Co(III) based surfactant complexes and their Dye, BSA and free radical activities

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Abstract

Study reports the preparation of metal/surfactant complexes or Metal Organic Ionic Framework (MOIF) based on ionic interaction of [Co(NH₃)₆]³⁺ and Dioctyl sulfosuccinate (AOT)/Sodium dodecyl sulfate (SDS). MOIF is result of strong ionic interaction between cationic and anionic moieties without disturbing their own structures. MOIF of [Co(NH₃)₆]³⁺ and SDS was found in solid powdery form while [Co(NH₃)₆]³⁺ + AOT produced sticky material. UV/Vis, FTIR, Raman and XRD measurements were used to characterize the MOIFs. The ionic interaction between cationic complex [Co(NH₃)₆]³⁺ and anionic sulphur of AOT/SDS was confirmed by comparing spectra with their parental moieties. MOIF containing hydrophilic and hydrophobic groups showed their dye interaction activity studied with methyl orange (MO) and methylene blue (MB) depicting impact of linear and iso-alkyl chain and hydrophilic amine groups. MOIF showed their protein binding nature, studied with bovine serum albumin (BSA), analyzed with spectrophotometric titrations revealing that hydrophobicity affects the interaction. In Dye and protein interactions, MOIF of [Co(NH₃)₆]³⁺ + AOT showed strong activities than MOIF of [Co(NH₃)₆]³⁺ + SDS due to more hydrophobicity associated with MOIF of [Co(NH₃)₆]³⁺ + AOT. MOIFs have also shown good scavenging effect tested in vitro against free radical, 2,2-diphenyl-1-picrylhydrazyl (DPPH), and the same, strong interaction for MOIF of [Co(NH₃)₆]³⁺ + AOT noticed.

Keyword: Inorganic chemistry
1. Introduction

In recent days a new concept of Metal Organic Ionic Framework (MOIF) is being emerged in the field of chemistry [1]. The term MOIF should not be confused with the MOF (Metal Organic Framework) because MOF is a coordinated framework ligand around to the centralized metal ion [2]. In the case of MOIF, a ionic framework is developed due to ionic interaction between cationic or anionic inorganic complex and cationic or anionic surfactants [1]. The preparation of MOIF is very simple and there is no need to have any special condition like temperature, pressure any special organic solvent. Since, MOIFs are formed due to ionic interaction; therefore the water is most suitable solvent for the same at room temperature [1]. Surprisingly, prepared MOIFs were found to be soluble in organic polar solvent like methanol and ethanol when compared with simple metal surfactants complexes, those are not [3, 4, 5]. Although MOIFs are ionic product but not ionized like salts, thus, their combine effect of hydrophobic (alkyl chains of surfactant) and hydrophilic (Polar ligands attached to the metal ion in complex; NH$_3$ in [Co(NH$_3$)$_6$]$^{3+}$) domains contribute a lot to material and medicinal activities [1]. This MOIF’s approach can stand valid for the construction of large synthetic molecules having desired properties like MOF [2] and can furnish many valuable applications [6]. Recent attempt in this field have revealed that the MOIF approach is an impressive tool to project new molecules as binding agents for protein and degradation of industrial organic waste like dye [1]. This synthetic strategy can afford a variety of structures ranging from host-guest complexes and organizations to linear Metallo-polymers through ionic bonding and metal-ligand bonds [7, 8, 9, 10, 11]. This ionic network is particularly interesting owing to their significantly different macroscopic properties emanating from the individual building blocks [8, 11]. Such kind of MOIF may also develop a supramolecular ionic network having much more applications and such kind of strategy has been applied to prepare supramolecular networks using hydrogen, ionic and metal – ligand bonding [12, 13, 14, 15]. The ionic network between two oppositively charged species can give a solid or liquid state to the compound depends upon strength of interaction [1, 13]. This ionic framework deals with that ionic molecular assembly where cationic charge is balanced by anionic species, and molecule becomes neutral and attains a steady state [12]. With such relevance, in present study, we prepared MOIFs (Fig. 1a and 1b) containing Hexamine Cobalt (III) cation and Dioctyl sulfosuccinate (AOT)/sodium dodecyl sulphate (SDS) as anion. The MOIF are studied for their interaction studies with dyes, BSA protein and free radical. For the preparation of MOIFs, we did not use any organic
solvent, and water was used for the same purpose. So, the use of water as solvent makes this preparation a green preparation or approach that describes the novelty of the work. Thus, the present study is an attempt to addition in the field of MOIF where it is the combination of cationic inorganic species and anionic organic species (see Scheme 1).
2. Experimental

