CHAPTER 3

MATERIALS & METHODS
Chapter 3
Materials & Methods

Introduction

This chapter is divided into seven sections. Section 3.1 deals with the materials and chemicals used in the present study. Section 3.2 details the methods for characterization of fatty alcohols and mono alkyl phosphates. Section 3.3 contains the methods used for the evaluation of performance properties. Section 3.4 illustrates the techniques used to determine the surface active properties of the surfactants. Section 3.5 depicts the assembly used to carry out the reaction and Section 3.6 demonstrates the experimental procedures used for preparing anionic phosphate gemini surfactants via phosphorylation. Section 3.7 describes the instrumental techniques employed for product characterization.

3.1 Materials / Chemicals

The various higher fatty alcohols used for the synthesis of anionic phosphate gemini surfactants were tetradecanol, hexadecanol and octadecanol. The \( \alpha-\omega \) alkyl dibromides used for the synthesis of anionic phosphate gemini surfactants were 1, 4 dibromo butane, 1, 6 dibromo hexane and 1, 8 dibromo octane.

3.1.1 Tetradecanol, hexadecanol and octadecanol: These fatty alcohols were of AR grade obtained from Sisco Research Lab, Mumbai.
3.1.2 Pyrophosphoric acid: Pyrophosphoric acid was of AR grade supplied by S.K Traders, Indore, India made by Fluka, Switzerland.

3.1.3 α-ω alkyl dibromides: 1, 4 dibromo butane (1,4 DBB), 1,6 dibromo hexane 1,6 DBH) and 1, 8 dibromo octane (1,8 DBO) were α-ω alkyl dibromides and these were of AR grade obtained from Spectrochemials, Mumbai, India.

3.1.4 Tetra methyl ammonium hydroxide (TMAH): TMAH was of AR grade obtained from Merck, Mumbai, India.

Some other chemicals used for the synthesis of anionic phosphate gemini surfactants were of AR/GR grade obtained from various manufacturers/suppliers as detailed below:

<table>
<thead>
<tr>
<th>S.No</th>
<th>Chemical</th>
<th>Grade</th>
<th>Manufacturer/Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Toluene</td>
<td>AR</td>
<td>Merck</td>
</tr>
<tr>
<td>2.</td>
<td>Diethyl ether</td>
<td>AR</td>
<td>Merck</td>
</tr>
<tr>
<td>3.</td>
<td>Hexane</td>
<td>AR</td>
<td>Merck</td>
</tr>
<tr>
<td>4.</td>
<td>Methanol</td>
<td>AR</td>
<td>Merck</td>
</tr>
<tr>
<td>5.</td>
<td>Acetonitrile</td>
<td>GR</td>
<td>Merck</td>
</tr>
<tr>
<td>6.</td>
<td>Ethanol</td>
<td>AR</td>
<td>s.d Fine Chem</td>
</tr>
<tr>
<td>7.</td>
<td>Sodium hydroxide</td>
<td>AR</td>
<td>Merck</td>
</tr>
<tr>
<td>8.</td>
<td>Hydrochloric acid</td>
<td>AR</td>
<td>Merck</td>
</tr>
</tbody>
</table>

Chemicals used for the analysis of fatty alcohols and for the performance evaluation of anionic phosphate gemini surfactants were also of AR grade. The details of which is given hereunder:
3.1.5 Materials used for evaluation of physico-chemical properties:

Water used in the experiment was doubly distilled. All the chemicals employed in the present study were used without any purification. Three different fabric substrates were used for the study of wetting ability of anionic phosphate gemini surfactants. These substrates were 100% cotton, 100% polyester and 66/33 cotton/polyester procured from local market and were selected on the basis of their uses by large segment of population. The details of the manufacturer of selected fabrics are given below:

<table>
<thead>
<tr>
<th>S.No</th>
<th>Name of fabric</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>100% Cotton</td>
<td>DCM Mills</td>
</tr>
<tr>
<td>2.</td>
<td>100% Polyester</td>
<td>Mafatlal Fabrics</td>
</tr>
<tr>
<td>3.</td>
<td>66/33 Cotton/polyester (blend)</td>
<td>JCT Phagwara</td>
</tr>
</tbody>
</table>
3.2 Methods

