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Thermodynamics of solvation for nano zinc ferrite in aqueous hydrochloric acid

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Abstract

The molar solubility and thermodynamic parameters of nano zinc ferrite nanoparticles have been studied at different concentration of aqueous hydrochloric acid at temperature ranging between 298 – 318 K. The nano zinc ferrite powder was prepared by thermal decomposition method. Structure and particle size of the reaction product was determined by XRD and TEM analysis. The prepared ferrite showed a spinel structure with particle size 45nm. The solubility of zinc ferrite nanoparticles in different concentrations of aqueous solutions of HCl was determined by the evaporation process. The solubility increased with increasing the temperature and the molar concentration of aq. HCl. The solvation thermodynamic parameters obtained were discussed.

Keywords: Molar solubility, Zinc ferrite, Molar ratio, Solubility, Solvation.

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1. Introduction

Zinc ferrite is one of the most important spinel ferrites that has attractive characteristics for the application such as soft magnets and low loss materials at high frequencies [1]. The characteristics of zinc ferrite always depend on the shape, size, purity and morphology that controlled by the synthetic process parameters [2–4]. In the present work zinc ferrite was synthesized by the sol gel method.

The solubility of solutes in mixed solvents has great importance in many industrial processes such as in laboratory uses and electronic manufactures and so on. The solubility of solutes in mixed solvents depends on its morphology and particle size and also on their constituent ions by the components of solvent mixtures [5].

Studying the thermodynamics of nano ferrite , is very important to evaluate the single ion thermodynamic parameters that assist in the discussion of the preferential solvation of ions [6] and also helps in the removal of heavy elements using solvent extraction which is necessary to get rid of the hard ions [7].

2. Experimental

2.1 Materials

Zinc nitrate hexa – hydrate $Zn(NO_3)_2$. 6 H_2O and Ferric (lll) nitrate [Fe (NO3)3.9H2O] were acquired from Oxford Laboratory, Mumbai. Glycine ($NH_2.CH_2.COOH$) and pure reagent hydrochloric acid 36% (HCl) were purchased from Adwic., was purchased from Adwic. CTAB (98%) was obtained from Aldrich. Double distilled water was used throughout all the experiments.

2.2 Synthesis of nano zinc ferrite by thermal decomposition Method: -

2.97 g of zinc nitrate [Zn $(NO_3)_2.6H_2O$], 8.08 g of [$Fe(NO_3)_3$. $9H_2O$] and 3.33 g of glycine were dissolved in distilled water at room temperature,then placed in oven at 100-150°C to prepare pure zinc ferrite gel, then the result material was calcined at 400°C for 1.30 h [8].

2.3. Preparation of saturated solutions and solubility measurements.

The saturated solutions of nano zinc ferrite were prepared by dissolving solid amount in closed test tubes containing different aqueous concentrations of hydrochloric acid (mole fraction of the solvent, ($HCl-H_2O$). The tubes were put in water thermostat for a period of three days at temperatures of 298, 303, 308, 313, 318K till equilibrium reached.

The solubility of zinc ferrite in each mixture was measured by taking 1 ml of each saturated solution putting in a small weighed beaker (10 ml) and evaporate under I.R lamp till dryness and then reweight [9 -11].

3. Results and Discussion

3.1. X-ray analysis:

The XRD patterns of the as-synthesized $ZnFe_2O_4$ powder is presented in Fig. (1). The XRD pattern showed characteristic planes: (220), (311), (400), (422), (511), and (440) for $ZnFe_2O_4$ spinel phase. The average particle size (D_{XRD}) is calculated by using the Debye- Scherrer's formula [12]:

$$D_{XRD} = 0.9\ \lambda / \beta \cos \theta \qquad (1)$$

Where λ is x-ray wavelength of the Cu Kα radiation (λ = 1.5406 Å), β is the full width of the most intense diffraction peak (311) at half of the greatest intensity determined in radians. The results show that the $ZnFe_2O_4$ sample is formed in nanocrystallite size of 45 nm.

