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Interaction of Sodium Sulfide with Zn^{2+}, Cd^{2+} and Hg^{2+} ions in Presence of Sun – light and Preparation of Nanoparticles in Ethylene glycol

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Abstract: *Interactions between $Na_2S\ 7H_2O$ and Zn^{2+}, Cd^{2+} and Hg^{2+} ions in solid state as well as in solution in presence of sun light ascertains tetrahedral structure instead of M_xS_y, with the help of their IR spectra, ESCA, TGA, DTA and XRD patterns. XRD patterns of cadmium and mercury compounds show possibility of two phases (α and β) of $[Cd(H_2O)_3S]$ and $[HgS]3H_2O$. Nanoparticles of ZnS, CdS and HgS were prepared in ethylene glycol indicating the particle size 10 – 20nm in TEM photograph.*

Keywords: *ZnS, CdS and HgS Nanoparticles, ethylene glycol, TEM photograph*

I. Introduction

White color of Zn^{2+} ion ($3d^{10}$) in compound might be due to overlapping of 3d filled metal orbital $3dM \xrightarrow{\text{to}} 3dL$ (3d S - orbital (oxidation type charge transfer band)[1] overlapping between $\xrightarrow{\text{empty}}$ orbital (3dM - orbital of Zn^{2+} ion and 3dL = S^{2-} ion) forms pure bonds. Such transitions [1-7] in UV – Visible spectrum of oxidation charge transfer type [2]. CdS is widely used as photo detector in visible spectrum. It is also used as buffer layer in thin film solar cells [8, 9]. The optical properties of nanoparticles of CdS shed some light on the surface properties of the materials [10, 11]. The photoemission of the CdS nanoparticle has much more importance on capped materials. [11].The variation in the photon energy in different capped compound is a function of bulk of surface particle and overlapping of S^{2-} ion (S) 2P orbital. HgS nanoparticles incorporated in polystyrene show high specific surface area and show a band gap 1eV compared to bulk HgS material (2ev) observed in optical spectra [12]. From fundamental and practical point of view, it is therefore important to synthesized and characterized new type of nanomaterials of ZnS, CdS, and HgS respectively..

II. Experimental

Reactants zinc sulphate ($ZnSO_4.7H_2O$) AR grade (purity 99.9% BDH). Sodium sulphide ($Na_2S\ 7H_2O$) purity 99.9%, Emerk. Cadmium chloride ($CdCl_2$) BDH (99.8% pure), and mercuric chloride ($HgCl_2$) BDH (99.9% pure) were used for preparing the final product in 1:1 molar ($Na_2S\ 7H_2O$ + M- salt) ratio in sun light. The final products were purified through vigorous washing with distilled water for several times. The final washing was completed with the removal of SO_4^{2-}, S^{2-} and Cl^- ions. Nanoparticles of ZnS, CdS and HgS were stabilized by ethylene glycol reducing agent.

Test tube containing nanoparticles of
ZnS, CdS and HgS in ethylene glycol

IR spectra of solutions were run in the range 4000 cm^{1-} to 400 cm^{1-} using polythene container on a Perkin FT-IR spectrophotometer RX- IB UK. The X-ray powder diffraction of thin films of solutions were carried on RIGAKU-Rota – Flex RAD/ Max-B, Rigaku, corporation, Japan, X-ray Diffractometer using Cu K radiation with $2\theta = 5 - 80^0$ with scanning speed of 1^0 per minute. Electronic spectrum of solutions of the complexes was recorded on a Shimadzu 160A Spectrophotometer in water (10^{2-} m molar TEM photographs have been produced from Transmission Electron Microscope, JEOL 2000 EX JEOL, corporation, Japan. The films were cut in appropriate size (10 mm approx.) and coated with gold to avoid charge accumulation on the surface of film.

