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Thermodynamics of solvation for nano zinc carbonate in mixed DMF–H_2O solvents at different temperatures

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***Abstract*—The molar solubility for nano zinc carbonate ($ZnCO_3$) in different percentages of dimethylformamide (DMF) and water were measured at 292.15, 303.15, 308.15 and 313.15 K. From the molar solubilities for nano $ZnCO_3$, the solvation parameters like, activity coefficient, solubility product, free energy of solvation, enthalpy of solvation and entropy of solvation were estimated. All these solvation parameters were discussed.**

***Index Terms*—Thermodynamics, molar solubility, nano zinc carbonate free energy, enthalpy, entropy of solvation, mixed DMF – H_2O solvents.**

I. INTRODUCTION

Zinc carbonate is very harmful salt by inhalation and is swallowed. It can also irritating eyes, respiratory system and skin [1]. It causes swelling of the cells and organelles, acute inflammation of cell clusters and cause cancer [2]. Our purpose is to try to estimate different concentrations of nano zinc carbonate to get rid from body and environment.

II. EXPERIMENTAL

A. Materials

$ZnCO_3$ from Al Nasr chemicals Co. was used without purification.DMF of the type Adwic was used.

B. Preparation of nano $ZnCO_3$

$ZnCO_3$ of the type Adwic was milled by ball - mill. The ball – mill was a retsch MM2000 swing mill with 10 cm^3 stainless steel, double – walled tube. Two stainless steel balls of 12mm diameter and 7 gm weight for each were used. Ball-milling was performed at 20225 Hz for half an hour at room temperature (with out circulating liquid and the temperature did not rise above 30^oC).

C. Preparation of saturated solutions and solubility measurement

The saturated solutions for nano $ZnCO_3$ were prepared by dissolving suitable amount of solid material in closed test tubes containing DMF – H_2O solvents. The tubes were placed in water thermostat for a period of four days till equilibrium reached. The solubility of $ZnCO_3$ in each mixture was measured by taking 1 ml of each saturated solution and putting in small weighed beaker (10ml) and evaporated under IR lamp till dryness and then weighted [3-25]. The molar solubilities for nano $ZnCO_3$ were calculated by subtracting the evaporated weights of samples minus that of empty beakers weight and calculation to changes to molar concentrations were done [26-40]. The same procedures were repeated at different temperatures.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

The X-ray diffraction of nano zinc carbonate in Fig. (1) Shows that it has about 72.1% of the structure is $Zn_5(CO_3)_2(OH)_6$ and 27.9% of the structure is $ZnCO_3$. The axial ratio of a : b : c in case of $Zn_5(CO_3)_2(OH)_6$ is 2.1327 : 1.0000 : 0.8493 . The crystal system is monoclinic – prismatic, the cell dimensions are : a = 13.479 , b = 6.32 , c = 5.368 , z = 2 , v = 455.1 and beta = 95.6^0 . The density calculated = 4.01 and the average density = 3.5 . The cleavage is { 1 0 0 } perfect. The axial ratio of a : c in case of $ZnCO_3$ is1.3229 . The crystal system is trigonal – hexagonal scalenohedrall and the forms are (1 0 2) (1 1^- 1) . The cell dimensions are : a = 4.653 , c = 15.028 , z = 6 , v = 281.77 . The density calculated = 4.43 . The cleavage is { 1 0 1 1 } perfect The crystal size calculated by the sum of values in table (1) then take the mean value which equal 9.4 nm .

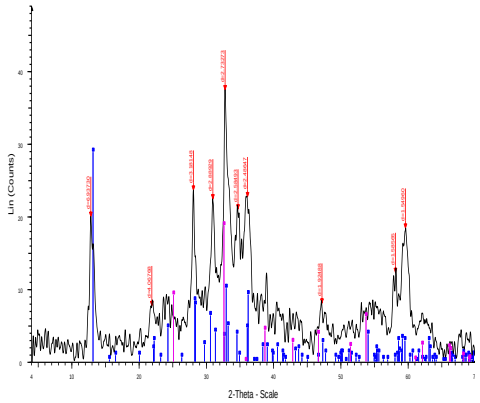

Fig (1) X-ray diffraction of nano zinc carbonate

Table (1) : The crystal size of nano zinc carbonate

Position	Area	Cry Size L(nm)	Microstrain	RMS Strain(%)
12.93132	16.58325	15.5	0.1	0.1