3.2.1 Methods for characterization of fatty alcohols

The standard procedures as per BIS specifications were used for different analysis of fatty alcohols and pyrophosphoric acid. BIS: 548 (Part I), 1964 was used for the determination of acid value, saponification value, refractive index, iodine value and specific gravity.

a) Determination of acid value

The number of milligrams of potassium hydroxide required to neutralize the free acids present in one gram of the oil or fat under prescribed conditions. Acid values of fatty alcohols were determined as per BIS: 548 (Part I), 1964, pp 29-30.

Reagent:

i) Ethyl alcohol

Ninety-nine percent, rectified spirit neutral to phenolphthalein indicator

ii) Phenolphthalein indicator solution

iii) Standard aqueous sodium hydroxide solution

Procedure: Mix the sample thoroughly before weighing. A suitable quantity of the sample was weighed in a 200 ml conical flask. The weight of the sample taken for the test and the strength of the alkali used for the titration shall be such that the volume of alkali required for the titration does not exceed 10ml. 25 ml of freshly neutralized hot ethyl alcohol, and about one millilitre of phenolphthalein indicator solution was added. The
mixture was boiled for about five minutes; titrated while as hot as possible with standard aqueous alkali solution, shaking vigorously during titration.

**Calculation**

\[
\text{Acid value} = \frac{56.1 N V}{W}
\]

where,

\[V = \text{Volume in ml of standard sodium hydroxide solution used,}\]

\[N = \text{Normality of standard sodium hydroxide solution used.}\]

\[W = \text{Weight in g of the material taken for the test}\]

**b) Determination of specific gravity**

The ratio of the weight in air of a given volume of the material at 30 °C to the weight in air of an equal volume of water at 30°C is known as specific gravity. Specific gravity of fatty alcohols was determined as per BIS : 548 (Part 1), 1964, pp. 39-41.

**Apparatus:**

i) **Specific gravity bottle or pyknometer**

ii) **Thermometer**

**Procedure:** The empty specific gravity bottle was weighed accurately. The bottle was filled with the sample, holding the bottle on its side in such a manner as to prevent the entrapment of air bubble after removing the cap of the side arm and weighed. The weight of specific gravity bottle with water in an identical matter was taken.
Calculation:

Specific gravity at 30°C = \( \frac{A-B}{C-B} \)

where,

\[ A = \text{Weight in g of the specific gravity bottle with sample at 30°C.} \]

\[ B = \text{Weight in g of the empty specific gravity bottle, and} \]

\[ C = \text{Weight in g of the specific gravity bottle with water at 30°C.} \]

c) Determination of saponification value

The number of milligrams of potassium hydroxide required to saponify completely one gram of the oil or fat. Saponification value of fatty alcohols was determined as per BIS: 548 (Part I), 1964, pp. 50-52.

Reagent:

i) **Alcoholic potassium hydroxide solution**: Dissolve 35 to 40 g of potassium hydroxide in 20 ml of distilled water, and add sufficient aldehyde free rectified spirit to make up to 1000 ml.

ii) **Phenolphthalein indicator solution**

iii) **Standard hydrochloric acid**: Approximately 0.5 N

Procedure: The sample was melted, and then dried completely. The sample was mixed thoroughly, and weighed accurately by difference about 1.5 to 2.0 g of the sample in a standard joint conical flask. 25 ml of the alcoholic potassium hydroxide solution was added and the reflux air condenser was connected to the flask. The flask was heated on a water bath
or an electric hot plate for one hour. The above mixture was boiled gently but steadily until the sample is completely saponified as indicated by absence of any oily matter and appearance of clear solution. After the flask and condenser have cooled somewhat, the inside of the condenser was washed out with about 10 ml of hot ethyl alcohol. One millilitre of phenolphthalein indicator solution was added and titrated with standard hydrochloric acid. A blank determination was also conducted at the same time in identical manner.

