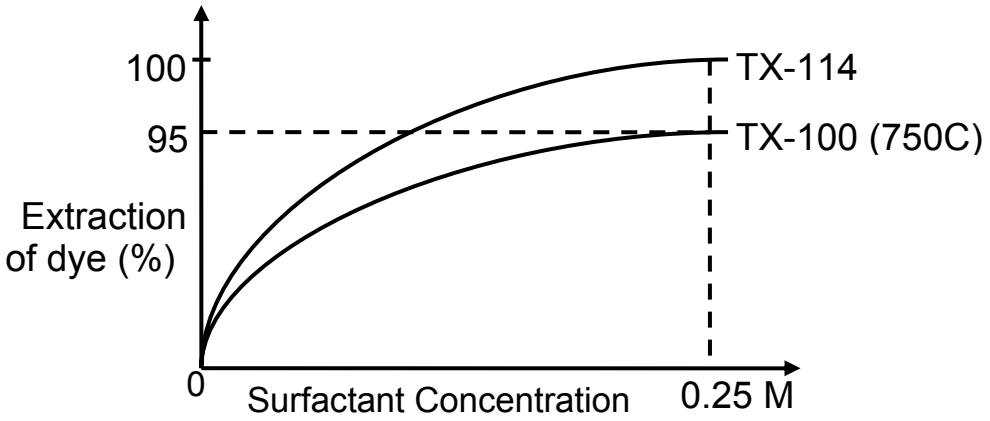

Fig. 6.1: Variation of extraction of dye with surfactant concentration

Surfactant partition coefficient (m):

The partition coefficient is defined as the ratio of concentration of surfactant in coacervate and dilute phase.

$$m = \frac{\text{Concentration of surfactant in coacervate phase}}{\text{Concentration of surfactant in dilute phase}} \qquad (6.3)$$

At constant temperature, surfactant concentration in dilute phase is nearly constant (near CMC) according to the Phase diagram of such systems. Thus, to maintain material balance, F_c increases as surfactant concentration in feed stream, $[S]_0$ increases. More micelles are formed in rich phase so that more extraction will takes place. A typical plot of distribution coefficient with feed surfactant concentration is presented in Fig. 6.2.

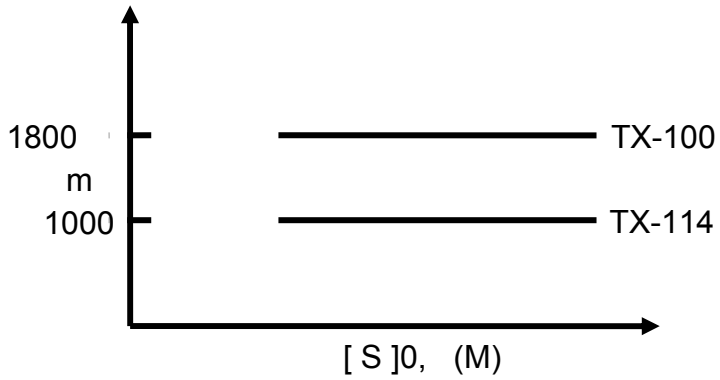

Fig. 6.2: Variation of surfactant partition coefficient with surfactant concentration in feed

Effect of temperature on extraction:

Temperature has pronounced effect on the extraction of solute. The effects are as follows:

(i) At high temperature, CMC of non-ionic surfactant decreases.

(ii) At high temperature, non-ionic surfactant becomes hydrophobic due to dehydration of ether oxygen. So, number of micelles increases and solubilization capacity increases with temperature.

Therefore, the extraction efficiency of the system increases with temperature. This is demonstrated in Fig. 6.3.

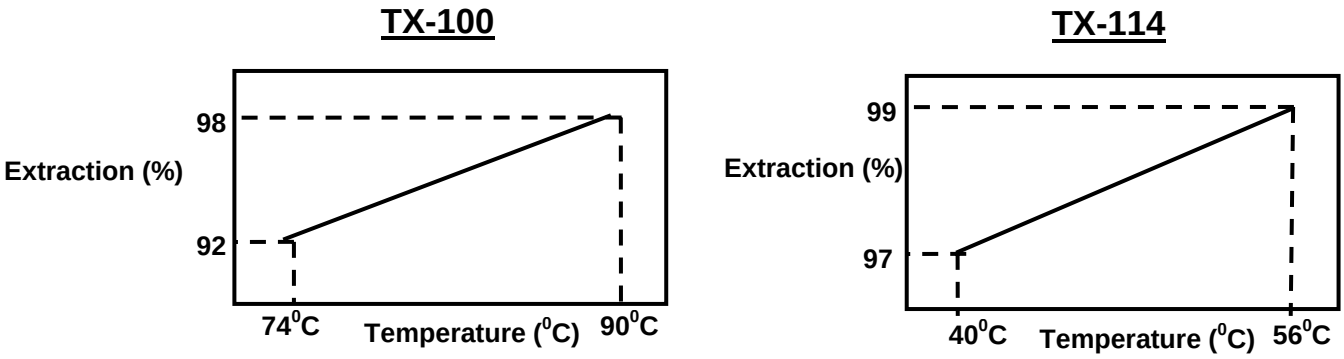

Fig. 6.3: Variation of dye extraction with temperature for Chrysoidine dye

Effect of pH:

The pK value of chrysoidine dye is about 6.0. Thus, at lower pH (< pK), dye is positively charged or protonated, thereby, increasing its ionic character. Therefore, at lower pH, the dye is less soluble in hydrophobic micelles. On the other hand, at higher pH dye is deprotonated and is more soluble in the micelles. Therefore, dye extraction is more at higher pH values. Fig. 6.4 shows that extraction increases significantly at higher pH values.

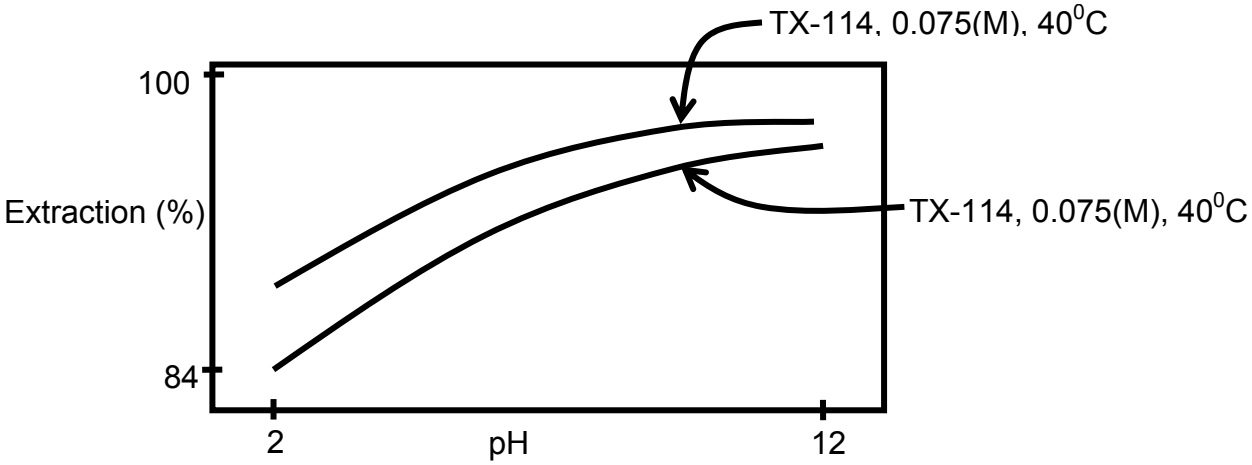

Fig. 6.4: Variation of dye extraction with pH for Chrysoidine dye

Effect of salt concentration:

Salts decrease cloud point of the surfactant due to salting out effect and promotes dehydration of ethoxy group on outer surface of micelles. Therefore, extents of solubilization in micelles are favoured at higher salt concentration. Cloud point of TX100

is 63^0C for 0.05(M) of NaCl and it is reduced to 54^0C for 0.5(M) of NaCl. The effect of divalent salt is stronger than monovalent salt. This effect for dye is shown in Fig. 6.5.

