CHAPTER: 7.0

Effect of different surfactants to remove Hexavalent Chromium by Emulsion Liquid Membrane

7.1 Introduction
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7.1 Introduction:

In ELM process, the membrane phase usually contains surfactants, additives and a base material that is a solvent for all the other ingredients. The surfactants and additives are chosen to enhance the stability, selectivity and permeability of the membrane. Surfactant is an abbreviation for surface active agent, which literally means active at a surface. A surfactant is composed of hydrophilic head and hydrophobic tail. They show a tendency to adsorb at liquid/solid, liquid/liquid and air/liquid interfaces. Above the critical micelle concentration (CMC), the surfactant monomers form a spherical or cylindrical aggregate, called a micelle. Heavy metal ions bind electrostatically on the surface of opposite-charged micelles. In general, the addition of surfactants helps lower the surface tension of the system making it easier to form the foam but this outcome does not, in itself, make the foam more stable (in fact, it does the reverse). The addition of surfactant also retards the loss of liquid from the lamellae through the Gibb-Marangoni effect which does make the foam more stable. The dependence of foam stability on surfactant depends upon a number of factors, including the chemical structure of the surfactant(s), methods of incorporation of surfactant into the interface, surfactant concentration, etc. The most widely used anionic groups are sulfate (–SO\(_4^–\)), sulfonate (–SO\(_3^–\)) and carboxylate (–CO\(_2^–\)), while the most widely used cationic groups are the quaternary ammonium groups (–NR\(_4^+\)), where R can be –CH\(_3\), –(CH\(_2\))\(_n\)CH\(_3\), or a variety of other alkyl groups[1-10].

Ionic surfactants are generally used as electrostatic stabilizing agents. By adsorbing ionic surfactant onto an oppositely charged surface in sufficient quantity that a bilayer of molecules is formed due to hydrocarbon chain interactions between adjacent molecules, a layer of charged hydrophilic groups will be extending into the aqueous solution. Since these charges are opposite in sign to the surface charge, this procedure has the effect of reversing the sign of the electrical potential at some distance prior to the second layer of adsorbed ionic head groups. As a result, the long range electrostatic forces between adjacent particles will be repulsive due to the repulsion of like charges opposite in sign from the surface charge. Nonionic surfactants have no charge associated with them. Nonionic surfactants will not provide a significant repulsive barrier to agglomeration. For a nonionic surfactant, increasing the hydrocarbon chain length results in an increased intermolecular hydrophobic interaction in the adsorbed surfactant and thus an increase in the foam film’s. They must form a bilayer if adsorbed on a hydrophilic surface in an aqueous
solution, similar to ionic surfactants. By contrast, increasing the relative size of the hydrophilic group causes a decrease in the hydrophobic interaction, resulting in less foam stability. In case of cationic surfactants, the same effect of hydrocarbon chain length on film stability has also been observed [11-23].

7.2 Experimental Procedure

7.2.1 Reagent:

Summary of experimental conditions for ELMs batch tests are given in Table 1. For the study of transport of chromium(VI) ions through emulsion liquid membrane, potassium dichromate (99.99% pure, Merck make) salt is used. Commercial kerosene of specific gravity 0.798 and boiling point range between 145 to 250 °C is used as a membrane phase. The extractant used is Aliquat 336 having 98.5% purity, n-heptane as a diluent and stabilizer for the membrane phase. Prior to the extraction reaction, the extractant (Aliquat 336), which is commercially available in chloride form, was converted to the hydroxide form. Sodium dodecyl sulphate (BDH, England), Cityl Pyridinium Chloride (CPC Loba Chemicals purity: 98%) and Sorbitan monooleate (SPAN 80 LOBO Chemicals, CAS No. 1338-43-8) was used as anionic, cationic and non ionic surfactant respectively. Earlier it was observed that the emulsion stability was improved with the increase in surfactant concentration. Earlier experiments proved that increasing concentration of surfactant from 2% to 4% increases the stability of the liquid membrane which leads to the decrease in the breakup rate, hence the extraction degree of chromium (VI) was also increased. However, increasing surfactant concentration from4% to 6% increased emulsion stability but the mass transfer was adversely reduced at 6%. Because, excessive surfactant tends to increase the resistance at the interface and this can be attributed to the increase in viscosity of the membrane phase.
Table 7.1: Summary of experimental conditions for ELMs batch tests

