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Removal of an Anionic Surfactant as an Iron (II) Complex

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Abstract. This work aims to remove an anionic surfactant by complexing it with Fe(II) ion. The objective was to trap sodium dodecylbenzene sulfonate (SDBS) by ferrous ions as a coordination complex. The isolated complex was characterized by spectroscopic, conductimetric and gravimetric methods to determine its structure. The results show that the complex obtained is very stable in air and has a tetrahedral geometry. Fe (II) is linked to two molecules of surfactant and two atoms of chlorine. Theoretical study of the complex structure confirms the results obtained by the experimental method. Molecular modeling aims to determine the most stable geometry and the structural parameters of the complex (bond lengths and bond angles). This work shows the efficiency of the elimination of surfactants in a homogeneous phase by complexation. Indeed, the complexation process allows eliminating 82.8% of the surfactant in an aqueous solution.

Keywords. Fe(II) complex, IR Spectrum, Absorbance, Structural study.

INTRODUCTION

Anionic surfactants representing 80 to 90% of detergents placed on the market are major contributors to urban pollution. The great use of synthetic detergents explains the high concentrations found in sewage: 10-15 mg/L (Martinez et al., 1989).

A part of these sewers flows without prior purification into the waterways. Studies carried out show that these compounds are not very toxic since their concentration remains below 3 mg/L (Kimerle, 1989).

However, their accumulation involves significant toxicity, therefore presents a real danger to the environment. One method of removing such compounds is complexation. Indeed, a surfactant is linked to metal ions forming a coordination complex, which is very stable and can be removed easily from the solution. This technique is interesting since the metal used does not present any danger.

Transition metals are present in infinitesimal quantities and play a fundamental physiological role in the body.

Iron, for example, plays a major role in the renewal of red blood cells and cellular respiration. Fe(II) chloride in aqueous solution has also been the subject of numerous studies and has shown significant effectiveness in water pollution control **(**de la Iglesia et al., 2015).

EXPERIMENTAL

Synthesis method

Fe(II) complex is prepared by dissolving separately precise amounts of sodium dodecylbenzene sulfonate and Fe(II) chloride in a minimum of water.

The solutions obtained are mixed by adding the iron solution to the ligand one. The reaction is carried out by stirring the solution without reflux until a green precipitate appears. The solid obtained is washed with water and dried.

Calculation method

To optimize the geometry of Fe (II) complex and minimize its energy, molecular mechanics calculations were carried out using Hyperchem (Hypercube Inc. Canada), and Fletcher Revees algorithm (Cobri et al., 2005; Brudzinska et al., 2004) and MM + force field.

The most stable geometry of the complex was determined and its structural parameters (bond lengths and bond angles) were calculated.

RESULTS AND DISCUSSION

Spectral study of the obtained complex

The isolated complex is green, stable in air, an insoluble in all common organic solvents except in DMF and ethanol (EtOH). It is a melting point greater than 300°C.

The molar mass determined experimentally by the Rast method is 840.019 g/mol (Kaushal et al., 2014; Rast, 1922; Smith and Young, 1927).

The conductivity value is 165.017 ms.cm2/mol. This value indicates that the complex formed is electrolytic, and it is more mobile than the free Fe^{2+} cation (Baize and Tercé, 2002).

Gravimetric analysis shows that two chlorine atoms are bonded to an iron ion.

The electronic spectrum of the Iron (II) complex dissolved in DMF is shown in figure 1. It shows a set of bands in [200 - 400nm] with a narrow band centered at 302nm; which indicates a tetrahedral structure for the isolated complex.

An infrared spectrum of the free ligand SDBS, compared with the Iron(II) complex spectrum (Fig. 2), shows the shift of S-O absorption band from 3441 cm-1(free ligand) to 3200 cm-1 (coordinated ligand). This indicates that the oxygen of S-O group is involved in the complexation. This is confirmed by the appearance of a band around 1154.27 cm^{-1} characteristics of the Fe-O bond.

IR spectrum shows that the SDBS ligand is a monodentate ligand, it binds to the metal through the oxygen of the S-O group. Two molecules of the surfactant and two atoms of chlorine surround the iron ion.

Based on the spectral study, the following formula for the obtained ion complex [Fe(DBS)2Cl2]2- (DBS: dodecylbenzene sulfonate) is suggested.

