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Thermodynamics of Solvation for Nano Barium Carbonate in Mixed DMF–H_2O Solvents at Different Temperatures

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Abstracts

The molar solubility for nano barium carbonate ($BaCO_3$) in different percentages of dimethylformamide (DMF) and water were measured at 292.15, 303.15, 308.15 and 313.15K. From the molar solubilities for nano $BaCO_3$, 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.

Keywords: Thermodynamics, molar solubility, nano barium carbonate, free energy, enthalpy, entropy of solvation, mixed DMF – H_2O solvents.

Introduction

Barium carbonate ($BaCO_3$), also known as Witherite, is an important material in industry for producing barium salts, pigment, optical glass, ceramic, electric condensers, as well as its close relationship with aragonite, biomineral and its use as a precursor for magnetic ferrites and/or ferroelectric materials. Witherite crystallizes in the orthorhombic system. The crystals are invariably twinned together in groups of three, giving rise to pseudo-hexagonal forms somewhat resembling bipyramidal crystals of quartz, the faces are usually rough and striated horizontally [1, 2].

Nanostructure materials have become attractive because of their unique characteristics that can hardly be obtained from conventional bulk materials owing to their quantum size and surface effects. So, there has been considerable interest in fabrication of low-dimensional nanosized
materials such as nanowires, nanorods and nanotubes because they possess distinctive geometries, novel physical and chemical properties, and have potential applications in nanodevices [3-6] and find diverse applications in nanotechnology [7, 8].

Most rare earth oxalates and carbonates have wide applications in electro-optical devices and some applications in industry for producing barium salts, pigments and barium ferrite [9]. Barium carbonate ($BaCO_3$) is also used as a precursor for producing superconductor and ceramic materials and other important applications in optical glass and electric condensers.

Solute solubilities in mixed solvents have great importance in many industrial processes as well as laboratory uses. The solubility of solutes in mixed solvents depends primarily on salvation of solutes or their constituent ions by the components of solvents mixtures [10-22]. Studying the thermodynamics of different salts, is important for evaluating the single ion thermodynamic parameters which help in explanation of the preferential solvation of ions [23]. Thermodynamic study helps in removing heavy elements using solvent extraction which necessary to get rid of the hard ions [24].

Experimental

Materials

$BaCO_3$ from Al Nasr chemicals Co. was used without purification.

DMF of the type Adwic was used.

Preparation of nano $BaCO_3$

$BaCO_3$ 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 (without circulating liquid and the temperature did not rise above 30°C).

Preparation of saturated solutions and solubility measurement

The saturated solutions for nano $BaCO_3$ 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.

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The solubility of $BaCO_3$ 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 [25, 35].
The molar solubilities for nano $BaCO_3$ were calculated by subtracting the evaporated weights of samples minus that of empty beakers weight and calculation to changes to molar concentrations were done [36]. The same procedures were repeated at different temperatures.

Results and discussion

X-ray diffraction
The X-ray diffraction of nano barium carbonate in fig. (1) shows that it has about 100% of the structure is $BaCO_3$. The axial ratio of a : b : c is 0.5966 : 1.0000 : 0.7221 . The crystal system is orthorhombic – dipyramidial, the cell dimensions are : a = 5.313 , b = 8.904 , c = 6.43, z = 4 , v = 304.18. The forms are (0 1 0) (1 0 2) (0 2 1) (1 0 0) . The density calculated = 4.31. The cleavage is { 0 1 0 } perfect . The crystal sizes calculated by the sum of values in Table (1) then take the mean value which equal 43.8 nm [9].

