
SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF SURFACTANT SCHIFF BASE ZINC (II) COMPLEX

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Abstract

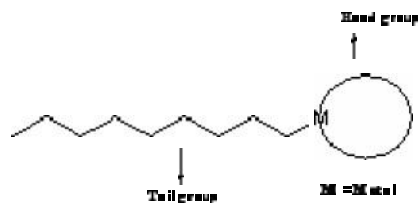
Octadecylamine Surfactant ligand and Metallosurfactant complex of Zinc (II) were synthesized and characterized by physico-chemical and spectroscopic methods. The surfactant Schiff base complex was screened in vitro for its bacterial activity against certain pathogenic bacteria and fungi species using disc diffusion method.

Keywords: *Octadecylamine, Metallosurfactant, Biological activity.*

Introduction

The Schiff bases derived from various aromatic and heterocyclic aldehydes were reported to possess cytotoxic, anticonvulsant, antiproliferative, anticancer and antifungal activities, while others have been identified as potential radio-protective agents, antimycobacterial agents and antioxidants. Transition metal complexes with Schiff base amphiphiles as ligands are of particular interest. Metal surfactant complexes have received a sustained high level of attention from the scientific community for the last few years [1-6] due to their relevance in various redox processes in biological systems, and also as promising agents for anthelmintic [7], antiparasitic [8] and antibiotic applications [9]. Metallosurfactants are a special type of surfactant where a coordination complex acts as the surfactant. In these surfactants, the metal complex part containing the central metal with its primary coordination sphere acts as the head group and the hydrophobic part of one or more ligands acts as the tail (Scheme 1).

Association colloids, such as, micelles, microemulsions and vesicles increase the rates of many nucleophilic and electrophilic reactions [10]. It is argued that the high charge and size of the head group of complexes having long paraffin tails give rise to detergent-like characteristics and such molecules are able to penetrate biological

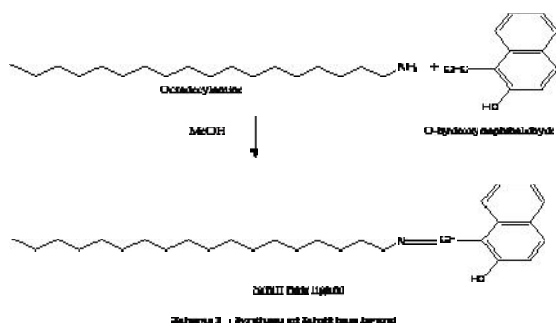


Scheme 1 METALLOSURFACTANT

membranes and so destabilize the exterior membrane of the organism [11]. Moreover, transition metal ions complexes with lipophilic ligands in micellar or vesicular aggregates have attracted considerable attention as catalysts for the cleavage of esters and amides and as biomimetic models of hydrolytic metalloenzymes [12].

In addition the presence of nitrogen and oxygen donor atoms in the complexes make these compounds effective and stereospecific catalysts for oxidation, reduction, hydrolysis and they can also show biological activities. Recently, there has been increasing interest in the use of these organized media to study the fundamental photochemical reactions of metal complexes, with relevance to the conversion of solar energy into other useful forms of energy through photochemical reactions [13, 14]. As part of our studies on transition metal based surfactants [3, 4, 15-21] in this paper, we report the synthesis, characterization and biological activity of zinc(II) surfactant complex.

Synthesis



Scheme 2 | Synthesis of Schiff base ligand

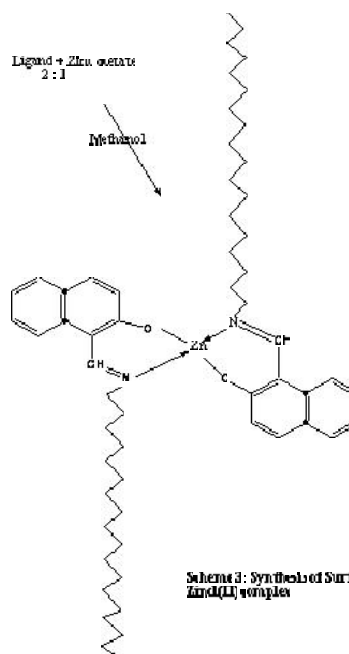
The Schiff base was synthesized (Scheme 2) by the condensation of 2-hydroxy naphthaldehyde and octadecylamine in 1:1 ratio. To the vigorously stirred solution of the octadecylamine in dry methanol, 2-hydroxy naphthaldehyde dissolved in methanol was added in drops. The reaction mixture was stirred for 5 hours.

