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Analysis of Cetyl Pyridinium Chloride (CPC) by Raman Spectroscopy Method

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Abstract

Surface active agents (surfactants) have found various critical technological applications, from helping infant lungs breathe to fugitive dust control at industrial sites. Surfactant molecules adsorb to an interface and facilitate a decrease in the surface free energy (interfacial tension) between two immiscible phases. However, a limited number of methods (e.g., holography and fluorescence microscopy) achieved qualitative visualization of surfactant molecule distribution in multiphase systems. To probe the efficacy and/or adsorption density of surfactants at such interfaces quantitatively, we demonstrate here a direct observation of surfactant adsorption by Surface-Enhanced Raman Scattering (SERS). This work details the development of a research platform to study surfactant adsorption using Raman imaging. The imaging and analysis were successfully benchmarked against conventional interfacial tension measurements and thermodynamic theory employed to estimate surfactant adsorption at equilibrium. This in situ Raman-based experimental method provides a platform to interrogate structure-function relationships that inform the design process for new surfactant species.

Keywords: *Surfactants, adsorption, interface, surface-enhanced Raman Scattering (SERS), imaging*

1. Introduction

Cetyl pyridinium chloride (CPC) is a water-soluble cationic surfactant with both antiseptic and surfactant properties. It has been used since 1930 in oral care, personal hygiene, cleaning, deodorization, and cosmetics, disinfectant products due to its effectiveness against a broad spectrum of microorganisms (Quisno & Foter,1946; Mao et al., 2020). The molecular structure of CPC comprises of cetyl group (a long alkyl chain with 16 carbon atoms) as a hydrophobic part and a pyridinium ring bonded to a chloride ion as a lipophilic part.

The structure of CPC can be shown in Figure 1.

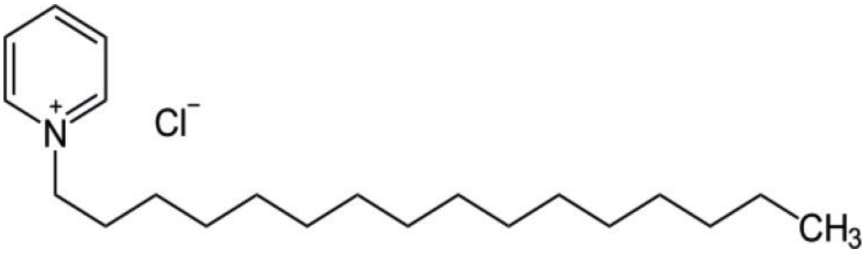

Figure 1: Representation of cetyl pyridinium chloride(CPC) showing long alkyl chain and pyridinium ring

The antimicrobial property of the CPC molecule is due to its amphiphilic nature comprising of polar head and non-polar tail. The polar head interacts with the negatively charged microbial cell membrane and the non-polar tail interacts with the lipid membrane resulting in cell disintegration and death (Gilbert & Moore, 2005; McDonnell & Russell, 1999). Being an economical biocide, CPC is commonly used as an ingredients in different personal care products and medicines.

Surface characterization is an analytical technique to quantify the physical chemical and structural properties of materials. The commonly used surface characterization techniques are optical microscopy, Scanning electron microscopy (SEM), Tunneling electron microscopy (TEM), Atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Raman spectroscopy, etc (Upadhyay & Kumaraswamidhas, 2018). These techniques are widely used in different fields like nanotechnology, material science, chemistry and catalysis, electronics, etc.

In pure water and ethanol-water mixed solvent media containing 0.10, 0.20, 0.30, and 0.40 volume fractions of ethanol at room temperature, cetylpyridinium chloride's critical micelle concentration was measured by Bhattarai et al (2013). Cetyl pyridinium chloride (CPC) was investigated for corrosion inhibition on mild steel (MS) in 0.5 M H2SO4 solution using weight loss and potentiodynamic polarization by Yadav et al (2024a). A UV-Vis spectrophotometer was used to study the interactions between methylene blue and cetylpyridinium chloride (CPC) in solvents containing 0.1, 0.2, and 0.3 volume fractions of methanol in water (Shrestha et al., 2018). Spectrophotometric measurements were carried out on methyl red (azo dye) and cetylpyridinium chloride (cationic surfactant) in the methanol-water system (Shahi et al., 2022). The interaction between sodium dodecyl sulfate and methylene blue was studied in the presence of cetylpyridinium chloride (CPC) in aqueous and methanol-water binary solvents by Shah et al. (2022). There was a study of the micellization behavior of cetylpyridinium chloride and dodecyl trimethylammonium bromide in methanol and water in the absence and presence of methyl red (Shahi et al., 2023). At 298 to 323 K, Bhattarai et al. (2017) determined the critical micelle concentration of CPC in water and methanol/DMSO-water. A conductivity measurement was used to investigate the interaction behavior among sodium dodecyl sulfate, cetyl pyridinium chloride, and dye methyl orange (Yadav et al., 2024b). An anti-corrosion study was conducted using sodium dodecyl sulfate and cetyl pyridinium chloride (Yadav et al., 2024c).

