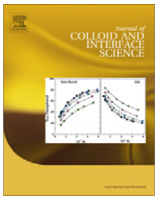
Journal of Colloid and Interface Science 393 (2013) 219–227

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis



Self-aggregation and solution behavior of synthesized organo transition metal (Co, Fe, Zn) amphiphilic complexes

S.K. Mehta *, Ravneet Kaur

Department of Chemistry & Centre of Advanced Studies in Chemistry, Panjab University, Chandigarh 160 014, India

ARTICLE INFO

Article history:
Received 9 August 2012
Accepted 1 November 2012
Available online 12 November 2012

Keywords:
Metallosurfactant
Ultrasonic studies
Self-aggregation
Thermal behavior
Compensation behavior
Redox activity

ABSTRACT

We report the aggregation behavior for the complexes of first row transition elements namely iron, cobalt, and zinc. Metal surfactant complexes of the type $[M(CH_3COO)_4]^{2-}[C_{12}H_{25}NH_3^+]_2$ have been synthesized, keeping the hydrophobic dodecyl chain same. The change in the thermal and redox behavior upon metal complexation with conventional surfactants has been analyzed. The influence of different metal ions on the physicochemical and solution properties of metal surfactant complexes has been explored by using techniques such as conductivity, surface tension, ultrasonic velocity, and cyclic voltammetry. The different metal surfactant complexes synthesized show different properties, which can be attributed solely to the change of metal (namely, cobalt, iron, and zinc) only.

1. Introduction

The advent of metal surfactant complexes has revolutionized the world of surfactants. The metallosurfactant chemistry had long remained an unexplored part because it combines two entirely dissimilar subject areas; organometallic chemistry and surface science. The grouping of the inorganic metal ion with the hydrophobic organic part imparts unusual properties to the surfactant. Although it is a relatively recent field, even in this short time scale, many applications of metallosurfactants have been reported in the field of catalysis, transport, sensing, etc. [1]. They also present numerous biomedical applications as MRI contrast agents, for DNA binding, etc. [2,3]. The self-assembly nature of this class of surfactants leads to unique properties, which have not been attained otherwise. The supramolecular assemblies formed as a result of aggregation, concentrate metal ion at the interface that can be put to a variety of uses. Micelles, reverse micelles, microemulsions, and other self-assembly structures created by these surfactants have been explored as templates for organic and inorganic nanoparticles and nanostructure material synthesis [4–6]. Recently, Lu and coworkers [7] reported a facile method for preparing ultrathin Au nanowires using [(oleylamine) AuCl] complex chains formed through aurophilic attraction. Martinez et al. [8] have shown that metallosurfactants are capable of showing excellent tuning emission properties as well.

In-depth knowledge into the characteristics and properties of these metallosurfactants is still required before they can be used for further applications. Although there are a number of recent interesting reports in the field of metallosurfactant chemistry, evaluating the effect of solvent [9], alkyl chain or head group [10–12] on aggregation behavior, the effect of metal has not really been investigated extensively. The focus of the present study is to look at the effect of first row transition metal ion change on the physicochemical as well as thermal characteristics of surfactant. Consequently, the metal complex formation possessing surfactant characters has been pursued. The incorporation of a metal ion into the conventional organic systems has been the most widely accepted approach to metallosurfactant synthesis. Ligands containing quaternary ammonium groups can be utilized as excellent tools to obtain complexes with surface active or physicochemical properties as they possess a long alkyl chain and a hydrophilic group, which makes them capable of forming a metal complex with surface-active properties [13].

The present report focuses on the relationship between properties and structure of a metal surfactant system. A range of metallosurfactants was prepared using the first row transition metal elements, namely iron, cobalt, and zinc. The hydrophobic dodecylamine chain has been kept the same in each case, in order to observe only the effect of metal. The results show interesting spectroscopic, thermal, redox, and self-aggregation properties, which are associated to the metal ion change.

---

* Corresponding author. Fax: +91 172 2545074.
E-mail address: skmehta@pu.ac.in (S.K. Mehta).

0021-9797/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2012.11.001

2. Materials and methods

2.1. Materials and techniques used

Cobalt(II)acetate, iron(II)acetate, zinc(II)acetate, and sodium acetate having purity >98% were purchased from Sigma. Dodecylamine and acetic acid of analytical grade were commercially available from Merck. The materials were used as received. Deionised doubly distilled water (using Labpure Analytica Bioage instrument and further distilled using $KMnO_4$) was used for conductivity measurements. The conductivity of water obtained was less than 3 $\mu S\ cm^{-1}$. Conductivity experiments were carried out on Pico Lab India Digital conductivity meter. FTIR (Fourier Transform Infra Red) measurements were performed on a Perkin Elmer (RX1) FT-IR spectrophotometer. For ^1H NMR spectra, Bruker Avance 300 spectrometer (300 MHz) was used. The elemental analyses were carried out using CHNS—O ANALYZER thermo scientific flash 2000 organic elemental analyzer. Thermal behavior was investigated using SDT-Q-600 (TA Instruments). Sample measurements were carried out in alumina pans under nitrogen atmosphere. For electrochemical studies, cyclic voltammeter Autolab Type III electrochemical system, with GPES software from Metrohm, was used. The counter electrode employed was Platinum wire, working electrode was Platinum electrode and as reference electrode Ag/AgCl was used. DSA 5000 instrument was used for ultrasonic velocity investigations at 25 °C ± 0.001 (Error limit: density $\pm 5 \times 10^{-6}$ g cm^{-3}; velocity $\pm 5 \times 10^{-2}$ ms^{-1}). Surface tension was measured on a K20 Krüss tensiometer (Germany) with an error limit of ±0.1 mN m^{-1} using the Ring Method at 298.15 K.