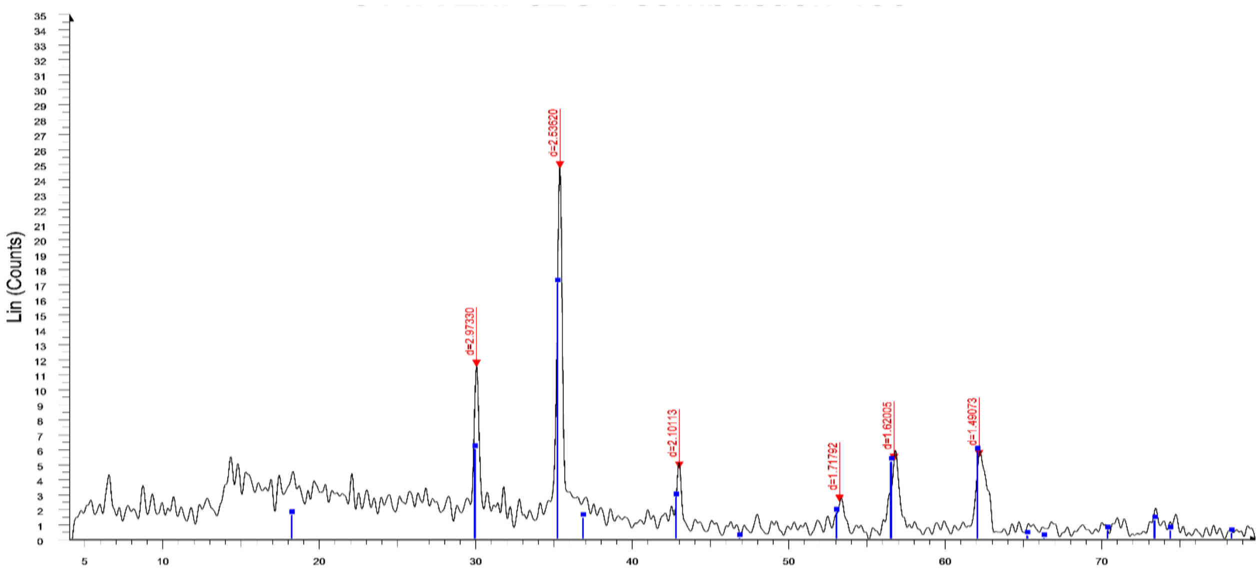

Fig (1): XRD for nano zinc ferrite prepared by thermal decomposition method calcinated at 400 ^{o}C.

3.2 TEM images :

The prepared $ZnFe_2O_4$ was also analyzed by TEM technique and the image obtained is given in Fig. (2).

It shows accumulated particle sizes with different morphologies most of them are cubic with an average particle size of 45 nm , which good match with that obtained from XRD.

