

Synthesis, characterization and micellization behaviour of some surface active mixed-ligand complexes of cobalt(III)

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Abstract

Micelle formation of some surface active mixed-ligand cobalt(III) complexes containing one of the chelating ligands ethylenediamine (en), triethylenetetramine (trien), 2,2 bipyridyl (bpy) or 1,10 phenanthroline (phen) as equatorial and with different axial amine ligands (dodecylamine or cetylamine) were synthesized and characterized by IR, NMR, UV–visible electronic absorption spectra and elemental analysis. The critical micelle concentration (CMC) values of these surfactant metal complexes in aqueous solution were obtained from conductance measurements. Specific conductivity data (at 303, 308 and 313 K) served for the evaluation of the temperature-dependent CMC and the thermodynamics of micellization (ΔG_m^0 , ΔH_m^0 and ΔS_m^0).
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1. Introduction

A feature of modern coordination chemistry is its expanding ability to mimic form and structure in biology. This has largely been achieved using a principle which has itself been borrowed from biology: the self-assembly of well-defined and complex molecular entities from constituent subunits in solution. Unlike biology, however, self-assembly in coordination chemistry occurs through the formation of coordinate bonds rather than weak inter- or intramolecular interactions. Self-assembly in coordination chemistry consequently provides an important and powerful entry into supramolecular engineering and the associated fields of solid-state and crystal engineering [1,2]. It potentially also affords novel catalytic systems [3] which may ultimately be induced to offer the selectivity and usefulness of biological catalysts. Recently, there has been a growing interest in the study of processes under con-

ditions globally referred to as restricted geometry conditions, that is under conditions in which a given ligand is forced (or different ligands are forced) to remain totally or partially bound at the surface of some substrate. In a broad sense, the restricted geometry conditions encompass phenomena such as homogeneous, heterogeneous and enzymatic catalysis [4,5], reactivity in micellar systems and microemulsions [6], molecular machines [7], molecular electronics [8], trapping of substrates by polyelectrolytes [9], conformational changes of DNA induced by the binding of solutes [10] and so forth. Numerous studies have been performed addressing the dependence of electron transfer on different environments including metalloproteins [11], Vitamin B₁₂ [12], liquids [13,14], micelles [15], vesicles [16] and DNA [17]. It is well known that amphiphilic molecules are characterized by their dual nature. On the same molecule two differentiated parts, the hydrocarbon (hydrophobic) and the ionic (hydrophilic), are found. This general structure, characteristic of surfactants, is responsible for the self-assembly process in solution. In the last century numerous works have been done on the nature of the self-assembly process and the interactions

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of these structures with salts, alcohols, proteins and other compounds [18]. Surface active materials are major building blocks of many physical, chemical and biological systems. They have been introduced into several commercial products such as antiseptic agents in cosmetics and as germicides [5], and also have found a wide range of applications because of their unique solution properties such as detergency, solubilization and surface wetting capabilities, in diverse areas such as mining, petroleum and pharmaceutical industries. It has been observed that several redox reactions in micellar media were influenced by the hydrophobic and electrostatic forces and for a given set of reactions the observed rate depends on the extent of association between the reactants and micellar aggregates [19–23]. A growing number of applications have been developed to study metallosurfactants in this content. They are a good enzymatic model for the catalytic hydrolysis of carboxylic acid esters, since they mimic not only the active center of the metalloenzyme but also the microenvironment of the metalloenzyme. In the course of studies on the effects of metallosurfactants on chemical reactions, catalytic effects were observed above a critical micelle concentration (CMC). Such systems offered the possibility to investigate the effects of the local reactant concentrations in the micellar subphase, as well as the local microenvironment on the reactivity [24–28].

Cobalt(III) complexes, by virtue of their abundance and diversity, have played a fundamental role in our understanding of the structural, spectroscopic and electrochemical properties of coordination compounds. We have been interested in the synthesis and micelle forming properties of Co^{III} complexes containing lipophilic ligands for a long time [29–31]. As in biology, such compounds may exhibit novel physical and chemical properties with interesting and useful associated applications. Studies on the chemistry of Co^{III} metallosurfactants have received a sustained high level of attention due to their relevance in various redox processes in biological systems and act as promising agents for antitumor [32], anthelmintic [33], antiparasitic [34], antibiotics [35] and antimicrobial activities [17], and

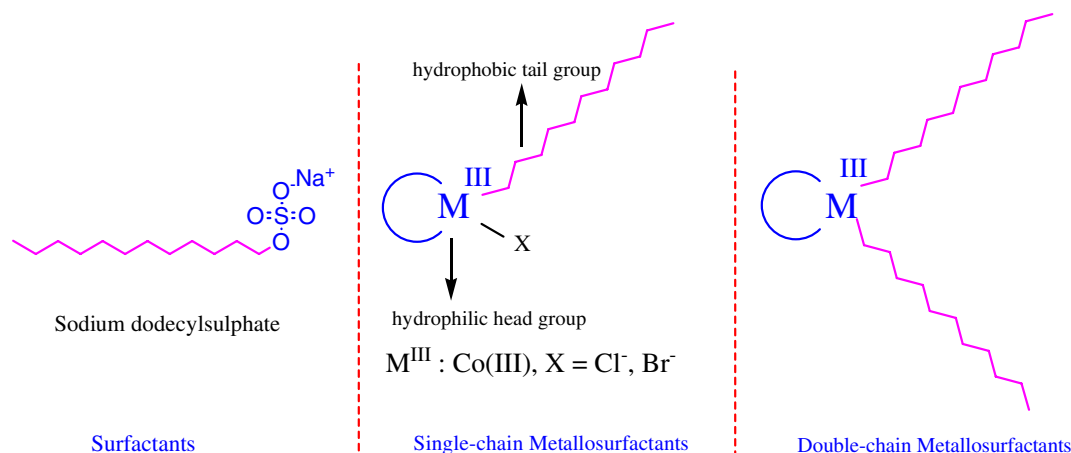
a boost of interest because of their multiple applications in fields such as medicine [36], magnetic resonance imaging [37] and drug delivery [38].

A characteristic feature of transition metals is their ability to form complexes with a variety of neutral molecules such as bpy and phen. These are widely used as a classical N,N' -bidentate ligand to prepare mixed-ligand complexes in coordination chemistry. A common feature of these ligands is the presence of a vacant π orbital that can accept electron density from the metal ion to form a type of π bonding that supplements the σ bonding arising from the donation of a lone pair of electrons. Most of the metal complexes containing bpy and phen chelators can act as potential anti-tumor agents. Intensive investigations of the coordination chemistry of metallosurfactants with chelating ligands continue to be stimulated by interest for metallobiomolecules, the search for appropriate systems for binding and activating simple molecules, catalysis, and magnetic interactions [39,40]. In spite of the greatest effort and success in the study of metallosurfactants of cobalt(III) complexes, such complexes still attract much attention due to their interesting properties and the relative simplicity of their synthesis (Scheme 1). Recently, there has been increasing interest in the use of these organized media to study the fundamental photochemical reactions of metal complexes in relevance to the conversion of solar energy into other useful forms of energy through photochemical reactions [41,42]. As a part of our studies on transition metal-based surfactants [29–31] in this paper we report the synthesis, characterization and determination of critical micelle concentration values of some more novel Co^{III} metallosurfactants.

2. Experimental

2.1. Materials

All the reagents were of analytical grade (Aldrich and Merck). Ultra pure water, obtained by deionising distilled water (conductivity $<10^{-6} \text{ S m}^{-1}$) using a Milli-Q Reagent



Scheme 1.

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