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# Magnetic Nanocomposites of Mixed Oxides of Iron and Zinc with a Copolymer of Aniline and Formaldehyde : Synthesis at Room Temperature

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Abstract - The paper describes the direct synthesis of magnetic nanocomposites of $\gamma$-$Fe_2O_3$ in presence of varying concentrations of zinc ions. Infrared, Mössbauer and pH measurement studies on these materials reveal the effect of zinc ions on clustering of the iron oxide particles resulting in nanosize particles of critical size to give paramagnetic and/or ferrimagnetic phases.

## I. INTRODUCTION

In recent years, composites based on nanosized magnetic materials are gaining increasing importance. The underlying reason is their unusual and new exciting properties [1] such as superplasticity, enhanced homogeneity, transparency in opaque ceramics, unusually soft ferromagnetism, giant magnetocaloric effects and magnetoresistance, etc. caused by the remarkable modifications of the electronic structures and formation of a great variety of structures ranging from high level ordered three dimensional periodic structures to stoichoimetrically dispersed medium. Some of the possible applications of magnetic nanocomposites viz. magnetic refrigeraion, high density information storage, smart structures(magnetostriction), ferrofluids, medical diagnosis, etc. are well recognised now [2-5].

The routes often employed for preparation of these materials are by co-sputtering of magnetic and non-magnetic species and chemical process [2] and recently by mimicking the process of bio-mineralization [7]. In any of these process, however, no plausible mechanism has emerged, for controlling the particle sizes. The present investigations report the chemical synthesis of nanoparticles of iron oxide with the control and the dependence of their sizes on the concentration of the added zinc ions.

## II. EXPERIMENTAL

### *A.Synthesis*

Five samples of nanocomposites of mixed oxides of iron and zinc in the copolymer matrix of aniline-formaldehyde were synthesised according to the method described elsewhere [8]. A typical preparation is described below :

To a solution of aniline (0.1 mole), HCl(0.12 mole) and formaldehyde(0.12 mole) in 200 $cm^3$ of distilled water was added another solution of $FeCl_3$(0.06 mole) and $ZnCl_2$ (0.0015 mole) in 100 $cm^3$ of distilled water. The resultant solution was allowed to stand at room temperature until traces of precipitate appeared and added, dropwise and with constant stirring, to a 200 $cm^3$ 10% NaOH aqueous solution. The resultant greyish yellow precipitate were filtered, repeatedly washed with distilled water until filterate give neutral pH and dried in air.

Four other samples were similarly obtained by varying molar ratio of $FeCl_3$:$ZnCl_2$ between 40:1 to 7.5:1 while keeping total weight of the two halides, taken together, as constant. The samples have been designated as given in Table I.

### *B.Physical Measurements*

The infrared spectra of all the samples were recorded in KBr pellets on Shimdzu Series 8000 FTIR spectrophotometer. $^{57}Fe$ Mössbauer spectra were recorded in standard transmission geometry. The fiting of the spectral data were carried out by using a computer program [9]. pH measurements were carried by suspending the nanocomposites in de-ionized water.

## III. RESULTS AND DISCUSSIONS

### *A.Infrared*

From the observed absorption peaks in the infrared spectrum of these samples, shown in Table I, it is apparent that the strong absorption around 580 $cm^{-1}$ can be attributed to presence of $\gamma$-$Fe_2O_3$. Since the possibility of $\alpha$-FeOOH