<table>
<thead>
<tr>
<th>Membrane Phase (O):</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>: 25 ml</td>
</tr>
<tr>
<td>Carrier Aliquat 336</td>
<td>:10% V/V</td>
</tr>
<tr>
<td>Surfactant</td>
<td>: 5% V/V</td>
</tr>
<tr>
<td>(Span 80, CPC &amp; SDS)</td>
<td>: 5%, V/V</td>
</tr>
<tr>
<td>Kerosene</td>
<td>: 80%.V/V</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Exterior phase (W):</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>: 200mL</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>: 50 ppm</td>
</tr>
<tr>
<td>pH</td>
<td>: 2–6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Interior phase (W):</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>25mL</td>
</tr>
<tr>
<td>Base conc.</td>
<td>1N (NaOH)</td>
</tr>
</tbody>
</table>

**For preparation of aqueous solutions double distilled water has been used. The ultra-pure deionised (DI) water, used in this study was obtained from Arium 611DI ultrapure water system (make: Sartorius A.G., Göttingen, Germany). The feed for DI water system was distilled water prepared by reverse osmosis (RO) system (Model: Arium 61315, make: Sartorius AG, Göttingen, Germany).**

Table 7.2: Characteristics of surfactants reviewed [23]

<table>
<thead>
<tr>
<th>Surfactant Name</th>
<th>Structural Formula</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetylpyridinium chloride</td>
<td>C_{16} H_{33} N(C_{2} H_{2})_{2} CHCl</td>
<td>CPC</td>
</tr>
<tr>
<td>Sodium dodecylsulphate</td>
<td>C_{12} H_{25} SO_{4}Na</td>
<td>SDS</td>
</tr>
<tr>
<td>Sorbiton monooleate</td>
<td>C_{24}H_{44}O_{6}</td>
<td>SPAN 80</td>
</tr>
</tbody>
</table>

![Fig.7.1: Structure of Span 80 (Sorbitan monooleate)[23]](image)
7.2.2 Membrane preparation and procedure:

Emulsion was prepared by emulsifying aqueous solution of acid (strip phase) with an organic phase (membrane phase). The membrane consisted of fixed proportions of, diluent (n-heptane), carriers (Aliquote 336) and varying concentration of surfactant, i.e. Span 80, CPC and SDS, in different pH. The pH of the membrane was maintained by adding acetic acid and sodium acetate buffer solution. A feed solution contained 50 ppm chromium (Cr^{+2}) was prepared with potassium di chromate. Same 200 ml feed (as external phase) was taken and mixed with 50 ml of membrane phase. The mixer was stirred at 100 % amplitude (frequency = 30000 hz) for 15 min using sonicator to form a uniform mixture. An excellent milky-white and stable emulsion was obtained. The emulsion was dispersed in feed phase containing Chromium(VI) ions from which chromium was to be extracted. 25 ml of 1 (N) NaOH solution was added as internal phase. Stirred the mixture again at 100% amplitude with help of sonicator. Samples of about 20 mL of mixture were withdrawn from the whole emulsified solution at different intervals of time and filtered through filter paper and collected the filtrate in a separating funnel. Collected the clear
aqueous phase from bottom of the separating funnel. Chromium concentration of bottom collected samples of aqueous phase, was analyzed by a spectrophotometer according to the standard methods [24].

7.3 Results and Discussion

7.3.1 Effect of Mixing speed:

When the W/O emulsion is dispersed by stirring in the continuous aqueous solution, the emulsion must be sufficiently stable in order to extract metal ions into the internal aqueous droplets. The emulsion breakdown will result in a lowering of extraction efficiency and loss of the extracted species. Three different amplitude, i.e. of sonocator were used to remove Cr(VI) from aqueous feed in presence of three different surfactants. Fig 7.2, is represented the results of removal efficiency of chromium from feed. Previous lab experiments confirmed, that 20 minutes was he best mixing time. In ELM separation the emulsion globules are stabilised by surfactants and the degree of enrichment for a target metal into a recovery phase is well known to be influenced by the stability of emulsions. The emulsion breakage decreases with the increase of the emulsification speed. An efficient emulsification gives a good dispersion as the internal phase drops into the membrane phase. The fact that these drops become smaller will take much more time to coalesce. This was conducive to good stability of the emulsion. In addition, the size of internal phase droplets is smaller at greater agitation intensity, creating a larger surface area for permeation and hence obtaining a higher fraction of recovery. The efficient speed was measured in terms of percentage of recovery of chromium.