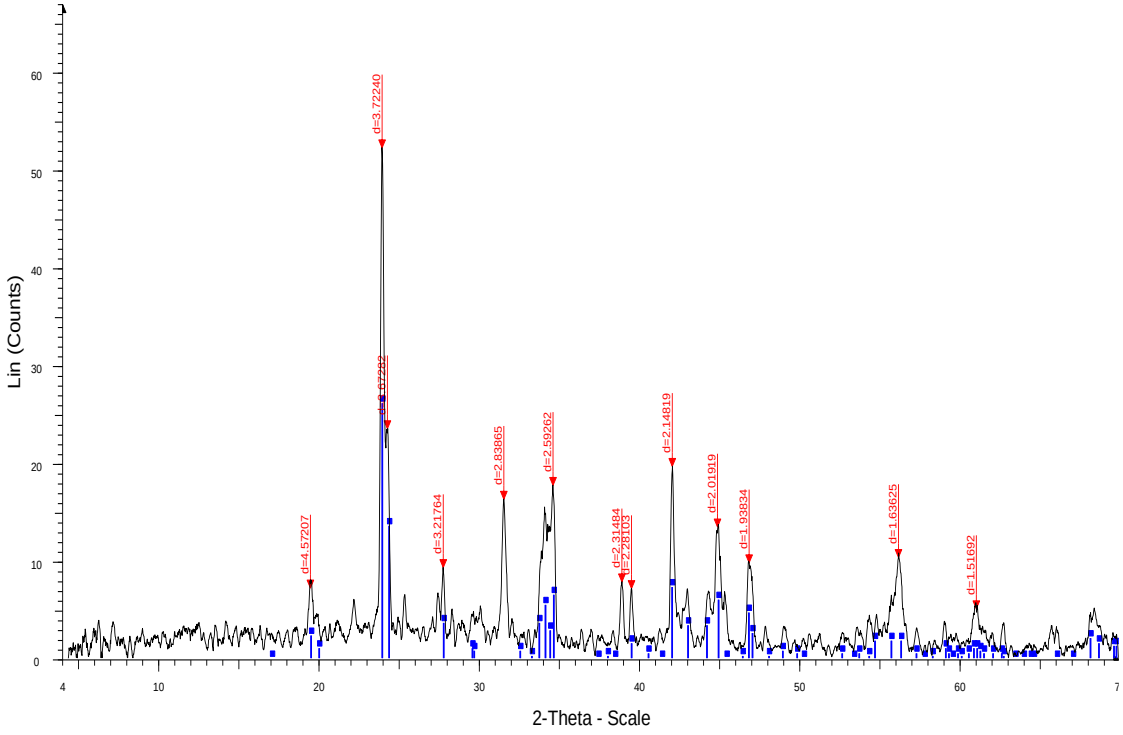

Figure (1) X-ray diffraction of nano barium carbonate

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

Position	Area	Cry Size L(nm)	Microstrain	RMS Strain(%)
19.492	4.358984	14.4	0.1	0.1
23.88099	16.27131	54	0.1	0.1
24.19925	5.508316	59.5	0.1	0.1
27.67062	11.62949	3	0.1	0.1
31.47716	5.749698	44.9	0.1	0.1
34.05669	8.365356	26.8	0.1	0.1
34.52773	4.636979	66.4	0.1	0.1
38.84429	1.765948	88.1	0.1	0.1
42.00933	6.546677	51	0.1	0.1
44.83335	8.212475	23.3	0.1	0.1

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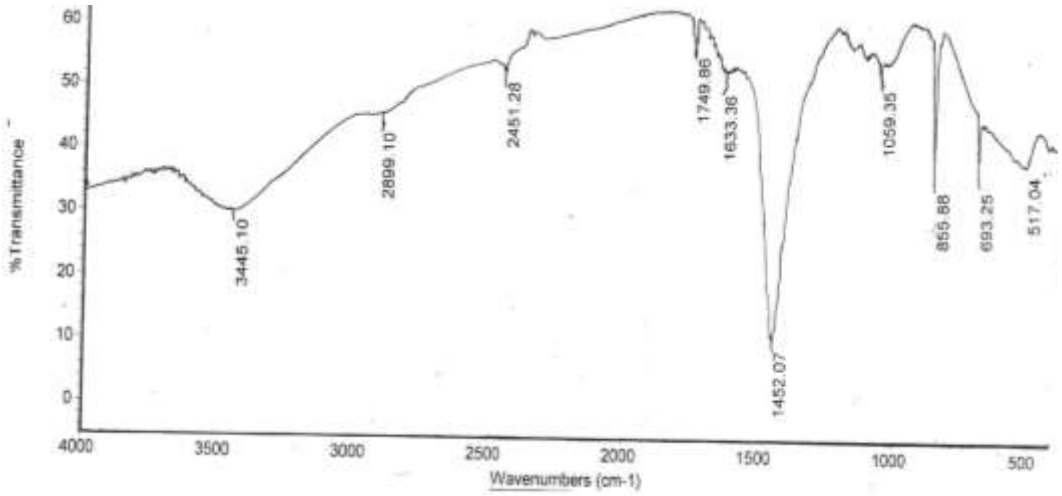
46.84754	3.135101	73.7	0.1	0.1
56.03141	7.167628	20.3	0.1	0.1

