Quaternary Pyridinium Salts: A Review

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Abstract: Cationic surfactants are being used in various applications industrially and domestically for a long time. Pyridinium salts come under the category of cationic surfactants. These are unsaturated heterocyclic compounds having different functional groups present either on pyridine ring or at nitrogen atom. Initially, they were only considered as effective germicides. Several researches have been done for the modification of the properties of these salts, making them important for various applications. This paper reviews the types, synthesis, properties, and applications of quaternary pyridinium salts.

Key words: cationic surfactants, quaternary pyridinium salts, micellization, adsorption, solubilization, antimicrobial activity

1 INTRODUCTION

Cationic surfactants first became important when the commercial potential of their bacteriostatic properties was recognized by Dogmark in 1935. Today, cationic surface active agents with antibacterial properties continue to play an important role as sanitizing and antiseptic agents, as components in cosmetic formulations and as germicides and fungicides. These surfactants are an important ingredient used worldwide as rinse added fabric softeners. They are effective at reducing microfibril static and inter-fiber friction. These surfactants are used less for their wetting abilities than for their pronounced germicidal properties and their ability to adsorb on the surface of hair, skin, and fabrics. Cationic surfactants represent a broad family of commercial compounds whose position has been raised from specialty chemicals to bulk industrial chemicals, which are being used as antistatic agents, corrosion inhibitors, textile softeners, foam depressants, flotation chemicals, asphalt and petroleum additives.

Cationic surfactants are a class of compounds having at least one hydrophobic group (R) attached directly or indirectly to a positively charged nitrogen atom. The hydrophobic groups are derived either from long chain fatty acids or from long chain alcohols derived from petrochemicals. Esterquats are a special class of novel cationic surfactants which have gained great importance in recent years.

2 TYPES

2.1 Ring unsubstituted compounds

These compounds can be produced by reaction of pyridine with alkyl halide. They are represented in Fig. 1.
2.2 Ring substituted

In these salts the pyridine ring is substituted at either 2 or 4 or 3 position by different groups such as NH\textsubscript{2}, CH\textsubscript{3}, SR. They are depicted in Fig. 2.

2.3 N-Substituted

In these salts the nitrogen atom of the heterocyclic ring is attached to various groups such as ester, alkoxy, benzyl, alkoxymethyl. They are represented in Fig. 3.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Pyridinium Derivatives.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S. No.</td>
<td>Derivative</td>
</tr>
<tr>
<td>1.</td>
<td>N-Alkylpyridinium</td>
</tr>
<tr>
<td></td>
<td>compounds.</td>
</tr>
<tr>
<td>2.</td>
<td>L-Alkyl-N-alkylpyridinium</td>
</tr>
<tr>
<td>3.</td>
<td>L-(Thio-ether)-N-alkylpyridinium</td>
</tr>
<tr>
<td>No.</td>
<td>Type of Quaternary Pyridinium Salts</td>
</tr>
<tr>
<td>-----</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>4.</td>
<td>Ring-acylated-N-alkylpyridinium compounds.</td>
</tr>
<tr>
<td>5.</td>
<td>N-Aralkylpyridinium compounds.</td>
</tr>
<tr>
<td>6.</td>
<td>N-Alkoxyalkylpyridinium compounds.</td>
</tr>
<tr>
<td>7.</td>
<td>N-(2-Alkoxyethylpyridinium compounds.</td>
</tr>
<tr>
<td>8.</td>
<td>N-Alkoxybenzylpyridinium chlorides.</td>
</tr>
<tr>
<td>9.</td>
<td>Ester substituted pyridinium compounds.</td>
</tr>
<tr>
<td>10.</td>
<td>N-Amide substituted pyridinium compounds.</td>
</tr>
<tr>
<td>11.</td>
<td>N-Thioether substituted pyridinium compounds.</td>
</tr>
</tbody>
</table>
3.1 Synthesis of ring unsubstituted pyridinium salts

3.1.1 N-Alkylpyridinium compounds

These salts can be prepared by the reaction of pyridine with alkyl halide or alkyl sulfate at 150°C for 2 hrs in the absence of solvent. The reaction follows S_N2 reaction mechanism and is shown in Scheme 1.

3.1.2 Acylenethenethyl pyridinium chlorides

The synthesis of these compounds utilizes Friedel Craft’s reaction to acylate β-phenethyl chloride that produces an intermediate, which is then reacted with pyridine to yield quaternary salt. The reactions are shown in Scheme 2.

3.1.3 N-Thioether pyridinium compounds

These compounds are formed by the sequence of reactions as shown in Scheme 3.

3.2 Synthesis of ring substituted pyridinium salts

3.2.1 2 or 4-Alkyl ring substituted pyridinium compounds

These salts are prepared by the reaction of 2 or 4-alkyl pyridine with alkyl halide at 180°C in the absence of solvent for 3 hrs. The reaction is depicted in Scheme 4.

As the chain length of the alkyl group, which is substituted at the ring, is increased higher temperatures and longer reaction times are needed for quaternization.

3.2.2 3-Alkyl ring substituted pyridinium salts

The synthesis of 3-alkylpyridinium salts requires 3-alkylpyridine, which is prepared synthetically and then quaternized. Synthesis of 3-alkyl pyridine begins with nicotinic acid, which is obtained from coal tar or by oxidation of 3-methyl pyridine, which also occurs in tar. Nicotinic acid is converted to ester, followed by reaction with base to form a ketone and subsequent reduction provides scheme for producing homologs of 3-methyl pyridine. The synthesis of 3-alkyl pyridine and its quaternization is given in Scheme 5.

An excellent review on the synthesis of 3-substituted pyridinium salts has been presented by Juliusz Pernak.

3.2.3 4-Amino ring substituted pyridinium salts

The aminopyridinium salts can be prepared in two ways:

a. By three step process

In this process, the amino group of 4-aminopyridine is...
firstly protected, followed by the reaction with alkyl halide and then further, alkaline hydrolysis of the intermediate yields aminopyridinium salt. The reactions are shown in Scheme 6.

b. By one step process

The process is shown in Scheme 7 in which 4-aminopyridine is directly reacted with alkyl halide at 180°C followed by crystallization of the product.

Mariana Viorica et al. prepared alkylpyridinium chlorides, with high transfection efficiency, from pure pyrylium perchlorate salts. Usually, pyrylium perchlorates are reacted with primary amines in the presence of ethanol or dimethylformamide to yield N-alkylpyridinium perchlorates which are soluble in fairly polar solvents such as lower alcohols, acetone, chloroform, etc.

