Colloid and Interface Science Communications 27 (2018) 26–34

Contents lists available at ScienceDirect

Colloid and Interface Science Communications

journal homepage: www.elsevier.com/locate/colcom

Spectroscopic, Conductometric and Biological Investigation of $[Ni(phen)_3]F_2.EtOH.MeOH.8H_2O$ Complex in Anionic Micellar Media

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A B S T R A C T

This manuscript reports the investigation of physicochemical behavior of $[Ni(phen)_3]F_2.EtOH.MeOH.8H_2O$ (Tris(1,10-phenanthroline)nickel(II) fluoride Ethanol(1/2)Methanol(1/2) octahydrate) complex with anionic surfactants (sodium dodecyl sulphate SDS and sodium stearate SS). Binding and partitioning parameters were determined by UV–Visible spectroscopy while CMC and thermodynamic parameters of complex-surfactant interactions were determined by electrical conductivity measurements. Ni-complex increased critical micellar concentration (CMC) of both surfactants. The investigated Ni-complex showed quite significant antioxidant activity against DPPH, hemolytic activity against RBCs, while there was no substantial cytotoxic activity against 3 T3 cell line.

1. Introduction

Transition metal complexes have numerous applications in molecular biology, biomedical and pharmaceutical research and biological activities, due to high coordination numbers and geometries [1–3]. Nickel is one of the essential trace metals in human body; it plays many biological functions and show synergetic interactions with the drugs. It has key role in hydrogenase biosynthesis, carbon monoxide dehydrogenase, glucose breakdown, enzyme production and in the field of chemical kinetics and surfactant science [4–6] to initiate some key chemical reactions. Transition metal forming complexes of such type $[M(LL)_3]$ (M represents Cobalt(III), Nickel(II) or Ruthenium(II) whereas "LL" symbolizes, 1,10-phenanthroline (phen/modified phen), have shown remarkable biological activities, most significantly antimicrobial, antifungal, antibacterial and antitumor activities. There is special interest in investigating *N,N*-bidentate phenanthroline type metal complexes mainly due to its ability to control biological properties. Formation of chelates and high affinity of phenanthroline type ligands to metal ions, ensure eminent position of such complexes in pharmaceutical and coordination chemistry.

Thus complexes of Nickel (II), Cobalt (III & II) and Ruthenium (II) with 1,10-phenanthroline (Phen) and its derivatives $[Co(ma)_2(phen)].5H_2O$, $Co(phen)(ma)]Cl.4H_2O$ (where "ma" represents maltolate) [7], $[Ni(phen)_3]^{2+}$, $[Ru(phen)_3]^{2+}$, $[Mn(valp)_2(phen)H_2O]$, $[Co(valp)_2(phen)H_2O]$, $[Co(phen)_3]^{3+}$ (where "valp" stands for sodium valproate) [8], $[Ni(phen)_2(dppz)]$(where "dppz" symbolizes dipyridophenazine) are known.

Surfactants are actually amphiphilic molecules which form colloidal-sized aggregations termed as micelles and they increase solubility of sparingly soluble or less soluble materials in water. Solubilization plays key role in many industrial and biological processes. The structures of Ni-complex and micellar media have a strong effect on partition coefficient. Micelle formation is distinctive property of surfactants which make it essential in pharmaceutical industry as these micelles help in simulating and act as substantial alternative of biological membranes due to their hydrophilic surface and its hydrophobic core and reveal drug-membrane interaction. Micelles resemble structurally with biological membranes which make them suitable to be used as models for conducting *in vitro* investigation on drug and biomembrane interactions. There are several drugs including anti-depressants, antibiotics, tranquilizers and local anesthetics agents which interact with biomembranes to exhibit biological activities [9–13]. Valuable information is available regarding these interactions from such investigations. Therefore, extensive research work is being conducted in this pharmaceutical science to study drug-surfactant interactions using various techniques and models [14–17].