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21.87766	6.385339	12.2	0.1	0.1
24.17547	17.89174	4.3	0.1	0.1
28.07026	24.04042	9	0.1	0.1
30.86505	23.92732	9.1	0.1	0.1
32.87991	45.0307	9.3	0.1	0.1
34.60966	22.79518	8.4	0.1	0.1
36.01647	28.12478	9.5	0.1	0.1
39.04919	26.14477	3	0.1	0.1
47.33825	9.397908	7.4	0.1	0.1
54.44555	31.57527	3	0.1	0.1
57.97841	5.129104	23.7	0.1	0.1
59.51628	31.25574	8	0.1	0.1

B. F.T.I.R Spectra

Fig. (2) shows FTIR spectra of $ZnCO_3$ in reverse micelles. The IR spectrum in the range 400-3500 cm^{-1} show well pronounced broad intense peaks in case of $ZnCO_3$. The observed IR bands and their assignments are shown in Table 2.

The IR bands at 693.3 and 856 cm^{-1} correspond to in plane and out plane bending CO_3^{-2}.The IR bands at 1462 cm^{-1} correspond to the asymmetric C-O stretching vibration mode, while the weak band at 1059 cm^{-1} is attributed to the symmetric C-O stretching vibration[41].

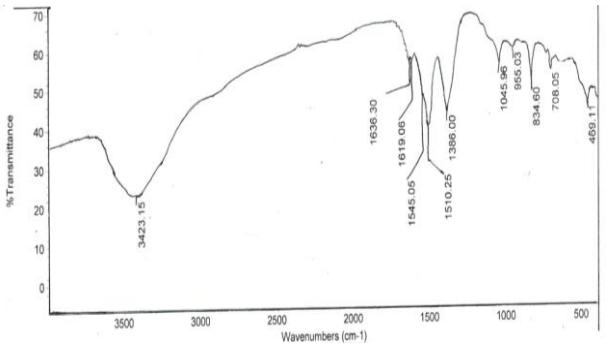
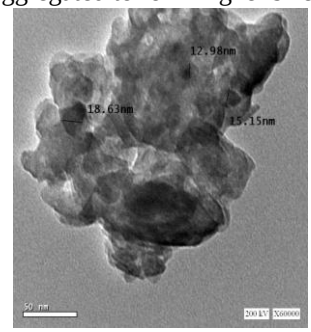


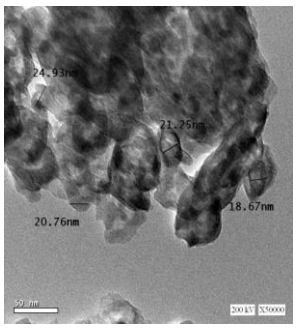
Fig (2) Fourier transform infra-red spectra of nano zinc carbonate

C. TEM Images

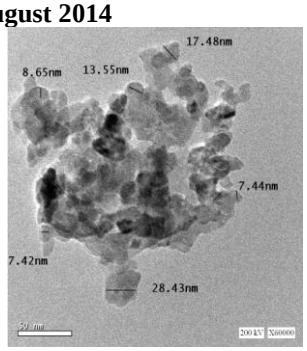
Fig. (**3**) shows that TEM images of $ZnCO_3$ obtained in ethanol solution are distorted spheres with diameters in the range from 7.44 to 36 nm. The small sizes particles are aggregated to form higher sizes

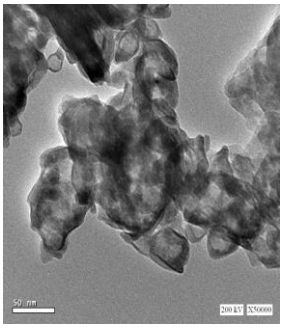


(A)



(B)





(C) (D)

D. Gibbs free energies of solvation

The molar solubility (S_M) for nano $ZnCO_3$ in mixed DMF – H_2O solvents were measured at 292.15 , 303.15 , 308.15 and 313.15 K, gravimetrically by taking mean value for three reading for each solution. The S_M values are listed in tables 3, 4, 5 and 6 at different temperatures. The activity coefficients were calculated by the use of Debye – Hückel equation (1) [42-62] and their values are given also in Tables 3, 4, 5 and 6.

$$\log \gamma_{\pm} = -0.5062 \sqrt{S_M} \quad \ldots\ldots (1)$$

Where S_M is the molar solubility. The solubility product pK_{sp} was calculated by the use of equation (2) [45-55].

$$pK_{sp} = -2 (\log \gamma_{\pm} + \log S_M) \quad \ldots\ldots (2)$$

From the solubility products, Gibbs free energies of solvation ΔG_s were calculated by using equation (3) [56-61].

$$\Delta G_s = 2.303RTpK_{sp} \quad \ldots\ldots (3)$$

All the data tabulated in Tables 3, 4, 5 and 6. Then data reveals that Gibbs free energies of solvation decrease in positivity by increasing the mole fraction of DMF in the (DMF-H_2O) mixtures. This may be due to the ease of solvation by increasing mole fraction of DMF.