Astrid Roosjen et al. prepared pyridinium amphiphiles having biodegradable ester linkages between cationic headgroups and a polar lipid tail. Isonicotinoyl chloride hydrochloride was treated with 1 equivalent of the appropriate double chain alcohol, followed by the reaction with 2.1 equivalents of triethylamine in the presence of dichloromethane. The product formed was then quaternized with methyl iodide in the presence of acetone to yield pyridinium amphiphile.

Cationic polyelectrolyte surfactants were prepared with poly(ethylene oxide) side chain by simultaneous polymerization of 4-vinyl pyridine in the presence of monotosylates or bromides. The products formed were fully PEO-grafted poly(vinylpyridinium) salts with high molecular weight and were soluble in water and organic solvents. These polymers present good thermal stability and their decomposition takes place in two steps.

Juliusz Pernak et al. prepared 1-alkylthiomethyl-3-carbamoyl pyridinium chlorides by the reaction of nicotinoyl chloride hydrochloride with 1 equivalent of the appropriate double chain alcohol, followed by the reaction with 2.1 equivalents of triethylamine in the presence of dichloromethane. The product formed was then quaternized with methyl iodide in the presence of acetone to yield pyridinium amphiphile.

Scheme 5

Scheme 6

Scheme 7
namide or isonicotinamide with chloromethyl alkyl sulfide. Nicotinamide or isonicotinamide (0.04mol) in 50 ml of dimethylformamide was added to chloromethyl alkyl sulfide. The mixture was stirred at 50°C for 2 hours and 30 ml dry ethyl acetate was added to it, followed by the extraction of product with hot dry hexane. The product obtained, showed strong antimicrobial activity similar to that of benzalkonium chlorides12).

4 MICELLE FORMATION IN AQUEOUS PHASE

4.1 Thermodynamics of micellization

The main thermodynamic quantities relevant to micellization are the changes of free energy, enthalpy, volume, and specific heat upon micellization. The quantities can be obtained from the variation of cmc with pressure and temperature or from the concentration dependence of thermodynamic quantities such as osmotic coefficient, the apparent molal enthalpy, and the volume and heat capacity using thermodynamic methods. For alkylpyridinium salts, ΔH_m increases linearly with ΔS_m and both the quantities become more negative with increase in temperature and chain length. The values of ΔG_m and ΔC_p_m are always negative and the values of ΔV_m and ΔS_m are always positive for micellization at room temperature and atmospheric pressure and sign of ΔH_m depends on the nature of surfactant. The values of ΔG_m increases as one moves in the lyotropic series to larger and more polarizable anions in the counterion sequence F⁻, Cl⁻, Br⁻, I⁻13). The thermodynamic properties of micellization of dodecylpyridinium bromide for different temperatures and cmc values have been provided in Table 2.

Jan Jaap H. Nusselder et al. studied the thermodynamic properties for micelle formation of four 1-methyl-4-(C_12-alkyl) pyridinium iodides in H_2O at 25 and 95°C. It was observed that the enthalpy of micellization was slightly affected by the large increase in temperature and remained invariant with alkyl chain branching, whereas entropy and enthalpy were dramatically influenced15).

The effect of counterions on thermodynamic properties had been studied for various 1-3, 3, 4, 5, 6, 6-nonafluoro hexylpyridinium chloride, bromide, and iodide surfactants16). The trends of thermodynamic properties vs molality and the micellization parameters confirmed that the effect of counterions were reduced with respect to the hydrogenated analogs and however, were strong and inversely proportional to the radius of the hydrated counterion. The trends of the free energies had shown that the degree of counterion binding and the aggregation number increased with increase in the radius of the counterion.

The thermodynamic behavior of micellization of single

<table>
<thead>
<tr>
<th>Temp. (ºC)</th>
<th>CMC (molality)</th>
<th>ΔG_m (kcal mol⁻¹)</th>
<th>ΔH_m (kcal mol⁻¹)</th>
<th>ΔS_m (cal K⁻¹ mol⁻¹)</th>
<th>ΔS_m (cal K⁻¹ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>278.2</td>
<td>0.0115</td>
<td>-4.69</td>
<td>1.33</td>
<td>21.6</td>
<td>4.78</td>
</tr>
<tr>
<td>283.2</td>
<td>0.0112</td>
<td>-4.79</td>
<td>0.60</td>
<td>19.0</td>
<td>2.12</td>
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<tr>
<td>288.2</td>
<td>0.0110</td>
<td>-4.88</td>
<td>0.02</td>
<td>17.0</td>
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<tr>
<td>293.2</td>
<td>0.0112</td>
<td>-4.96</td>
<td>-0.54</td>
<td>15.0</td>
<td>-1.86</td>
</tr>
<tr>
<td>298.2</td>
<td>0.0114</td>
<td>-5.03</td>
<td>-0.97</td>
<td>13.6</td>
<td>-3.25</td>
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<tr>
<td>303.2</td>
<td>0.0118</td>
<td>-5.10</td>
<td>-1.31</td>
<td>12.5</td>
<td>-4.32</td>
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<tr>
<td>308.2</td>
<td>0.0122</td>
<td>-5.16</td>
<td>-1.57</td>
<td>11.6</td>
<td>-5.09</td>
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<td>313.2</td>
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<td>-5.21</td>
<td>-1.77</td>
<td>11.0</td>
<td>-5.64</td>
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<tr>
<td>318.2</td>
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<td>-5.26</td>
<td>-1.90</td>
<td>10.6</td>
<td>-5.99</td>
</tr>
<tr>
<td>323.2</td>
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<td>-5.32</td>
<td>-2.02</td>
<td>10.2</td>
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<td>328.2</td>
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<td>-2.11</td>
<td>9.93</td>
<td>-6.43</td>
</tr>
<tr>
<td>333.2</td>
<td>0.0154</td>
<td>-5.42</td>
<td>-2.21</td>
<td>9.64</td>
<td>-6.63</td>
</tr>
<tr>
<td>338.2</td>
<td>0.0163</td>
<td>-5.47</td>
<td>-2.34</td>
<td>9.23</td>
<td>-6.93</td>
</tr>
<tr>
<td>343.2</td>
<td>0.0172</td>
<td>-5.51</td>
<td>-2.54</td>
<td>8.67</td>
<td>-7.39</td>
</tr>
</tbody>
</table>

* Used in its broad sense. The actual process with which this table is concerned is the addition of a single surfactant ion to a micelle having the most probable aggregation number at cmc.
chain bearing one (P₁), two (P₂), and three (P₃) pyridinium headgroups surfactants had been investigated. Exothermic enthalpies were found to be more negative for cetylpyridinium bromide than for P₁ and it increased with a negative sign from P₁ to P₂ and decreased for P₃. The values of ΔS°m decreased with increase in number of headgroups, whereas the values of ΔG°m became less negative with increase in number of headgroups. These values show that micelle formation becomes less favorable as more headgroups are incorporated in the surfactant.