7.3.2 Effect of pH

The extraction reaction in the feed solution plays an important role in the extraction of metal ion from the feed phase to the stripping phase. Therefore, the effect of pH in the feed solution on extraction percentage of chromium was studied in the pH range of 2.0 – 6.0. The pH of the feed solution was adjusted using acetic acid/sodium acetate buffer. Three different surfactants namely, Span-80, SDS and CPC of concentration 5% to membrane volume, were used at different pH to study the extraction efficiency. The results are plotted in Fig.7.3. At pH 6 the maximum removal of chromium was happened in presence of Span 80.
Fig. 7.3: Effect of mixing speed (Sonicator speed) on different Surfactants, Time = 20 minutes, pH= 6.0, carrier : 10% (V/V), temperature = 34 deg C.

Fig. 7.4: Effect of pH on different Surfactants, Time = 20 minutes, Mixing speed = 100% (30000 Hz), carrier : 10% (V/V), temperature = 34 deg C.
7.3.3 Effect of surfactant concentration

Surfactant concentration is an important factor as it directly affects the stability of ELM. Fig 7.4, Fig 7.5 & Fig 7.6 represents the variation of percentage extraction of chromium for various surfactant concentrations. As shown in Fig. 7.4, by increasing surfactant concentration, i.e. concentration of SPAN 80, from 1 to 5%, removal efficiency is increased while by increasing surfactant concentration from 5 to 7%, the removal efficiency is partly decreased. Removal efficiency is decreased steadily by adding more surfactant more than 7%. The figure also shows that the effect of surfactant concentration on removal efficiency has a marginal effect for the concentration range of 1–5 wt% with an offset of less than 8% in removal efficiency. Although it is not shown here, the results of other tests with different conditions also indicate the same trends, and it was found that the optimum concentration of surfactant is about 5 wt% of membrane phase. The effect of other two surfactants, i.e. SDA and CPC are not so appreciable.

7.3.4 Effect of Cr concentration in feed solution :

The effect of initial Cr (VI) concentration in the feed solution on the extent of extraction is shown in Fig. 7.7, using the optimum parameters (Table 7.3). The optimum conditions (Table 7.3) were obtained from the earlier experiments.

Table : 7.3 Optimum condition for extraction of Chromium

| Feed volume | 200 ml |
| Mixing Speed | 100 % amplitude of Sonicater ( 30000 hz) |
| pH of the Feed | 6.0 (maintained by Acetic acid & Sodium acetate buffer) |
| Surfactant | 5% V/V Span 80, SDS & CPC |
| Carrier | 10 % V/V Aliquote 336 |
Fig. 7.5: Effect of different concentration of Span 80 to remove Cr(VI) with time, Mixing speed, = 100 % (30000 Hz), carrier : 10% (V/V), temperature = 34 deg C

Fig. 7.6: Effect of different concentration of SDS to remove Cr(VI) with time, Mixing speed, = 100 % (30000 Hz), carrier : 10% (V/V), temperature = 34 deg C
Fig. 7.7: Effect of different concentration of CPC to remove Cr(VI) with time, Mixing speed, = 100 % (30000 Hz), carrier: 10% (V/V), temperature = 34 deg C

Fig. 7.8: Effect of different feed concentration with different Surfactants, Mixing speed, = 100 % (30000 Hz), carrier: 10% (V/V), temperature = 34 deg C
7.4 Conclusion

The removal of Chromium(VI) from its dilute aqueous solution through ELM is studied with respect to using different surfactants in different pH of the feed solution. Adjustment of the solution pH may also affect several factors in the surfactant system during separation. This is indicated the level of dissociation of surface groups, the degree of binding to micelles, and the overall ionic strength. The head-group charge present on ionic surfactants (here CPC & SDS) results in a more complicated adsorption process when compared to nonionic amphiphiles. Ionic surfactant adsorption is particularly sensitive to the interactions of counter- and co-ions with the charged groups of the surface. If the affinity of co-ions for surface groups is sufficiently high, then the co-ions can compete for adsorption sites at the surface. It is observed that the non ionic surfactant like Span 80 (5% volume) is the most suitable surfactant to form a stable emulsion membrane at pH 6.0. The experimental results obtained also showed the validity / feasibility of the ELM method for the treatment of wastewaters contaminated with chromium (VI) ions. Further studies can be done on the effect of different concentration of surfactant to separate chromium by ELM.
7.5 Reference