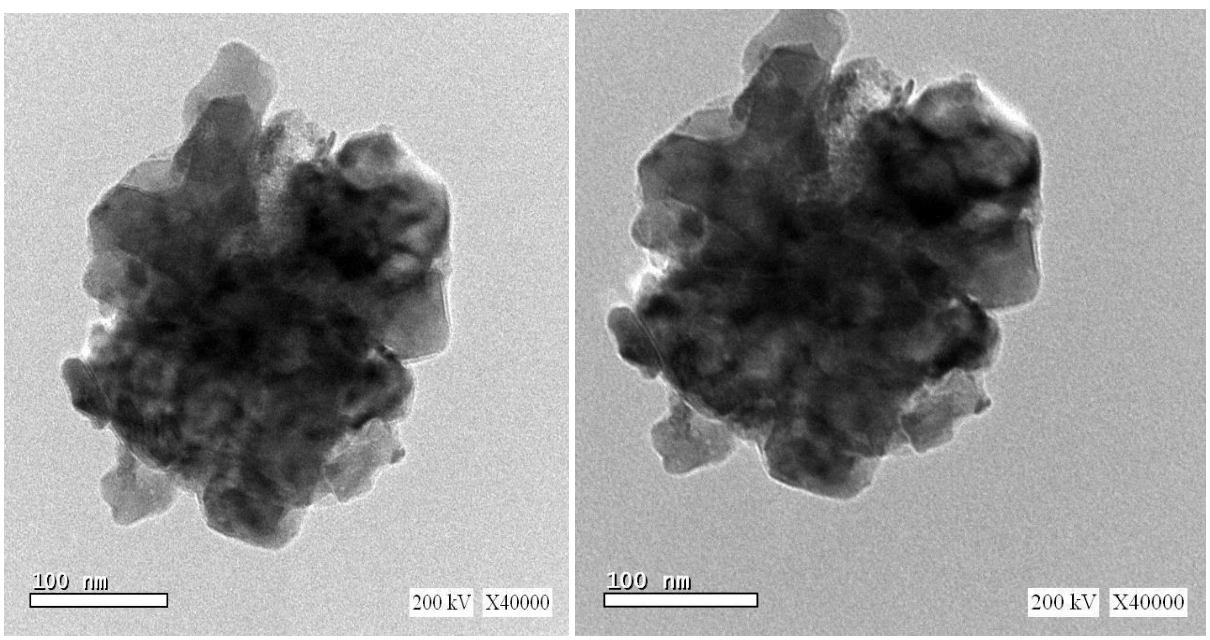

Fig (2): TEM images for nano zinc ferrite prepared by thermal decomposition method calcinated at 400 ^{o}C

3.3. Thermodynamic solvation parameters

3.3.1 Molar solubility:

The molar solubility of $ZnFe_2O_4$ nanoparticles in different concentration of aqueous hydrochloric acid was calculated according to Eq. (1)

Molar solubility (S) = (W×1000)/(M.wt) …… (1)

Where W is the weight of one ml. of the saturated solution after the evaporation process in the small cups using I.R. lamp and M.wt is the molecular weight of nickel ferrite and the data obtained are tabulated in Tables 1-5 .

3.3.2 Solubility product

The solubility product PK_{sp} was calculated using Eq. (2) and the results obtained are listed in Tables 1-5.

$$pksp = -Log\ S \qquad \ldots\ldots \qquad (2)$$

3.3.3. Activity coefficient

The activity coefficients were calculated using Debye – Hückel equation (3) [13] and the evaluated values are given in Tables 1-5.

$$\log \gamma_{\pm} = -0.5062 \times (S)^{0.5} \quad \ldots\ldots\ldots\ldots..(3)$$

3.3.4. Free energy of solvation

From the solubility products the Gibbs free energies of solvation and the transfer Gibbs free energies from water to mixed solvents were calculated by using equations 4 and 5 .The computed data are also listed in Tables 1-5

$$\Delta G = 2.303\ RT\ pKsp \quad \ldots\ldots\ldots\ldots..(4)$$

$$\Delta G_t = \Delta G_S - \Delta G_w \quad \ldots\ldots\ldots\ldots\ldots..(5)$$

3.3.5. Enthalpies and entropies of solvation

Using the solubility measurements at different temperatures and from the plots of log K_s versus 1/T, the enthalpy (Δ H) values are calculated from the slope (Slope= -ΔH/2.303R). Thus, the entropy (Δ S) of solvation for different nano zinc ferrite sample can be obtained using Gibbs-Helmholtz [14-17].

$$\Delta G = \Delta H - T \Delta S \quad \ldots\ldots \quad (6)$$

The data obtained are given in Tables 6-10.

3.3.6. Different volumes of nano zinc ferrite

The molar volumes (V_M) for $ZnFe_2O_4$ nanoparticles were calculated from density measurements after subtracting the weight of 1ml of saturated solutions from the empty weights of beakers. The V_M were obtained by dividing the molecular weight by the extract solution densities. The packing density (P) as explained in literature [18-22] is equal to the ratio of van der Waals volumes (V_w) to the molar volume (V_M) and equal to 0.664.

$$P = Vw/Vm = o.664 \quad \ldots\ldots \quad (7)$$

The data obtained are listed in Table s 11- 15.

Table (1): Solubility S, Log Solubility, log activity coefficient (log γ), solubility product (pK_{sp}), Gibbs free energy (ΔG) and Transfer Gibbs free energy (ΔG_t) for zinc ferrite nanoparticle at different concentrations (X_s) of hydrochloric acid at 298 K.

X_s (HCl)	S	Log S	$\log \gamma_{\pm}$	pK_{sp}	Δ G, J/mol	ΔG_t, KJ/mol
0.1275	0.0187	-1.7270	-0.0693	1.7270	9854.6646	0
0.2803	0.0229	-1.6394	-0.0767	1.6394	9354.6988	-0.5
0.4671	0.0311	-1.5077	-0.0892	1.5077	8603.1959	-1.2515
0.7003	0.0396	-1.4021	-0.1008	1.4021	8000.4094	-1.8543

Table (2): Solubility S, Log Solubility, log activity coefficient (log γ), solubility product (pK_{sp}), Gibbs free energy (ΔG) and Transfer Gibbs free energy (ΔG_t) for zinc ferrite nanoparticle at different concentrations (X_s) of hydrochloric acid at 303 K.

