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Adsorption Dynamics of Surfactant on Nanoparticles

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ABSTRACT : This Work Is Carried Out For Finding The Dynamics Of Surfactant Adsorption On Surface Of Nanoparticles. Experiments Were Carried Out On Ferrofluid For Given Concentration With Various Particle Sizes. Nanoparticles Were Synthesized With Different Ph Like 8,10,11.5 And 12.5 And Ferrofluid Suspension Was Prepared. The Ferrite Particles Were Coated By Oleate Ionsto Avoid Agglomeration Of The Particles. Different Particle Sizes In Accordance With Ph Of Solutions Were Confirmed By Using Tem,Xrd. The Coating Was Confirmed By Ftir. Kerosene Was Taken As Hydrocarbon Carrier.More Adsorption Of Surfactant Molecules Were Witnessed On Nanoparticles Made With Higher Ph Solution. Ftir Was Carried Out On All Four Samples To Investigate The Adsorption Of Oleic Acid Molecules.It Was Observed That Sharpness Of The Ftir Peaks Were Dependent On Size Of The Nanoparticles. The Ftir Spectrum Shows Adsorption Band At 1710cm^{-1} Which Presents The Stretching Vibration Of The Carboxylic Group(C=0) Associated To The Oleic Acid Molecules Which Are Adsorbed On To The Surface Of The Crystallites. Ftir Range Shows The H-O-H Bonding Vibration At About 1000-1600cm^{-1}, Typically Of H_2o Molecules Which Is Less Intense. Thus, Ftir Absorption Spectroscopy Allowed Identifying The Presence Of Certain Types Of Chemical Substances Adsorbed On Surface Of Nanoparticles. It Was Concluded That Ftir Peaks Were More And More Sharper As Diameters Of Particles Were Reduced. This Was Attributed To The Fact That For A Given Concentration, The Surface Area Of Smaller Nanoparticles Was More And Hence More Adsorption And Orderly Intense Peak Was Observed On Ftir.

Keywords-*Fe_2o_4, Ftir, Xrd, Surfactant Dynamics.*

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I. INTRODUCTION

Ferrofluid Is A Stable Colloidal Suspension Of Magnetic Nanoparticle. These Particles Can Be Prepared With Various Techniques Like Physical Methods, Chemical Methods, Biological Methods. These Nanoparticles Are Single Domain And Exibit Super Paramagnetism. These Particles Are Dispersed In Hydrocarbon Carrier And Stabilized With The Help Of Surfactant Coating To Avoid Agglomeration Of Particles. There Are Various Applications Of Ferrofluids Which Includes Its Use In Biology And Medicine {Proteins, Genes, Radio Pharmaceuticals, Magnetic Resonance Imaging [1], Diagnostics, Separation, And Controlled Drug Release [2-4]}. Ferrofluids Characteristically Posses Both, Magnetic And Fluidic Properties And Thus Have A Diverse Range Of Applications In Various Branches Of Engineering Including The Electrical Engineering [5, 6]. It Also Has Specific Applications In Sensors [7, 8], Optical Fibres [9, 10], Audio Speaker Devices [11] And In The Study Of Electrical Conductivity [12]. Effect Of Surface Area Of Particle On Conductivity Of Ferrofluid Has Already Been Studied [13]. It Is Interesting To Compare Other Form Of Electronic Conduction In Conducting Polymer Which Is Mainly Due To Hopping Mechanism Of Electrons [14, 15].

This Work Is About The Relation Of Ftir Absorption Peaks With Particle Size. The Synthesis Of Oleate-Coated Ferrimagnetic Nanoparticles Have Been Reported For Various Sizes Of Particles And Adsorption Dynamics On Surface Of Nano Particles. Claim Has Been Supported By Experimental Data.

II. MATERIALAND METHODS

2.1 Materials:

Ferrous Chloride Tetra-Hydrate ($Fecl_2$:$4h_2o$), Ferric Chloride Hexahydrate ($Fecl_3$:$6h_2o$), Oleic Acid $C_{18}h_{34}o_2$ (Anionic Surfactant) And Ammonium Hydroxide (Nh_4oh) Were Obtained. Milli-Q Water Was Re-Deionized (With Specific Conductance < 0.1 S/Cm). 0.1m Hcl Was Used For Adjustment Of Surface Charge On Nanoparticles Prepared With Ph8, Ph10, Ph11.5 And Ph12.5.