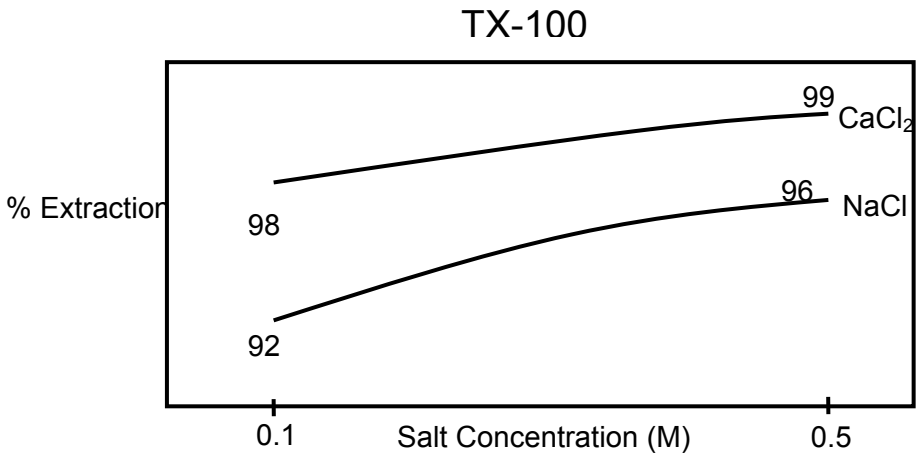

Fig. 6.5: Variation of dye extraction with salt concentration for Chrysoidine dye

Solubilization isotherm:

Moles of solute solubilized per mole of surfactant can be expressed in terms of solubilization isotherm. Such an isotherm qualitatively is presented in Fig. 6.6 for solubilization of chrysoidine dye.

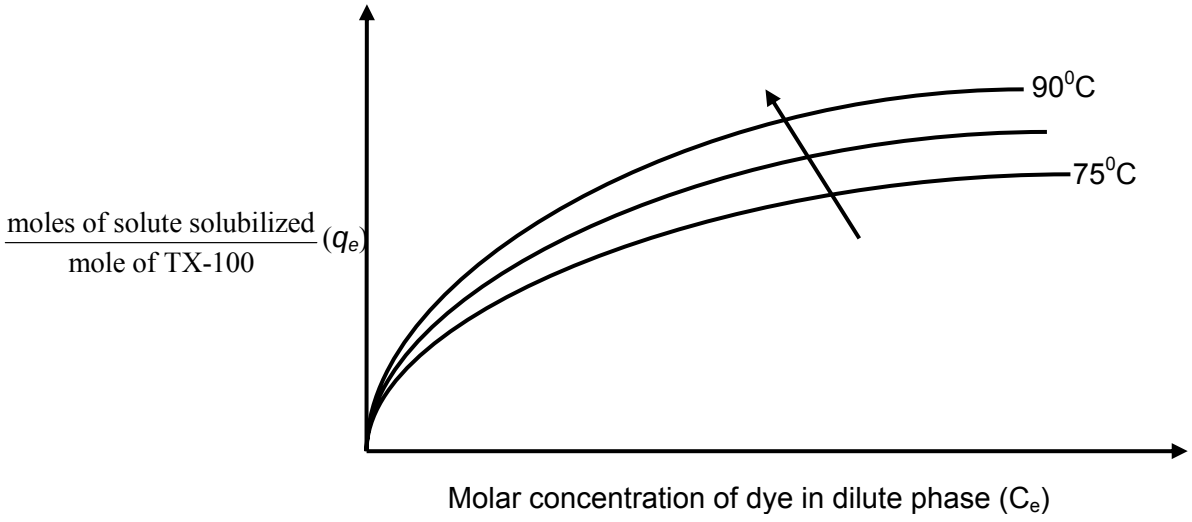

Fig. 6.6: Solubilization isotherm of chrysoidine dye at various temperature for TX-100

The isotherm can be expressed using the following Langmuir type expression:

$$q_e = \frac{mnc_e}{1+nc_e} \qquad (6.4)$$

Where, both m and n are functions of temperature. For chrysoidine- TX100 system,

$$m = 0.24 - 6\times10^{-3}T + 3.7\times10^{-5}T^2 \quad (T \text{ is in } {}^0\text{C}) \qquad (6.5)$$

$$n = -5\times10^{4} + 1.3\times10^{3}T - 5.9T^2 \quad (T \text{ is in } {}^0\text{C}) \qquad (6.6)$$

Variation of fractional coacervate volume (F_c):

As discussed above, the fractional coacervate volume is a function of surfactant concentration and it can be expressed by the following equation:

$$F_c = aC_s^b \qquad (6.7)$$

Where, C_s is the molar concentration of feed surfactant. The parameters *a* and *b* in above equation are functions of temperature. These variations are generally linear as follows:

$$a = P + QT; \qquad (6.8a)$$

$$b = R + ST \qquad (6.8b)$$

The parameters P, Q, R and S are functions of feed concentration of the surfactants or they are almost constant. For TX-100, these are presented below,

$$P = 5.9 - 200C_s - \frac{1.9\times10^{-8}}{C_s^2} \qquad (6.9)$$

$$Q = -0.05 \qquad (6.10)$$

$$S = 0.09 \qquad (6.11)$$

$$R = 0.4 + 6.9C_s + \frac{4\times10^{-9}}{C_s^2} \qquad (6.12)$$

Knowing the variation of various process parameters with the operating variables, it is possible to design a cloud point extractor. This is demonstrated below.

Design of Cloud Point Extractor

In this section design procedure of a cloud point extractor is outlined. The definition of the solubilization isotherm is given below.

$$q_e = \frac{\text{moles of solute solubilized}}{\text{moles of surfactant used}} = \frac{A}{X} \qquad (6.13)$$

Where, the moles of dye solubilized is presented as,

$$A = V_0C_0 - V_dC_e \qquad (6.14)$$

V_0 is initial volume of the extractor, C_0 is initial concentration of solute, V_d is the volume of dilute phase and C_e is final solute concentration in dilute phase. A rearrangement of Eq.(6.14) leads to the following equation,

$$A = V_0\left[C_0 - \frac{V_d}{V_0}C_e\right] \qquad (6.15)$$

Now, invoking the definition of fractional coacervate volume the above equation becomes,

$$A = V_0\left[C_0 - \left(1 - F_c\right)C_e\right] \qquad (6.16)$$

$$= V_0\left[C_0 - \left(1 - aC_s^b\right)C_e\right] \qquad (6.17)$$

Variation of F_c with surfactant concentration is given in Eq.(6.7). Using that definition, Eqs.(6.13) and (6.15) are combined to the following equation.

$$X = \frac{A}{q_e} = \frac{V_0}{q_e}\left[C_0 - \left(1 - aC_s^b\right)C_e\right] \qquad (6.18)$$

C_s is the initial feed concentration of surfactant and is defined as $C_s = \frac{X}{V_0}$. Using Eq.(6.17) and definition of isotherm, the following equation of surfactant feed concentration is obtained.

$$C_s = \frac{C_0 - \left(1 - aC_s^b\right)C_e}{q_e}$$

$$= \frac{\left[C_0 - \left(1 - aC_s^b\right)C_e\right]\left(1 + nC_e\right)}{mnC_e} \qquad (6.19)$$

The above equation is the required design equation. Knowing, the operating temperature, isotherm equation, and target value of solute in dilute phase (C_e), one can calculate the concentration of surfactant C_s required to achieve that.

6.2 Micellar Enhanced ultrafiltration

Surfactants are surface active agents. There are generally three types of surfactants.

(i) Ionic surfactants – They have ionic head and non-ionic tail (Sodium dodecyl sulphate)

(ii) Non-ionic surfactants – They are non-ionic in nature (polyethoxylates)

(iii) Zwetternic Surfactants – They are having both ionic and non-ionic characteristics

Ionic surfactants are two types.

(i) Cationic surfactants (eg. is CPC - Cetyl pyridinium chloride): These surfactants have positively charged heads when put in the aqueous solution.

(ii) Anionic surfactants (eg. is SDS – Sodium dodecyl sulfate): These surfactants have negatively charged heads when put in the aqueous solution.

In aqueous solution CPC and SDS both are divided in to ionic forms.

$$CPC \rightarrow CP^{+} + Cl^{-}$$

$$SDS \rightarrow Na^{+} + DS^{-}$$

Critical micellar concentration (CMC):

When surfactant monomers are dissolved in aqueous solution, the hydrophilic heads point towards the friendly aqueous environment and hydrophobic tails point towards air. This is shown in Fig. 6.7.

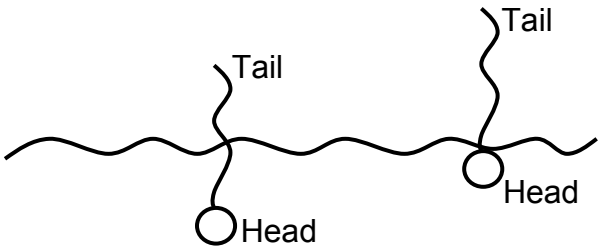

Fig. 6.7: Alignment of surfactant monomers

Beyond a particular concentratin of monomer, monomers form globules and they enter into the bulk of the solution. These globules or agglomerates of monomers are of spherical in shape to have the minimum surface energy and are known as micelles. This concentration of surfactants is known as critical micellar concentration (CMC). Typical micelle diameter is nearly 2-10 nm. There exists a size distribution of micelles. CMC of SDS is 8.1 mM and M_w of SDS monomer is 288. CMC of CPC is 0.88 mM and M_w of CPC monomer is 340. For non-ionic surfactants CMC is very small.