E. Fisicaro et al. compared the thermodynamic properties of aqueous micellar solutions of N-[1H,1H,2H,2H-perfluorocetyl] and decylpyridinium chloride with corresponding N-alkylpyridinium and N-alkylnicotinamide halides. The differences in thermodynamic parameters of micellization between fluorinated surfactants and their protiated counterparts confirmed the more pronounced hydrophobic character of the perfluoroalkane moiety, due to the positive free energy of transferring the -CF₂- group from the single headgroups surfactants had been investigated. Exothermic enthalpies were found to be increasing with decrease in partial charge in related surfactants. It was observed that the presence of alkyl groups on the pyridine ring lowered the aggregation numbers for decylpyridinium bromide were found to be increasing with decrease in partial charge in alkyl tails and it decreased with an increase in positive charge on the pyridinium ring atom to which decyl chain was attached.

4.2 Critical micelle concentration

The cornerstone of all surfactants research is the critical micelle concentration (cmc). The cmc is the concentration above which monomeric surfactant molecules abruptly assemble into aggregate called micelle. “Abruptly” is, of course a subjective term, if the micelles are small (e.g. 10 molecules) then the cmc may embody a concentration range, if the micelles are more useful size of 50-100 molecules, then the cmc is indeed sharply defined owing to the highly cooperative nature of the aggregation process. The cmc is useful as it reveals the propensity of surfactants to assemble in water. Longer the surfactants tail, the lower the cmc. Hydrophobic forces opposed by electrostatic repulsion among the ionic headgroups at the micelle surface, drive the micellization. Micelles are known to be disorganized assemblies with interior consisting of mobile hydrocarbon chains.

Generally for alkylpyridinium salts, the values of cmc and α (degree of ionization) decrease with increase in alkyl chain length. Surface tension and conductivity measurements for tetrahydroperfluoroalkylpyridinium chlorides had shown that the cmc’s of the perfluorinated surfactants were only about 0.02 times than that of hydrocarbons with the same carbon number. The micelle ionization degrees decreased with the increase in length of the alkyl chain. It has been observed that cmc values and degree of counterion dissociation of the micelles increase with the increase in number of pyridinium headgroups of the surfactants. The 50% reduction in the cmc values of aqueous solutions of cetylpyridinium chloride have been observed by the addition of certain organic compounds such as MeCN (methyl cyanide), urea, lauryl alcohol, Na lauryl sulfate to them.

Varadade et al. studied the effect of added salts, NaCl and NaBr on the micelles of cetylpyridinium chloride (C₆PyCl). Critical micelle concentration of C₆PyCl decreased with increase in salt concentration, whereas counterion dissociation increased with increase in temperature. The effect of NaBr on the micelles of C₆PyCl was more than that of NaCl because of the higher hydration of Cl[–] ions, which renders them less effective to neutralize the charge on the micellar surface.

The effect of temperature on the cmc values for N-alkylpyridinium halides containing a nonionic polar group at 4-position of pyridine ring had been investigated. It was noted that the change of anion from bromide to chloride, increased the temperature at which minimum cmc occurred. Unsaturation in the alkyl chains of alkylpyridinium surfactants affects the aggregation behavior of the surfactant molecules. The cmc values of the surfactant increase with the introduction of a double bond or a triple bond in the tail. Introduction of unsaturation also increases exothermic enthalpies.

4.3 Aggregation behavior

The number of surfactant monomers required to form a micelle is termed as aggregation number (N). The aggregation number (N) is affected by the nature of the counterions. For decylpyridinium micelles, the N value increase closely follows the lyotropic series, i.e. IO₃⁻ < HCO₂⁻ < BrO₂⁻ < F⁻ < CI⁻ < NO₃⁻ < Br⁻ < ClO₄⁻ < SCN⁻. An increase in temperature results in decrease in N. The effects of iodide, bromide, and chloride counterions on the aggregation of vesicle forming 1-methyl (1-4-2-(pentyheptyl)pyridinium halide surfactants have been studied.

Arthur E. Westwell et al. determined the aggregation numbers of decylpyridinium bromide and 18 structurally related surfactants. It was observed that the presence of alkyl groups on the pyridine ring lowered the aggregation number, whereas corresponding alkanol raised it. The aggregation numbers for decylpyridinium bromide were found to be increasing with decrease in partial charge in alkyl tails and it decreased with an increase in positive charge on the pyridinium ring atom to which decyl chain was attached.

4.4 Rheology of micellar solutions

Viscosity of solutions of cationic micelles of near-spherical shape or slightly anisometric is Newtonian. However, as micellar growth takes place upon increasing surfactant concentration, ionic strength or upon addition of anions with a large lyotropic number, the solutions become first very viscous, then viscoelastic.

Candau et al. studied the effect of salt content on the rheological properties of wormlike micelles formed by cetylpyridinium chloride CPC₁₀₅. They observed maximum

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zero shear viscosity upon increasing the salt concentration\(^{27}\). Similar study has been performed on micellar solution of cetylpyridinium chloride by the addition of NaClO\(_3\)\(^{28}\). The addition of salt induced an increase in zero shear viscosity and investigations were made on linear and non-linear rheological behavior of micellar system. The effects of various organic additives on the viscosities for aqueous and 0.1 M KBr solutions of 0.05 or 0.1 M cetylpyridinium have been noted under Newtonian flow conditions\(^{29}\). The viscosities were changed dramatically in the presence of KBr by the favorable conditions, and it also assisted the micellar growth by organic additives, with concomitant enhancement in viscosity.

5 MICELLE FORMATION IN NON-AQUEOUS PHASE

Many cationic surfactants are soluble in apolar organic solvents such as chloroform, carbon tetrachloride, or benzene. A very few studies had been conducted comparing cationic surfactants dissolved in such solvents with respect to solution in water. Moreover, micellization of cationic surfactants in these non-aqueous media is different from micellization in water and there exist several differences between solubilization behavior and aggregation behavior among non-aqueous and aqueous solutions of cationic surfactants\(^{30}\).

R. Nagarajan et al. studied the solution behavior of \([\text{C}_{12}, \text{C}_{14}, \text{C}_{16}]\) alkyl pyridinium surfactants in ethylene glycol utilizing the thermodynamic approach. Estimations have been made for various free energy contributions in ethylene glycol and were used to compute the size distribution of aggregates of alkyl pyridinium bromides. Calculations were made for cmc values, free energy, and aggregation numbers\(^{31}\) and the results are shown in Fig. 4 - Fig. 11 and Table 3. The theoretical cmc of cetylpyridinium bromide in ethylene glycol (Fig. 4) and in water (Fig. 5) has been estimated using the calculated size distribution data. The size-dependent quantities plotted in Fig. 4, for ethylene glycol, do not show a very sharp transition as the total surfactant concentration is increased. Although, all the curves reflect the presence of aggregates, the physical properties change only gradually over a wide range of concentrations. Table 3 summarizes the cmc values estimated by using the curves drawn in Fig. 4 and Fig. 5.