Raman spectroscopy is a powerful analytical and spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system. It deals with the inelastic scattering of monochromatic light, usually from a laser, known as Raman scattering. The technique provides a molecular fingerprint that can be used for the identification and characterization of materials including solids, liquids, and gases along with the estimation of their composition and chemical environment (Czaplinski et al., 2023). This sensitive and non-destructive technique is also used in the detection and quantification of adulterants in many fields, including structural properties of polymers, semiconductors, and nanomaterials (Wong et al., 2007).

Surface-enhanced Raman scattering (SERS) is a powerful and effective sensing method that provides ultra-sensitive characterization of sample surfaces that produce a large enhancement to the Raman scattering (Chen et al., 2012). It is emerging as a promising analytical tool to determine chemical composition, structure, orientation, and chemical reaction at surfaces. Moreover, it has high utility as a characterizing tool in several prominent research fields such as materials and analytical sciences, medicine, the environment, food, gems, cultural relics, and archaeology (Fan et al., 2011). In the present study, the surface morphology, molecular structure, and interactions of CPC were analyzed by using the versatile and effective tool i.e. SERS.

There are some literature reported earlier which used SERS as the characterization tool such as Olson and Harris (2008) in determining the kinetics of adsorption of the cationic surfactant cetylpyridinium chloride (CPC), Botti et al (2018) for characterization of pristine and functionalized Carbon Nanotubes and Graphene and Koglin et al. (1994) in studying adsorption mechanism of cationic surfactants, p-nitrophenol, and CPC on the charged surface using SERS. CPC has gained marked recognition and acceptance for its antiviral effects possessing a wide range of applications in the global context. However, studies exploring the structure and utility of surfactant CPC are limited in our country (Yadav et al., 2024d). Hence, the present study is carried out to utilize Surface-enhanced Raman spectroscopy (SERS) to evaluate the surface morphology, molecular structure, and interactions of CPC molecules.

2. Materials and Methods

2.1 Materials

The material used in this study is Cetyl pyridinium chloride monohydrate (CPC) ($C_{16}H_{33}H^{+}C_5H_5CI^{-}$) having a molecular mass of 358g/mol with 96% purity which was obtained from Hi Media Laboratories, Mumbai, India.

2.2 Methods

A SERS instrumentation comprises of a laser excitation source, the potential-controlled electrochemical cell, the optical system for focusing laser into sample, the computer controlled spectrometer, a detector that captures dispersed light from the spectrophotometer, and the display unit for processing and displaying Raman spectra.

Working of SERS: The laser light is focused on the nanostructured metallic surface which is mostly composed of coinage (Ag, Au, and Cu) having high amplification. Then, the excitation of plasmons takes place with the amplification of the electric field resulting in the emission of Raman scattered light. Finally, scattered light is transferred back to plasmons and again get scattered in air resulting effective surface enhancement (Botti et al., 2018).

Raman spectra are representations of Raman scattering, a process where light interacts with molecular vibrations, rotations, or other low-frequency modes within a material. This interaction causes a shift in the wavelength of the incident light, which is detected and plotted as a spectrum. The Raman spectrum of a substance provides a molecular fingerprint that can be used to identify and characterize its chemical structure.