The yellow precipitate formed was filtered, washed with little ether and dried. The four coordinated Zinc (II) (Scheme 3) was prepared under ambient condition. To a stirred solution of surfactant Schiff base (1.5mmol) in methanol, solution of zinc acetate (1.5 mmol) dissolved in methanol was added in drops. The mixture was stirred for 2-3 hour at room temperature. The precipitate was filtered and washed with methanol and dried in vacuum.

RESULTS AND DISCUSSION

Estimation of Zinc

The organic part of the metal complex was completely eliminated before estimation of the metal. The following procedure was used to estimate the organic part of the complexes. A known weight of the metal complex (0.2 g) was treated with con. Sulphuric acid (5 mL) followed by con. nitric acid (20ml). After the completion of the vigorous reaction, perchloric acid (5 mL, 60%) was added. This mixture was maintained at the boiling temperature for 3 h. The clear solution thus obtained was evaporated to dryness. After cooling concentrated nitric acid (5 mL) was added evaporated to dryness on a water bath. The residue was dissolved in water and this solution was used for the estimation of the metal. Zinc was estimated as Zinc dimethylglyoximate complex by adding an alcoholic solution of dimethylglyoxime followed by ammonia solution (Theoretical: 7.15%, Calculated 6.98%).



Scheme 3: Synthesis of Surfactant Schiff Base Zinc(II) complex

Electronic Absorption Spectra

The electronic absorption spectrum was recorded in chloroform and showed absorption maxima due to (Fig. 1) $n-\pi^*$ and $\pi-\pi^*$ transitions. The absorption in the region 403-421nm is assigned to $n-\pi^*$ transitions. The absorption in the region 255-308 nm is due to $\pi-\pi^*$ transition. The electronic absorption spectrum of the complex was recorded in chloroform and showed absorption maxima due to (Fig.2) $n-\pi^*$ and $\pi-\pi^*$ transitions. The absorption in region 422-497nm is assigned to $n-\pi^*$ transitions. The band in the region 195-277nm is assigned to $\pi-\pi^*$ transitions.

IR Spectra

The assignments of characteristic IR frequencies for Schiff base compound (Fig. 3) shows the IR spectrum of ligand. Comparison of the IR spectrum of this compound was made with those of aromatic aldehyde and primary amine (octadecylamine). The Infrared spectra of the compound showed no characteristic absorption assignable to C=O and NH₂ groups. This confirmed the formation of Schiff base compound.

The IR spectra (Fig 4) of the free Schiff base showed a strong band at 1614 cm⁻¹ characteristic of the azomethine (C=N) group. A band around 1369 cm⁻¹ was characteristic of the (C-O) group. The band at around 2920 cm⁻¹ showed the CH stretching of alkyl chain [23,24].

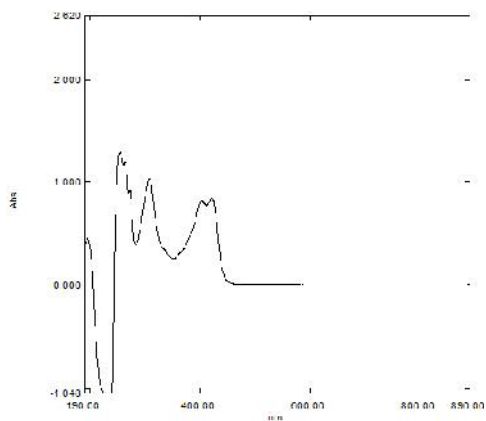


Fig. 1: Electronic Spectrum of Octadecylamine Ligand

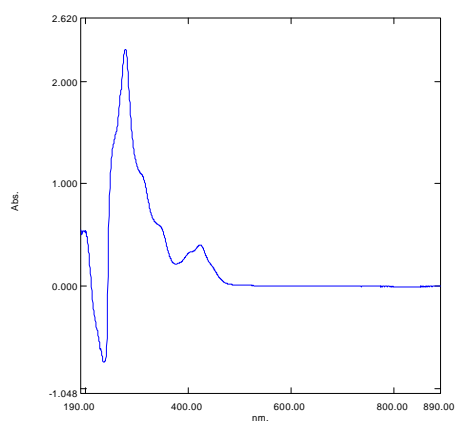


Fig. 2: Electronic Spectrum of Octadecylamine Zn(II) complex

The IR spectrum of the complex, in comparison with those of the free ligand, displayed certain changes, which gave an idea about the type of coordination and the structure. Free Schiff base showed a very strong band around 1637 cm^{-1} characteristic of azomethine (-C=N) group [Ramesh and Maheswaran (2003)].