Determination of critical micellar concentration (CMC):

It may be noted that various physical properties of the solution changes slope around the CMC concentration. Surface tension drastically decreases beyond CMC. Osmotic pressure and conductivity of the solution increase slowly beyond CMC. Some of these typical variations with surfactant concentration are shown in Fig. 6.8.

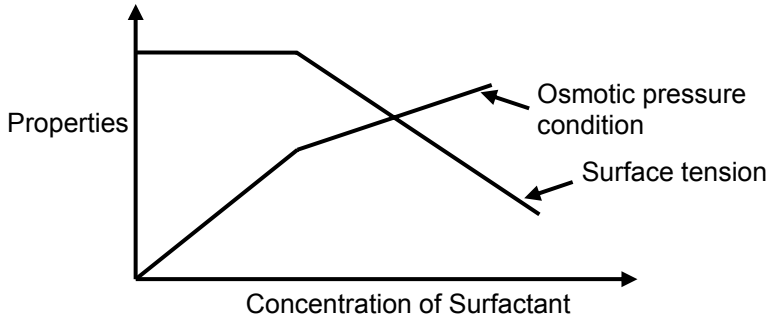

Fig. 6.8: Property variations with surfactant concentration

Therefore, measurement of such properties can lead to the determination of CMC by observing the surfactant concentration where the slope of the curve changes.

Micellar enhanced ultrafiltration (MEUF):

Thus, in case of anionic micelles (SDS), the outer surface of the micelles are negatively charged and for cationic micelles (CPC), the outer surface of the micelles are positively charged. Now, in case of oppositely charged pollutants present in the system, for example, cations like zinc, cadmium, arsenic, etc., they will be attached on the outer surface of anionic micelles of SDS. Anionic pollutants (like cyanidie, CN^{-1}, manganate, MnO_4^{-1}, dichromate, $Cr_2O_3^{-2}$, etc.), get attached to the cationic micelles of CPC, CTBr, etc., by electrostatic attraction. Therefore, for removal of cationic pollutants anionic surfactants and for anionic pollutants, cationic surfactants should be used. If there are some non-ionic, organic pollutants present in the solution, they can be dissolved within the hydrophobic core of the micelles. Now, the transfer of the pollutants from the solution phase to the micelle phase is almost instantaneous. Micelles being larger in size (nano-colloids), their sizes also increase with solubilization of the pollutant solutes. These larger

aggregates can now be separated by a more open pore sized membranes, like, ultrafiltration at the expense of lower pumping cost. The micelles with solubilized pollutants are retained by the membrane and the filtrate will be devoid of pollutants and has the surfactant concentration to the level of CMC which is generally extremely low. In fact, there are methods exist tom remove the left over surfactants in the filtrate stream by suitable chemical treatments. The process of MEUF is depicted in Fig.6.9.

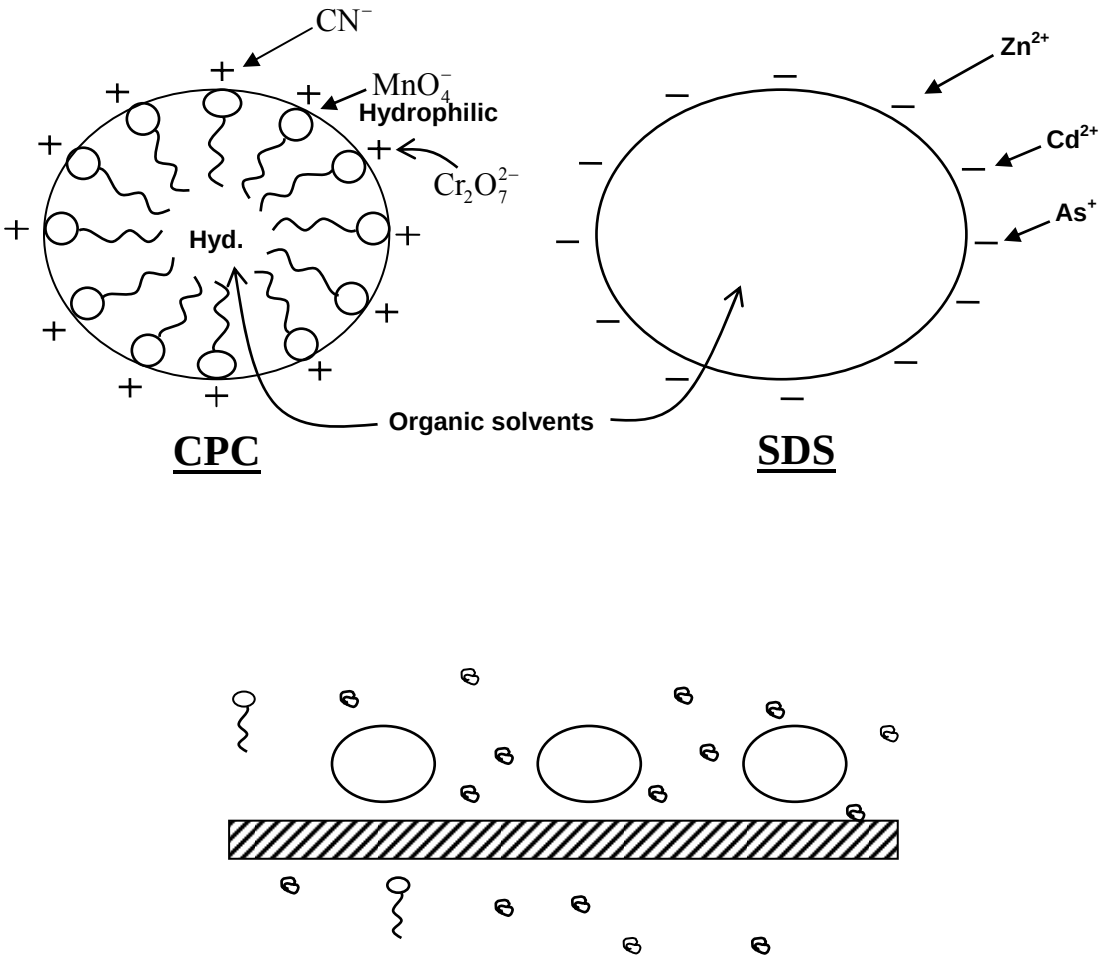

Fig. 6.9: Schematic of MEUF process

``Quantification of MEUF

Extent of solubilization of the solutes within the micelles

The solubilization coefficient of the solutes in the micelle can be defined as,

$$S = \frac{C_0 - C_p}{C_0^s - CMC} = \frac{\text{Amount of solute solubilized}}{\text{Amount of micelles}} \qquad (6.20)$$

Where, C_0 is the feed and C_p is the permeate concentration of the solute. C_0^s is the feed concentration of the surfactants and CMC is the critical micellar concentration of the surfactant.

For single component solute system

A Langmuir type isotherm is proposed. Following equation holds for a single component system.

$$\frac{C_0 - C_p}{C_0^s - CMC} = \frac{QbC_p}{1 + bC_p} \qquad (6.21)$$

Q and b are the coefficients of the isotherm.

For multi component solute system

An extended Langmuir isotherm type of equation is proposed for multicomponent solute system

$$\frac{C_{01} - C_{p1}}{C_0^s - CMC} = \frac{Q_1 b_1 C_{p1}}{1 + b_1 C_{p1} + b_2 C_{p2}} \qquad (6.22)$$

$$\frac{C_{02} - C_{p2}}{C_0^s - CMC} = \frac{Q_2 b_2^{'} C_{p2}}{1 + b_1^{'} C_{p1} + b_2^{'} C_{p2}} \qquad (6.23)$$

In the above equations, subscripts 1 and 2 indicate the solutes 1 and 2.