E. Enthalpies and entropies of solvation

From the linear plots of log K_{sp} vs 1/T of nano $ZnCO_3$, the enthalpies were calculated from the slopes (slopes = $-\Delta H/2.303R$) [61] and their values given in Table 7. The entropies of solvation were calculated by use of Gibbs-Helmholtz equation (4) [60,61]

$$\Delta G_s = \Delta H_s - T\Delta S \quad \ldots\ldots (4)$$

Their values were also shown in Table 7 as example at 313.15K. More exothermic character (i.e. $-\Delta H$) could be obtained by adding more DMF, more negative entropies favour, less solvation behavior.

F. Different volumes of nano $ZnCO_3$

The molar volumes (V_M) for nano $ZnCO_3$ were obtained from density measurements. The V_M as calculated by dividing the molecular weight of $ZnCO_3$ by exact solution densities

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and their values were given in table 8. The packing density (ρ) as explained by Kim [52-61] , the relation between Van der Waals volumes (V_W) and the molar volumes (V_M) for relatively large molecules was found to be constant [52] and equal to 0.661.

$\rho = V_W/V_M = 0.661 \pm 0.017$ ……(5)

The electrostriction volumes (V_e) [51-56] which is the volume compressed by the solvent can be calculated by using equation (6) as follows:

$V_e = V_W - V_M$ ……..(6)

All different volumes for nano $ZnCO_3$ are presented in table 8 which reveals that the above results demonstrate that solubilities of nano $ZnCO_3$ decrease by increase DMF percentages due to less solvation. This is supported by volume measurements.

Table (2): Assignment of IR Band Frequencies.

S. No.	Zinc Carbonate	Assignments
1.	693.3 and 856 cm^{-1}	In plane and out plane bending CO_3^{-2}
2.	1059 cm^{-1}	Symmetric C-O stretching vibration
3.	1462 cm^{-1}	Asymmetric C-O stretching vibration

Table (3) : Molar solubility (S_M), log activity coefficient ($\gamma_\pm$) , solubility product (pK_{sp}) and Gibbs free energies of salvation (ΔG) for nano $ZnCO_3$ in mixed DMF –H_2O solvent at 292.15K^0

X_s	S_M	log $\gamma_\pm$	pK_{sp}	ΔG kj/mole
0.1894	6.3810 X10^{-3}	-0.0404	4.4710	24.9980
0.2595	14.3560 X10^{-3}	-0.0587	3.8596	21.5796
0.3528	27.9150 X10^{-3}	-0.0469	4.2234	23.6136
0.4831	1.5950 X10^{-3}	-0.0202	5.6349	31.5056
0.6774	3.9880 X10^{-3}	-0.0320	4.8625	27.1869

Table (4) : Solvation parameters for nano $ZnCO_3$ in mixed DMF –H_2O solvent at 303.15 K^0

X_s	S_M	log $\gamma_\pm$	pK_{sp}	ΔG kj/mole
0.1894	9.5710 X10^{-3}	-0.0495	4.1371	24.0021
0.2595	14.3560 X10^{-3}	-0.0607	3.8073	22.0887
0.3528	16.7490 X10^{-3}	-0.0510	4.0889	23.7224
0.4831	11.1660 X10^{-3}	-0.0535	3.7972	22.0301
0.6774	5.5830 X10^{-3}	-0.0378	4.5819	26.5826
1.0000	12.7610 X10^{-3}	-0.0572	3.9026	22.6416

Table (5) : Solvation parameters for nano $ZnCO_3$ in mixed DMF –H_2O solvent at 308.15 K^0

X_s	S_M	log $\gamma_\pm$	pK_{sp}	ΔG kj/mole
0.1894	11.9640 X10^{-3}	-0.0554	3.9550	23.3240
0.2595	15.1540 X10^{-3}	-0.0623	3.7635	22.1947
0.3528	12.7610 X10^{-3}	-0.0572	3.9026	23.0150
0.4831	18.3440 X10^{-3}	-0.0686	3.6102	21.2906
0.6774	9.5710 X10^{-3}	-0.0495	4.1371	24.3979
1.0000	17.5470 X10^{-3}	-0.0671	3.6458	21.5006