Coordination of the surfactant Schiff base to the zinc ion through azomethine nitrogen atom is expected to reduce the electron density in the azomethine link and thus, lower (C=N) absorption frequency. Hence this band underwent a shift to lower frequency to 1614 cm^{-1} after complexation (Fig.8), indicating coordination of the azomethine nitrogen to cobalt [25, 26]. The free ligand exhibited a broad band at 3425 cm^{-1} , which might be assigned to the (OH) and this band was absent in the spectra of all the complexes, indicating the deprotonation of the surfactant Schiff base prior to coordination. The hydroxyl proton was displaced by the metal leading to higher (C-O) (1355 cm^{-1}) suggesting that the other coordinating atom was phenolic oxygen [27]. The hydroxyl proton was displaced by the metal leading to higher (C-O) (1462 cm^{-1}). The binding of the metal to the ligand through nitrogen and oxygen atom was further supported by the appearance of new band at 518 cm^{-1} due to (M-O) stretching [28], in the complex.

^1H NMR Spectra

The ^1H NMR spectrum of ligand is shown in Fig4. The ^1H NMR spectrum of the compound taken in deuteriochloroform solution was consistent with the expected structure. In ^1H NMR data of the surfactant Schiff base, a sharp singlet at around 8.6 ppm was assigned to the azomethine proton(C=N). Multiplets observed around 6.8-7.8 ppm were assigned to the aromatic protons. The methylene protons of the alkyl chain appeared in the region 1.2-1.8 ppm for the Schiff base, while the methyl protons appeared in the region 0.86-0.89 ppm [29].

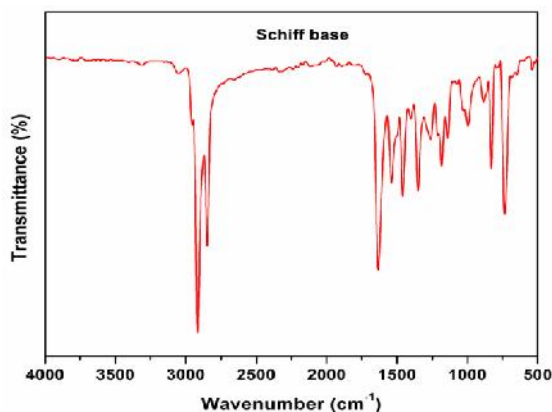


Fig. 3: IR Spectrum of Octadecylamine Ligand

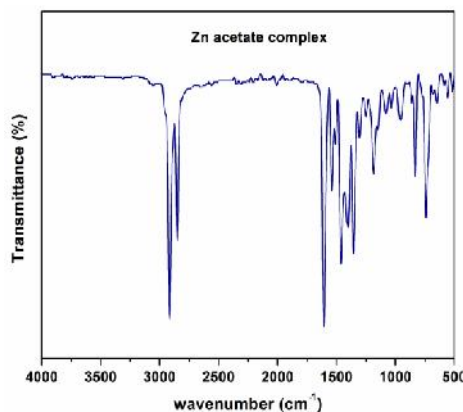


Fig. 4: IR Spectrum of Octadecylamine Zn(II) complex

The ^1H nuclear magnetic resonance spectrum of the Zinc(II) surfactant Schiff base complex taken in D_2O confirmed the formation of complex. In the spectrum of the free surfactant Schiff base ligand, a sharp singlet appeared at around 9.1 ppm which was assigned to azomethine proton ($-\text{C}=\text{N}$). The position of azomethine signal in the complex appeared upfield at around 8.2 ppm compared to that of the free ligand indicating coordination [30] through the azomethine nitrogen atom. A multiplet observed around 6.9-7.9 ppm in the complex has been assigned to the aromatic protons of benzene in Schiff base ligand [29]. The methylene protons of the alkyl chain appeared in the region 1.12-3.65 ppm in the Schiff base. In the case of complex, the methylene protons of the of the alkyl chain appeared in the region of 1.12-3.36 ppm. The methyl protons of the alkyl chain appeared in the region 0.8 ppm for the complex.