Calculation

\[
\text{Saponification value} = \frac{56.1 \times (B-S) \times N}{W}
\]

where,

\[B = \text{Volume in ml of standard hydrochloric acid required for the blank},\]

\[S = \text{Volume in ml of standard hydrochloric acid required for the sample},\]

\[N = \text{Normality of the standard hydrochloric acid, and}\]

\[W = \text{Weight in g of the material taken for the test}.\]

d) Determination of refractive index

The ratio of the velocity of light in vacuum to the velocity of light in the oil or fat; more generally, it is expressed as the ratio between the sine of the angle of incidence to the sine of the angle of refraction when a ray of light of a known wavelength (usually 589.3 m\(\mu\), the mean of the D lines of sodium) passes from air into the oil or fat. Refractive index of fatty alcohols was determined as per BIS : 548 (Part I), 1964, p. 35.

Apparatus
i) **Refractometer**: In the present investigation Abbe’s refractometer was used for the determination of refractive index.

ii) **Light source**: Sun light

**Procedure**: The sample was melted, and filtered through a filter paper to remove any impurities and the last traces of moisture. The temperature of the refractometer was adjusted to 40.0 ± 0.10°C. The prism was cleaned and completely dried and then few drops of the sample were placed on the lower prism. The prism was closed tightly with the screw head, and allowed to stand for two minutes. The instrument was adjusted and the refractive index was determined.

**Temperature corrections**

\[ R = R' + K (T' - T) \]

where,

- \( R \) = The reading of the refractometer reduced to the specified temperature \( T^\circ \text{C} \),
- \( R' \) = The reading at \( T^\circ \text{C} \)
- \( K \) = Constant
- \( T' \) = The temperature at which the reading is taken,
- \( T \) = The specified temperature.

e) **Determination of hydroxyl value**
The number of milligrams of potassium hydroxide required to neutralize the acetic acid capable of combining by acetylation with one gram of the oil or fat. Hydroxyl values of fatty alcohols was determined as per BIS : 548 (Part I), pp.52-56.

Reagents

i) Pyridine: Refluxed with powdered barium oxide and distilled using the fractional distillation above 114°C.

ii) Acetic anhydride

iii) Acetylation reagent: Mix one volume of acetic anhydride and seven volumes of pyridine.

iv) Alcoholic sodium hydroxide solution: Prepare by dissolving sufficient aqueous caustic soda (60 percent w/v) in 95% alcohol to make a 0.30 to 0.35N solution. Remove the precipitated carbonate by filtering.

The solution should be standardized against standard acid in the presence of phenolphthalein before use. The solution remains colourless for a long time if kept below 25°C.

v) Normal butyl alcohol

vi) Phenolphthalein

Apparatus

A round bottomed acetylation flask made of glass of capacity 150 to 200 ml with a 100 cm ground- in air condenser tube.

Procedure:
Weigh accurately 0.5 to 3.0 g of fat in the acetylation flask. Add 5 ml of the pyridine – acetic anhydride mixture. Before attaching the condenser, moisten the neck of the flask with pyridine to act as a seal, and make sure that the seal is maintained during acetylation. Mix the sample and the acetylation agent by shaking well. Add one or two small pieces of pumice, and boil the contents of the flask gently during 60 minutes, maintaining the boiling so that the vapour rises no higher than the bottom end of the condenser. Cool the flask to about 50°C with a rotatory motion to assist in washing the condenser tube, and add 5 ml of distilled water from the top of the condenser. Shake the mixture well, and then boil it gently for 5 to 10 minutes, shaking the flask two or three times during the boiling. After cooling the flask and the contents to room temperature and before detaching the condenser, wash the condenser with 30 ml of butyl alcohol. Detach the condenser and wash the neck and mouth of the flask and the tip of the condenser with a further 20 ml butyl alcohol and then if the contents of the flask are not homogenous, add butyl alcohol until they become homogenous. Titrate the free acetic acid with carbonate-free 0.35N sodium hydroxide solution, in the presence of a few drops of phenolphthalein as indicator.