The true weight-average aggregation number \(g_w\) and polydispersity index \((g_w/g_n)\) \((g_n = \text{number-average aggregation number})\) Table 3 CMC of Alkyl Pyridinium Bromides in Ethylene Glycol at 25°C.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Predicted CMC (M) based on a plot of (*g_w,\text{app}) vs (**C_{tot})</th>
<th>Predicted CMC (M) based on a plot of (**C_1) vs (C_{tot})</th>
<th>CMC (M) based on emf measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_{16})PBr</td>
<td>0.148</td>
<td>0.124</td>
<td>0.10</td>
</tr>
<tr>
<td>C(_{14})PBr</td>
<td>0.246</td>
<td>0.222</td>
<td>0.18</td>
</tr>
<tr>
<td>C(_{12})PBr</td>
<td>0.446</td>
<td>0.372</td>
<td>0.65</td>
</tr>
</tbody>
</table>

* \(g_w,\text{app}\) denotes apparent weight-average aggregation number
** \(C_{tot}\) denotes total surfactant concentration
*** \(C_1\) denotes concentration of the singly dispersed surfactant

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**Fig. 4** Calculated Size-dependent Variables for Cetyl Pyridinium Bromide Solutions in Ethylene Glycol as a Function of the Total Surfactant Concentration. A denotes the apparent weight average aggregation number, B denotes the apparent number average aggregation number, C denotes the monomer concentration \(X_1\), D denotes the total concentration of the surfactant in the form of aggregates, \(\Sigma gX_g\), and \(X_1+\Sigma gX_g\) denotes the total concentration of surfactant. All concentration are expressed in mole fraction units.
tion number) of cetyl pyridinium bromide, in ethylene glyco-
col, were calculated as a function of total surfactant con-
centration and are shown in Fig. 6 and Fig. 7, respectively. 
Around the cmc, the occurrence of small aggregates such as
dimers, trimers and tetramers can be observed. Even at
large surfactant concentrations, the aggregation numbers
are very small compared to the typical behavior in water.
The polydispersity index in Fig. 7 shows values apprecia-

Fig. 5 Calculated Size-dependent Variables for Cetyl
Pyridinium Bromide Solutions in Water as a
Function of the Total Surfactant Concentration.
The lines denoted by A, B, C, and D refer to the
same size-dependent variables as in Fig. 4.

Fig. 6 True Weight-average Aggregation Number of Cetyl
Pyridinium Bromide Aggregates in Ethylene Glycol
as a Function of the Total surfactant Concentration.
C_{tot} denotes total surfactant concentration.

Fig. 7 Polydispersity Index of Cetyl Pyridinium Bromide
Aggregates in Ethylene Glycol as a Function of the
Total Surfactant Concentration.

Fig. 8 Contributions to the Standard Free Energy Change
Associated with Aggregation of Cetyl Pyridinium
Bromide in Ethylene Glycol as a Function of the
Aggregation Number. \((\Delta \mu^a/kT)_{int}\) denotes aggregate
core-solvent interfacial free energy, \((\Delta \mu^a/kT)_{ion}\) denotes free energy of headgroup ionic interactions,
\((\Delta m/kT)_{def}\) denotes deformation free energy of the
surfactant tail, \((\Delta m/kT)_{ste}\) denotes free energy of
headgroup steric interactions, \((\Delta \mu^a/kT)_{tot}\) denotes transfer free energy of the surfactant tail, \((\Delta \mu^a/kT)_{tot}\) denotes total free energy on aggregation, \(g\) denotes
aggregation number for spherical micelle.

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bly larger than unity, indicating considerable polydispersity in the aggregate sizes. The increasing portion of the curve corresponds to the fact that as the concentration increases, increasing amounts of dimers, trimers, and other smaller oligomers are being formed.

The free energy curves of cetyl pyridinium bromide in ethylene glycol and in water are shown in Fig. 8 and Fig. 9, respectively. The transfer free energy contribution is negative and is responsible for the aggregation and this aggregation is independent of the aggregate size and thus has no influence on the size or shape of the equilibrium aggregate formed. Comparison between the Fig. 8 and Fig. 9 show that the ionic interactions are lower in ethylene glycol solution compared to in water, thus causing a reduction in cmc in ethylene glycol. The interfacial free energy is smaller in the case of ethylene glycol solutions, compared to that in water because of the considerable smaller ethylene-hydrocarbon interfacial tension compared to water-hydrocarbon interfacial tension. This is responsible for the smaller aggregation numbers of the equilibrium aggregates formed in ethylene glycol.

Figure 10 provides a plot of the concentration $C_1$ of the singly dispersed surfactant as a function of the total surfactant concentration $C_{tot}$ for dodecyl, tetradecyl, and cetyl pyridinium bromides in ethylene glycol solutions. Even at very high concentration of about 1 M, the aggregation numbers are quite small.

### 6 ADSORPTION

Adsorption of cationic surfactants at the liquid/vapor and liquid/liquid interface is not as commercially important as adsorption at the solid/liquid interface. Foaming and emulsification are the two most important practical applications which depend on adsorption at the fluid interfaces, but they are rarely involved in cationic surfactants. However, the importance of adsorption of cationic surfac-
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The adsorption phenomenon of cationic surfactants has been affected by various parameters such as:

a) Molecular structure of surfactants (chain length and type of alkyl group)
b) Nature of substrates
c) Time of action
d) Temperature
e) pH value
f) Presence of other substances (electrolytes, surfactants)

6.1 Adsorption at mineral/water interface

The phenomenon of adsorption at mineral/water interface by pyridinium salts has been applied in flotation of minerals. These surfactants modify the wetting behavior of mineral surfaces and also affect the stability of mineral suspensions. They transform the hydrophilic surfaces into hydrophobic ones by adsorption at the mineral/solution interface.

The adsorption process in these systems is controlled by the electrical characteristics of both, the mineral surface and the composition of the cationic surfactant solution. Electrostatic forces are responsible for the attraction of the positively charged polar group of the surfactant ion and negatively charged site on the mineral surfaces. Therefore, the surface of the mineral particles acquires a net electric charge upon the immersion of these materials into aqueous solution of minerals. To maintain the system electrically neutral, the surface charge is always compensated by the charge of an ionic diffusion layer, equal in magnitude, but opposite in sign, located in the solution side of the interface. The surface electric charge and the ionic diffuse layer constitute the interfacial double layer.