Table I IR spectral data in range of 1000 - 400 $cm^{-1}$ of nanocompsites with varying concentration of zinc ions

| Molar ratio $FeCl_3$:$ZnCl_2$ | Sample | Frequency ($cm^{-1}$) |
|---|---|---|
| 40:1 | 1 | 816(s), 583(vs), 509(w) |
| 20:1 | 2 | 814(s), 581(vs), 507(w) |
| 13:1 | 3 | 815(s), 581(vs), 511(w) |
| 10:1 | 4 | 814(s), 581(vs), 509(w) |
| 7.5:1 | 5 | 815(s), 583(vs), 510(w) |

is ruled out due to the absence of its characterisitic absorption at 800 $cm^{-1}$ and 890 $cm^{-1}$ [10]. The absorption bands observed at 815 $cm^{-1}$ and 510 $cm^{-1}$ were also found in the pure copolymer [11]. Though pure $\gamma$-$Fe_2O_3$ has been reported to show characteristic absorptions at 555 $cm^{-1}$ and 468 $cm^{-1}$, the shift of the former band to higher frequency and disappearance of the later may be attributed to the formation of fine particles of $\gamma$-$Fe_2O_3$ and their interactions with the polymer chain.

*B.Mössbauer Studies*

All the samples give relaxed and complex Mössbauer specra (Fig. 1). Fitting of the spectral data, by assuming the lines to be Lorentzian in shape, show the presence ot two sextets due to magnetic phase and a doublet due to paramagnetic phase in all samples except for sample 3. Furthermore, values of Mössbauer parameters (Table II) change on varying zinc ion concentration without following a clear trend. However, the appearance of broad lines (relaxed spectra) with a paramagnetic doublet indicate the presence of iron oxide particles in size range of < 10 nm with a particle size distribution [13]. Whereas in sample 3 the particles are of size below the critical size which shows paramagnetic behaviour may not be present.

Further, Mössbauer studies also indicate the presence of $\gamma$-$Fe_2O_3$ in these materials [14]. Since observation of lower values of $H_{eff}$ and zero values of quadrupole splitting of the two sextets rules out the presence of $\alpha$-$Fe_2O_3$ - another possibility of formation during the reaction.

It has been observed in authors' laboratory that coprecipitation of only iron oxide with copolymer and oxides of zinc and iron without the polymer show the formation of pure paramagnetic phases [11]. These observations thus make clear that presence of both zinc ions and the copolymer plays definite roles in formation of ferrimagnetic phases in these samples through clustering of colloidal particles of iron oxide. Moreover, sizes of the clusters depend very much on the concentration of zinc ions.

It has been reported earlier that reduction of particle size of metal oxides to colloidal size ($\sim$100 A°) gives rise to enhanced surface phenomena with occurrence of particular features viz. redox response against surface acid-base phenomena, exceptional catalytic activity, etc. [15]. However, no report is available on the surface hydration of the colloidal particles in aqueous medium. In this study we report the pH behaviour of colloidal particles of the nanocomposites of $\gamma$-$Fe_2O_3$ suspended in water of neutral pH. The plot of mole fraction of zinc ions, used in clustering of $\gamma$-$Fe_2O_3$ in samples 1 - 5, versus pH value and paramagnetic component (Fig. 2), obtained from Mössbauer studies (Table II), present some very interesting observations. Firstly, with increasing zinc ion mole fraction the pH value increases while paramagnetic component drops down to zero at zinc ion mole fraction value of $7.4 \times 10^{-2}$. However, on further increasing the zinc ion mole fraction the pH value decreases and paramagnetic component increases.