Carry out the same series of operations with 5 ml of pyridine – acetic anhydride mixture alone, also with a corresponding weight of the sample plus 5 ml of pyridine.

**Calculation:**

\[
\text{Hydroxyl value} = \frac{56.1NY}{W}
\]

where,

\[
N = \text{Normality of sodium hydroxide solution};
\]

\[
Y = \text{Volume of sodium hydroxide solution in ml correspond to the amount of acetylated sample formed}
\]
\[ a = V \text{olume in ml of sodium hydroxide solution required with pyridine-acetic anhydride.} \]

\[ b = V \text{olume in ml of sodium hydroxide solution required with sample and pyridine.} \]

\[ c = V \text{olume in ml of sodium hydroxide solution required with sample, pyridine and acetic anhydride.} \]

\[ W = W \text{eight in g of sample for test} \]

**f) Determination of iodine value**

The sample was weighed accurately into 500ml iodine value flask. The weighed sample was dissolved in 25 ml carbon tetrachloride. Then 25 ml of wijs solution (Iodine monochloride in glacial acetic acid) was added and glass stopper was replaced after wetting it with potassium iodide solution (freshly prepared by dissolving 10 gm potassium iodide, free from potassium iodate, in 90 ml of water). The flask was swirled and allowed to stand in dark for about 45 minutes. After taking out the flask, 15 ml of potassium iodide and 100ml of distilled water was added, rinsing in the stopper also. The iodine, which liberated, was titrated against standard sodium thiosulphate solution until the colour of the solution was straw yellow. 1 ml of (1%) starch solution was added as an indicator at this stage. The titration was continued until the blue colour formed on addition of starch disappeared after thorough shaking with the stopper on. A blank determination was also made simultaneously under similar conditions and the iodine value of the sample was calculated using the following relationship:

\[ \text{Iodine value} = 12.69 \times \frac{N \times (B-S)}{W} \]

where,
N = Normality of sodium thiosulphate
B = Volume of standard sodium thiosulphate solution (in ml) used in blank determination
S = Volume of standard sodium thiosulphate solution (in ml) used with sample
W = Weight of the sample (in g)

3.2.2 Methods for characterization of mono alkyl phosphates and anionic phosphate gemini surfactants

a) Determination of anionic matter

The anionic matter of anionic phosphate gemini surfactants was determined as per IS: 548 (Part II), 1964, pp35-38.

Apparatus

i) Volumetric flasks: 1000, 500, & 250ml.
ii) Stoppered graduated cylinder: 100ml.
iii) Burette: 50 ml.
iv) Pipette: 10 ml.

Reagents

i) Chloroform

ii) Standard sodium lauryl sulphate solution: (0.004 M)
Weigh to the nearest 1 mg, between 1.14 and 1.16g of sodium lauryl sulphate and dissolved in 200 ml of water. Transfer to a ground glass- stoppered 1 litre one mark volumetric flask and dilute to the mark with water.

iii) **Standard benzethonium chloride solution:** Hymine solution of (0.004M) was procured from market.

iv) **Methylene blue solution (0.005%):** 0.05 g of methylene blue, 50 gm of sodium sulfate and 6.8 ml of concentrated sulfuric acid were dissolved in water and the solution was made up to volume of 1 litre with water.

v) **Synthesized anionic gemini surfactant solution (0.004M):** Adequate quantity of synthesized anionic gemini surfactant was weighed and dissolved in water and then the solution was made up to 250 ml using distilled water.

**Procedure**

a) **Standardization of sodium lauryl sulphate solution:** Pipette out 10 ml of benzethonium chloride solution in a 100 ml graduated cylinder provided with a glass stopper. 15 ml of chloroform and 25 ml of methylene blue solution were added to the cylinder and shaked well. The lower chloroform layer shall be coloured (blue).