2.2 Preparation Of Fe_3o_4 Nanoparticles:

Chemical Co-Precipitation Method Was Used For Synthesis Of Ferrofluid Nanoparticles Which Is Bottomup Approach**.** 1.28m $Fecl_3$:$6h_2o$, 0.64m Of $Fecl_2$:$4h_2o$ Stock Solutions Were Prepared As A Source Of Iron By Dissolving The Respective Salts In Milli-Q Deionised Water. 1.5m Nh_4oh Stock Solution Was Prepared And An Iron Source Was Added Slowly Into The Alkaline Solution With Vigorous Stirring For 30 Min At 90^0c Till The Complete Reaction Took Place. The Ph Of The Reaction Was Maintained By Using Buffer Solution. Here Hydrolysis Process Is Designated With Ammonium Hydroxide's Reaction With Iron Source, This Forms Ferric Hydroxide $Fe(Oh)_3$ And Ferrous Hydroxide $Fe(Oh)_2$.

Here The Oxidation Process Progressed The Formation Of Feo And Fe_2o_3 Molecules And Thus Ferritisation Took Place Easily. The Reaction Was Carried Out At Room Temperature And Final Product Of Fe_3o_4 Particles Was Obtained. The Dark Black Powder Was Attracted Towards Weak Magnet; Thus The Precipitate Was Confirmed To Be Fe_3o_4. The Concentration Of Fe^{2+} And Fe^{3+} Must Be In The Ratio Of 1:2 Respectively [16]. 1.5m Oleic Acid Was Used As Anionic Surfactant For Preparation Of Oleate Ions At Ph = 9.4 . Coating Was Carried Out Using Oleate Ions Under Vigorous Mechanical Stirring For 30 Minutes At 97^oc To Acquire Steric Repulsion. Oleic Acid In Excess Was Removed From The Mixture By Washing Sample Three Times With Acetone. Peptization And Centrifugation Of The Solution Was Carried Out. The Shade Of The Powder Was Observed To Be Brown Due To Coating Of Surfactant Molecules. The Chemical Reaction Of Fe_3o_4 Precipitation As Well As The Principle Reaction Is As Follows[17,18]:

$Fecl_2$+2[$Fecl_3$]+8[Nh_4oh] Fe_3o_4+8[Nh_4cl]+4[H_2o]

The Magnetic Powder That Obtained Was Dried In The Oven At 80 ^{O}c. This Work Was Carried Out For Consecutive Four Batches Of Nanoparticles At Ph8, Ph10, Ph11.5 And Ph12.5

III. CHARACTERISATIONOFFE$_3$O$_4$NANO PARTICLES

The Prepared Batches Were Characterized And Tem, Xrd And Ftir Were Carried Out On These Samples. Fig.3.1 – Fig.3.4 Shows Characterization Of Tem Performed On Jem 2100, Jeol Make.

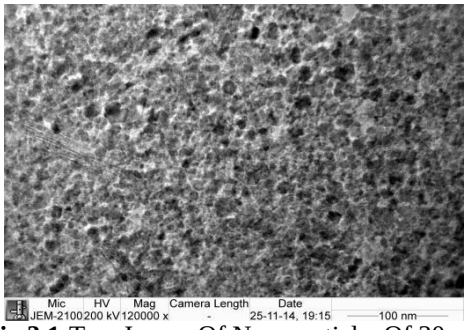

Fig.3.1: Tem Image Of Nanoparticle Of 30nm Prepared With 8 Ph.

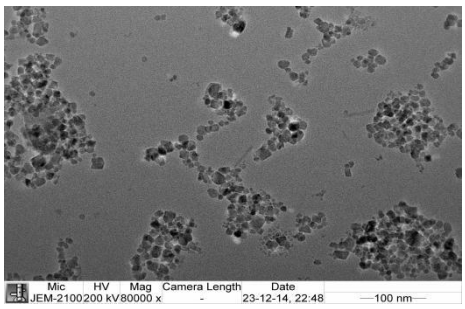

Fig.3.2: Tem Image Of Nanoparticle Of 24nm Prepared With 10 Ph.