2.1. Materials

Chemicals, $\text{[Co(NH}_3\text{)_6]}\text{Cl}_3$, SDS, AOT, DMSO, MO, MB were procured from Merck and Sigma having 99.99% purity. All chemicals were used as received without any purification. The double distilled water of conductivity $10^{-7}$ Scm$^{-1}$ was used.

2.2. Method

2.2.1. General consideration for preparation of MOIF

As below mentioned scheme, initially, aqueous solutions of $\text{[Co(NH}_3\text{)_6]}\text{Cl}_3$ and SDS/AOT were prepared separately with 1: 3 molar ratio respectively. Then these were mixed in 50 mL round bottom flask at 800 rpm at magnetic stirrer for an hour or till complete precipitation. The powder and reddish sticky states of MOIFs of SDS and AOT were obtained respectively. The precipitate was washed with water several times and dried in vacuum oven. MOIF were found to be soluble in Dimethyl Sulfoxide.

2.2.2. Characterization of MOIF

UV/Vis spectra were recorded with a Spectro 1800 plus model UV/Vis spectrophotometer from 200 to 600 nm using 1 cm path length cuvette. DMSO was used for solution preparation and concentration of MOIF was $1 \times 10^{-3}$ M. FTIR (Perkin Elmer) spectra were taken in KBr plates with polystyrene thin film as calibration standard. The XRD measurements were carried out using Bruker D8 Advance X-ray Diffractometer. The x-rays were produced using a sealed tube and the wavelength of x-ray was 0.154 nm (Cu K-alpha). The x-rays were detected using a fast counting detector based on Silicon strip technology (Bruker Lynx Eye detector). Raman measurements were carried out with Micro Raman system from Jobin Yvon Horibra LABRAM-HR visible instrument with range from 50 cm$^{-1}$ to 700 cm$^{-1}$ at 473 nm wavelength.
2.2.3. Dye interaction study

Stock solutions of chosen dyes were prepared in DMSO having concentration $1 \times 10^{-4}$M, and solutions of MOIF were also prepared in DMSO from 50 to 200 μM with an interval of 50 μM. Then in 1:1 ration (2 mL of each), the dye and MOIF solutions were mixed and after half an hour UV spectra were recorded.

2.2.4. BSA interaction

Stock solution of BSA 60μM was prepared in DMSO-phosphate buffer (1:2 ratio) where concentration was determined by taking absorbance at 280 nm with molar extinction coefficients of BSA ($\varepsilon_{280} = 44,300 \text{ M}^{-1}\text{cm}^{-1}$) [16, 17], and mixed with MOIF solution in DMSO of 50−200μM with an interval of 50μM in 1:1 ratio separately for half an hour, then spectrophotometric titrations were carried out.

2.2.5. Scavenging activity

Antioxidant or scavenging activities were determined on the basis of a free radical 1,1-diphenyl-2-picrylhydrazyl (DPPH) scavenging effect [18, 19, 20, 21, 22, 23, 24, 25]. Stock solution of DPPH (0.002%) was prepared with DMSO. 1 mL of 0.002% DPPH solution was added into 1 mL of complex of 50, 100, 150, 200μM separately. The reaction mixtures were thoroughly mixed by shaking the test tubes vigorously and incubated for 60 min keeping in the dark. Absorbance was measured at 517 nm in a spectro 2060 plus modeled UV/Vis spectrophotometer. The radical scavenging activity was determined as a result of the decrease in absorbance of DPPH [18] and calculated with the following formula:

$$\text{Scavenging activity} \% = \left( \frac{A_0 - A_S}{A_0} \right) \times 100$$

$A_S$ is the absorbance of DPPH with a tested compound and $A_0$ is the absorbance of DPPH without a tested compound (control). The data calculated for anti-oxidation are presented as means SD of three determinations. The percentage error in experimental data of all interaction analysis was found ±0.01–0.05%.