The ionic species move freely across the solid/liquid interface, which develops some electric potential and electrokinetic effects are resulted from the relative motion between solid and liquid phases in a charged system. This causes transport of counterions in the diffuse layer and zeta potential (\(\zeta\)) serves as a tool to estimate their adsorption effect on electric double layer phenomenon. A zeta potential study for the adsorption of quaternized polyvinylpyridine and subsequent binding of perfluorinated anionic surfactants on silica had been carried out. The \(\zeta\)-potential became negative with increase in concentration of poly(2-vinyl-1-methyl) [P2VP] pyridinium bromide at pH values of 4, 6.6, and 9.2. Surfactant anions were adsorbed on that silica surface which was modified with P2VP and \(\zeta\)-potential of P2VP changed from positive to negative with increase in concentration of anionic surfactant.

The hydrocarbon chain length plays an important role in adsorption process. High surface coverage is obtained due to hydrocarbon association. A.H. Herz et al. noted the increase in reversible adsorption of alkylpyridinium salts on AgBr-gelatin with increase in length of alkyl chain. Longer alkyl chain enhanced adsorbability without influencing the saturation coverage. The rates of adsorption and desorption for four alkylpyridinium bromide (C10, C12, C14, C16) surfactants had been evaluated in the presence and absence of salts (NaCl, CaCl2 and Na2SO4). The rates of adsorption for the surfactants on sand surface were very high and were almost same at low concentration for different chain length.

Inorganic electrolytes and pH influence the adsorption phenomenon to a great extent. The electrolytes modify the interaction between the surfactant and mineral surface and enhance the adsorption due to reduction in electrostatic repulsions among headgroups, whereas pH of the system determines the degree of ionization of the surfactant and also the electrical nature of mineral/water interface. The flotation of quartz has been studied for various electrolyte concentrations.

M. Szekeres presented a report on the study of adsorption of dodecylpyridinium chloride (DPCI) on monodisperse Stober silica particles dispersed in an aqueous medium as a function of pH and electrolyte concentration (KCl). The charge density increased with increase in electrolyte concentration. In the absence of DPCI, silica did not approach the zero axis, but seemed to reverse sign between pH = 4.3 - 4.5. Addition of 0.01M DPCl had no significant effect on the charge as a function of pH. The surfactant ions could not penetrate into major part of the porous core of the particles due to the presence of K+ ions and were excluded from the bulk of the Stober silica particles and were present at the outer surface. The \(\zeta\)-potential study gives the indication and extent of surfactant adsorption at the outer surface.

The surfactant molecules, which are adsorbed on to the mineral surface, arrange themselves in a definite pattern. The arrangements are affected by the presence of electrolytes. For the adsorption of cetylpyridinium bromide at silica aqueous, spherical surface structures are obtained in the absence of electrolyte, whereas presence of electrolyte leads to elongated cylindrical structures. Adsorption study of cetylpyridinium on montmorillonite reveals that the surfactant molecules are arranged in monolayers and the bonding of surfactant is due to interaction of pyridinium rings via \(\pi - \pi\) bonding.

6.2 Adsorption at miscellaneous substrates

The adsorption of cationic surfactants also involves various substrates which include carbonaceous material, organic compounds, pigments, polymers, non-cellulosic fibers and textiles, biological nutrients, plants, human skin and hair. These substrates are generally hydrophobic in nature and adsorption of cationic surfactants on them covers variety of applications, including dispersions and tex-
tile processing, antimicrobials, personal care products and cosmetics, biological and dermatological problems and detergency, covering both soil and substrate.

The adsorption of surfactants on the above said substrates increases with length of the alkyl chain. The presence of solutes and nature of counterions of the surfactants affect the adsorption on these substrates. Generally, inorganic electrolytes increase the adsorption and lower the cmc value. D. Goralczyk studied the effect of inorganic electrolytes (NaCl, NaBr, NaI) on the adsorption of decylpyridinium ions. It was found that presence of NaI in the solution affected the adsorption of surfactant due to high specific adsorbability of I(–) ions.

The effect of pH on the adsorption of pyridinium surfactants is negligible. However, the adsorption is effective in the pH range of 8-10 and percentage adsorption depends upon the type of substrate. The effect of pH and surfactant concentration on the adsorption of pyridinium salts on fabrics is shown in Table 4 and Fig. 12, respectively.

### Table 4 Adsorption of Cetylpyridinium Bromide by Wool.

<table>
<thead>
<tr>
<th>pH</th>
<th>Wool % adsorbed (15 min)</th>
<th>Chlorinated wool % adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.125</td>
<td>0.50</td>
</tr>
<tr>
<td>6</td>
<td>0.625</td>
<td>0.812</td>
</tr>
<tr>
<td>10</td>
<td>0.812</td>
<td>1.06</td>
</tr>
</tbody>
</table>

### Fig. 12 Sorption of Dodecylpyridinium Bromide (DPyB) by Various Fibers at pH 9.8.

7 SOLUBILIZATION

Solubilization by aqueous micellar solution is defined as the phenomenon of incorporating water insoluble hydrocarbons (mainly alkanes, arenes, alcohols) by dissolution in the micelles. Kaufman proposed the more general definition that solubilization is a process occurring in the presence of a solvent, whereby the solubilizing agent diminishes the activity of the solubilize, after which both species remain soluble.

Many studies deal with the partition of a variety of solutes between micelles and intermicellar solution. In most of studies the micelles are considered as a pseudophase and the results analyzed in terms of a solute partition coefficient $K_p$, defined as the ratio of the solute mole fraction in micelles and in the bulk. The main results are as follows:

1. $K_p$ increases with the size of the hydrophobic moiety of the solute for a homologous series of compounds (alcohols, polycyclic arenes, etc.).
2. $K_p$ decreases upon increasing the solute mole fraction in micelles.
3. Electrolytes can strongly affect $K_p$.
4. Solubility goes through a maximum upon increasing pressure, at $p \cdot 10^3$ atm.
5. The solubility of dyes and gases by micellar solutions has been found to be nearly independent of the nature of the counterion and size of the surfactant head group, and has been found to increase slightly with the surfactant alkyl chain length.
6. The expressions for the thermodynamic functions for transfer of a solubilize from water to micellar solutions have been obtained by extending existing models. The fitting of the data to these expressions provides the value of $K_p$ and of the partial molal thermodynamic properties of the solubilize in micelles.
7. Large changes of solubility can occur upon changes of micelle shape. Thus the sphere-to-rod transition has been found to be accompanied by a large increase of dye solubilization. In general, rod-like micelles appear to have a larger capacity for solubilization than spherical micelles.