Permeate flux

It is assumed that the surfactant micelles form a gel type of layer over the membrane surface. At the steady state, the permeate flux of gel controlled filtration is given as,

$$J_s = k \ln \frac{C_g}{C_0^s} \qquad (6.24)$$

Where, Cg is gel layer concentration . k is the mass transfer coefficient. The gel layer concentration of CPC micelles is about 366 kg/m^3 and that for SDS micelles is about 210 kg/m^3. In presence of counter ions eg., Zn^{2+}, Ca^{2+}, Cu^{2+}, etc., two phenomena occur. (i) Presence of counter ions decreases CMC of the surfactants due to reduced electrostatic repulsion; (ii) the gel layer concentration of the micelles decreases. The first phenomenon is well known. The second one is newly found. This occurs as the multivalent counter ions act as bridge between two charged micellar entities. Therefore, micelles tend to precipitate at lower concentration due to this "bridging effect". This is schematically shown in Fig. 6.10

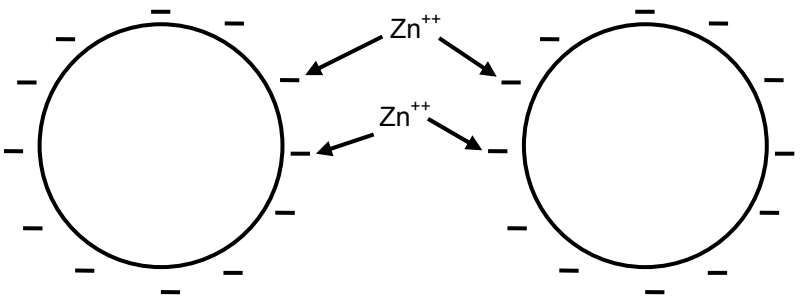

Fig. 6.10: Bridging effect of micelles in presence of counter ions

This, results into onset of gel layer formation at lower gel concentration. So, gel layer concentration decreases from pure component. Therefore, a typical flux versus feed concentration of the surfactants in presence of micelles looks like Fig. 6.11.

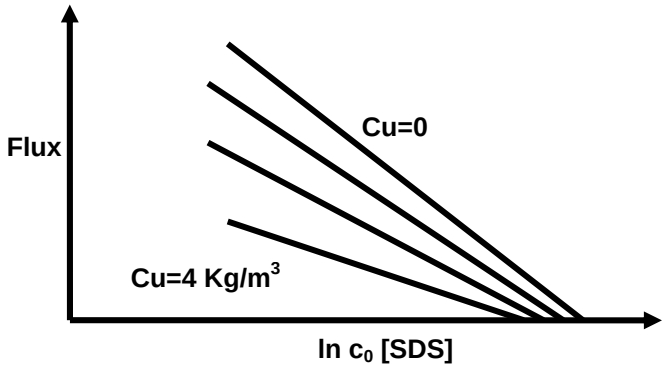

Fig. 6.11: Permeate flux with feed concentration of the surfactant during MEUF

From the work of Das et al. [2008], it is observed that the gel layer concentration of SDS micelles decrease with counter ions as follows:

For Cu^{2+} : $C_g = 366\left(1-0.21C_{Cu}\right)$ for $C_{Cu} < 1$ Kg/m^3

$= 292 - 3C_{Cu}$ for $1 < C_{Cu} < 4$ Kg/m^3 (6.25a)

For Ca^{2+} : $C_g = 366\left(1-0.14C_{Ca}\right)$ for $C_{Ca} < 1$ Kg/m^3

$= 318 - 4.37C_{Ca}$ for $1 < C_{Ca} < 4$ Kg/m^3 (6.25b)

The mass transfer coefficient can be calculated from the following equations under laminar flow conditions:

$$Sh = \frac{kd_e}{D} = 1.86\left(\text{Re Sc}\ \frac{d_e}{L}\right)^{\frac{1}{3}}\left(\frac{\mu_b}{\mu_g}\right)^{0.27} \qquad (6.26)$$

Effect of binary mixture on C_g

The reduction of gel layer concentration in presence of mixture of counter ions is also important. This is presented for SDS and copper-calcium mixture in Table 6.1

Cu^{++}:Ca^{++} (kg/m^3)	C_g^{mix} (kg/m^3)
0.5:3.0	311
1:2.5	302
2:2	298
3:1	291
4:0.5	281

Table 6.1: Change in gel layer concentration in presence of mixture of counter ions

Effects on change viscosity in presence of counter ions

It is to be noted that in presence of surfactant micelles and counter ions the viscosity of the solution get affected. It has been experimentally observed that viscosity of the surfactant solution increases in presence of counter ions. A typical such behavior is shown in Fig. 6.12.

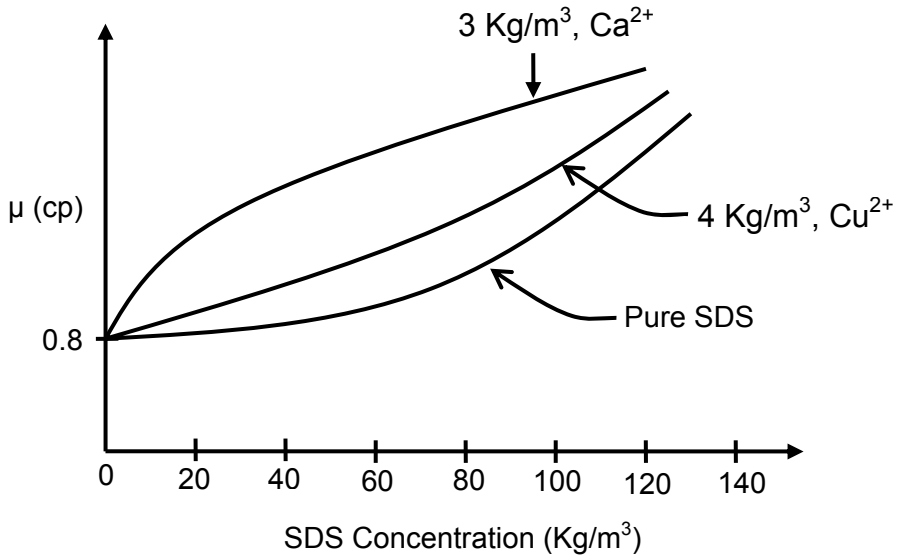

Fig. 6.12: Change in gel layer concentration in presence of mixture of counter ions

Determination of the viscosity of the solution in presence of counter ions at the gel point is a complex phenomenon. The relevant calculation procedure is outlined in Das et al. (2008). These viscosity variations need to be considered to estimate the mass transfer coefficient.

Model for counterion binding localized adsorption model

The counter ion binding model of Rathman and Sacmehorn can be extended to evaluate the amount of counter ions bound on the micelles by electrostatic attraction. In case of SDS micelles and one solute (say, copper), the binding ratio of the solute is defined as,

$$\beta_i = \frac{K_i C_i e^{-\frac{z_i \psi}{K_B T}}}{1 + K_i C_i e^{-\frac{z_i \psi}{K_B T}} + K_{Na} C_{Na} e^{-\frac{z_i \psi}{K_B T}}} \qquad (6.27)$$

Where, C_i is the bulk concentration of the solute; K_i is binding constant of i[th] component; K_{Na} is binding constant of Na and Ψ is the zeta potential of the micelle.

For a two component mixture, the above concept is extended and the following expression is resulted.

$$\beta_i = \frac{K_i C_i e^{-\frac{z_i \psi}{K_B T}}}{1 + K_{Na} C_{Na} e^{-\frac{z_i \psi}{K_B T}} + \sum_{i=1}^{2} K_i C_i e^{-\frac{z_i \psi}{K_B T}}} \qquad (6.28)$$

The binding coefficient of i[th] component can be experimentally obtained as,

$$\beta_i^{\exp} = 2\left(\frac{C_i - C_{p_i}}{C_0^s - CMC}\right) \qquad (6.29)$$

It may be noted that CMC of the surfactant decreases with counter ion concentration. The associated constants K's and zeta potential of the micelles can be estimated by optimizing the data over number of experimental data points.

$$S = \sum_{i=1}^{n} \left(\beta_{i,Cu}^{\exp} - \beta_{i,Cu}^{cal}\right)^2 + \sum_{i=1}^{n} \left(\beta_{i,Ca}^{\exp} - \beta_{i,Ca}^{cal}\right)^2$$

(6.30)

Some typical values of these coefficients are presented below.

For single component system (SDS and copper): The values of the isotherm constants are: $K_{Cu} = 70.87;\ K_{Na} = 0.06;$ and $\psi = 11.15$ mV. These values are for SDS and calcium system, $K_{Ca} = 192;\ K_{Na} = 0.06;$ and $\psi = 16$ mV. Similar results are obtained for SDS micelles and copper-calcium mixture. It is observed that in case of mixture, Ca^{2+} is more

favourably bound than Cu^{2+}. The typical plots of binding / retention of counter ions on the micelles are presented in Fig. 6.13.

6.3 Liquid Membranes

In this chapter, only emulsion liquid membrane is discussed. In this case, membrane is a liquid phase involving an emulsion configuration. The emulsion is essentially a double emulsion, *i.e.*, water/oil/water or oil/water/oil system. For water/oil/water system: Oil phase separating two aqueous phases is the liquid membrane. For oil/water/oil system: Water is the liquid membrane. Surfactants are used for stabilizing the emulsion.

Applications of liquid membranes:

Some typical applications are listed below:

1) Removal of zinc from wastewater in viscose fibre industry.
2) Removal of phenol from wastewater.
3) Recovery of nickel from electroplating solution.
4) Removal of heavy metals.