III. Results and Discussion

These reactions were carried out in the solid state as well as in solution in presence of sun-light. The reactants were interacted in solid state. The observations are given bellow-

$$MSO_4 + Na2S.\ 7H_2O \xrightarrow[\text{Sun Light (35 minute)}]{\Delta T=20^0\,C} [MS\ (H_2O)_3]$$

(M = Zn, Cd, Hg)

The scheme may follow the following route MSO_4 is broken in to ions. ($M^{2+} + SO_4^{2-)}$ and $Na_2S.\ 7H_2O$ as $2Na^+ + S^{2-} + 7OH^- + 7H^+$ ions and forming the final product [MS $(H_2O)_3$] with ions.

The yellow colour of the compounds [CdS $(H_2O)_3$] (photographs) might be due to overlapping of $(4dM \longrightarrow 3dL)$ [2] orbital to empty 3d (3dS) orbital (charge transfer bands) that is $(4d \longrightarrow 3d)$impure overlapping is between filled 4dM to 3dL empty orbital. The black color and orange color (photographs) of the compounds [$Hg(3H_2O)S$] $(5d \longrightarrow 3d)$are in 34000 cm^{1-} region shows overlapping of filled 5d(Hg) and with empty 3d(S) orbital. The metal ions having completely filled d-orbital do not show co-ordinating [3-7] ability. In order to see the effect of sunlight on transition metal ions the interaction between $Na_2S\ 7H_2O$ and Zn^{2+}, Cd^{2+} and Hg^{2+} ions in solid state as well as solution[13] has been undertaken. Their structures have been established by XRD pattern. The presence of two peaks in ESCA has been discussed for either two phases or two compounds of Cd^{2+} ion. ESCA of all the compounds has been done. The presence of coordinated ions (SH^-) to transition metals ions, TGA and DTA have been carried out to show the thermal stability and phase changes. In the XRD pattern of the zinc compound showed their similar structure in solid state as well as in solution. The peak of oxygen in ESCA ascertains the presence of H_2O molecule in coordination sphere. Since there is no peak for phase change in DTA of all the compounds therefore the possibility of two phases in ruled out. TEM photograph show 10 - 20 nm size nanoparticle.

One strong peak (I / I_O =100) at 3.358A appears in XRD pattern (Table-2 Fig.-2) of compound of Cd^{2+} ion prepared in solution while reported value for CdS is at $3.16A^0$. Therefore the compounds prepared in presence of sun light in solid state as well in solution have a molecular structure different from that of CdS in solid state two peaks at 3.650 and 3.571 I/I_O= 100 (Table-2 Fig-2) might be due to cubic and hexagonal $Cd(OH)_2$ type structures[3]. CdS shows a peak[4] ($4d_{5/2}$) at 405 ev only while our compound shows two peaks at 419.4 ev (Table- 5, Fig.-5) and 410.0ev indicating presence of two new compounds $CdS(H_2O)_3$ and $[Cd(OH)_2(H_2O)]$. Thermal stability [5,14] of oxides has been reported as CdO > HgO ie 700^0C for CdO and 360 ^{0}C for HgO. Similar order of stability in TGA might be for CdS $(H_2O)_3$ > $HgS(3H_2O)$ which follows the sequence 481.70C and 391.2 ^{0}C respectively (Fig. 8-9). Similar order of thermal stability is also followed in TGA (Table. 7-9) while the compounds prepared in solid state show $CdS(H_2O)_3$ > $HgS(3H_2O)$ 486.4 ^{0}C and 386.1 ^{0}C. A mass gain in TGA (Table-7) might be due to absorbed oxygen on non – stoichiometric sites in case of compound of Zn^{2+} ion. Since there is no peak for O^{2-} ion in ESCA of Hg^{2+} ion the formula would be $[HgS]3H_2O$. Results of elemental analysis are given in Table-10 by ESCA. Two peaks in XRD pattern indicate α and β phases

IR spectra of compounds of Zn^{2+}, Cd^{2+} and Hg^{2+} ions (Fig. 10 -12) indicate the absence of ν (SH) and ν (OH) modes of vibrations suggesting the molecular formula[MS $(H_2O)_3$] with coordination number four due to presence of IR bands of T_d symmetry in region 1110, 1010, 900 and 800 cm^{1-}. While M_xS_Y compound do not show T_d bands. Splitting and shifting in main frequencies may occur due to lowering [6] in symmetry, $Td \longrightarrow C_{3v}$ or $T_d \longrightarrow C_{2v}$. The IR bands at 490 and 350cm^{1-} are due to ν M – O and ν M – S respectively. The magnetic susceptibility measurement shows diamagnetic character (nd^{10}). Since these compounds are insoluble in any solvent (Tetrahydrofuran THF, DHSO, $CHCl_3$, CCl_4, C_2H_5OH, NaOH, HCl) UV – Visible spectra could not be recorded.