Taking into consideration, the biological properties shown by nickel and 1,10-phenanthroline and their complexes, it was envisaged to investigate the interactions of $[Ni(phen)_3]F_2.EtOH.MeOH.8H_2O$ with anionic micellar media of SDS and SS using UV/Visible spectroscopic and conductometric techniques. Although Ni-complex under investigation has already been synthesized and structurally characterized [18], but its biological activities invited us to study its interactions with

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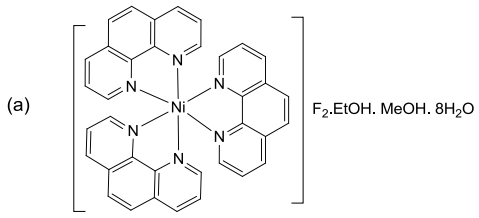
https://doi.org/10.1016/j.colcom.2018.09.004
Received 13 June 2018; Received in revised form 9 September 2018; Accepted 25 September 2018



Tris(1,10-phenanthroline)nickel(II) fluoride Ethanol(1/2)Methanol(1/2) octahydrate

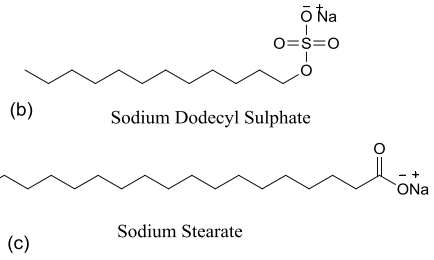


Fig. 1. Structures of (a) Ni-complex (b, c) anionic surfactants.

the anionic micellar media of SDS and SS so that its interaction with biomembranes can be foreseen. We are reporting the interaction of [Ni(phen)$_3$]F$_2$.EtOH.MeOH.8H$_2$O complex (NPC) with SDS and SS by spectroscopic and conductometric measurements. This interaction will be helpful in getting more information about its binding with biomembranes. Previously reported literature does not include such interactions of Ni fluoride complex with surfactants [18,19]. The structures of the complex and anionic surfactants are given in Fig. 1.

2. Experimental Section

2.1. Chemicals and Preparation of Solution

Nickel(II)fluoride tetrahydrate (98%; CAS, 13940–83-5; Sigma Aldrich, Germany), sodium dodecyl sulphate (SDS: CAS, 151–21-3, 99%; Sigma Aldrich, Germany), sodium stearate (SS: CAS, 822–16-2; 98%; Sigma Aldrich, Germany) and ligand 1,10-phenanthroline (CAS: 66–71-7; 99%, Alfa Aesar, Germany) were purchased and used without any further purification. Methanol and ethanol and were purified by repeated distillations over CaO. Water was distilled by using still apparatus. The solutions of the Ni-complex were prepared in deionized water for conductometric and spectroscopic measurements. An aqueous solution of Ni-complex (primary solution) was prepared and secondary solution was prepared by dissolving anionic surfactants ranging from pre- to post-micellar concentrations. The concentration range was 7.5–15 mM and 2.5–8.0 mM for SDS and SS respectively. The stock solution was diluted to keep absorbance below 1 holding Lambert-Beer's law.