Preparation:

An emulsion is prepared between two immiscible phases (under high stirring). Then the emulsion is dispersed in a third (continuous) phase under continuous agitation. Membrane phase is the liquid phase that separates the encapsulated, internal droplets in the emulsion from the external phase. Membrane phase must not be miscible with either of internal and external phase. To stabilize emulsion, membrane phase generally contains some surfactants and additives as stabilizing agents. Typical sizes of internal droplets are 1-3 μm diameter and those for emulsion gobule are 100-2000 μm diameter. The schematic of an emulsion droplet is shown in Fig. 6.14.

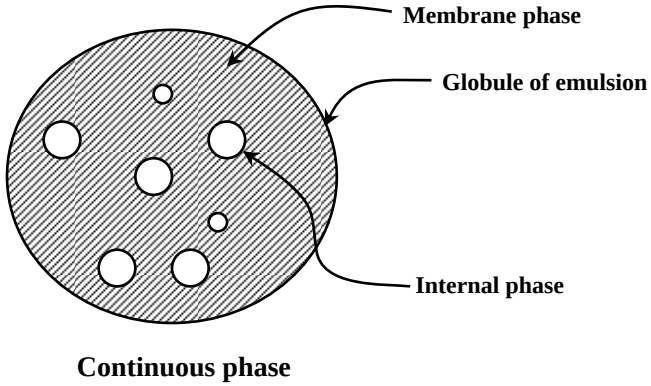

Fig. 6.14: A typical liquid membrane emulsion droplet

The system works like this. As shown in Fig. 6.14, the aqueous phase is present both inside the emulsion droplet and as a continuous phase outside. Typically, internal phase contains a species that reacts with the pollutant present in the external continuous phase. The pollutant diffuses through the membrane phase, gets into the internal phase. As it reacts with the reagent present in the external phase, the product cannot diffuse out the membrane phase. In the process, the concentration gradient of pollutant species is maintained at its maximum between the internal and external phase. Thus the removal of pollutant occurs from the external phase. A typical example of removal of phenol by this technique is described below.

ELM system for phenol removal:

A typical emulsion liquid membrane system for removal of phenol is shown in Fig. 6.15. Phenol diffuse through membrane phase (hexane) and reacts with NaOH forms sodium phenolate which is insoluble in oil phase and trapped inside. Extracted component can be recovered from the "loaded" internal phase of emulsion by breaking the emulsion, usually by the electrostatic coalescer.

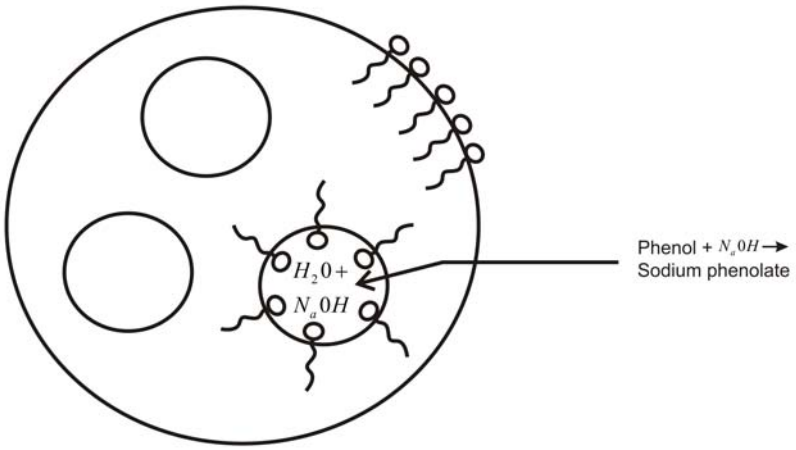

Fig. 6.15: A typical liquid membrane emulsion droplet for removal of phenol

From breaking the emulsion, membrane phase recovered can then be recycled to the emulsification step for preparation of the emulsion with fresh internal agent.

Facilitated Mechanism & driving force:

Type I facilitation:

Reaction in the internal phase maintains a solute concentration of effectively zero and this make the driving force of solute transport maximum. Reaction of diffusing species with a chemical reagent in internal phase forms a product which is incapable of diffusing out (through the membrane), for example, sodium phenolate in the above example.

Type II facilitation:

Diffusing species are carried across the membrane phase by incorporating a ‘carrier’ compound (complexing agent), in the membrane phase, as shown in Fig. 6.16.

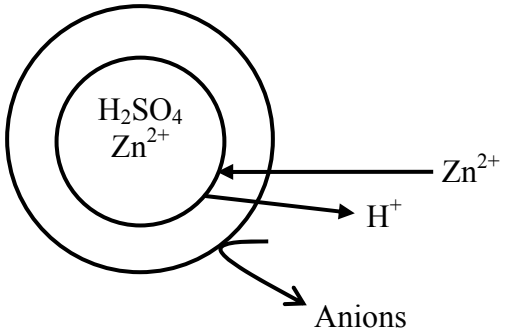

Fig. 6.16: Transport of cations in presence of carrier in the membrane phase

Reaction takes place at external interface between external and membrane phase and also at the internal interface between membrane and internal phase. Following reaction takes place,

$$Zn^{++} + 2HR \rightarrow ZnR_2 + 2H^+$$

(aq.) (org.) (org.) (aq.)

Zn^{++} in the external phase reacts at external interface with carrier compound, HR in the membrane phase to form complex ZnR_2. Here the carrier compound is D_2EHPA (). This reaction forms zinc complex in organic phase and releases protons to external aqueous phase. Zinc complex diffuses across membrane phase to concentrated H_2SO_4 in internal phase. At internal interface, stripping reaction takes palce:

$$ZnR_2 + 2H^+ \rightarrow Zn^{++} + 2HR$$

(org.) (aq.) (aq.) (org.)

Concentrated acid in internal phase strips Zn from the membrane phase to become Zn^{++} ion and donates protons to extractant in membrane phase. Concentrated acid drives stripping reaction to right and maintain a low concentrated of zinc complex, ZnR_2, at internal interface high driving force in terms of ZnR_2.

In this case, driving force of proton transport "pumps" the transport of metal ion against its own concentration difference between feed and receiving phase. Concentration of Zn in internal phase becomes almost 70 times of feed. The schematic of the driving force is shown in Fig. 6.17.

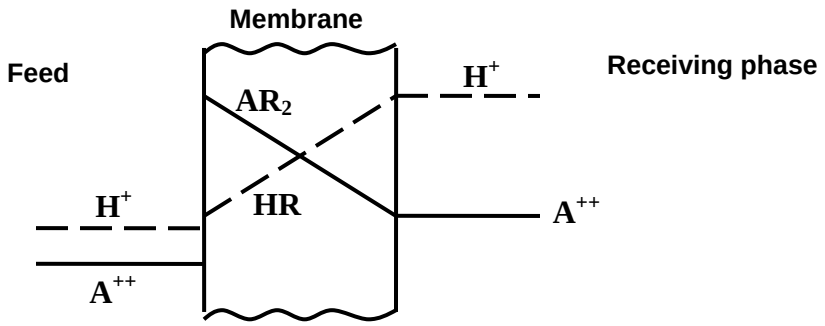

Fig. 6.17: Driving forces in Type II facilitation

The advantage of ELM

Simultaneous extraction and stripping occur in one single step rather than two separate steps as required by solvent extraction. Schematic of a continuous ELM process is shown in Fig. 6.18.

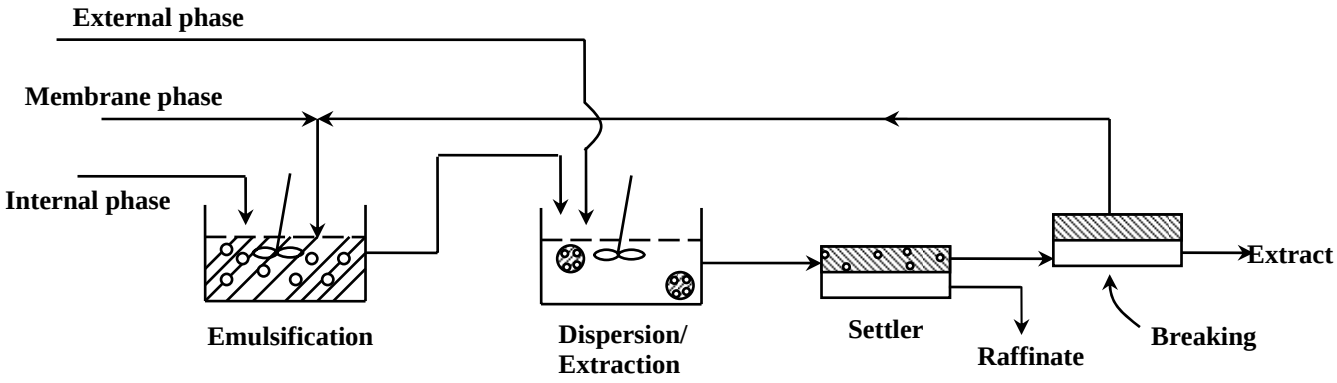

Fig. 6.18: Schematic of a continuous ELM process

Modeling of Batch Extraction of Type I Facilitation:

The main transport mechanism involves in Type I facilitation is diffusion type of transport. A Spherical shell approach is commonly used to quantify this phenomena.