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Table-1: d- values of compound of Zn^{2+} ion prepared in solid state as well as in solution

d – values of the compound prepared in Solid State					
I/I_o	100	95	88	86	45
d A^o	3.135	3.124	3.116	3.163	3.084
d – values of the compound prepared in Solution					
I/I_o	100	95	64		
d A^o	3.181	3.116	3.103		

Table-2: d- values of compound of Cd^{2+} ion prepared in solid state as well as in solution

d – values of the compound prepared in Solid State					
I/I_o	100	100	92	69	
d A^o	3.65	3.57	2.11	2.09	
d – values of the compound prepared in Solution					
I/I_o	100	59			
d A^o	3.358	2.06			
Reported d – values of the compound Cadmium Sulphide					
I/I_o	100	75	60	55	
dA^o	3.16	3.58	3.36	2.06	

Table-3: d-values of compound of Hg^{2+}ion prepared in solid state as well as in solution

d – values of the compound prepared in Solid State					
I/I_o	100	40	52	44	
d A^o	3.37	2.567	2.069315	1.763	
Abs	597	242		264	
d – values of the compound prepared in Solution					
I/I_o	100	66	58	50	48
d A^o	3.383	2.066	1.264	2.568	2.578
Abs	898	467	387	3.57	337

Table-4 ESCA of the compounds of Zn^{2+}ionprepared in Solid State as well as in Solution

Elements	Compound from Solid State	Compound from solution
Zn ($3d_{3/2}$)	1029.5ev	1030.0ev
S ($2P_{1/2}$)	168.5ev	169.5ev
O ($2P_{1/2}$)	539.5ev	539.5ev

Table-5 ESCA of the compounds of Cd^{2+}ionprepared in Solid State as well as in Solution

Elements	Compound from Solid State	Compound from solution
CdS ($4d_{3/2}$),($4d_{5/2}$)	419.4,410.0.ev	418.7, 412.1ev
S ($2P_{1/2}$)	178.0,168.0 ev	178.2, 168.4ev
O ($2P_{1/2}$)	538.6ev	539.8ev

Table-6 ESCA of the compounds of Hg^{2+}ion prepared in Solid State as well as in Solution

Elements	Compound from Solid State	Compound from solution
Hg ($5d_{3/2}$),($5d_{5/2}$)	110.3, 106..3 ev	109.2, 106.0,107, 103ev
S ($2P_{1/2}$)	171.5, 164.0ev	167.1,160.8ev

Tabble-7: Exotherm and Endotherm in DTA of both the compounds of Zn^{2+} ion

Compound from Solid State	Compound from solution
Exotherm 248.7 ^{0}C, 251.8 ^{0}C	362, 390, 450 ^{0}C
Endotherm 101.2 ^{0}C, 217.3 ^{0}C	90.4 ^{0}C

Tabble-8: Exotherm and Endotherm in DTA of both the compounds of Cd^{2+} ion

Compound from Solid State	Compound from solution
Exotherm 243.1^{0}C, 486.4 ^{0}C 2.1 ca 1/g ΔH, 64.5 ca 1/g ΔH	481.7 ^{0}C 99.5 ca 1/g ΔH
Endotherm 98.0 ^{0}C	95.0 ^{0}C