X_s (HCl)	**S**	**Log S**	**$\log \gamma_{\pm}$**	**pK_{sp}**	**ΔG, J/mol**	**ΔG_t, KJ/mol**
0.1275	0.0240	-1.6199	-0.0784	1.6199	9398.4318	0
0.2803	0.0290	-1.5371	-0.0863	1.5371	8917.8821	-0.4805
0.4671	0.0377	-1.4231	-0.0983	1.4231	8256.7927	-1.1416
0.7003	0.0465	-1.3322	-0.1092	1.3322	7729.0587	-1.6694

Table (3): Solubility S, Log Solubility, log activity coefficient (log γ), solubility product (pK_{sp}), Gibbs free energy (ΔG) and Transfer Gibbs free energy (ΔG_t) for zinc ferrite nanoparticles at different concentrations (X_s) of hydrochloric acid at 308 K

X_s (HCl)	S	Log S	$\log \gamma_\pm$	pK_{sp}	ΔG, J/mol	ΔG_t, KJ/mol
0.1275	0.0303	-1.5182	-0.0881	1.5182	8954.0520	0
0.2803	0.0369	-1.4328	-0.0973	1.4328	8449.9639	-0.5041
0.4671	0.0456	-1.3408	-0.1081	1.3408	7907.3639	-1.0467
0.7003	0.0539	-1.2682	-0.1175	1.2682	7479.4851	-1.4746

Table (4): Solubility S, Log Solubility, log activity coefficient (log γ), solubility product (pK_{sp}), Gibbs free energy (ΔG) and Transfer Gibbs free energy (ΔG_t) for zinc ferrite nanoparticle at different concentrations (X_s) of hydrochloric acid at 313 K.

X_s (HCl)	S	Log S	$\log \gamma_\pm$	pK_{sp}	Δ G, J/mol	ΔG_t, KJ/mol
0.1275	0.0394	-1.4044	-0.1005	1.4044	8417.3242	0
0.2803	0.0476	-1.3222	-0.1105	1.3222	7924.2092	-0.4931
0.4671	0.0559	-1.2530	-0.1196	1.2530	7509.5786	-0.9077
0.7003	0.0632	-1.1990	-0.1273	1.1990	7185.9052	-1.2314

Table (5): Solubility S, Log Solubility, log activity coefficient (log γ), solubility product (pK_{sp}), Gibbs free energy (ΔG) and Transfer Gibbs free energy (ΔG_t) for zinc ferrite nanoparticle at different concentrations (X_s) of hydrochloric acid at 318 K

X_s (HCl)	S	Log S	$\log \gamma_\pm$	pK_{sp}	ΔG, J/mol	ΔG_t,KJ/mol.
0.1275	0.0498	-1.3030	-0.1129	1.3030	7933.9968	0
0.2803	0.0592	-1.2280	-0.1231	1.2280	7477.6874	-0.4563
0.4671	0.0701	-1.1545	-0.1340	1.1545	7030.0051	-0.9040
0.7003	0.0828	-1.0817	-0.1457	1.0817	6586.7107	-1.3473

Table (6): Enthalpies and entropies of solubility parameters for zinc ferrite nanoparticles in aqueous hydrochloric acid at 298 K

X_s (HCl)	Δ H, J/mol	Δ S, J/mol.K
0.1275	37534.3585	92.8381
0.2803	37063.3121	92.9351
0.4671	29710.3921	70.7938
0.7003	23628.9146	52.4182

Table (7): Enthalpies and entropies of solubility parameters for zinc ferrite nanoparticles in aqueous hydrochloric acid at 303 K.