3. Results and discussion

3.1. Synthesis and charaterizations

Mixing of aqueous solution of $[\text{Co(NH}_3)_6]\text{Cl}_3$ and anionic surfactants AOT and SDS at 500 rpm produced the MOIF of CoAOT $[\text{Co(NH}_3)_6][\text{CH}_3(\text{CH}_2)_3\text{CH(C}_2\text{H}_5)\text{CH}_2\text{O}_2\text{CCH}_2\text{CH(SO}_3\text{)}\text{CO}_2\text{CH}_2\text{CH(C}_2\text{H}_4)(\text{CH}_2)_3\text{CH}_3]$ and CoSDS $[\text{Co(NH}_3)_6][\text{C}_{12}\text{H}_{25}\text{SO}_4]_3$ respectively as per ion exchange mechanism. Since MOIF are product of ionic interaction formed quickly in aqueous solution, so to check the sustainability of inorganic unit within the MOIF, the UV/Vis spectra of MOIF and pure salt
[Co(NH₃)₆]Cl₃ have been analyzed as shown in Fig. 2. Two UV/Vis absorbance peaks at 340 and 470 nm were found for the [Co(NH₃)₆]Cl₃ and respective MOIF, those are assigned for transition from t₂g (5D) to e₉ (5D) as cobalt has +3 oxidation state and d⁶ system. The patterns for the MOIF and pure salt are the same for UV/Vis that inferred the presence of hexamine cobalt (III) unit within the MOIF. In spectra having the same concentration, the difference in absorbance of [Co(NH₃)₆]Cl₃ and respective MOIF is almost 69%. This reduction in absorbance infers that the three chloride ions have been replaced by anionic part of SDS and AOT in MOIF of CoSDS and CoAOT respectively. Similarly, the difference in absorbance at 340 and 470 nm for [Co(NH₃)₆]Cl₃ is 0.182 while the same is very low for MOIF, may be due to that in [Co(NH₃)₆]Cl₃ the amino ligand and metal ion feel the little bit free environment but in the case of MOIF central metal and ligand are surrounded by larger anionic part of SDS and AOT. Similarly, in FTIR spectra (Table 1) the weak bands near 426 and 535 cm⁻¹ are components of the T₁u Co-N stretching mode which has been split by site-symmetry interactions [26]. In both

Table 1. Infrared absorption band assignments for MOIF of SDS and AOT with [Co(NH₃)₆]³⁺.

| Wave number cm⁻¹ | CoSDS | CoAOT | IR band assignment |
|------------------|-------|-------|--------------------|
| 426              | 535   |       | T₁u, Co-N          |
| 585              | 582   |       | Co³⁺−···OSO₃⁻       |
| 723              | 738   |       | ν(SO)              |
| 828              | 881   |       | ν(SO)              |
| 1070             | 1048  |       | ν(OSO₃⁻)           |
| 1242             | 1262  |       | ν(OSO₃⁻)           |
| 1472             | 1472  |       | δ(CH₂)             |
| 1651             | 1651  |       | δ(CH₂)             |
| 2856             | 2902  |       | ν(CH₂)             |
| 2954             | 2934  |       | ν(CH₃)             |
| 3381             | 3458  |       | -NH                |
the MOIF, IR frequencies around 3458 and 3381 cm\(^{-1}\) are assigned for the NH stretching while 2934, 2902, 2856, 2954 cm\(^{-1}\) for alkyl CH stretching. IR bands at 1242 and 1262 cm\(^{-1}\) may be assigned for sulphur-oxygen (S-O) bonds present in SDS and AOT with in MOIF respectively. The vibrational frequencies for interaction of Co\(^{3+}\) and anionic oxygen of SDS and AOT which are characteristic for the formation of MOIF were found at 582 and 585 cm\(^{-1}\) respectively [27, 28]. Thus, UV/Vis and FTIR spectral data has confirmed the formation of MOIF by ionic combination of inorganic unit ([Co(NH\(_3\))\(_6\)]\(^{3+}\) and organic unit (RSO\(_3\)-) as well as sustainability of both units within MOIF. For further confirmation, in Raman spectra the frequencies near around 442 and 500 are assigned for \(E_g\), Co-N stretching and \(A_{lg}\), Co-N stretching respectively for pure [Co(NH\(_3\))\(_6\)]Cl\(_3\) [26] while in the case of MOIF the same frequencies are obtained for the CoAOT but they have been found to be lowered in intensity as well as a strong peak has been found at 600 cm\(^{-1}\) as shown in Fig. 3. This is may be due to that the interaction between cobalt (III) ion and \(-\)ve oxygen of AOT that created a compact environment in MOIF that disabled the vibrations at some extent. In the case of CoSDS there are no peaks found at the mentioned wavelengths. A typical XRD pattern for MOIF is illustrated in Fig. 4a,
from which it can be understood that many sharp peaks are attributed for the crystalline nature of synthesized MOIF where it shows diffraction peaks at 15.83, 18.85, 22.48, 23.24 corresponding to the cubic structure [29, 30]. In powder XRD pattern the below 10 degree of 2 theta values may be attributed for organic part in MSIN while more than this shows the crystalline nature of the MOIF [29]. Table 2 shows the the lattice parameters calculated using following equations (see Fig. 5).