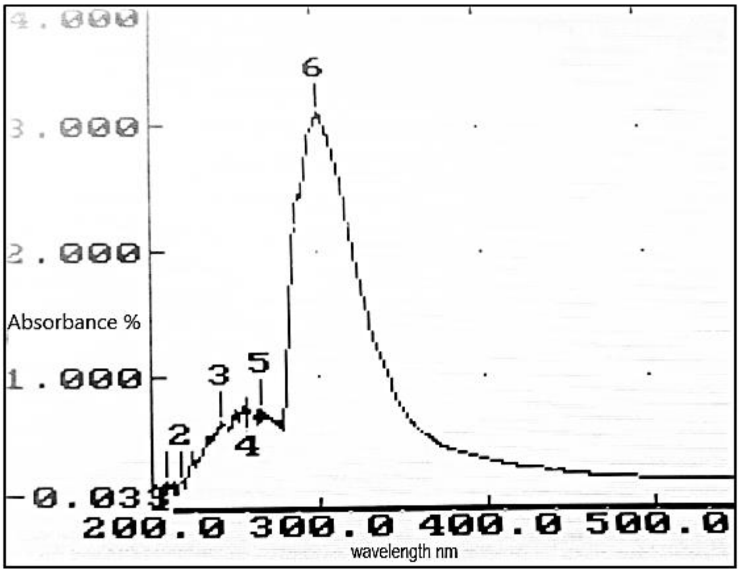

Fig.1. Electronic spectrum of Fe(II) complex.

The formula of the obtained complex will be Na_2 $[Fe(DBS)_2Cl_2]$; with a molar mass of 823.703 g/mol . The comparison between this value and calculated mass using the Rast method, which is 840.019 g/mol, suggests that one water molecule outside the coordination sphere. So the proposed formula for the obtained complex is Na_2 $[Fe(DBS)_2Cl_2]H_2O$

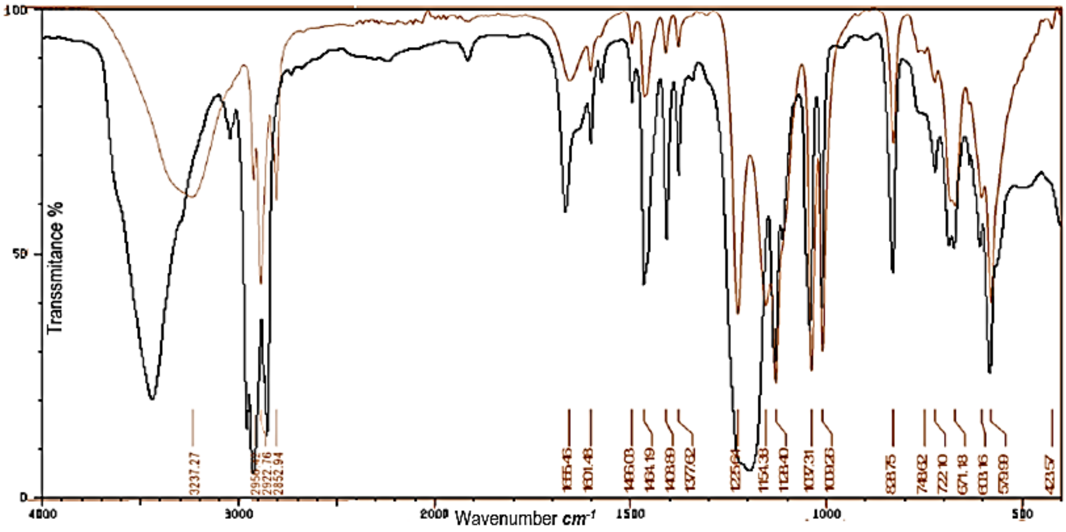

Fig.2. IR spectrum of Fe(II) complex:
Ligand SDBS ▬
Fe(II) Complex ▬

Determination of the percentage of surfactant removal

The determination of uncomplexed surfactant concentration remaining in solution and then a percentage of removal of SDBS by complexation, a spectrophotometric dosage is carried out. The maximum wavelength is 312 nm with an absorbance of 2.953.

Absorbance is determined for different concentrations from the filtrate (the solution recovered after filtration) as shown in table1.

The calibration curve is linear over the chosen concentration interval (Fig.3), which indicates that the Beer-Lambert law is verified in this concentration range.

The correlation coefficient; R^2 = 0.99726 is very close to 1 indicating that the results obtained are well defined.

The absorbance of the filtrate solution of unknown concentration is 2.953, and by extrapolation at 6.88 g/L.

Table 1. Absorbance values at different concentrations.