X_s (HCl)	Δ H, J/mol	Δ S, J/mol.K
0.1275	37534.3585	92.81189745
0.2803	37063.3121	92.84324576
0.4671	29710.3921	70.76892434
0.7003	23628.9146	52.44880712

Table (8): Enthalpies and entropies of solubility parameters of zinc ferrite nanoparticles in aqueous hydrochloric acid at 308 K

X_s (HCl)	Δ H, J/mol	Δ S, J/mol.K
0.1275	37534.3585	92.7480
0.2803	37063.3121	92.8552
0.4671	29710.3921	70.7545
0.7003	23628.9146	52.4076

Table (9): Enthalpies and entropies of solubility parameters of zinc ferrite nanoparticles in aqueous hydrochloric acid at 313 K

X_s (HCl)	Δ H, J/mol	Δ S, J/mol.K
0.1275	37534.3585	92.9811
0.2803	37063.3121	93.0515
0.4671	29710.3921	70.8951
0.7003	23628.9146	52.5084

Table (10): Enthalpies and entropies of solubility parameters of zinc ferrite nanoparticles in aqueous hydrochloric acid at 318 K

X_s (HCl)	Δ H, J/mol	Δ S, J/mol.K
0.1275	37534.3585	93.0390
0.2803	37063.3121	92.9926
0.4671	29710.3921	71.2883
0.7003	23628.9146	53.5665

Table (11): Density (d), Molar volume (V_M) and Van der Waals volume (V_W) for zinc ferrite nanoparticles at different concentrations of hydrochloric acid at 298 K

X_s (HCl)	Molarity	D (gm/cm^3)	V_M (cm^3/mol)	V_w (cm^3/mol)
0.1275	2.32	0.799	284.6427	200.3402
0.2803	4.64	0.8469	268.7200	189.0027
0.4671	6.96	0.8971	251.9997	178.4301
0.7003	9.28	0.9567		167.3278

Table (12): Density (d), Molar volume (V_M) and Van der Waals volume (V_W) for zinc ferrite nanoparticles at different concentrations of hydrochloric acid at 303 K

Xs (HCl)	Molarity	D (gm/cm3)	VM (cm3/mol)	Xs (HCl)
0.1275	2.32	0.8844	272.5838	180.9956
0.2803	4.64	0.9325	258.5235	171.6596
0.4671	6.96	0.9826	245.3579	162.9176
0.7003	9.28	1.0398	231.8462	153.9459

Table (13): Density (d), Molar volume (V_M) and Van der Waals volume (V_W) for nano zinc ferrite at different concentrations of hydrochloric acid at 308 K

Xs (HCl)	Molarity	D (gm/cm3)	VM (cm3/mol)	Xs (HCl)
0.1275	2.32	0.9587	251.4548	166.9660
0.2803	4.64	1.0147	237.5746	157.7495
0.4671	6.96	1.0648	226.4123	150.3378
0.7003	9.28	1.1160	216.0230	143.4393

Table (14): Density (d), Molar volume (V_M) and Van der Waals volume (V_W) for zinc ferrite nanoparticles in different concentrations of hydrochloric acid at 313 K

Xs (HCl)	**Molarity**	**D (gm/cm3)**	**VM (cm3/mol)**	**Xs (HCl)**
0.1275	2.32	1.0360	232.7004	154.5131
0.2803	4.64	1.0894	221.2845	146.9329
0.4671	6.96	1.1414	211.2110	140.2441
0.7003	9.28	1.1970	201.3946	133.7260

Table (15): Density (d), Molar volume (V_M) and Van der Waals volume (V_W) for nano zinc ferrite at different concentrations of hydrochloric acid in at 318 K

Xs (HCl)	Molarity	D (gm/cm3)	VM (cm3/mol)	Xs (HCl)
0.1275	2.32	1.2290	196.1620	130.2515
0.2803	4.64	1.3036	184.9332	122.7956
0.4671	6.96	1.3767	175.1116	116.2741
0.7003	9.28	1.4212	169.6347	112.6375

4. Conclusion

The nano-sized zinc ferrite with cubic spinel crystal structure (confirmed from XRD and TEM) were prepared using thermal decomposition method. The Gibbs free energies of transfer(ΔG_t) for the solubility of nano zinc ferrite in HCl aqueous solutions are increased with an increase in the mole fraction of HCl favoring more solvation. Increasing temperature caused a decrease in ΔG_t and other thermodynamic parameters due to the increase in solubility. The prepared zinc ferrite nanoparticles have great solvation volumes in HCl solutions favoring more solvation and interaction in this medium. The solvation volumes V_M & V_w decreased with the rise of the temperature favouring less solvation. Positive values of enthalpies and entropies for nano zinc ferrite showed that the reaction process occurred spontaneously and it is not exothermic and not endothermic and depend on the values of temperatures and ΔG. The decrease in volumes for nano salt by increasing the temperature is due to the migration of the solvated sphere around away from the field of the ions.

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