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Synthesis and Characterization of Trasition Metal Dodecyl Sulphates by Infrared Technique.

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ABSTRACT

Synthesis of anionic surfactants, copper dodecyl sulphate, zinc dodecyl sulphate, (Cu(DS)2, Zn(DS)2) by the direct metathesis of sodium dodecyl sulphate. The present paper deals with the preparation of copper, dodecyl and zinc dodecyl sulphate and their chara¬cterization by infrared technique. Various group frequencies (cm-1) have been reported.

KEYWORDS : copper dodecyl sulphate (Cu(DS)2,); zinc dodecyl sulphate (Zn(DS)2); Group frequencies (cm-1).

Introduction:

Surfactants have been widely studied due to its significance in both applied and fund amental processes: detergency, catalysis, flotation, lubrication, colloid stabilization, foaming, emulsification, protein denaturation, tension moderation in membranes, membrane permeation, and drug delivery (1). Infrared spectroscopic studies of sodium dodecyl sulphate permeation and interaction with stratum corneum lipids in skin studied by P. Saad et al. (2). M. Kieke et al. worked on Intercalation of dodecyl sulphate into layered double hydroxides (3). Fourier transform infrared attenuated total reflection spectroscopy linear dichroism study of sodium dodecyl sulfate adsorption at the alumina/water interface using alumina-coated optics were carried by R. P. Sperline et al (4). Infrared spectroscopic study of the crystalline phases of sodium dodecyl sulfate was conducted by R. P. Sperline (5). However, Synthesis, characterization and analytical applications of sodium dodecyl sulphate cerium (IV) phosphate was pointed out by Amita Somya et al. (6). Wall and Kirschnek (7) reported an interesting analytical method based on the paramagnetic proton resonance of surfactants. However, a critical weakness of many analytical methods is the fact that they are not capable of giving evidence of the bond state of H-atoms and their next behaviour in a molecule. The infrared spectroscopy has however been found to be the most successful tool to analyze and identify the molecular structure. There had been a renaissance of interest in infrared spectra of metal surfactants in order to obtain structural information's in crystalline state . Hummel (8) in his painstaking studies has reviewed the identification and analysis of various classes of surface active agents following the infrared and chemical methods which now-a-days serves as reference spectra for the identification, characterization and analysis of various surfactants. Snyder et al (9) studied that vibrational spectra in the CH stretching region and the structure of the polymethylene chain. Padalkar et al (11) reported that the characterization of mixed micelles of sodium cumene sulfonate with sodium dodecyl sulfate and cetyl trimethylammonium bromide by SANS. A fourier transform infrared spectroscopic study of dodecyltrimethylammonium chloride/sodium dodecyl sulfate surfactant mixtures by Scheuing et al (12). Infrared Spectroosocopy of Anionic, Cationic and Zwitterionic Surfactants studied by Rommel et al (13). Kumar et al (14, 15) Reported that effect of urea and butanol on the micelle formation of anionic surfactants at different temperature.

Experimental:

(a) Materials:

Extra pure sodium dodecyl sulphate (B.D.H. product) after its recrystallization was used for the preparation of other anionic surfactants. Potassium chloride, copper (II) chloride was AnalaR B.D.H. chemicals used as such to carry out the metathesis with sodium dodecyl sulphate.

(b) Preparation of surfactants:

The metal dodecyl sulphates (zinc and copper dodecyl sulphates) were prepared by direct metathesis of sodium dodecyl sulphate with the calculated amount of metal salts at 50-60ºC. The products were recrystallized 4 or 5 times from water and then finally washed with petroleum ether. The completion of metathesis was further checked by negative flame test for sodium in the various dodecyl sulphates formed. The products were recrystallized and dried in an air oven.

The characterization of surfactants was made by recording their infrared spectra on Themo Nicolet FTIR NEXUS™.

Results and discussion:

Although the infrared spectrum is characteristic of the entire molecule, it turns out that certain groups of atoms give rise to bands at or near the same frequency regardless of the structure of the rest molecule. It is the, persistence of these characteristic bands that permits to obtain the useful structural information by simple inspection and reference to generalized chart of characteristic group frequencies.