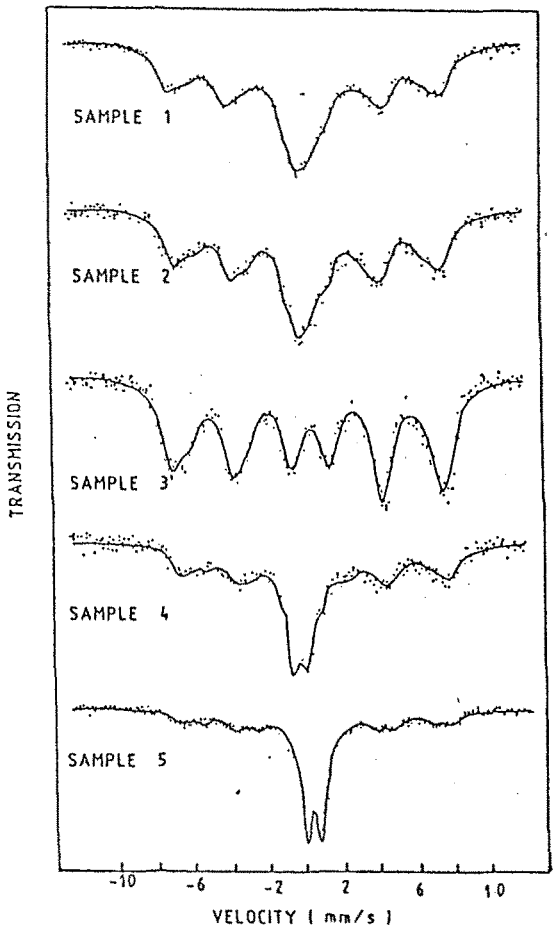


Fig. 1 : Room temperature $^{57}Fe$ Mössbauer spectra of nanocomposites (1 - 5) with varying concentration of zinc ions

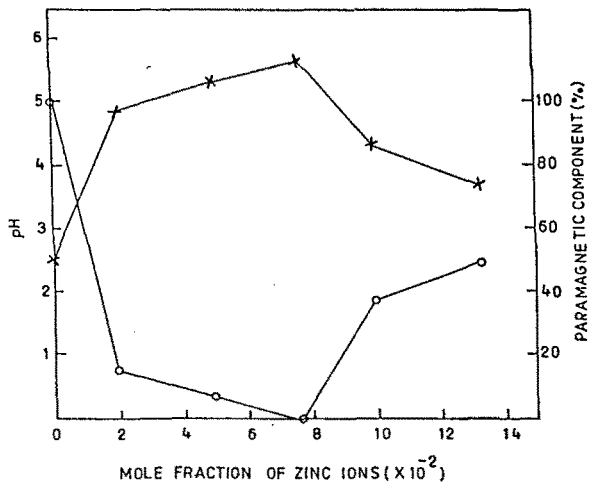


Fig. 2 : Plot of pH values (x) and paramagnetic component (o) versus mole fraction of zinc ions in samples 1 - 5.

Table II Mössbauer parameters of nanocompsites with varying concentration of zinc ions

| Sample | Doublet | | | Sextet 1 | | | Sextet 2 | | |
|---|---|---|---|---|---|---|---|---|---|
| | I.S. (mm/s) | Q.S. (mm/s) | Area (%) | I.S. (mm/s) | $H_{eff}$ (kOe) | Area (%) | I.S. (mm/s) | $H_{eff}$ (kOe) | Area (%) |
| 1 | 0.23 | 0.70 | 15.0 | 0.36 | 461 | 42.7 | 0.39 | 400 | 42.3 |
| 2 | 0.24 | 0.63 | 7.4 | 0.45 | 445 | 55.9 | 0.45 | 377 | 36.7 |
| 3 | - | - | - | 0.38 | 460 | 59.3 | 0.59 | 416 | 40.7 |
| 4 | 0.31 | 0.74 | 38.1 | 0.31 | 449 | 53.9 | 0.38 | 408 | 33.4 |
| 5 | 0.35 | 0.76 | 49.8 | 0.46 | 450 | 26.3 | 0.51 | 385 | 24.1 |

Isomer shift values are with respect to natural iron.

## IV. Conclusions

Characterization of these nanocomposites of iron oxide reveals the following : i) formation of fine particles of $\gamma$-$Fe_2O_3$ with their particle size in the range of 10 nm results in giving both ferri- and paramagnetic phases, ii) formation of these phases takes place in the presence of zinc ions and the polymer phase, and iii) zinc ions through their clustering effects control the particles sizes of $\gamma$-$Fe_2O_3$, showing varying degree of paramagnetic and ferrimagnetic behaviours. This study first time shows the effect of zinc ions in controlling the particle size of an oxide of iron at nanoscale.


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