Katsuhiko Fujio et al. studied the solubilization of water insoluble dye (Orange OT) in aqueous NaBr solutions of dodecylpyridinium bromide (DPB), decylpyridinium bromide (DCPB), tetradecylpyridinium bromide (TPB) and hexadecylpyridinium bromide (CPB). It was observed that solubilization powers of DCPB and DPB micelles increased with increase in NaBr concentrations up to 2.86 and 3.07 mol dm$^{-3}$, respectively, and above these concentrations they remained unaltered. On the other hand, solubilization powers for TPB and CPB increased in the whole range of concentration studied and their solubilization dependency on counterion concentration changed at 0.10 and 0.03 mol dm$^{-3}$ NaBr, and their micelles took the rod-shape.
The effect of HLB and electrostatic forces have been studied on the solubilization of neutral and electric charged liposomes by a series of alkylpyridinium surfactants (C_{10} - C_{14})\textsuperscript{46}. The cmc and the HLB increased with decrease in alkyl chain length of surfactant, regardless of the bilayers electric charge. The solubilization of liposomes was greatly influenced by HLB, whereas it was minorly influenced by electrostatic forces. Another study by M. Angeles Urbaneja et al. had shown that the solubilization of liposomes by alkylpyridinium micelles do not largely depends upon electrostatic forces but is chiefly influenced by hydrophobic interactions\textsuperscript{49}.

Solubilization of water in organic solvents has also been achieved by pyridinium surfactants. The water is blended into organic solvents with formation of hydrogen bonds with cationic surfactant molecule. These hydrogen bonds may be formed in chloroform but not in nitrobenzene which competes for donor oxygen. However, this mechanism of solubilization is not general because solubilization occurs due to excess free energy. Such interactions occur due to free energy and are also known as "hydrophobic effect". The amphiphilic molecules undergo cooperative self association to form large aggregates in equilibrium with surfactant monomers. The effect favors the formation of aggregates of randomly mixed surfactant molecules with their hydrophobic chains in the interior of the aggregates and the hydrophilic headgroups at the surface in contact with aqueous solution. The effect applies equally to both pure and mixed systems of amphiphiles and can be viewed as leading to "ideal mixtures" of surfactants in aggregate.

1. Interactions between like head groups: These interactions occur due to free energy and are also known as "hydrophobic effect". The amphiphilic molecules undergo cooperative self association to form large aggregates in equilibrium with surfactant monomers. The effect favors the formation of aggregates of randomly mixed surfactant molecules with their hydrophobic chains in the interior of the aggregates and the hydrophilic headgroups at the surface in contact with aqueous solution. The effect applies equally to both pure and mixed systems of amphiphiles and can be viewed as leading to "ideal mixtures" of surfactants in aggregate.

2. Interactions between unlike head groups: These interactions occur due to excess free energy. Such interactions within the aggregate may lead to significant changes in the behavior of the overall surfactant solution. The effect is regarded as "nonideal" mixing in the aggregate.

The formation of mixed micelles in surfactant solution leads to striking changes and these effects are more pronounced in the region of cmc\textsuperscript{46}. The influence of headgroups on the mixed micellization has been observed for pyridinium salts and quaternary ammonium salts\textsuperscript{47}. It was concluded that bulky pyridinium headgroups created steric incompatibility and mixed micelle formation was favorable for quaternary ammonium salts.

The binding of alkylpyridinium ions to sodium dodecyl sulfate micelles had been investigated\textsuperscript{48}. The increase in number of carbon atoms in the alkyl chain (ethyl, propyl, butyl, and hexyl) of counterions led to the reduction of both, intramicellar mobility and exchange rate with aqueous phase.

M. Bhat et al. studied the interactions between butyl benzene sulfonates and cetylpyridinium chloride (CPyCl) in mixed aggregate system. It was observed that steric hindrance due to butyl group to the interaction with CPyCl was highest for tertiary butyl benzene sulfonate as compared to butyl benzene sulfonate and iso-butyl benzene sulfonate. The mixtures formed rod-like micelles and were highly viscous, even at very low concentration\textsuperscript{49}.

8 INTERACTION WITH OTHER SURFACTANTS

Mixtures of different surfactants are used in almost all practical applications. This is due to the performance advantages that often result from deliberately mixing the different surfactants. The micellar aggregation in these systems occurs same as that in single-specie surfactant system. The cmc or onset of micellar aggregates in a solution provides a useful measure of both the tendency of surfactant to aggregate and of strength of interactions between surfactant types. The interactions of cationic surfactants with other surfactant in aqueous solutions are of two types:

1. Interactions between like head groups: These interactions occur due to free energy and are also known as "hydrophobic effect". The amphiphilic molecules undergo cooperative self association to form large aggregates in equilibrium with surfactant monomers. The effect favors the formation of aggregates of randomly mixed surfactant molecules with their hydrophobic chains in the interior of the aggregates and the hydrophilic headgroups at the surface in contact with aqueous solution. The effect applies equally to both pure and mixed systems of amphiphiles and can be viewed as leading to "ideal mixtures" of surfactants in aggregate.

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9 ANTIMICROBIAL ACTIVITY

Pyridinium salts show antimicrobial activity with no odor or toxicity, when used in recommended concentration. They are quite stable and do not contain any phenol, iodine, active chlorine, mercury or other heavy metals. Their activity restricts or inhibits the growth of various microorganisms such as bacteria, viruses, fungi, protozoa etc. However, they do not fulfill the requirements of a "universal" antimicrobial agent and do not always provide complete destruction of various sundry organisms under all conditions of use.

9.1 Mode of antimicrobial action

The activity of pyridinium salts is governed by various mechanisms. They are adsorbed on the cell membranes of microorganisms and promote various changes in their cell organization. The important changes that take place are:

1. Alteration in cell structure
2. Interference in respiration and glycolysis of microorganisms, particularly inhibition of oxidative system

In general, these salts are adsorbed on the cell wall and are bound to one of the biochemical components. Adequate binding results in disruption of cellular process leading to cessation of bacterial growth and thus causes cell death. It has been also noticed that there is leakage of cellular constituents, such as nitrogen, phosphorus, free glycine etc. by the action of these salts on microbial cells.

The antimicrobial activity of alkylpyridinium salts gener-
ally increases with the length of the alkyl chain and for substituted pyridine it also depends upon the nature of the groups and position at which they are substituted on the pyridine ring. The antimicrobial activity and electrostatic effect of 1-alkoxymethyl-3-substituted pyridinium chlorides had been examined with different substituents at 3-position\(^5\). It was observed that salts with dimethylamino group at 3-position showed higher antimicrobial activity and high electrostatic effect as compared to the salts having hydroxy group at 3-position.