Since infrared spectra contain large number of bands, the possibility that two different compounds will have the same infrared spectrum is exceedingly small. For this reason an infrared spectrum has been called the finger print of a molecule. Thus, if two pure samples give different infrared spectra, the compounds must be different. If they give the supreimposable spectra then they represent the same compound. The region from 4000-1500 cm^{-1} (high frequency part) to the left in an infrared spectrum is useful for the identification of functional group. This region shows absorption arising from stretching modes. The region to the right of 1500 cm^{-1} (1500-500 cm^{-1}) is usually complex since both stretching and bending modes give rise to absorption here. In this region correlation of an individual band with a specific functional group is often difficult. Even for organometallic compounds the infrared region (4000-500 cm^{-1}) is of prime importance. Table 1 however shows a clear cut compression of infrared spectra for transition metal dodecyl sulphates with the infrared spectrum of potassium, sodium dodecyl sulphates. As no crystal structure information is available on any of the transition metal dodecyl sulphates one has to make use of correlations which have been established with known crystal structures of related compounds. Thus is can be seen that the infrared spectra (Fig. 1-5) of these compounds when compared with infrared wave numbers of n-hexadecanol show clear splitting of the CH_2 scissoring (1468-1465 cm^{-1}) and the CH_2 rocking modes (724-665 cm^{-1}). These spectra resemble those of n-alkanes (16-19).

Sundell suggested that in case of sodium dodecyl sulphate (20), the molecular arrangement in the system is too highly irregular to allow any formal subcell description for the whole

molecule. The head group vibrations in these dodecyl sulphates involve four sulfur-oxygen stretching and five S-O angle bending modes of the SO_4 group; some of the vibrations could, in principle, degenerate. The bands in the infrared spectra of the dodecyl sulphates appear in the (1265-1200cm^{-1}) region and are due to the asymmetric SO_3 stretching modes. However, from the crystal structure of sodium dodecyl sulphate is evident that the sulphate groups of adjacent molecules are alternately displaced by about 2Å (20).

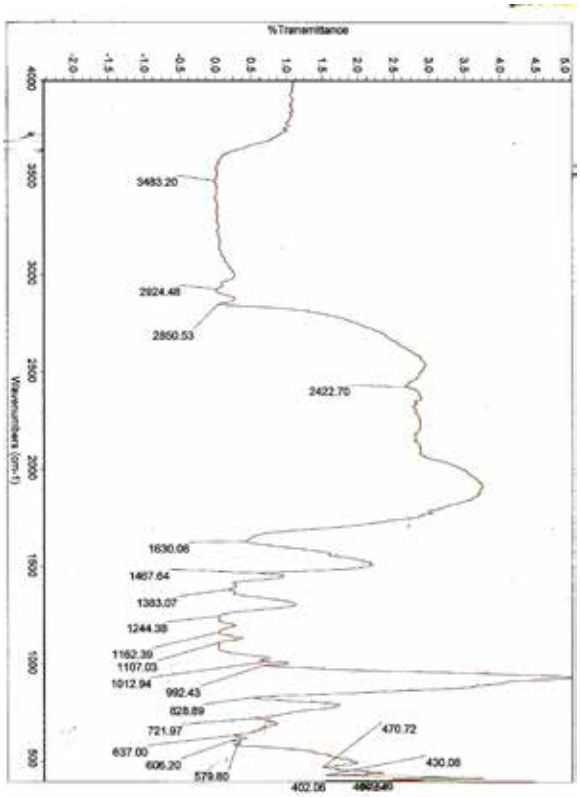

FIGURE 1: Infrared spectrum of $Cu(DS)_2$.