Salient features of the model:

(i) Solute 'A' from external phase diffuses to the internal phase and after reaction becomes 'B'. (with mass transfer coefficient k_A)

(ii) B diffuses to the external phase via (a) diffusion (with mass transfer coefficient k_B) and (b) breakage (with breakage coefficient φ).

(iii) In the external phase, B gets converted to A.

Thus, 'A' can exist only in external phase and 'B' can exist only in internal phase. In the internal phase, the following reaction takes place

$NaOH$ + Phenol $\rightarrow$ Phenolate

The mechanism is shown in Fig. 6.19.

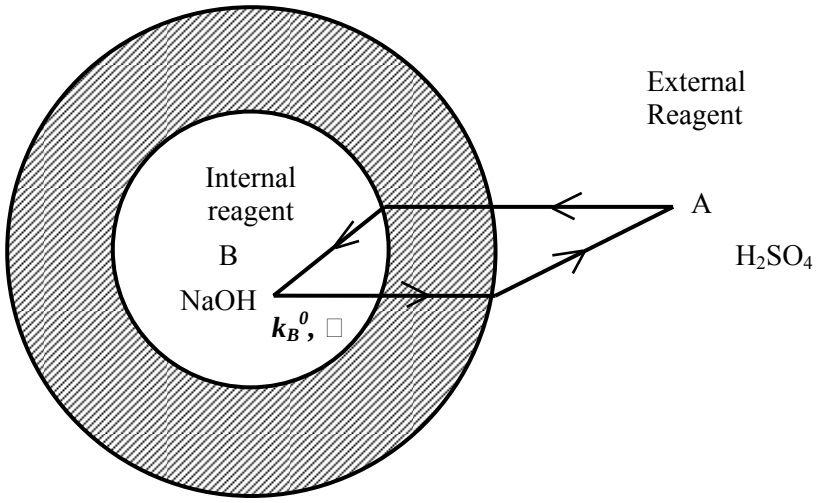

Fig. 6.19: Schematic of Type I reaction in an emulsion droplet

Breakage:

Breakage of internal phase in terms of internal phase volume with time is assumed to proportional to internal phase volume,

$$-\frac{dV_i}{dt} = \phi V_i \qquad (6.31)$$

Where, φ is the breakage coefficient. Integrating of above equation results in the following time variation of internal volume

$$V_i = V_{i0} e^{-\phi t} \qquad (6.32)$$

The total volume can be written as,

$$V_0 = V_{e0} + V_{i0} \qquad (6.33)$$

Where, V_0 is total initial volume; V_{e0} is volume of external phase initially and Vi0 is initial volume of internal phase. At any point of time, the following equation holds.

$$V_e + V_i = V_0 \qquad (6.34)$$

Combining Eqs. (6.32) and (6.34) the following equation is resulted.

$$V_e = V_0 - V_{i0} e^{-\phi t} \qquad (6.35)$$

In this example, the external phase consists of Phenol + H_2SO_4. The internal phase is aqueous solution of NaOH. In the internal phase, sodium phenolate is produced. Some amount of Sodium phenolate comes to the solution through breakage and reacts with sulphuric acid present in the external phase to produce phenol and sodium sulphate. Concentration of A in internal phase is zero, $C_{iA}=0$ (A exists only in external phase). Concentration of B in external phase is zero $C_{eB}=0$ (B exists only in internal phase). $k_B^0 = 0$, because ionic species B cannot diffuse through oil-type membrane phase.

Balance equations in external phase:

We can write species A balance in the external phase,

$$\frac{d}{dt}\left(V_e C_{eA}\right) = -k_A^0 C_{eA} + \phi V_i C_{iB} \tag{6.36}$$

At $t=0$, $C_{eA}=C_{eA0}$, $C_{iB}=C_{iB0}$

Overall solute mass balance results the following:

Total solute mass at't' = Total initial mass

$$V_i C_{iB} + V_e C_{eA} = V_{e0} C_{eA0} + V_{i0} C_{iB0} \tag{6.37}$$

The expression of species "B" is then obtained as,

$$C_{iB} = \frac{1}{V_i}\left(V_{e0} C_{eA0} + V_{i0} C_{iB0}\right) + \frac{V_e}{V_i} C_{eA} \tag{6.38}$$

Small Breakage

Assuming small breakage, for $\phi \le 1.4\times10^{-5}$ s^{-1}, change in internal phase volume is less than 5%. Thus, V_i and V_e can be assumed to be constant as,

$$V_i \simeq V_{i0}; \qquad V_e \simeq V_{e0}$$

From Eq. (6.38), the following equation is obtained.

$$C_{iB} = \frac{V_{e0}}{V_{i0}} C_{eA0} + C_{iB0} + \frac{V_{e0}}{V_{i0}} C_{eA} \tag{6.39}$$

From Eq. (6.36), time variation of concentration of "A" is obtained.

$$\frac{dC_{eA}}{dt} = -\frac{k_A^0}{V_{e0}} C_{eA} + \phi \frac{V_{i0}}{V_{e0}} C_{iB} \tag{6.40}$$

$$\frac{dC_{eA}}{dt} = -\frac{k_A^0}{V_{e0}} C_{eA} + \phi \frac{V_{i0}}{V_{e0}} \left[\frac{V_{e0}}{V_{i0}} C_{eA0} + C_{iB0} + \frac{V_{e0}}{V_{i0}} C_{eA}\right]$$

$$= -\frac{k_A^0}{V_{e0}} C_{eA} + \phi C_{eA0} + \phi \frac{V_{i0}}{V_{e0}} C_{iB0} - \phi C_{eA} \tag{6.41}$$

By simplifying this we finally get,

$$\frac{dC_{eA}}{dt} + \alpha C_{eA} - \beta = 0 \tag{6.42}$$

Where, $\alpha = \frac{k_A^0}{V_{e0}} + \phi$ and $\beta = \phi\left(C_{eA0} + \frac{V_{i0}}{V_{e0}} C_{iB0} \right)$.

The above equation is a non-homogeneous ordinary differential equation with two parts, homogeneous solution and particular integral.

Homogeneous solution:

$$\frac{dC_{eA}^h}{dt} + \alpha C_{eA}^h = 0 \tag{6.43}$$

$$C_{eA}^h = k_1 \exp(-\alpha t) \tag{6.44}$$

Partial integral:

$$C_{eA}^p = \frac{\beta}{\alpha} \tag{6.45}$$

So, the final solution is obtained by linear superposition of above two solutions.

$$C_{eA} = C_{eA}^h + C_{eA}^p = k_1 \exp(-\alpha t) + \frac{\beta}{\alpha} \tag{6.46}$$

At $t=0$, $C_{eA}=C_{eA0}$. Thus, the integration constant is obtained.

$$C_{eA0} = k_1 + \frac{\beta}{\alpha} \tag{6.47}$$

$$k_1 = C_{eA0} - \frac{\beta}{\alpha} \tag{6.48}$$

Thus, the final solution is

$$C_{eA}(t) = C_{eA0}e^{-\alpha t} + \frac{\beta}{\alpha}\left(1 - e^{-\alpha t}\right) \tag{6.49}$$

Large Breakage

In this case, the variation of internal volume with time is

$$V_i = V_{i0}e^{-\phi t} \tag{6.50}$$

The time variation of external phase becomes,

$$V_e = V_0 - V_{i0}e^{-\phi t} \tag{6.51}$$

From the overall material balance, the following expression of concentration of "B" in the internal phase becomes,

$$C_{iB} = \frac{V_{e0}}{V_i}C_{eA0} - \frac{V_{i0}}{V_i}C_{iB0} - \frac{V_e}{V_i}C_{eA}$$

$$= \frac{1}{V_{i0}e^{-\phi t}}\left\{\left(V_{e0}C_{eA0} - V_{i0}C_{iB0}\right) - \left(V_0 - V_{i0}e^{-\phi t}\right)C_{eA}\right\} \tag{6.52}$$

The time variation of species "A" is obtained by undertaking "A" balance

$$\frac{d}{dt}\left(V_e C_{eA}\right) = -k_A^0 C_{eA} + \phi V_i C_{iB} \tag{6.53}$$

Combining Eqs. (6.52) and (6.53), the following equation is resulted.

$$C_{eA}\frac{dV_e}{dt} + V_e\frac{dC_{eA}}{dt} = -k_A^0 C_{eA} + \frac{\phi V_i e^{-\phi t}}{V_{i0}e^{-\phi t}}\left\{\left(V_{e0}C_{eA0} - V_{i0}C_{iB0}\right) - \left(V_0 - V_{i0}e^{-\phi t}\right)C_{eA}\right\} \tag{6.54}$$

The final solution is obtained by simultaneous solution of Eq. (6.51) and (6.54).