Table (6) : Solvation parameters for nano $ZnCO_3$ in mixed DMF –H_2O solvent at 313.15 K^0

X_s	S_M	log $\gamma_\pm$	pK_{sp}	ΔG kj/mole
0.1894	40.6770 X10^{-3}	-0.1021	2.9855	17.8922
0.2595	19.1420 X10^{-3}	-0.0643	3.7127	22.2503
0.3528	15.9520 X10^{-3}	-0.0639	3.7222	22.3073
0.4831	24.7250 X10^{-3}	-0.0796	3.3729	20.2139
0.6774	12.7610 X10^{-3}	-0.0572	3.9026	23.3884
1.0000	27.9150 X10^{-3}	-0.0846	3.2775	19.6422

Fig (4) and (5) show the relation between log K_{sp} and 1/T for different concentrations of DMF and water

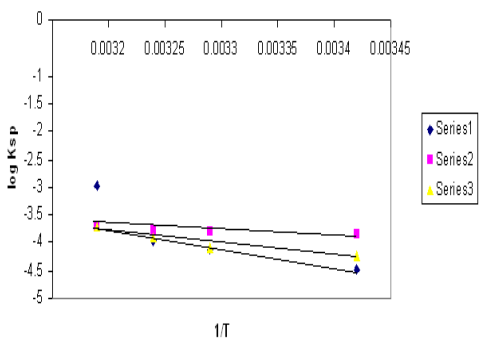

Fig (4) shows the relation between log K_{sp} and 1/T for different concentrations of DMF and water where:

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Series 1: 50% DMF – 50% H_2O
Series 2: 60% DMF – 40% H_2O
Series 3: 70% DMF – 30% H_2O

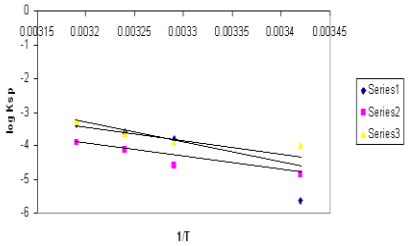

Fig (5) shows the relation between log K_{sp} and 1/T for different concentrations of DMF and water where:

Series 1: 80% DMF – 20% H_2O
Series 2: 90% DMF – 10% H_2O
Series 3: 100% DMF –0% H_2O

Table (7): Enthalpies and entropies of solvation for nano $ZnCO_3$ in mixed DMF –H_2O solvent at 313.15 K^0

X_s	ΔH kJ/mole	TΔS
0.1894	123.6061	105.7094
0.2595	12.2233	-10.0269
0.3528	41.6707	19.3634
0.4831	81.2022	60.9883
0.6774	130.0039	106.6155
1.0000	56.3736	36.7314

Table (8) : The different volumes for nano $ZnCO_3$ at 292.15 , 303.15 , 308.15 and 313.15 K^0

Temperature	Concentration	V_M	V_W	V_e
292.15K	100 % DMF	13.0076	8.5980	-4.4096
	90 % DMF	13.1676	8.7038	-4.4638
	80 % DMF	12.8303	8.4808	-4.3495
	70 % DMF	13.3797	8.8439	-4.5358
	60 % DMF	13.4650	8.9003	-4.5647
	50 % DMF	13.4178	8.8691	-4.5487
303.15K	100 % DMF	13.1920	8.7199	-4.4721
	90 % DMF	13.5437	8.9524	-4.5913
	80 % DMF	13.6898	9.0489	-4.6409
	70 % DMF	13.3451	8.8211	-4.5240
	60 % DMF	12.9234	8.5423	-4.3811
	50 % DMF	12.7467	8.4255	-4.3212
308.15K	100 % DMF	13.7581	9.0941	-4.6640
	90 % DMF	13.5959	8.9869	-4.6090
	80 % DMF	13.7028	9.0575	-4.6453
	70 % DMF	13.6643	9.0321	-4.6322
	60 % DMF	13.5851	8.9797	-4.6054
	50 % DMF	13.6562	9.0267	-4.6259
313.15K	100 % DMF	13.2838	8.7806	-4.5032
	90 % DMF	13.6507	9.0231	-4.6276
	80 % DMF	13.4582	8.8958	-4.5624
	70 % DMF	13.3691	8.8369	-4.5322
	60 % DMF	13.1788	8.7111	-4.4677
	50 % DMF	12.6553	8.3651	-4.2902

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