Concentration (g/L)	Absorbance
1	0.516
2	0.875
3	1.24
4	1.76
Unknown	2.953

The initial concentration of SDBS was 40 g/L, and the final concentration is 6.88 g/L, therefore, sodium dodecylbenzene sulfonate (SDBS) was removed at 82.8%.

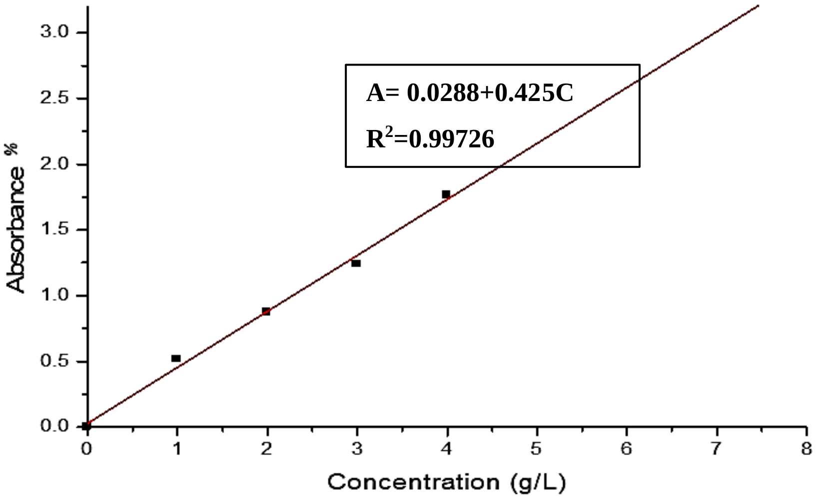

Fig.3. Calibration curve.

Theoretical study of Fe(II) complex structure

The most stable geometry of Fe(II) complex as shown in figure 4 , confirms the results obtained by the experimental study.

The ligands form a tetrahedral environment around the metal ion. Iron(II) is linked to two DBS molecules and two chlorine atoms.

The ligand is monodentate, it is bonded to Fe(II) by oxygen of S-O group.

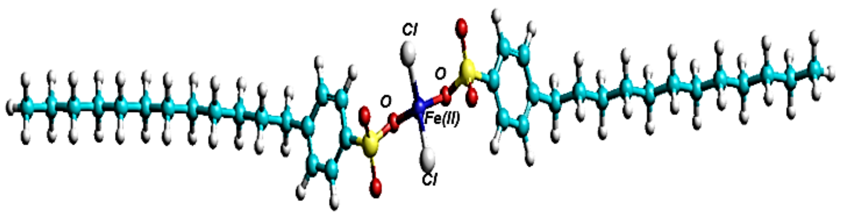

Fig.4. Optimized structure of $[Fe(DBS)_2Cl_2]^{2-}$; using Hyperchem.

Bond length and bond angle are listed in table 2. The bond angles values confirm the tetrahedral structure.

Table 2. Bond length and Bond angles in $[Fe(DBS)_2Cl_2]^{2-}$.

Atoms	Bond length (Å)	Atoms	Bond angles (degrees)
Fe(53)-O(54)	1.8351	Cl(66)-Fe(53)-O(54)	109.593
Fe(53)-O(23)	1.8351	Cl(66)-Fe(53)-O(23)	110.533
Fe(53)-Cl(65)	2.1637	Cl(66)-Fe(53) Cl(67)	109.857
Fe(53)-Cl(66)	2.1636	O(54)-Fe(53)-Cl(67)	110.579
		O(23)-Fe(53)-O(54)	106.623
		O(23)-Fe(53)-Cl(67)	109.611

CONCLUSION

The interaction between iron(II) chloride and the surfactant (SDBS) in solution gives a coordination complex. The obtained complex is a very stable solid, insoluble in all usual organic solvents, except in DMF and ethanol, with a melting point above 300 ° C. Spectral study showed that the isolated Fe(II) complex has a tetrahedral structure. The gravimetric analysis shows the presence of two chlorine atoms in the obtained complex. Therefore, the central metal is linked to two molecules of surfactant and two chlorine ions. The surfactant acts as a monodentate ligand. The appearance of the characteristic band of Fe-O; in the infraRed spectrum; suggests that; DBS molecule binds to the metal through the oxygen of the S-O group. The structure of the obtained complex is $Na_2[Fe(DBS)_2Cl_2]H_2O$. Theoretical study of the complex structure confirms the result obtained by the experimental study. The complexation allowed to removal 82.8% of the 40 g/L of surfactant initially present in the water. This result indicates that complexation appears to be operative in wastewater treatment.

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