3. Results and discussion

3.1 Analysis of Raman spectra of cetyl pyridinium chloride (CPC)

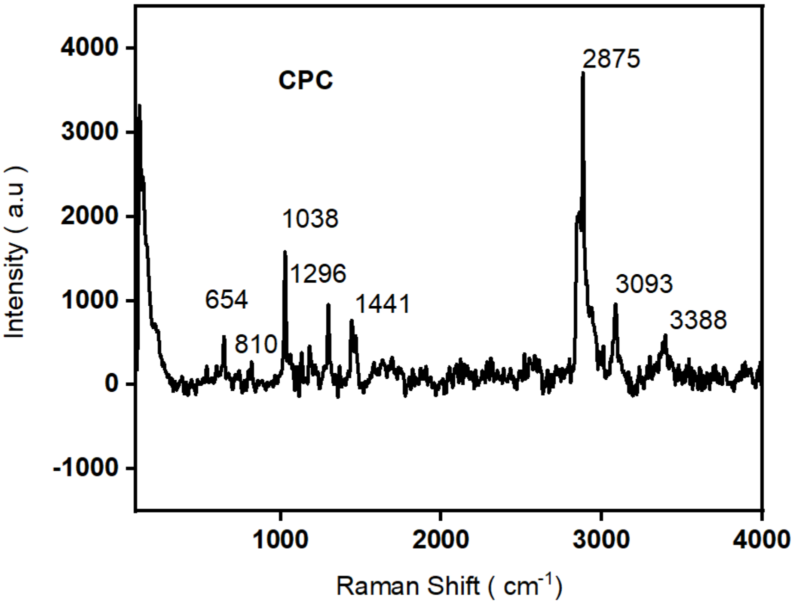

Figure 2: Representative Raman spectrum of CPC showing characteristic bands

Raman spectroscopy is a powerful analytical tool for analyzing molecular structures by examining vibrational, rotational, and other low-frequency modes in a molecule. Cetyl pyridinium chloride (CPC), a quaternary ammonium compound, can be analyzed using Raman spectroscopy to understand its molecular structure, interactions, and environment. It is an amphiphilic cationic surfactant composed of a long alkyl chain acting as a hydrophobic part and an ammonium ion as a polar part. So, from the Raman spectra, it is expected to obtain the peaks corresponding to C-H stretching and C-C stretching in the long alkyl chain and C-C stretching, C=C stretching, C-H stretching, C-N stretching, N-H stretching referring to the pyridinium ion. The Raman spectra of the CPC molecule in Figure 2 represent the vibrations of different bonds present in the molecule. The Raman spectra of pure cationic surfactant (CPC) were recorded in the transmittance mode in the range of 4000-500 cm^{-1}. The representative Raman spectrum for CPC with characteristic absorption bands of different intensities is depicted in Figure 2.

In the Raman spectrum of CPC, the intense peak at 2875 cm^{-1} represented the stretching of aliphatic C-H bonds in CH_2 and CH_3 groups (Petrov et al., 2018; Sun et al, 1990). The C-H stretching in the cetyl chain is due to the change in C-H distance as a result of stretching and compression of the C-H bond in the cetyl chain. The high intensity of peak obtained in this region is the indication of the presence of a hydrophobic part in CPC with a long alkyl (hexadecyl) chain containing carbon and hydrogen bonds. Similarly, the next intense peak at 1441 cm^{-1} indicated a bending vibration of the C-H bond due to the presence of CH_2 and CH_3 groups. The peak at 1296 cm^{-1} is due to the wagging and twisting vibrations of the CH_2 group. The peaks obtained in these regions are an indication of the interaction of CH_3 and CH_2 groups in the long alkyl chain of the CPC molecule. The bands obtained at (1038, 1296, 1441, and 2875) cm^{-1} refer to the vibration of the long hydrocarbon chain of the cetyl group in CPC (Sun et al, 1990; Koglin et al.,1996; Liu et al., 2013).

The less intense peak at 3388 cm^{-1} indicates the presence of the N-H group in the CPC molecule. The characteristic absorption bands and intense peak at 1038 cm^{-1} are due to the stretching vibration of the C-N bond in the pyridinium ring due to the symmetrical and trigonal ring breathing mode of CPC molecules which confirms the presence of the C-N group and pyridinium (Liu et al., 2021; Castellucci et al.,1969; Liu et al., 2013). The peaks at 3093 cm^{-1} and 1441 cm^{-1} are due to the stretching of the C-H bond and C=C bond in an aromatic ring (Castellucci et al.,1969; Liu et al., 2021). Similarly, the peak at 810 cm^{-1} presents the in-plane ring bending vibration of the head group in the CPC molecule (Heyns & Venter,1985; Liu et al., 2021). These peaks refer to the characteristics of the pyridinium ring. The peaks responding to (1000-1500) are due to the stretching of C-C bonds within the alkyl and pyridinium ring (Vu et al., 2019). The C=C stretching takes place in the pyridine ring due to the lengthening of the bonds connecting the C atoms in the molecule. The in-plane bending in the aromatic ring occurs due to the bending of C−H bonds in the plane of the pyridine aromatic ring (Czaplinski et al., 2023). The C−C stretching region is comprised of C−C vibrational motions for both cetyl and pyridine molecules. Similarly, the peak at 654 cm^{-1} corresponds to the stretching of the C-Cl bond in which chlorine is directly involved in the vibration. The resulting band provides information about the interaction and bonding environment due to the presence of chorine. The data obtained in Raman Spectroscopy is used in determining the composition of CPC.

3.2 Effect of chlorine on CPC

The characteristic peak of the cetyl group due to C-H stretching is obtained at 2875 cm^{-1} instead of 2850 cm^{-1} in the presence of chlorine. Similarly, there is a shift in symmetrical stretching of the pyridine ring from 1000 cm^{-1} to 1038 cm^{-1} due to the electron withdrawing nature of chlorine. There is also a shift in C-C from 1060 cm^{-1} to 1038 cm^{-1}, C=C and C=N stretching from 1580 cm^{-1} to 1441 cm^{-1} in the pyridine ring in the presence of chlorine. There is the appearance of a new peak around (600-800) cm^{-1} due to C-Cl stretching vibration. Hence, the presence of chlorine causes shifts in the characteristic peaks, their intensity, and the appearance of new peaks in Raman spectra.

4. Conclusions

The fast and efficient SERRS method is used in the present study for the identification of the functional groups and bonds in the CPC molecule to deduce information on its molecular composition. From the data obtained from the Raman spectra, the significant peaks obtained at (1038, 1296, 1298) cm^{-1} confirm the vibration due to the long alkyl chain in the CPC molecule. Similarly, the less intense peak at 3388 cm^{-1} indicates the presence of the N-H group in the CPC molecule. The characteristic absorption bands at 1038 cm^{-1} are due to the stretching vibration of C-N. The peaks at 3093 cm^{-1} and 1441 cm^{-1} are due to the stretching of the C-H bond and C=C bond in an aromatic ring. No significant peak changes and new peak appearance indicate the purity of CPC.

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