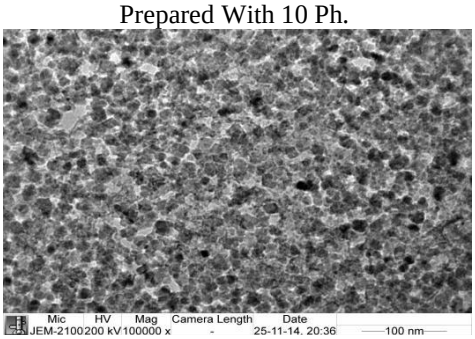

Fig.3.3: Tem Image Of Nanoparticle Of 19nm Prepared With 11.5 Ph.

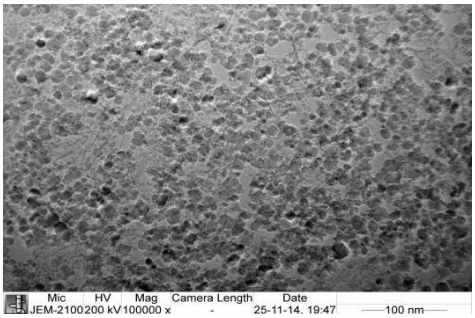

Fig.3.4: Tem Image Of Nanoparticle Of 13nm Prepared With 12.5 Ph.

Now, Fig.3.5 – Fig.3.8 Shows Characterization Of Xrd Performed On X-Ray Diffractometer Phillips Pw 1800, Range 6-80^o. The

Properties Of Produced Nanoparticals Were Analyzed By Xrd Taken On Philipsmake X'pert Pro Model Xrd Machine. The Size Of The Crystal Is Calculated By Scherrer's Formula And The Xrd Wavelength **Λ** Of 0.15406nm Was Used For Characterization.

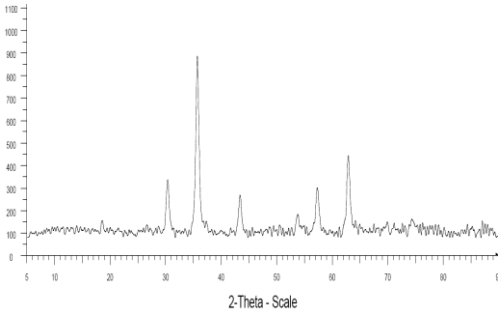

Fig.3.5: Xrd Pattern Of Fe_3o_4 Nanoparticle Of 27.6nm(8ph) X-Axis: 2 Theta Y-Axis: Intensity A.U.

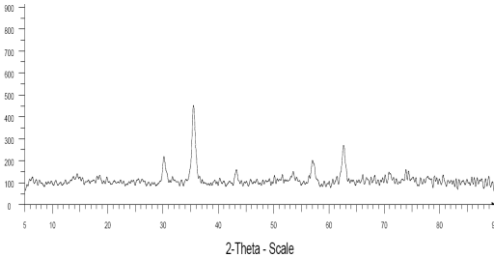

Fig.3.6: Xrd Pattern Of Fe_3o_4 Nanoparticle Of 23.7nm(10ph) X-Axis:2 Theta,Y-Axis: Intensity A.U.

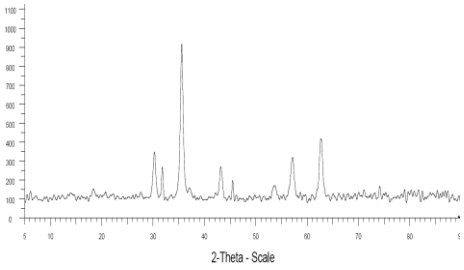

Fig.3.7: Xrd Pattern Of Fe_3o_4 Nanoparticle Of 19nm(11.5ph) X-Axis: 2 Theta Y-Axis: Intensity A.U.

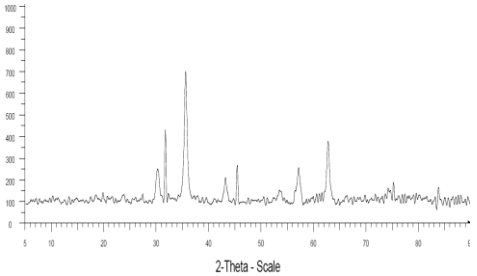

Fig.3.8: Xrd Pattern Of Fe_3o_4 Nanoparticle Of 12.7nm(12.5ph)X-Axis:2-Theta,Y-Axis:Intensity A.U.