2.2. Synthesis of metal surfactant complexes

Metallosurfactant of the type: $[M(CH_3COO)_4]^{2-}[C_{12}H_{25}NH_3^+]_2$; M: metal was synthesized via a two-step process [14]. It involved the preparation of dodecylamine acetate by addition of 1 mM acetic acid to 1 mM dodecylamine, with continuous stirring at room temperature. Further, refluxing 1 mM metal acetate with 2 mM dodecylamine acetate in ethanol resulted in the formation of metal surfactant complex. The obtained residue was recrystallized using dichloromethane–ethyl acetate mixture. The synthesized metallosurfactants have been characterized by various techniques as discussed in the next section.

3. Results and discussion

3.1. Spectroscopic techniques

3.1.1. FTIR spectroscopy

FTIR spectroscopy has been essentially used to determine the binding site of the dodecylammonium chain to the metal ion. The IR spectra (Fig. A1, Supplementary information) are dominated by peaks in the regions 3000–2800 cm^{-1} and 1600–1350 cm^{-1}. Two peaks present at 2850 cm^{-1} and 2925 cm^{-1} are due to the C—H stretching within the methylene and methyl group of dodecyl chain. Only the C=O stretching frequency (1560 cm^{-1}) for free dodecylammonium acetate shows a change on complexation with the metal ion and shifts to a higher frequency for the surfactant metal complexes. All the other IR peaks are observed at approximately the same positions. This confirms that the acetate group of dodecylammonium acetate coordinates with the metal ion in the metal surfactant system.

3.1.2. ^1H NMR spectroscopy

^1H NMR spectra for free and metal complexed dodecylammonium acetate are quite different. Compared to the well-defined spectrum of free dodecylammonium acetate, the metal complexes show a few broad signals due to interference from the paramagnetic character of iron and cobalt. In contrast, the spectrum for zinc is very well resolved because of its diamagnetic nature. Upon complexation with the metal ions, all the proton signals of the ligand do not undergo chemical shift. The NMR spectrum of the free dodecylamine acetate shows a broad singlet at 5.5 ppm corresponding to ammonium protons. However, metal complexes show this signal in the 1.4–4.8 ppm range (Fe 1.5, Co 1.54, Zn 4.8). The shift of this signal is consistent with the coordination of ammonium group to metal ion. Different magnitudes indicate the strong interaction of iron with the dodecylammonium chain and the weak interaction of zinc. This suggests that metal is coordinated to nitrogen.

3.2. Thermogravimetric analysis (TGA)

3.2.1. Thermal behavior

The thermal analysis of the metallosurfactants has been carried out using thermogravimetry (TG) and differential thermogravimetry (DTG). Typical TG plots (with overlapped DTG curves) obtained for the cobalt and iron surfactant complexes have been depicted in Fig. 1. It can be inferred by the well-defined curves obtained that the cobalt and iron surfactant complexes follow step wise decomposition and exhibit high thermal stability. (Due to waxy nature of zinc surfactant complex, TG measurements could not be done at room temperature.)

The TG plots demonstrate that the decomposition takes place in two steps. The first step, between room temperature and 250 °C approximately, initiates the complex decomposition along with the breakdown of quaternary ammonium structure. The second mass loss step eventually results in the formation of metal oxide or metal. For iron complex, decomposition in the temperature range of 160–367 °C consists of two overlapping peaks with a net weight loss of 81.5%. The percentage weight loss is consistent with the elimination of two acetic acid, two dodecylamine, and one acetone molecule. After the second step, the material decomposition finally yields iron whereas in the case of cobalt complex successive weight losses end with the formation of cobalt oxide. The transition temperatures for decomposition, DTG_{max}, obtained from the peak values in DTG graphs along with the corresponding mass loss of species have been given in Table 1. The TG results obtained experimentally are in excellent agreement with the calculated values as summarized. The expected decomposition species from the three steps are indicated in Scheme 1.

3.2.2. Thermodynamic parameters of decomposition

Numerous methods viz. Horowitz–Metzger, Madhusudanan–Krishnan–Ninan, van Krevelen, Ozawa and Wanjun–Yuwen–Hen–Cunxin are available for the determination of thermodynamic decomposition parameters. The integral method by Coats and Redfern [15] (Eqs. (1) and (2)) has been used for the assessment of thermodynamic parameters of decomposition for the metal surfactant complexes in the present work.

$$-\log\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} = \log\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303RT} \quad \text{for } n \neq 1 \qquad (1)$$

$$-\log\frac{-\log(1-\alpha)}{T^2} = \log\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303RT} \quad \text{for } n = 1 \qquad (2)$$

The parameters α, β, T, E, A, R represent the degree of reaction, heating rate (K min^{-1}), temperature (K), activation energy (kJ mol^{-1}), pre-exponential factor (min^{-1}), and gas constant (8.314 J mol^{-1} K^{-1}), respectively. In general, $2RT/E \ll 1$ exhibits a small variation with T. Practically, it is assumed that the term $(1–2RT/E)$ is approximately constant and equal to unity [16].