F.T.I.R Spectra

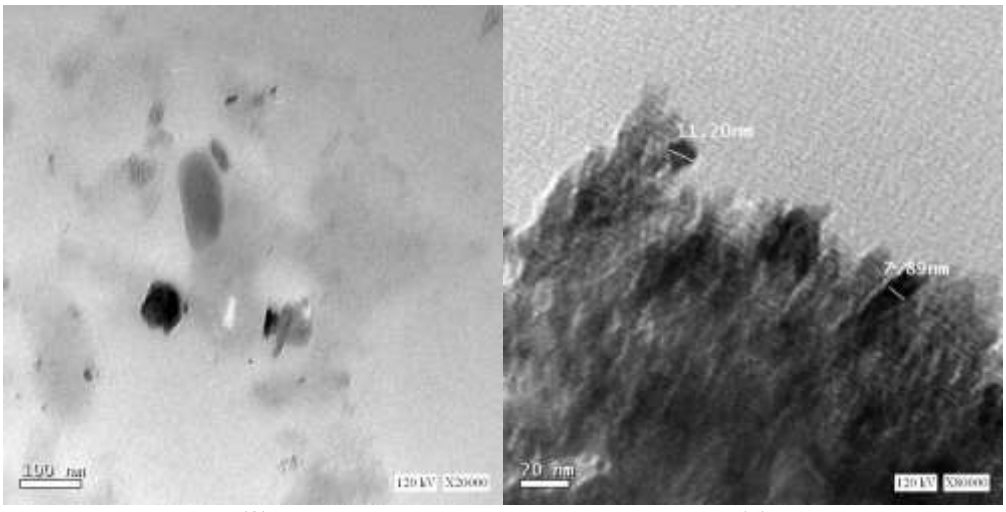
Fig. (2) shows FTIR spectra of $BaCO_3$ done by NICOLET IS10 apparatus was used by forming potassium bromide . The IR spectrum in the range 400-3500 cm^{-1} show well pronounced broad intense peaks in case of $BaCO_3$. The observed IR bands and their assignments are shown in Table 2.

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[9].



TEM Images

Fig. (3) in all images measured by using JEOL HRTEM – JEM 2100 (JAPAN) show that TEM of $BaCO_3$ obtained in ethanol are aggregated rod-like in the form of small trees with an average length of 3 µm and diameter in the range of 100 nm. The nm aspect ratio that is the ratio of length to diameter is on the order of 30. It has been reported [9] that aspect ratio of $BaCO_3$ is 15 and diameter in the range of 5.95-66.87nm.The small sizes in the range between 5.9 to 14.59 nm are collected to give sizes between 20 to 66.87 nm .These different sizes were proved also by x- ray diffraction which gave crystal sizes in the same order .The non homogeneity in sizes for nano barium carbonate need controlling during the primary preparation of the samples.