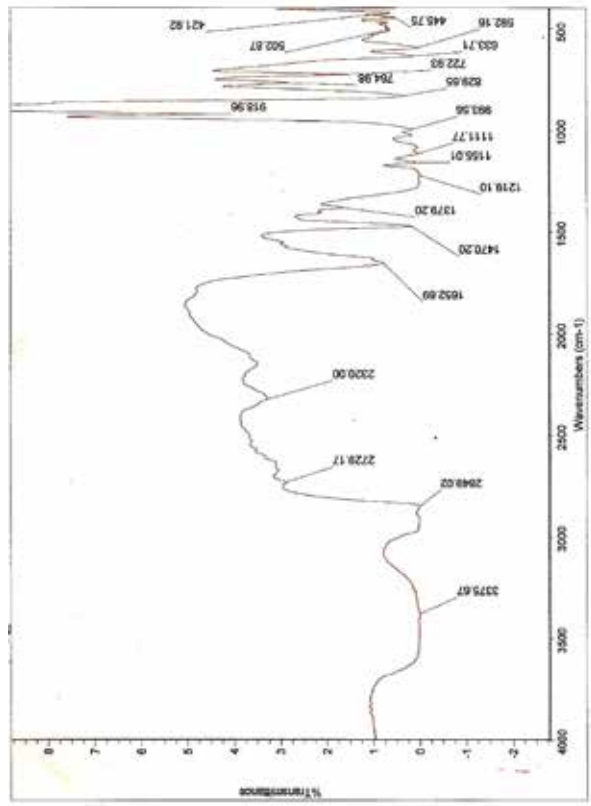

FIGURE 2: Infrared spectrum of $Zn(DS)_2$.

The similarity of the infrared spectra of sodium dodecyl sulphate andtransition metal dedecyl sulphates make it not unrealistic to expect that this staggered structure also occurs in the transition metal dodecyl sulphates. Thus transition metal dodecyl sulphates will have different environments, i.e. different sets of sites are occupied, producing an effect analogous to factor group splitting. Transition metal dodecyl sulphates display broad intense OH stretching absorption in the range of (3483-3376 cm^{-1}) suggesting the presence of water of crystallization of copper and zinc dodecyl sulphates.

Furthermore, bands near 3448 cm^{-1} frequently appear in all the spectra might be due to the moisture (21) (and not water of crystallization) and are obtained by the pressed disc technique which depends upon the fact that dry powdered KBr can be pressed under pressure in vacuum to form transparent pallets. Furthermore, the presence of water as moisture was further confirmed by heating the each surfactant at 700 for about 2 hrs and slight loss in weight for each corresponding sample was observed which excludes the possibility of water of crystallization.

S. No.	Surfactants	M-O Str.	SO_4 def	(CH_2) rock	C-O-S Str	C-C and O Str.	Sym. SO_3 Str.	C-C Str.	Sym. C-C Str.	Asy. SO_3 Str.	C-H def. in CH_3 asy	C-H def. in CH_2 asy	S-H Str. Sym.	C-H Str. In CH_2	OH Str.
01	KDS	580.0 (VS)	630.97 (S)	762.16 (MS)	812.64 (VS)	865.83 (W) 918.83 (W)	1065.6 (S)	1098.56 (W)	1208.68 (S)	1378.9 (W)	-	1470.05 (S)	2322.02 (W)	2848.52 (W)	3443.96 (MB)
02	NaDS	591.82 (VS)	634.36 (S)	722.82 (MS)	834.01 (VS)	914.87, 996.24 1012.943 (W)	1982.72 (S)	1114.51 (W)	1132.91 (W) 1156.38 (VW)	1222.87 (W)	1380.07 (W)	1469.78 (S)	2849.39 (S)	2915.27 (S)	3467.28 (MB)
03	$Cu(DS)_2$	470.72 (S)	606.20 (B)	721.97 (S)	828.89 (S)	992.43 (W)	-	1107.03 (B)	-	-	1383.07 (S)	1467.64 (S)	2422.64 (S)	2924.48 (MB)	3483.20 (VB)
04	$Zn(DS)_2$	502.87 (WB)	592.16 (S) 631.80 (S)	722.93 (W)	829.65 (MS)	918.96 (W) 1018.39 (S)	993.56 (VS)	-	1111.77 (W)	1219.10 (VS)	1379.20 (VS)	1470.20 (S)	2729.17 (W) 2356.06 (B)	2849.02 (S)	3375.67 (VB)
05	NaBDS	584.49 (W)	668.02 (MS)	761.69 (MS)	834.59 (VS)	1008.70 1041.85 (S)	1134.11 (W)	1187.10 (W)	1398.40 (W)	1465.00 (S)	1496.34 (W)	1601.36 (W)	2221.41 (W)	2864.02 (W)	3436.37 (MB)

Table 1. Assignment of frequencies in the infrared spectrum of dodecyl sulphates of Na, K, Cu a Zn and Sodium dodecyl benzene sulphonate.

S- Sharp
B-Broad
W- Weak
MS- Medium Sharp
MB- Medium Broad
WB- Weak Broad
VS- Very Sharp
VB- Very Broad
VW- Very Weak

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