From the burette sodium lauryl sulphate solution was added slowly; initially in portions of 0.2 ml. After each addition, the cylinder was stoppered, shaked well and allowed the phase to separate. Initially the chloroform phase will be coloured blue. Towards the end, the colour would start migrating to the aqueous layer. The reading at which the colour intensity in both the phase is the same was noted, when viewed under standard conditions of light.
Calculate the molarity of sodium lauryl sulphate (SLS) solution as follows:

\[
\text{Molarity of SLS (T_2)} = \frac{10 \times T_1}{V_1}
\]

where,

\[T_1 = \text{Molarity of hymine solution (i.e. 0.004M)}\]

\[V_1 = \text{Volume of SLS solution added}\]

b) **Determination anionic matter in anionic phosphate gemini surfactant:** Pipette 10 ml of sample solution and transferred into 100 ml graduated cylinder provided with a glass stopper. Add 15 ml of chloroform and 25 ml of methylene blue reagents to the cylinder and shake well. The chloroform layer shall colored blue.

Benzethonium chloride solution was slowly added from the burette, initially in portion of 0.2 ml. After each addition, the cylinder was stoppered and allowed the phases to separate. Initially, the chloroform phase was blue in colour. Towards the end point the colour would start migrating to the aqueous layer. Reading was noted when the color intensity in both the phases was the same when viewed under standard conditions of light.

**Calculation**

Anionic active matter, percent by mass = \(326 \times V_2 \times T_2 \times 5/M_2\)

where,

\[V_2 = \text{Volume of benzethonium chloride solution,}\]

\[T_2 = \text{Molarity of benzethonium chloride solution,}\]

\[M_2 = \text{Mass in gram of sample taken,}\]
326 = Molecular mass of the alkyl benzene sulfonic acid taken for calculation.

**b) Determination of melting point**

Melting point was determined with the help of melting point apparatus. A small quantity of finely powdered compound was taken in capillary tube closed at one end. The compound melts at a certain temperature and becomes almost transparent and this temperature was recorded as melting point.

**3.3. Methods used for evaluation of physico-chemical properties**

Foaming stability, emulsification ability, dispersing power and solubility was determined. Wetting ability was evaluated on different types of fabric.

**Foaming stability:** The foaming properties were measured at 0.1% wt solution of surfactants (Ahmed et al., 2002, and Ahmed, 2004). The foaming power of 0.1% solution was determined by pouring the surfactants into 100 ml stoppered measuring cylinder and whipping with a perforated plunger, giving 30 constant vigorous strokes by hand. The volume of the foam produced was read immediately and after 5 minutes.

**Emulsion stability:** Emulsion stability determination was done from 10 ml of 20 mmol aqueous solution of the surfactant and 5 ml toluene at 40°C. The emulsion stability was determined as the time of separation of water (9 ml) from the emulsion layer (Takeshi, 1970).
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Dispersing power: The dispersing power of anionic phosphate bisphosphodiester surfactants was determined according to BIS: 5785, (Part I) 1970. pp3-6. Take a 250 ml graduated cylinder. Weigh 4 g of carbon black and transfer it to the cylinder. Add 5 ml of white oil to it and also 40 ml of 2.5 per cent solution of the surface active agent. Make up the volume to 200 ml by adding more water. Stopper the cylinder and hold it upright and tilt in the clock wise direction to invert with stopper down and restore back in the same way. Repeat the procedure 10 times and keep the cylinder stationary without disturbing the contents. After a period of two hour pipette out exactly 5 ml of solution from the centre of each cylinder and transfer each aliquot portion to a previously tared Petri dish. Evaporate the solution on the water bath and dry the residue at 105°C to 110°C to constant weight.

Calculations

\[ C = \frac{W - D}{4000} \]

where,

\( C \) = percentage of the solid dispersed

\( W \) = weight in mg of the residue

\( D \) = weight in mg of surface active agent present in 5 ml of the solution of surface active agent when dried at 105°C to 110°C to constant weight.

Solubility: 0.1 g surfactants were placed in a test tube, to which then 5 ml solvent was added. The test tube was heated on a water bath. The system was stirred and the results were recorded (Zhina et al., 2008).
**Wetting ability:** Wetting time was determined by immersing a sample of fabric (4×4) in 0.1% aqueous solution of surfactant at 25°C. The time was recorded from the moment fabric was put into the solution until the moment it started going down (Cohen and Rosen, 1981).