Ftir Was Carried Out On All Four Samples To Investigate The Adsorption Of Oleic Acid Molecules As Per Fig.3.9 – Fig.3.12. The Ftir Spectrum Here Shows The Absorption Band At 1710cm^{-1} Which Presents The Stretching Vibration Of The Carboxyl Group (C = O), Associated To The Oleic Acid Molecule, Adsorbed On To The Surface Of The Crystallites. Ftir Spectrum In Figures Below Shows That The H-O-H Bending Vibration At About 1000 - 1600 Cm^{-1}, Typical Of The H_2o Molecule, Is Less Intense. Thus, Ftir Adsorption Spectroscopy Allowed Identifying The Presence Of Certain Types Of Chemical Substances Adsorbed On The Surface Of Nanoparticles.

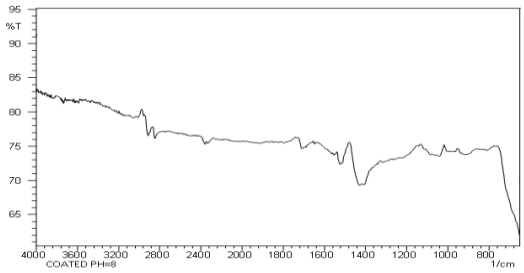

Fig.3.9: X-Axis: Cm^{-1}, Y-Axis:Transmittance

Ftir Of Coated Fe_3o_4 Nanoparticles Of 30nm (8ph). Absorption Peak Around 1710 Cm^{-1} Is Indication Of C=O Bonding. Shows Evidence Of Oleic Acid Adsorption On Nanoparticles. Size Of Peak: Very Low.

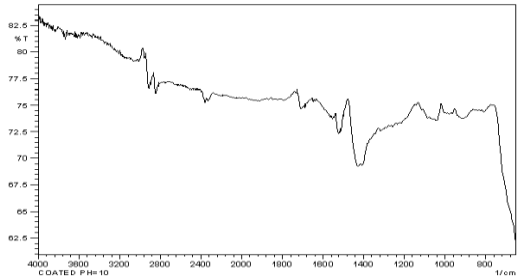

Fig.3.10: X-Axis: Cm^{-1}, Y-Axis:Transmittance

Ftir Of Coated Fe_3o_4 Nanoparticles Of 24nm (10ph). Absorption Peak Around 1710 Cm^{-1} Is Indication Of C=O Bonding. Shows Evidence Of Oleic Acid Adsorption On Nanoparticles. Size Of Peak: Low.

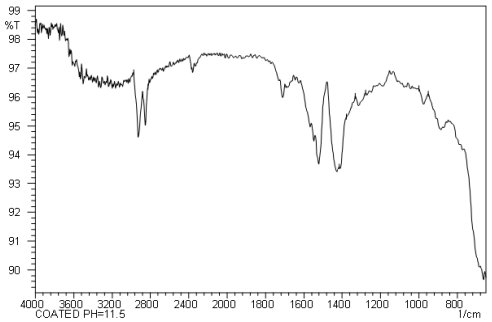

Fig.3.11: X-Axis: Cm^{-1}, Y-Axis:Transmittance

Ftir Of Coated Fe_3o_4 Nanoparticles Of 19nm (11.5ph). Absorption Peak Around 1710 Cm^{-1} Is Indication Of C=O Bonding. Shows Evidence Of Oleic Acid Adsorption On Nanoparticles. Size Of Peak: Moderate.

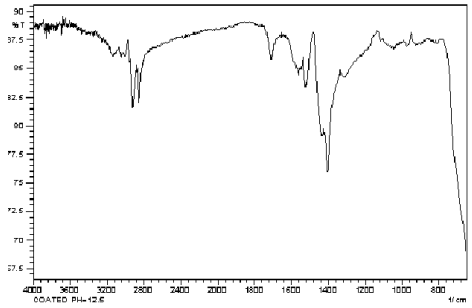

Fig.3.12: X-Axis: Cm^{-1}, Y-Axis:Transmittance

Ftir Of Coated Fe_3o_4 Nanoparticles Of 13nm (12.5ph). Absorption Peak Around 1710 Cm^{-1} Is Indication Of C=O Bonding. Shows Evidence Of Oleic Acid Adsorption On Nanoparticles. Size Of Peak: Higher.