^{13}C NMR Spectra

The ^{13}C NMR spectrum of compound was recorded in deuteriochloroform. Fig. 5 shows the ^{13}C NMR spectrum of ligand. In the ^{13}C NMR spectrum of surfactant Schiff base ligand, a sharp singlet appeared at around 157 ppm and it was assigned to azomethine carbon. The aromatic carbon signals of surfactant Schiff base ligand appeared at around 131-117 ppm. The methyl carbon of the surfactant Schiff base ligand appeared around 14 ppm. The methylene carbons of the surfactant Schiff base ligand appeared around 41-22 ppm. The ^{13}C NMR spectrum of surfactant Schiff base complex taken in D_2O were consistent with the expected structure. Fig: 10 shows the ^{13}C NMR spectrum of the complex. In the ^{13}C NMR spectra of the free Schiff base ligand the sharp singlet that appeared at around 157 ppm has been assigned to azomethine carbon. The position of azomethine carbon signal in the complex appeared up field at around 165 ppm compared to that of the free ligand indicating coordination through the azomethine nitrogen atom. The aromatic carbon signals of the complex appeared at around 137-117 ppm. The methylene carbons of the ligand

appeared around 30-22 ppm. But in the case of complex, the methylene carbons appeared around 31-22 ppm. The methyl carbon of the complex appeared around 14 ppm. The carbon signal in (C-O) bond appeared around 165 ppm for the complex.

Antimicrobial Activities

Antimicrobial activity was evaluated by measuring the diameter of the zone of inhibition in mm against the test microorganisms and the solvent. DMSO was used as solvent control. Ciprofloxacin was used as reference antibacterial agent. The tests were carried out in triplicates. The ligand showed no significant activity against microorganisms (Fig.6).

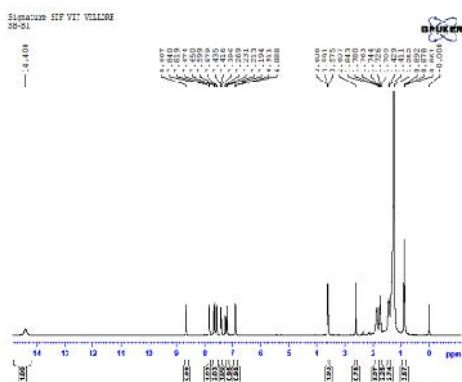


Fig. 5: ¹H NMR spectrum of octadecylamine ligand

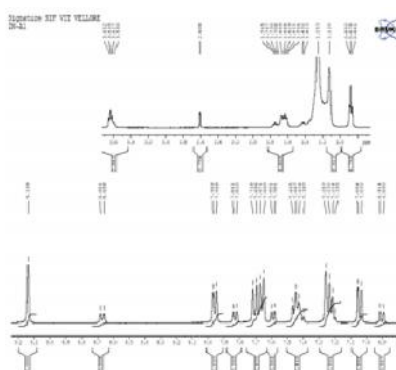


Fig. 6: ¹H NMR spectrum of octadecylamine ligand

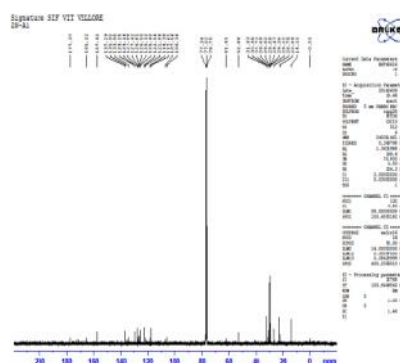
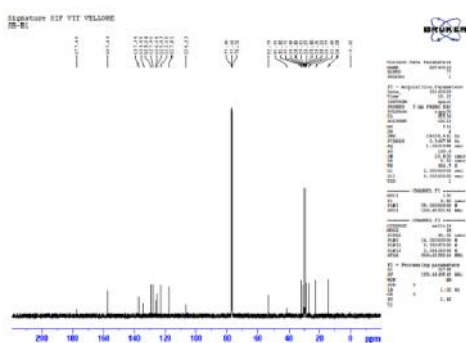
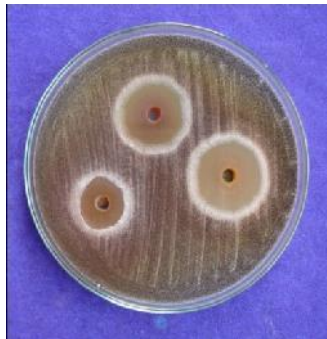


Fig. 5 & 6: ¹³C NMR Spectrum of Octadecylamine Ligand and complex

The surfactant Schiff base complex was screened in vitro for its bacterial activity against certain pathogenic bacteria and fungi species using disc diffusion method. The surfactant Schiff base complex was found to exhibit significant activity against Gram positive, Gram negative bacteria and fungi.

Summary and Conclusion



A study on the synthesis of surfactant Schiff base ligand, metallosurfactant zinc (II) complex and biological activities were carried out in this research work. The characterization of ligand and the complex were achieved through Physico-chemical and spectroscopic methods. The Schiff base ligand is stable and can be used for the synthesis of a large number of metal complexes.

Fig. 7: Antibacterial activities of surfactant Schiff base ligand & zinc (II) complex against *Escherichia coli*

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