Consumption of Chemical Reagent in external phase: *(e.g. H_2SO_4 for conversion of phenolate to phenol):*

Consumption of H_2SO_4 in external phase is the amount required to convert phenolate to phenol through leakage as well as to convert IR(NaOH) to salt through leakage.

$$W_e = \int_0^t \left(\phi V_i C_{iB} + \phi V_i C_{ir}\right) dt \qquad (6.55)$$

Where, C_{ir} is concentration of internal reagent. A balance of internal reagent results:

$$\frac{d}{dt}\left(V_i C_{ir}\right) = -k_A^0 C_{eA} + \phi V_i C_{ir} \qquad (6.56)$$

For Small Breakage:

$$\frac{dC_{ir}}{dt} = -\frac{k_A^0}{V_{i0}} C_{eA} + \phi C_{ir}$$

$$\frac{dC_{ir}}{dt} + \phi C_{ir} = -\frac{k_A^0}{V_{i0}}\left[C_{eA0}e^{-\alpha t} + \frac{\beta}{\alpha}\left(1 - e^{-\alpha t}\right)\right]$$

$$e^{\phi t}\frac{dC_{ir}}{dt} + \phi e^{\phi t} C_{ir} = -\frac{k_A^0}{V_{i0}} e^{\phi t}\left[C_{eA0}e^{-\alpha t} + \frac{\beta}{\alpha}\left(1 - e^{-\alpha t}\right)\right]$$

$$\frac{d}{dt}\left(e^{\phi t} C_{ir}\right) = -\frac{k_A^0}{V_{i0}}\left[C_{eA0}e^{-(\alpha-\phi)t} + \frac{\beta}{\alpha}\left(e^{\phi t} - e^{-(\alpha-\phi)t}\right)\right]$$

By integrate this equation we get,

$$C_{ir} = -\frac{k_A^0}{V_{i0}}\left[\frac{\beta}{\alpha\phi} - \frac{e^{-\alpha t}}{(\alpha-\phi)}\left\{C_{eA0} + \frac{\beta}{\alpha\phi}\right\}\right] + k \qquad (6.57)$$

At $t=0$, $C_{ir}=C_{ir0}$

$$k = C_{ir0} + \frac{k_A^0}{V_{i0}}\left[\frac{\beta}{\alpha\phi} - \frac{1}{(\alpha-\phi)}\left\{C_{eA0} + \frac{\beta}{\alpha\phi}\right\}\right] \qquad (6.58)$$

But,

$$W_e = \int_0^t \left(\phi V_i C_{iB} + \phi V_i C_{ir} \right) dt$$

Consumption of chemical reagent (e.g. NaOH for conversion of phenol to phenolate) in internal phase:

$$W_i = \int_0^t \left(k_A^0 C_{eA} + \phi V_i C_{ir} \right) dt$$

For small breakage, $V_i = V_{i0}$ and can be used as constant and the above integration can be evaluated numerically.

Solved Problems

1) Phenol is removed from SDS micellar solution of 10 *kg/m*^{3}. Feed concentration of phenol is 20 *mg/l*. Solubilization of phenol in micelle, *S=2.34 mg/gm*. The solubilization isotherm is given as, $S = \frac{Qb_1C_p}{1+b_1C_p}$, where, *S* is in mg/mg, *Q=0.1 mg/mg*; b_1*= 9*10*$^{-2}$ *l/mg*. If gel concentration of SDS is *280 kg/m*^{3} and mass transfer coefficient is *2*10*$^{-5}$ *m/s* and CMC of SDS is *2.3 kg/m*^{3}, find the permeate flux and permeate concentration of phenol?

Solution:

Flux is $v_w = k \ln \frac{C_g}{C_0^s}$

$$= 2 \times 10^{-5} \ln \frac{280}{10}$$

$$= 6.66 \times 10^{-5} \frac{m^3}{m^2.s}$$

$$S = \frac{Qb_1C_p}{1+b_1C_p}$$

$$2.34\times10^{-3} = \frac{0.1\times9\times10^{-2}C_p}{1+9\times10^{-2}C_p}$$

$$2.34\times10^{-3} + 2.1\times10^{-4}C_p = 9\times10^{-3}C_p$$

$$8.79\times10^{-3}C_p = 2.34\times10^{-3}$$

$$C_p = 0.266\ mg/l$$

$$\text{Observed retention of phenol} = \left(1-\frac{0.266}{20}\right)100\%$$

$$= 98.67\%$$

2) Copper is removed from an SDS micellar solution of 4 kg/m^3. Copper concentration in feed is 4 kg/m^3. If mass transfer coefficient is 10^{-5} m/s find the permeate flux and observed retention of copper?

$C_g = 292 - 3C_{Cu}$; $\quad CMC = 2.3\ kg/m^3$

Use localized adsorption model and binding rates of copper on SDS micelle is given as,

$$\beta = \frac{\kappa_{Cu}C_{Cu}\exp\left(-\frac{z_{Cu}e\psi}{K_BT}\right)}{1+\kappa_{Cu}C_{Cu}\exp\left(-\frac{z_{Cu}e\psi}{K_BT}\right)+\kappa_{Na}C_{Na}\exp\left(-\frac{z_{Na}e\psi}{K_BT}\right)}$$

$\kappa_{Cu} = 71; \quad \kappa_{Na} = 0.06; \quad z_{Cu} = 2; \quad z_{Na} = 1; \quad \psi = 11\ mV; \quad T = 300\ K$

Permeate flux = $J = K\ln\frac{C_g}{C_0^s}$

$$C_g = 292 - 3\times4 = 292 - 12 = 280\ kg/m^3$$

$$J = 10^{-5}\ln\frac{280}{10} = 3.33\times10^{-5}\frac{m^3}{m^2.s}$$

$$\beta = \frac{\kappa_{Cu} C_{Cu} \exp\left(-\frac{z_{Cu} e\psi}{K_B T}\right)}{1 + \kappa_{Cu} C_{Cu} \exp\left(-\frac{z_{Cu} e\psi}{K_B T}\right) + \kappa_{Na} C_{Na} \exp\left(-\frac{z_{Na} e\psi}{K_B T}\right)}$$

$$= \frac{71 \times 4 \times \exp\left(-\frac{2 \times 11 \times 10^{-3} \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 300}\right)}{1 + 71 \times 4 \times \exp\left(-\frac{2 \times 11 \times 10^{-3} \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 300}\right) + 0.06 \times 20 \times \exp\left(-\frac{1 \times 11 \times 10^{-3} \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 300}\right)}$$

$$= \frac{284 \times \exp(-0.85)}{1 + 284 \times \exp(-0.85) + 1.2 \exp(-0.425)}$$

$$= \frac{284 \times 0.427}{1 + 284 \times 0.427 + 0.78} = 0.985$$

$$\beta = 2\left(\frac{C_{01} - C_{p1}}{C_0^s - CMC}\right)$$

$$0.985 = 2\frac{\left(4 - C_{p1}\right)}{\left(10 - 2.3\right)}$$

$$3.79 = 4 - C_{p1}$$

$$C_{p1} = 0.21\ kg/m^3$$

$$R_0 = 1 - \frac{0.21}{4} = 94.75\%$$

3) Design of a cloud point extractor:

Cloud point extraction of a dye is carried out using TX-100 surfactant at 70^0C. Dye concentration has to be reduced to $3.8*10^{-6}$ (M) from $4*10^{-4}$ (M) concentration. Find the concentration of surfactant TX-100 required for this purpose?

Data: Solubilization isotherm of dye in surfactant micelle, $q_e = \frac{mnC_e}{1 + nC_e}$

C_e = molar concentration of dye in final dilute solution.