IV. RESULTSAND DISCUSSION

It Is Observed From The Above Analyses That The Particles Sizes Obtained From Tem And Xrd Matched. The Calculated Size Of Particles From Xrd Is Lesser Than The Average Size In Case Of Tem.

Ftir Of Coated Fe_3o_4 Nanoparticles Of 30nm (8ph) In Which Absorption Peak Around 1710 Cm^{-1} Was Observed. It Showed Evidence Of Oleic Acid Adsorption On Nanoparticles With A Very Low Peak.

Ftir Of Coated Fe_3o_4 Nanoparticles Of 24nm (10ph) In Which Absorption Peak Around 1710 Cm^{-1} Was Observed. It Showed Evidence Of Oleic Acid Adsorption On Nanoparticles With A Considerably Low Peak.

Ftir Of Coated Fe_3o_4 Nanoparticles Of 19nm (11.5ph) In Which Absorption Peak Around 1710 Cm^{-1} Was Observed. It Showed Evidence Of Oleic Acid Adsorption On Nanoparticles With A Moderate Peak.

Ftir Of Coated Fe_3o_4 Nanoparticles Of 13nm (12.5ph) In Which Absorption Peak Around 1710 Cm^{-1} Was Observed. It Showed Evidence Of Oleic Acid Adsorption On Nanoparticles With A High Peak.

Thus While Going Through The Ftir, With The Reduction In The Size Of The Particle, It Was Observed That The Ftir Peaks Were Increasing At 1710cm^{-1} In The Same Order With Respect To The Decreasing Trend Of The Particle Size.This Was Due To The Fact That As The Particle Sizes Were Reduced, More And More Surface Area Was Attained. And Therefore More Oleate Ions Were Absorbed On The Increased Area Of The Surface And Thus More Ftir Peaks Were Observed.

For Comparing These Ftir, An Amount Of Samples Taken Were Normalised As Well As Ftir Were Performed On Same Machine At (Ict) Institute Of Chemical Technology, Matunga, Mumbai-For Comparing These Ftir, An Amount Of Samples Taken Were Normalised As Well As Ftir Were Performed On Same Machine At Institute Of Chemical Technology, Matunga, Mumbai-400019, India. 400019, India.

V. CONCLUSION

It Is Observed From The Above Analysis That The Particles Sizes Obtained From Tem And Xrd Matched. The Calculated Size Of Particles From Xrd Is Lesser Than The Average Size In Case Of Tem.Ftir Of Coated Fe_3o_4 Nanoparticles Of 30nm Prepared In 8 Ph, Shows Absorption Peak Around 1710 Cm^{-1}. It Showed Evidence Of Oleic Acid Adsorptionon The Surface Of These Magnetic Nanoparticles With A **Very Low Peak**.Ftir Of Coated Fe_3o_4 Nanoparticles Of 24nm Prepared In 10 Ph In Which Absorption Peak Around 1710 Cm^{-1} Was Observed. It Showed Evidence Of Oleic Acid Adsorption On Nanoparticles With A **Considerably Low Peak**. Ftir Of Coated Fe_3o_4 Nanoparticles Of19nm Prepared With 11.5 Ph,Shows Absorption Peak Around 1710 Cm^{-1}. This Also Showed Evidence Of Oleic Acid Adsorption On Nanoparticles With A **Moderate Peak**. Ftir Of Surfactant Coated Fe_3o_4 Nanoparticles Of 13nm Prepared With 12.5 Ph Shows Absorption Peak Around 1710 Cm^{-1}. This Shows Evidence Of Oleic Acid Adsorption On Nanoparticles With A **Considerably High Peak**.

With The Reduction Trend In The Size Of Nano Particles, It Was Observed That The Respective Ftir Peaks Were Showing Increasing Trend At Around 1710cm^{-1}. This Was Due To The Fact That While Particle Sizes Were Reduced, More And More Surface Area Were Attained. Therefore More Oleate Ions Were Adsorbed On The Increased Area Of The Surface Of Particles And Thus Increasing Stretching Ir Absorption By C=O Of Oleatemolecule Were Observed.

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