2.2. Synthesis of [Ni(phen)$_3$]F$_2$.EtOH.MeOH.8H$_2$O

The [Ni(phen)$_3$]F$_2$.EtOH.MeOH.8H$_2$O complex [NPC] (Fig. 1), was prepared by slight modification in the reported method. Ligand, 1,10-phenanthroline (30 mmol; 5.4 g) was refluxed with 50 mL methanolic suspension of nickel fluoride NiF$_2$.4H$_2$O (10 mmol, 1.7 g) for 15 h until all the salt have dissolved leading to the formation of purple-blue solution. Cooled filtrate was reduced to 1/3 of its volume with rotary evaporator. The product appeared as pink powder with a yield (75%) after keeping the solution at room temperature for 10 days. This powder was dissolved in ethanol to get red colored crystal of Ni-complex [18]. In the electronic absorption spectra of Ni- complex there appeared three well resolved bands at 8630, 14450 and 2430 cm^{-1}. These were assigned to spin allowed transitions: ^3A_2g (F) ➔ ^3T_2g (F); ^3A_2g (F) ➔ ^3T_1g (F) and ^3A_2g (F) ➔ ^3T_1g (P) respectively and these transitions are consistent with octahedral configuration [18,19]. Elemental Analysis (EA) for $C_{75}H_{90}F_4N_{12}O_{16}Ni_2$, Calcd: C; 54.89, H; 5.52, N; 10.24%. Found: C; 54.83, H; 5.54, N; 10.22%. In the IR spectra of the complex characteristic bands were observed due to functional groups of 1,10-Phenanthroline. The three broad continua were observed centered at 3400, 1625 and 636 cm^{-1} due to –OH hydrogen bonds [18,20]. A medium intensity band in the range of 435 cm^{-1} was present in the far IR region due to ν(Ni—N) vibrations. There were no band attributable to Ni—F was found in the far IR region, which indicated absence of F$^-$ coordination to metal ion [18,21].

2.3. Apparatus and Methods

2.3.1. Specific Conductivity

Specific conductivity of the solutions was measured with Hanna Cond HI-99301 (USA) in temperature range from 298 to 328 K with and an increment rate of 10 K while accuracy was maintained up to ± 0.5% ± 2 and ~ ± 0.5 K. The conductometer was equipped with a platinum black coated electrode (for avoiding polarizations) for specific conductivity measurement from 0.01 μS to 199.9 mS. The electrode of instrument was calibrated with solution of KCl within the required concentration range using molar conductivity data [22,23].

2.3.2. UV/Visible Spectroscopy

All the absorption spectra of complex in pure H$_2$O and at various concentrations of surfactants were measures on Perkin Elmer's computer interfaced double beam UV–Visible spectrophotometer (USA). All simple and differential spectra were recorded in square quartz cells (10 mm thick; 1 nm slit width) at 298 K with ± 0.5 K accuracy control. While recording absorption spectra by differential UV/visible spectroscopy, distilled water was taken as blank and aqueous solution of Ni-complex was kept the reference, while the ternary solution of complex in the surfactants was taken in sample cell.

2.4. Biological Activities

2.4.1. Antioxidant Assay

Antioxidant activity of Ni-complex was determined with DPPH. Stock solution was prepared in DMSO (40 mg/mL). Then the solution of complex was added to the solution of DPPH (100 μL/5 mL), 0.004% methanol and incubated for about 30 min at ambient temperature. Absorbance of the sample was observed at 517 nm. Triplicates of the assay were run [24]. Antioxidant activity of Ni-complex in micellar solution of SDS and SS was determined with DPPH.

$$I\% = [(A\ \text{blank} - A\ \text{sample})/A\ \text{blank}] \times 100$$

2.4.2. Hemolytic Assay

For *Hemolytic assay*, blood sample (3 mL) was obtained from some healthy donors and then centrifuged in sterile, screw-caped polystyrene tube (15 mL) for 5 min at 2000 rpm while supernatant was cast off. From the remaining material, viscous pellets were washed thrice with a sterile and chilled isotonic solution of PBS (PBS preparation: KH_2PO_4, 0.2; NaCl 8; KCl, 0.2 and Na_2HPO_4 were homogenized for 1 h in order to maintain pH at 7.4). The RBCs were calculated with haemacytometer (Fisher ultraplane, Neubauer ruling instrument USA) after suspending the washed blood cells in chilled isotonic PBS solution making final volume up to 20 mL. RBCs count was maintained to 7.068 × 10^8/mL by diluting with sterile PBS in an ice bath. Ni-complex (20 μL) was then aseptically transferred to microfuge tubes having 2 mL capacity. 0.1% Triton (X-100) was taken as positive (100% lytic control) and PBS taken as negative (0% lytic control). After incubating RBCs, the percentage hemolysis was determined at 576 nm. Hemolytic activity of Ni-complex in micellar solution of SDS and SS was also determined. This procedure for the Ni-complex was run in replicates [25].