$m = 2.4 \times 10^{-1} - 5.9 \times 10^{-3} T + 3.7 \times 10^{-5} T^2$, T in ^0C

$$n = -5\times10^{4} + 1.3\times10^{3}T - 5.9T^{2}$$

$$a = P + QT \qquad\qquad b = R + ST$$

Where, $P = 5.9 - 200C_0 - 1.9\times10^{-8}C_0^{-2}$; $\qquad Q = -0.05$

$$R = 0.39 + 6.9C_0 + 4\times10^{-9}C_0^{-2}; \qquad S = 0.09$$

Here, C_0 = Molar concentration of dye in feed

Solution:

C_s = Surfactant concentration required

$$= \frac{\left[C_0 - \left(1 - aC_s^b\right)C_e\right]\left[1 + nC_e\right]}{mnC_e}$$

$$T = 70^{0}C$$

$$m = 0.24 - 5.9\times10^{-3}\left(70\right) + 3.7\times10^{-5}\left(70^2\right)$$

$$= 8.3\times10^{-3}$$

$$n = -5\times10^{4} + 1.3\times10^{3}\times70 - 5.9\times\left(70^2\right)$$

$$= 1.21\times10^{4}$$

$$C_0 = 4\times10^{-4} \text{ (M)}$$

$$P = 5.9 - 200\times4\times10^{-4} - \frac{1.9\times10^{-8}}{\left(4\times10^{-4}\right)^2} = 5.7$$

$$a = 5.7 - 0.05\times70\times = 2.2$$

$$R = 0.39 + 6.9\times4\times10^{-4} + \frac{4\times10^{-9}}{\left(4\times10^{-4}\right)^2} = 0.418$$

$$b = 0.418 + 0.09\times70 = 6.718$$

$$C_s = \frac{\left[4\times10^{-4} - \left(1 - 2.2C_s^{6.718}\right)3.8\times10^{-6}\right]\left[1 + 1.21\times10^{4}\times3.8\times10^{-6}\right]}{8.3\times10^{-3}\times1.21\times10^{4}\times3.8\times10^{-6}}$$

$$= \left(3.96\times10^{-4} + 8.36\times10^{-6}C_s^{6.718}\right)2740.8$$

$$C_s \simeq 1.085 \text{ (M)}$$

4) A dye is removed from $3*10^{-4}$ *(M)* concentration using cloud point extraction with *0.05 (M)* TX-114 solution at 40^0C. Find out the dye concentration in dilute phase?

Solution:

$$C_s = \frac{\left[C_0 - \left(1 - aC_s^b\right)C_e\right]\left[1 + nC_e\right]}{mnC_e}$$

Dye- TX 114:

$$m = 0.47 - 1.9\times10^{-2}T + 2.1\times10^{-4}T^2$$

$$n = -1.6\times10^{5} + 5.9\times10^{3}T - 37.4T^2$$

$$a = P - 0.11T; \qquad b = R + 0.09T$$

$$P = 9.4 - 8\times10^{3}C_0 + \frac{1.8\times10^{-8}}{C_0^2}$$

$$R = 4.2\times10^{-1} - 2.4\times10^{3}C_0 + \frac{2.2\times10^{-9}}{C_0^2}$$

Given that, $P = 7.2; \qquad R = -0.276$

At $T = 40^0C$, $m = 0.046$

$n = 16160$

Given that, $C_0 = 3*10^{-4}$ (M)

So, $a = 7.2 - 0.11\times40 = 2.8$

$b = -0.276 + 0.09\times40 = 3.324$

Given as, $C_s = 5*10^{-2}$ (M)

So, $$5\times10^{-2} = \frac{\left[3\times10^{-4} - \left(1 - 2.8\times\left(5\times10^{-2}\right)^{3.324}\right)C_e\right]\left[1 + 16160C_e\right]}{0.046\times16160\times C_e}$$

$$37.17C_e = \left(3\times10^{-4} - C_e\right)\left(1 + 16160C_e\right)$$

$$37.17C_e = 3\times10^{-4} - C_e + 4.85C_e - 16160C_e^2$$

$$16160C_e^2 + 33.32C_e - 3\times10^{-4} = 0$$

$$C_e = \frac{-33.32 + \sqrt{33.32^2 + 4\times16160\times3\times10^{-4}}}{2\times16160}$$

$$= 8.96\times10^{-6} \text{ (M)}$$

5. Phenol is removed in an emulsion liquid membrane system from its initial concentration of 10 *ppm*. The volume of external phase (sulfuric acid) is 50 *ml* and that od internal phase (sodium hydroxide) is 10 *ml*. The internal reagent concentration initially was 6 *ppm*. Breakage coefficient is $1*10^{-5}\ s^{-1}$ and $\kappa_A^0 = 10^{-3}\ ml/s$. Find phenol concentration in the bulk phase after 5 hours?

Solution:

$$C_{e_A} = C_{e_{A0}} e^{-\alpha t} + \frac{\beta}{\alpha}\left(1 - e^{-\alpha t}\right)$$

$$\alpha = \frac{\kappa_A^0}{V_e^0} + \phi; \qquad \beta = \phi\left(C_{e_{A0}} + \frac{V_i^0}{V_e^0} C_{i_{B0}}\right)$$

ϕ = Breakage coefficient $= 1.0\times10^{-5}\ s^{-1}$

A= Phenol; $C_{e_{A0}}$ = initial phenol concentration $= 10\ ppm$

V_e^0 = Volume of external phase = 50 *ml*

V_i^0 = Volume of internal phase = 10 *ml*

$\kappa_A^0 = 10^{-3}\ ml/s$

$$\alpha = \frac{10^{-3}}{50} + 1.0\times10^{-5} = 3\times10^{-5}\ s^{-1}$$

$$\beta = 1.0\times10^{-5}\left(10 + \frac{10}{50}\times6\right) = 11.2\times10^{-5}$$

$$C_{e_A} = 10e^{-3\times10^{-5}t} + \frac{11.2\times10^{-5}}{3\times10^{-5}}\left(1 - e^{-3\times10^{-5}t}\right)$$

$$= 10e^{-3\times10^{-5}t} + 3.73\left(1 - e^{-3\times10^{-5}t}\right)$$

$$= 3.73 + 6.27e^{-3\times10^{-5}t}$$

$$t = 5\ hrs = 5\times3600\ s$$

$$C_{e_A} = 7.38\ ppm$$

References

1. A. K. Agrawal, C. Das and S. De, “Modeling of extraction of dyes and their mixtures from aqueous solution using emulsion liquid membrane”, Journal of Membrane Science, 360 (2010) 190-201.
2. C. Das, S. DasGupta and S. De, “Prediction of permeate flux and counterion binding during cross flow micellar enhanced ultrafiltration”, Journal of Colloids & Surfaces A: Physicochemical Aspects, 318 (2008) 125-133.
3. C. Das, S. DasGupta and S. De, ”Simultaneous separation of mixture of metal ions and aromatic alcohol using cross flow micellar enhanced ultrafiltration and recovery of surfactant”, accepted in Separation Science and Technology, 43(1) (2008) 71-92.
4. M. K. Purkait, S. DasGupta, S. De," Performance of TX-100 and TX-114 for the separation of chrysoidine dye using cloud point extraction ", Journal of Hazardous Materials, 137, 827-835, 2006.
5. M. K. Purkait, S. DasGupta, S. De," Micellar enhanced ultrafiltration of eosin dye using hexadecyl pyridinium chloride ", Journal of Hazardous Materials, 136, 972-977, 2006.
6. M. K. Purkait, S. DasGupta, S. De," Determination of design parameters for the cloud point extraction of congo red and eosin dyes using TX-100 ", Separation & Purification Technology, 51, 137-142, 2006.

7. M. K. Purkait, S. Banerjee, S. Mewara, S. DasGupta, S. De, "Cloud point extraction of toxic eosin dye using Triton X-100 as nonionic surfactant", Water Research, 39, 3885-3890, 2005.
8. M. K. Purkait, S. DasGupta, S. De, "Simultaneous separation of two oxyanions from their mixture using micellar enhanced ultrafiltration", Separation Science & Technology, 40, 1439-1460, 2005.
9. M. K. Purkait, S. DasGupta, S. De, "Micellar enhanced ultrafiltration of phenolic derivatives from their mixture", Journal of Colloid & Interface Science, 285, 395-402, 2005.
10. M. K. Purkait, S. DasGupta and S. De, "Separation of aromatic alcohols using micellar enhanced ultrafiltration and recovery of surfactant", Journal of Membrane Science, 250, 47-59, 2005.
11. M. K. Purkait, S. S. Vijay, S. DasGupta, S. De, "Separation of congo red by surfactant mediated cloud point extraction", Dyes & Pigments, 63, 151-159, 2004.
12. M. K. Purkait, S. DasGupta and S. De, "Micellar enhanced ultrafiltration in phenolic derivatives", Research & Innovations, Issue 13, 23-28, 2004.
13. M.K.Purkait, S DasGupta, S. De, "Resistance in series model for micellar enhanced ultrafiltration of eosin dye" Journal of Colloid & Interface Science, 270, 496-506, 2004.

14. M.K.Purkait, S DasGupta, S. De," Removal of dye from wastewater using micellar enhanced ultrafiltration and regeneration of surfactant", Separation & Purification Technology, 37, 81-92, 2004.