(A) ***(B)***

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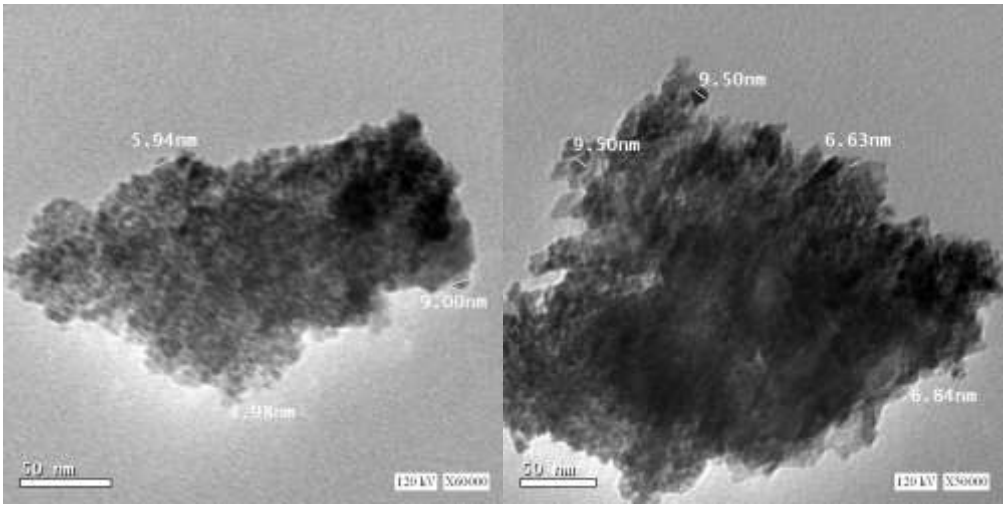
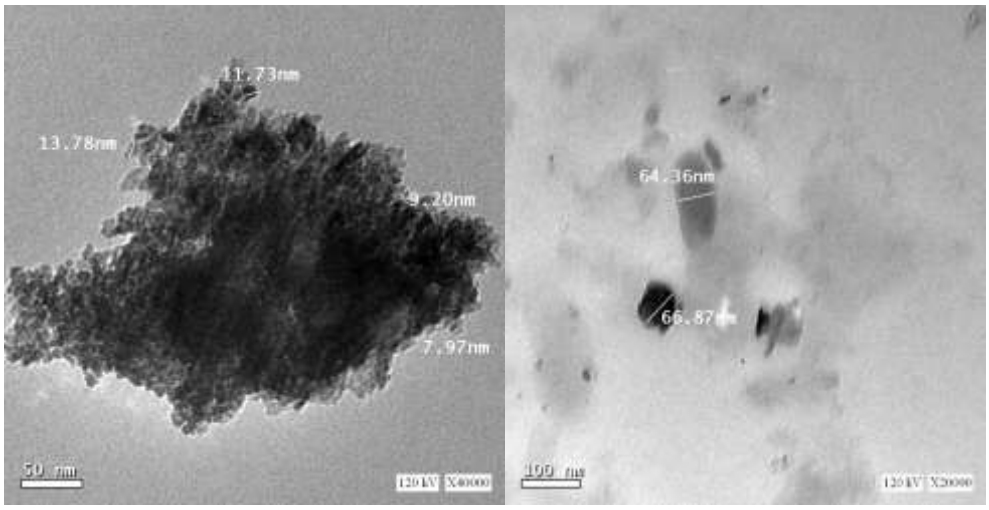
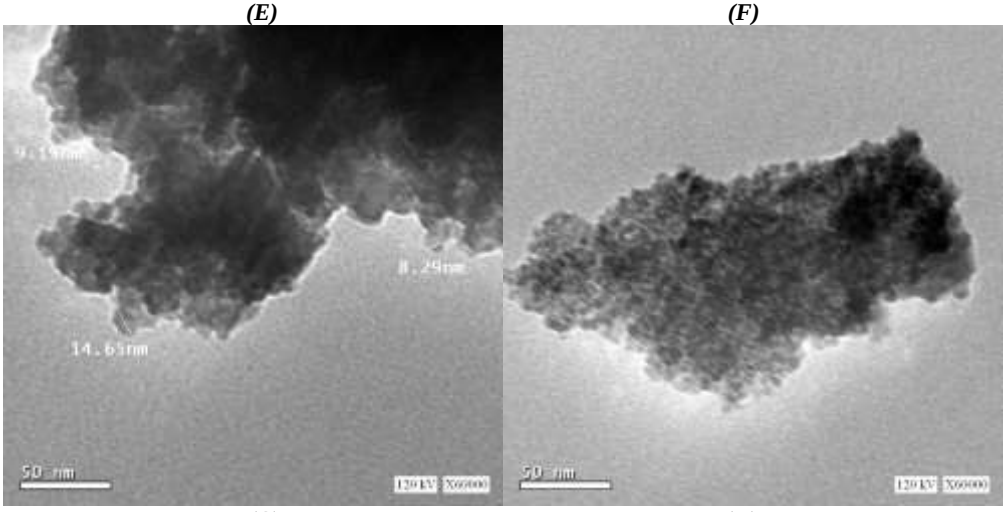