Antimicrobial activity has been found to be dependent upon the number of headgroups present in pyridinium amphiphiles. It increases with increase in number of headgroups. Haldar \textit{et al.} compared the antimicrobial properties of two sets of novel cationic amphiphiles with one, two, and three trimethylammonium headgroups (T\(_1\), T\(_2\), T\(_3\)) and pyridinium headgroups (P\(_1\), P\(_2\), P\(_3\)). It was noted that the amphiphiles having triple headgroups were most effective to kill both gram-negative and gram-positive bacteria and required much less time to kill them than that required by single headed salt. However, the multihedged pyridinium amphiphiles were more active as compared to their trimethylammonium counterparts\(^3\).

Kanji Fugimoto \textit{et al.} evaluated the in vitro antimalarial activity of N,N-hexamethylene bis(4-carbamoyl-1-decylpyridinium bromides) and their derivatives against the plasmodium falciparum FCR-3 strain. The amphiphiles exhibited antimalarial activity over a concentration range of 3.5 \(\mu\)M to 10 \(\mu\)M and it was dependent upon the chain length of N-alkyl moiety. The most appropriate N-alkyl chain length was found to be eight\(^4\).

Significant antimicrobial activity of butyl, hexyl, octyl pyridinium bromide ionic liquids were observed against pure cultures of Escherichia coli, Staphylococcus aureus, Bacillus subtilis, Pseudomonas fluorescens and Saccharomyces cerevisiae. However, butylpyridinium bromide was less antimicrobial than ionic liquids with longer alkyl chain lengths to all the microorganisms examined\(^5\).

I. Mancini \textit{et al.} tested monomeric, dimeric and tetrameric compounds of linear 3-alkylpyridinium salts for their antibacterial and anti-cholinesterase activities. It was observed that antibacterial and anti-cholinesterase activities increased with degree of oligomerization\(^6\).

Klaus Schoene \textit{et al.} studied the protective effects of a series of pyridinium salts against soman (O-Pinacolyl methylphosphonofluoridate) poisoning in female mice. 130 nmol/kg of the salt reduced the toxic effect of a LD\(_{50}\) of soman to the 50\% mortality level. The compounds with in vivo protective activity also protected acetylcholinesterase (AChE) from soman in vivo\(^7\).

## 10 Applications

### 10.1 Corrosion inhibition

Pyridinium salts are effectively used to inhibit the corrosion of ferrous surfaces in highly acidic medium. They act as cathodic inhibitors and lead to increase in cell resistance and cathode polarization, and decrease in apparent circuit potential. The inhibition is generally attributed to the adsorption and formation of insoluble films by the salts at the surfaces and their interaction with the atoms of the surface of metal. M.L. Free \textit{et al.} studied the relationship between corrosion inhibition of mild steel in acidic medium with the aggregation of cetylpyridinium chloride at the interface and in solution. Various factors that affect the aggregation of surfactants have also been investigated\(^8\). Incorporating pyridinium salts and other cationic surfactants in acidic medium of ferrous surfaces inhibit their corrosion by forming a bilayer on them. Highly quaternized pyridinium salts are useful for such inhibition\(^9\).

### 10.2 Asphalt emulsions

Quaternary pyridinium salts are employed in preparations of asphalt emulsions. Such emulsions are used for automotive undercoating preparations or as water proofing coatings on concrete. The emulsion usually contains:

- Asphalt: 50-70\%
- Cationic emulsifier: 0.1 - 2\%
- Water: q.s.

They are used in highway construction, since they improve the adhesion of asphalt to acidic aggregate and road becomes more resistant to water. These emulsions can be applied on roads, while it is raining. Surfactant mixture comprising alkyl benzene pyridinium chlorides, alkyl napthyl pyridinium chlorides, and alkyl anthracyl pyridinium chlorides are added to the emulsions, increases the adhesive strength between the bitumen and mineral components of black top road surface by a factor of 1.5 times than that obtained without them\(^10\).

### 10.3 Liquid - liquid extraction

It is the process by means of which one or more components of a liquid are transferred to another liquid. The rapid and simple liquid-liquid extraction of palladium (II) has been carried out using hexadecylpyridinium bromide (HDP). It was observed that the extraction was fast and required shaking time of few minutes with an average 99\% recovery of palladium from an aqueous solution containing 10 \(\mu\)g/ml of analyte with a residual percentage of 0.15. The percentage recovery of 0.2 \(\mu\)g/ml palladium was 96\% \(^11\).

Cetylpyridinium surfactant along with 1-pentanol is used to extract vanadium from a colored compound, which is formed by the action of tannic acid and vanadium during the spectrophotometric determination of vanadium in edible oils and petroleum products\(^12\).

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10.4 Styrene polymerization

Alkyl pyridinium bromide maleate and succinate diester surfactants are used as stabilizers in free radical polymerization of styrene to enhance the rate of polymerization. Incorporation of these surfacmers into the polymer particles yield stable latex emulsions and the stability of lattices against the electrolytes also gets enhanced\(^{61}\). Fairly highly stable lattices with monodisperse particle size distribution (1.01 to 1.1) with particle diameters ranging from 70 to 160 nm have been obtained during the emulsion polymerization of styrene in the presence of series of pyridinium salts with N-substituted with W-[4-methoxy-4-bisphenyloxy) alkyl group\(^{62}\). Polystyrene nanocomposites with higher degradation temperature than virgin polymer are prepared by insitu bulk polymerization of modified clays based on pyridinium salts\(^{63}\).

10.5 Dye removal from waste water

Anionic organic dyes are insoluble in water but are soluble in micelles of cationic surfactants. These also get solubilized in the micelle of pyridinium salts. Their solubility in micelle is generally related to the aggregation number of surfactant molecules. M.K. Purkait et al. studied the removal of dye from waste water using enhanced ultrafiltration technique. Cetylpyridinium chloride micelle was used to solubilize eosin (dye). It was observed that retention of the dye at the membrane without surfactant was only 10% as compared to 73.4% retention with surfactant micelle. The maximum retention of dye was obtained at surfactant to eosin ratio of 2000. The recovery of surfactant molecules present in permeate began with precipitation of former by potassium iodide followed by addition of cupric chloride\(^ {64}\).

10.6 Drug delivery

Pharmaceutical industry applies various systems for delivery and uptake of drugs in the body systems. Pyridinium salts are employed in pharmaceuticals for effective drug delivery. They carry the drugs to central nervous system and improve uptake of drugs by brain, thus enhancing pharmacologic activity with no side effects. They also act as redox targetors.

Nicholas Badar et al. achieved brain-enhanced delivery of chlorthalidone through biological membranes using pyridinium salt chemical delivery system\(^ {65}\). Improved targeting of penicillin to the central nervous system has been achieved using dihydropyridine pyridinium salts. The drugs are temporarily linked to the salt moieties and are carried to the target with redox mechanism\(^ {66}\).