**Fig. 4.** (A) Powder XRD pattern of MOIF of CoSDS and (B). A probable portion of the unit cell of CoSDS illustrating intermolecular contacts.

**Table 2.** Lattice parameters for selected peaks obtained through XRD patterns for CoSDS.

| 2θ  | θ  | Sinθ | Sin squareθ | Ratio 1 | Ratio 2 | hkl | a (nm) | d (nm) | R (radius, nm) |
|-----|----|------|-------------|---------|---------|-----|--------|--------|----------------|
| 5.8897 | 2.9449 | 0.0513 | 0.0026 | 1.00 | 2 | 110 | 2.12 | 1.50 | 1.50 |
| 8.8215 | 4.4108 | 0.0769 | 0.0059 | 2.25 | 4 | 200 | 2.12 | 1.00 | 1.50 |
| 15.5554 | 7.7777 | 0.1353 | 0.0183 | 6.96 | 14 | 321 | 2.12 | 0.57 | 1.50 |
| 18.8910 | 9.4455 | 0.1641 | 0.0269 | 10.24 | 20 | 420 | 2.12 | 0.47 | 1.50 |
| 22.2270 | 11.1135 | 0.1927 | 0.0371 | 14.12 | 28 | 432 | 2.12 | 0.40 | 1.50 |
| 23.5011 | 11.7506 | 0.2036 | 0.0415 | 15.76 | 32 | 440 | 2.12 | 0.38 | 1.50 |
\[
\sin^2 \theta = \left( \frac{\lambda^2}{4a^2} \right) \left( h^2 + k^2 + l^2 \right)
\]

\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}
\]

\[
a = 2\sqrt{2}R \text{ and } V = a^3
\]

The calculated lattice parameters depict the crystalline nature of MOIF and Fig. 4b shows a probable portion of unit cell of MOIF of CoSDS with intermolecular ionic contacts between hexaamine cobalt (III) cation and loryl sulphate anion.

### 3.2. Interaction studies

Prepared MOIFs were analysed for their interacting activities with dyes, BSA and free radicals for proving their applicability in the field of sciences. Since MOIFs were soluble in DMSO only so it may be their limitation but by dispersing them into suitable emulsion system their properties can be more utilised.
3.2.1. Dye interaction study

MO has shown its characteristic absorption peaks at 430 nm in UV/Vis, and upon interaction with Co-SDS and Co-AOT, this absorbance has been found to be decreased as shown in Fig. 6. Since, equal volumes of dye and MOIF solutions were mixed, so dilution factor become nullified, and decrease in absorbance was attributed for interaction between MO and MOIF but not any structural changes [1]. This interaction may be hydrophobic-hydrophobic-interaction as well as hydrophilic-hydrophilic-interaction since both hydrophobic and hydrophilic parts are present in dye and MOIF [30]. The same has been noticed for interaction with MB where it showed characteristic absorbance maximum at 670 and 300 nm and upon interaction with MOIF such absorbance got decreased as shown in Fig. 6. The quantitative analysis for such interaction was estimated as follows.