Tabble-9: Exotherm and Endotherm in DTA of both the compounds of Hg^{2+} ion

Compound from Solid State	Compound from solution
Exotherm 386.1 ^{0}C 279.61 ca 1/g ΔH, 64.5 ca 1/g ΔH	391.2 ^{0}C 151.53 ca 1/g ΔH
Endotherm 99.0 ^{0}C	98.1^{0}C 4.92 ca 1/g ΔH

Table-10 Molecular formula and molecular weights of Zn^{2+}, Cd^{2+} an d Hg^{2+}

Molecular Formula	M %	H %	O %	S %
[Zn $(H_2O)_3$S] cal. Mol. wt.= 151.0 Obs.	Zn =43.2 43.1	3.9 3.7	31.5 31.3	21.1 20.9
[Cd $(H_2O)_3$S] cal. Mol. wt.= 198.0 Obs.	Cd = 56.7 58.7	3.0 3.2	24.0 30.0	16.1 15.1
[Hg (H_2O)S] cal. Mol. wt.= 250.4 Obs.	Hg = 80.0 80.2	0.7 0.8	6.3 6.1	12.7 12.5

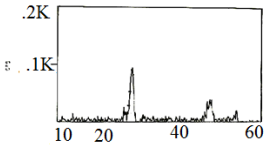

Fig. 1a. XRD pattern of compound of Zn^{2+} ion in solid state

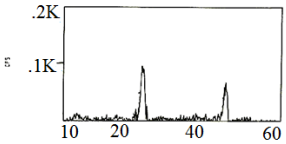

Fig. 1b. XRD pattern of compound of Zn^{2+} ion in solution

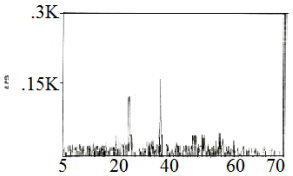

Fig.2a. XRD pattern of compound of Cd^{2+} ion in Solid State

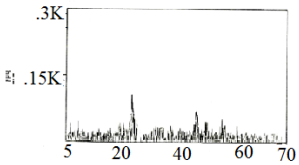

Fig.2b. XRD pattern of compound Cd^{2+} ion in solution

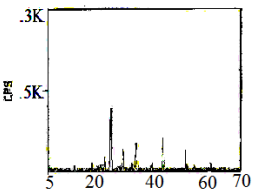

Fig.3a. XRD pattern of compound of Hg^{2+} ion in Solid-State

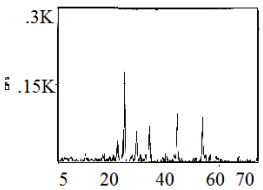

Fig.3b. XRD Pattern of compound of Hg^{2+} ion in solution

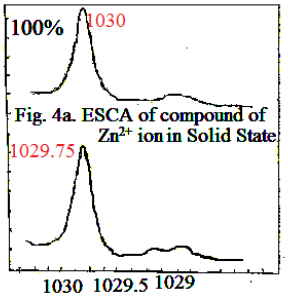

Fig. 4a. ESCA of compound of Zn^{2+} ion in Solid State

Fig.4b. ESCA of compound of Zn^{2+} ion in solution

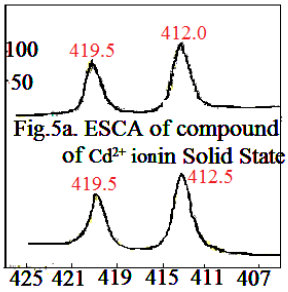

Fig.5a. ESCA of compound of Cd^{2+} ion in Solid State

Fig.5b. ESCA of compound of Cd^{2+} ion in solution