The enhanced transport of transdermal drugs has been achieved by using equal molar mixtures of dodecyldimethylpyridinium chloride and sodium lauryl sulfate, which increase the skin permeability\(^ {67}\).

10.7 Electrolyte for lithium batteries

Certain pyridinium salts act as liquid electrolytes, which conduct Li ions in lithium batteries and carry them between the cathode and the anode when a battery passes an electric current through an external circuit. Mixture of 1-butyl-4-methyl pyridinium tetrafluoroborate and 1-butyl-3-methyl imidazolium tetrafluoroborate or hexafluoro-phosphate, when added to organic solvents such as butyro-lactone and acetonitrile act as electrolyte for lithium batteries containing lithium salt as LiBF\(_{4}\) or LiPF\(_{6}\). Low viscosity and high conductivity were obtained with mixture having BF\(_{4}\) anion\(^ {68}\).

10.8 Textile processing

Pyridinium salts are being adsorbed on the fibers of textile due to their positive charge on them and impart certain properties to them. They act as antistatic agents and are used as dry cleaning additives. Cotton cloths are made oil repellent by treatment with certain pyridinium salts. 1% aqueous solution of 6-(heptafluoro-2-propoxy)-3, 3, 4, 4, 5, 5, 6 - octafluoroethyl pyridinium iodide makes the cotton print cloth oil repellent. The salt can be prepared by heating (CF\(_{3}\))\(_{2}\)CFO (CF\(_{3}\))\(_{2}\)(CH\(_{2}\))\(_{3}\) with C\(_{6}\)H\(_{5}\)N\(_{6}\)\(^ {69}\).

10.9 Flotation of minerals

Quaternary pyridinium salts form monomolecular films on the surface of negatively charged ore particles in such away that cationic nitrogen is attached to the ore surface resulting in hydrophobic coating of the ore particles, hence they act as flotation collectors. They are used to separate the minerals. In froth flotation process, the air bubbles cause the hydrophobic components of ore to float on the surface of water and are thus, scrapped off.

The pyridinium salts are used in the flotation of potash ore, phosphate rock, sulfide ores, oxide ores, silicate ores, and coal. The flotation of the minerals depends upon the concentrations of surfactants and electrolytes\(^ {70}\).

10.10 Biological applications

a. Modification of membranes

The transport properties of exchange membranes are being affected by the presence of pyridinium salts. They make the membranes more permeable for monovalent ions than for multivalent ions. So, these salts are applied for electrodialysis of salt solutions\(^ {71}\).

The properties of the membranes in mammalian cells can be modified by the presence of alklypyridinium sponge toxin which increases their porosity\(^ {72}\). The action of alkylypyridinium salts on the membranes of tumor cells have also been reported\(^ {73}\).

b. Gene delivery

Gene therapy is helpful for the treatment of various diseases including cancer, AIDS, arthritis, and many more. The transfer of gene in this therapy to particular cell has
been attributed to pyridinium cationic lipids. They have low cytotoxicity and improved efficiency across different cell lines. Equal molar ratio of pyridinium lipid and cholesterol can transfect several cancer cell lines with similar or better efficiency than its tetraalkyl ammonium congener.64.

Highly efficient DNA transfections are also promoted by novel, double chain pyridinium surfactants. These compounds increase the efficiency of transfection and enhance DNA delivery. The increase in above said quantities is much more than that produced by conventional cationic lipid system, lipofectin.75.

10.11 Dewatering of waste oil
Quaternary pyridinium salts are used to break water-in-oil emulsions or oil-in-water emulsions. Mixture of pyridinium and ammonium salts and betaine having at least one alkyl group with 6 to 22 carbon atoms with tertiary or quaternary polyamines can separate the two phases.76

10.12 Cleaning of nonadsorbent articles
Mixture of 0.25% cetylpipridinium bromide, 1% H2O and trichloroethylene is used to remove Ca-stearate from extruded Al or pitch CeO2 or ZrO2 from optical lenses. Other substances such as waxes, metallic soaps can be removed from metals, porcelain, glass, and plastic using a combination of trichloroethylene, perchoroethylene, CH2Cl2 with 0.05-70.05% cationic surfactant in less than 5% H2O at elevated temperature.77

10.13 Antimicrobial agents
Pyridinium salts are effective against number of microorganisms. Their applications as antimicrobial agents may be described as:

a. Surgical applications
i. They are used to sterilize surgical instruments and to remove congealed blood from them.
ii. Wound irrigation can be done effectively using pyridinium salts with rapid recovery with reduce chances of secondary infection.
iii. Quaternary pyridinium salts are applied effectively for the treatment of urological infections.

b. Medicinal use
Pyridinium salts are used to control certain infections in our body. Cetylpyridinium chloride is formulated in certain medicines such as griseofluvin tablets for rapid and effective curing of ringworm. It also controls supragingival plaque and gingivitis. Moreover, it also has direct anti-inflammatory activity and inhibits action of several matrix metalloproteinase proteins which cause inflammation.

c. Sanitizers
Quaternary pyridinium salts are used as disinfectant for eating and drinking utensils and food processing equipment. Moreover, their germicidal action has also been employed in dairy industry for sanitization of milk cans and milking machines.

d. Cosmetics
The antiseptic action of quaternary pyridinium salts makes them important ingredient for cosmetic products. They are added to aftershave lotions, shaving creams, skin creams, shampoos, and body lotion etc. Moreover, antimicrobial brushes can also be used to prevent certain skin problems. They can be prepared by dipping animal hairs in 0.2-7.5% of alkylpyridinium salt in the presence of heat.78

A composition containing 0.5-30% laurylpipridinium chloride, 30-98.5% cetyl alcohol lactic acid ester improves the combability, the luster and the touch of the hair.79 Pyridinium salts also improve hair conditioning when added to Henna coloring composition. A composition containing 75-95% Henna powder, 1.5-5% non-ionic surfactant, 2.5-15% H2O soluble polymer, 0.5-75% laurylpipridinium chloride or laurylpipridinium bromide improves coloring and conditioning.80

11 CONCLUSION
This paper includes several aspects of quaternary pyridinium surfactants. Their importance lies in their effective antimicrobial activity. However, bispyridinium salts show variable solubility and micellization behavior depending upon the length of methylene group.81 Besides this, these surfactants find various useful industrial applications.

References
8. Zhao, T.; Sun, G. Synthesis and characterization of...


33. McNamme, C.E.; Matsumoto, M.; Hartley, P.G.; Nakahara, M. Adsorption of quaternized polyvinylpyridine


Quaternary Pyridinium Salts: A Review

(2002).