### 3.4. Methods used for evaluation of surface active properties

**Surface Tension:** Surface tension was measured with DCAT tensiometer using 0.1% weight solution. The measurement of the surface tension was done with a Whilmey plate, made of platinum–iridium. To measure the surface tension, the DCAT first detects the surface of test liquid by moving the sample vessel with the liquid up until the balance detects a weight difference. This position of this stage was kept at the position where the plate meets the surface. The vessel moves further up. The stage moves down to the stored position of the surface and waits until the stop criteria for the surface tension is reached.

**Interfacial tension:** Interfacial tension was measured with a DCAT tensiometer using 0.1% weight solution. Whilmey plate was used to determine the interfacial tension. The determination of interfacial tension consist three steps. In the first step buoyancy of the probe in the liquid with lower density oil was determined. The second step carried the measurement of surface tension of the liquid with surfactant solution. The third step involves detection of interfacial tensions between the two immiscible liquids.

**Critical micelle concentration:** Conductivity measurements were carried out using a Decibel direct reading conductivity meter. The conductivity cell was calibrated with KCl
solutions in the appropriate concentration range. A concentrated surfactant solution (~10-20 times the critical micelle concentration) was progressively added to 25 ml of water-organic solvent medium in a thermostat container (having a temperature accuracy of ±0.01°C) using a micropipette. After ensuring thorough mixing and temperature equilibration of 300-320 K, the specific conductance (k) was measured (Deepti et al., 2009).

3.5 Description of experimental set up

3.5.1 Assembly for preparation of mono alkyl phosphates (MAP)

A round bottom flask was taken with a thermometer. The round bottom flask was kept on copper water bath filled with water. This system was fitted on magnetic stirrer having heater with regulator for stirring the contents of the flask as shown in Fig.1.

Figure 1  Assembly used for preparation of mono alkyl phosphates
3.5.2 Assembly for preparation of anionic phosphate gemini surfactants

Adequate quantity of mono alkyl phosphate and tetra methyl ammonium hydroxide was taken in standard joint flask. The requisite quantity of α-ω-alkyl dibromides were added to the flask. The reaction mixture was stirred on magnetic stirrer having heater with regulator for stirring the contents of the flask and then reaction mixture was refluxed on water bath. Water condenser was fitted to flask, and cotton wetted with water was kept at the mouth of condenser to avoid any escape of solvent vapours from reaction mixture as shown in Fig. 2a.

Figure 2a
Figure 2 a. Assembly used for preparation of phosphate gemini surfactants

Figure 2 b. Assembly used for decantation of solvent (acetonitrile)

3.6 Experimental procedures

The various experimental procedures used for the preparation of mono alkyl phosphate, phosphate gemini surfactants and conversion of gemini surfactants to their disodium salts are given hereunder.

3.6.1 Preparation of mono alkyl phosphates

Mono alkyl phosphates were synthesized according to the method described by Nelson and Toy (Nelson and Toy, 1963) but with slight modification. In the present work, the preparation of mono alkyl phosphates was carried out at 35°C instead of room temperature. Fatty
alcohol (60 mmol) and pyrophosphoric acid (60 mmol) were dissolved in 20 ml of toluene in an Erlenmeyer flask, after which the mixture was vigorously stirred for four days at 35°C temperature. The toluene was then evaporated and the viscous liquid produced was dissolved in 200 ml of ether. The ether solution was then added to 200 ml of 1.5 M NaOH solution to extract the product, after which the ethereal layer was separated from aqueous layer. The pH of the aqueous solution, 12.5 was then changed to 0.5 by the addition of concentrated hydrochloric acid. The mono alkyl phosphoric acid thus precipitated was extracted with 150 ml of ether. The ether was then evaporated and the crude product was vacuum distilled. Recrystallization from hexane gave white, crystalline product. Finally yield of mono alkyl phosphates was determined.