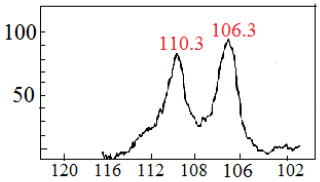

Fig6 a. ESCA of compound of Hg^{2+} ion in Solid State

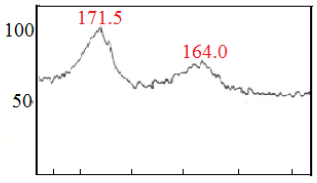

Fig.7a. ESCA of compound S^{2-} ion in Solid State

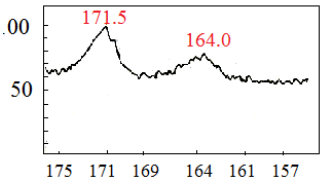

Fig.6b. ESCA of compound of Hg^{2+} ion in solution

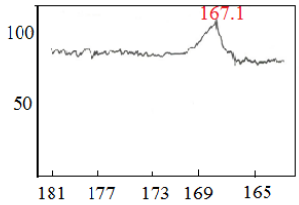

Fig.7b. ESCA of compound of S^{2-} ion in solution

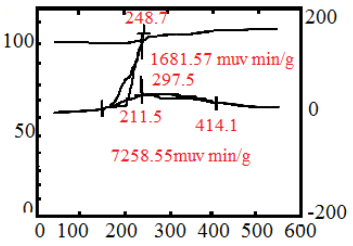

Fig.8a. TGA - DTA of compound of Zn^{2+} ion in Solid State

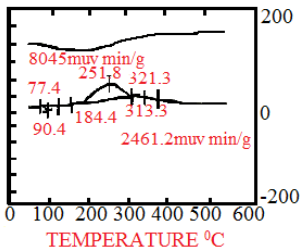

FIG.8b. TGA - DTA of compound of Zn^{2+} ion in solution

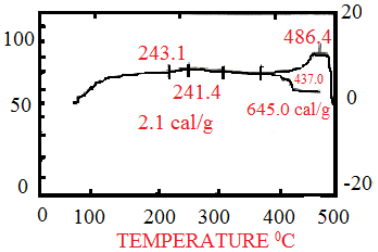

Fig.9a TGA - DTA of compound of Cd^{2+} ion in Solid State

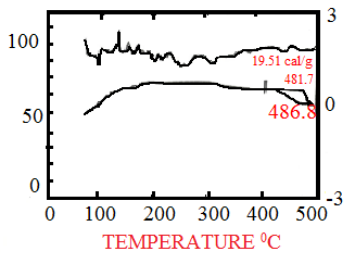

Fig.9b. TGA - DTA of compound of Cd^{2+} ion in solution

Fig.10a.IR spectra
Of Zn^{2+} ion in Solid State

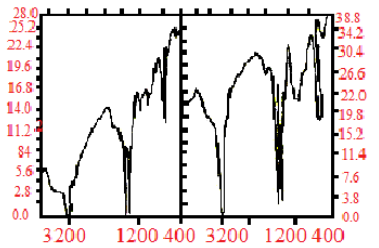

Fig.10b. IR spectra of
Zn^{2+} ion in solution

Fig.11a. IRspectra of
Cd^{2+} ion in Solid State

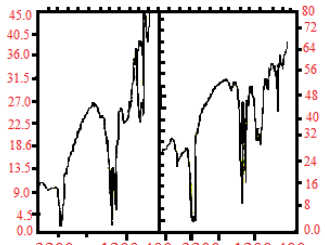

Fig.11b. IR spectra of
Cd^{2+} ion in solution

Fig.12a. IR spectra of
Hg^{2+} ion in Solid State

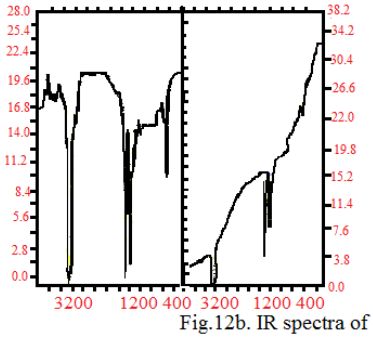

Fig.12b. IR spectra of
Hg^{2+} ion in solution

Fig.13a.Test tube containing nanoparticles of
ZnS, CdS and HgS in ethylene glycol

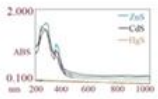

Fig.13b. uv- visible spectra of
nanoparticles of ZnS, CdS and HgS

ZnS nanoparticle CdS nanoparticle HgS nanoparticle

Fig.14 TEM of nanoparticles of ZnS, CdS and HgS