\[
\% \text{Interaction} = \left( \frac{\text{Absorbance}_{\text{DYE}} - \text{Absorbance}_{\text{DYE+MSN}}}{\text{Absorbance}_{\text{DYE}}} \right) \times 100
\]

For instance with 100µM of MOIF and MO, the 63.67 and 76.98% interaction was found for Co-SDS and Co-AOT MOIF respectively at 670 nm while 48.31 and 60.17% at 300 nm for the same MOIF respectively. In the case of MB the 46.15 and 49.11% interaction was found for Co-SDS and Co-AOT respectively at 430 nm.
nm (Fig. 7). In case of Co-AOT, the interaction was found to be greater than Co-SDS with both the dyes. It may be due to the hydrophobic part in AOT is more than SDS (Fig. 1) so hydrophobic-hydrophobic-interaction was higher in Co-AOT than Co-SDS.

### 3.2.2. Protein binding study

All MOIF have expressed binding potential with BSA, and showed hypochromic effect (Fig. 8). Generally, the hypochromic effect tells that binding nature of compound while a hyperchromic effect reveals the unfolding of bio-molecules [29, 30, 31, 32]. It inferred that the structure of MOIF is attributed for the binding
with BSA. The MOIF of CoAOT has bound BSA strongly than CoSDS that may be due to greater hydrophobicity of AOT. It gives information that more hydrophobicity causes greater interaction.

3.2.3. Free radical interaction

Antioxidant activities were analyzed by the scavenging effect of a stable free radical di(phenyl)-(2,4,6-trinitrophenyl) iminoazanium as per standard procedure [18, 19] with a slight modification. The percentage scavenging activity of MOIF was determined in a concentration-dependent mode with a comparison with the DPPH free radical’s absorption at 517 nm. The DPPH free radical’s absorption at 517 nm in DMSO was 0.417, a maximum. The MOIF from 50 to 200 mM at an interval of 50 mM, showed a decrease in absorption, from which their antioxidant activities could be inferred (Fig. 9). The MOIF of CoAOT has shown more scavenging effect as compared to CoSDS, may be that hydrophobicity which is high for CoAOT than CoSDS, became more effective to interact with free radical. The interaction of BSA, dyes and free radical with prepared MOIFs may also be because of physisorption. Since MOIF is a framework system so it can have pore sizes or surface activity which may be responsible for absorption of such chosen materials. Because of this property these could be very effective as an alternative of MOF.

4. Conclusion

We have developed novel MOIF with ionic attraction of cationic complex, hexaamine cobalt (III), and anionic surfactant SDS and AOT. Such MOIFs have both hydrophilic and hydrophobic parts responsible for the physisorption of Dye, BSA and free radical. Such interactions were found to be stronger with high hydrophobicity as Co-AOT > Co-SDS. The interaction tendency of MOIF with dye, protein and free radical show their application for dye degradation from industrial waste, protein binding and scavenging effect respectively. The comparative analysis of interaction activity of MOIFs of CoSDS and CoAOT with Dye, protein and free radical infer that CoAOT has expressed stronger activity than CoSDS. It is due to higher

![Fig. 9. DPPH interaction of MOIF of Co-AOT and Co-SDS.](https://doi.org/10.1016/j.heliyon.2019.e01568)
hydrophobic domain with branching associated with CoAOT could able to make strong interaction with Dye, BSA and free radical. In this regard their anticancer activity and other catalytically activities are under progress.

Declarations

**Author contribution statement**

Rakesh Ameta: Conceived and designed the experiments; Performed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Man Singh: Analyzed and interpreted the data.

**Funding statement**

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

**Competing interest statement**

The authors declare no conflict of interest.

**Additional information**

No additional information is available for this paper.

**Acknowledgements**

Authors are highly thankful to Central University of Gujarat for providing infrastructure and laboratory facilities. R. K. Ameta is highly thankful to Council of Scientific & Industrial Research, CSIR, India, for associating as SRA, Scientist’s pool scheme.

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