\[
\text{ROH} + \begin{array}{c} \text{O} \\
\text{\|} \\
\text{\|} \\
\text{OH} \\
\text{OH} \\
\end{array} \text{OH} \rightarrow \begin{array}{c} \text{OH} \\
\text{\|} \\
\text{\|} \\
\text{OH} \\
\text{OH} \\
\end{array} \text{P=O} + \text{H}_3\text{PO}_4 \\
\text{Toluene} \quad \text{35°C} \\
\]

3.6.2 Preparation of anionic phosphate gemini surfactants

Anionic phosphate gemini surfactants were synthesized according to the method described by Bauman (Bauman, 1974) but with slight modification and the preparation of this type of gemini surfactants was carried out at 35°C. Mono alkyl phosphate (5 mmol) was dissolved in a 25% methanolic tetra methyl ammonium hydroxide solution (containing exactly 10 mmol of tetra methyl ammonium hydroxide), and the methanol was removed in vacuo over a period of 20 minutes. The oily residue was taken up in acetonitrile (20-40 ml) and the \(\alpha-\omega\)-alkyl
dibromide (2.5 mmol) was added with stirring. The reaction mixture was refluxed for 4 hours at 35°C with the formation of a white precipitate. The solvent was then removed in vacuo, and the white solid was dissolved in water. The aqueous solution was acidified with HCl to a pH of < 0.5, and the white precipitate was collected on a buchner funnel and washed thoroughly with water. The filtrate was extracted once with diethyl ether, and phosphate gemini surfactants were crystallized from 99% ethanol, yielding the 14-s-14, 16-s-16 and 18-s-18 surfactant in 78-90 % yield.

\[
\begin{align*}
2 \text{RO-P=O} & \overset{\text{N(CH}_3)_4\text{OH}}{\rightarrow} \text{Br(CH}_2)_n\text{Br} \\
\text{OH} & \quad \text{O} \\
& \quad \text{O} \\
\text{OH} & \quad \text{OH}
\end{align*}
\]

3.6.3 Preparation of disodium salts of anionic phosphate gemini surfactants

It is the conversion of phosphate gemini surfactants to their disodium salts. The physico-chemical and surface active properties were studied with the disodium salts of synthesized gemini surfactants. These were prepared by dissolving phosphate gemini surfactants by refluxing in absolute ethanol with stirring and neutralizing the solution with an ethanolic NaOEt solution. The solution was refluxed for 15 minutes with stirring. After removal of ethanol in vacuo the white solid was crystallized from 99 % ethanol. These salts were collected on a buchner funnel, yielding the disodium salts in > 95% yield.
3.7 Instrumental analysis

Identification and characterization of unknown anionic often require the most sophisticated instrumental methods. The following instrumental techniques were used for this purpose:

3.7.1 FT-IR spectroscopy

Infra-red spectroscopy is an instrumental tool for verification of organic compounds. FT-IR spectra of MAP, anionic phosphate gemini surfactants and disodium salts of anionic phosphate gemini surfactants were obtained by using model vector 22, BRUKER, Germany. KBr pellets of samples were subjected to analysis at 20 scans. FT-IR work was done at IIT Kanpur, India.

3.7.2 FT-NMR spectroscopy

NMR spectroscopy especially $^1$H NMR is important for structure elucidations of surfactants. $^1$H NMR and $^{13}$C NMR spectra of MAP, anionic phosphate gemini surfactants and disodium salts of anionic phosphate gemini surfactants were obtained by using model JNMLA 500 FT-NMR multiproab system, JEOL company. The samples were injected in liquid state using CDCl$_3$ and deuterated chloroform as solvent. NMR spectroscopic analysis was also conducted at IIT Kanpur, India.
3.7.3 Elemental analysis

Elemental analysis of compounds was carried out with the help of Elemental-analyzer CE-440 EL. Elemental analysis was also carried out at IIT Kanpur, India.
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References


CHAPTER 4

TETRADECANOL BASED PHOSPHATE GEMINI SURFACTANTS