(C) *(D)*

Fig.3 a : TEM for nano barium carbonate



(E) *(F)*



(G) *(H)*

Fig.3 b : TEM for nano barium carbonate

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Gibbs free energies of solvation

The molar solubility (S_M) for nano $BaCO_3$ 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) [37-44] and their values are given also in tables 3, 4, 5 and 6.

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

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

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

From the solubility products, Gibbs free energies of solvation ΔG_s were calculated by using equation (3) [56-68].

$\Delta G_s = 2.303RTpK_{sp}$…….(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.

Enthalpies and entropies of solvation

From the linear plots of log K_{sp} vs 1/T of nano $BaCO_3$, the enthalpies were calculated from the slopes (slopes = $-\Delta H/2.303R$) [69] and their values given in Table 7.

The entropies of solvation were calculated by use of Gibbs-Helmholtz equation (4) [70-72]

$\Delta G_s = \Delta H_s - T\Delta S$ ……..(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.

Different volumes of nano $BaCO_3$

The molar volumes (V_M) for nano $BaCO_3$ were obtained from density measurements. The V_M as calculated by dividing the molecular weight of $BaCO_3$ by exact solution densities and their values were given in table 8. The packing density (d) as explained by Kim [73-79] , the relation between Van der Waals volumes (V_W) and the molar volumes (V_M) for relatively large molecules was found to be constant [80] and equal to 0.661.

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

The electrostriction volumes (V_e) [81-86] 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 $BaCO_3$ are presented in table 8 which reveals that the above results demonstrate that solubilities of nano $BaCO_3$ decrease by increase DMF percentages due to less solvation. This is supported by volume measurements.

Table (2): Assignment of IR Band Frequencies.

S. No.	Barium 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_s) for nano $BaCO_3$ in mixed DMF –H_2O solvent at 292.1K.

X_s	S_M (g.mol/1000g solvent)	log $\gamma_{\pm}$	pK_{sp}	ΔG_s (kJ/mole)
0.1894	$1.5200X10^{-3}$	-0.0197	5.6757	31.7337
0.2595	$1.0130 X10^{-3}$	-0.0161	6.0210	33.6643
0.3528	$4.5600 X10^{-3}$	-0.0341	4.7503	26.5596
0.4831	$5.0670 X10^{-3}$	-0.0360	4.6625	26.0687
0.6774	$2.5360 X10^{-3}$	-0.0255	5.2427	29.3127
1.0000	$3.5470 X10^{-3}$	-0.0301	4.9605	27.7349

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Table (4): Solvation parameters for nano $BaCO_3$ in mixed DMF –H_2O solvent at 303.15K.

X_s	S_M (g.mol/1000g solvent)	Log $\gamma_{\pm}$	pK_{sp}	ΔG_s (kJ/mole)
0.1894	$3.0400 X10^{-3}$	-0.0279	5.0901	29.5310
0.2595	$2.5340 X10^{-3}$	-0.0255	5.2434	30.4204
0.3528	$4.0540 X10^{-3}$	-0.0322	4.8486	28.1299
0.4831	$5.5740 X10^{-3}$	-0.0378	4.5832	26.5902
0.6774	$3.5470 X10^{-3}$	-0.0301	4.9605	28.7791
1.0000	$7.0940 X10^{-3}$	-0.0426	4.3834	25.4310

Table (5): Solvation parameters for nano $BaCO_3$ in mixed DMF–H_2O solvent at 308.15 K.

X_s	S_M (g.mol/1000g solvent)	log $\gamma_{\pm}$	pK_{sp}	ΔG_s (kJ/mole)
0.1894	$7.6010 X10^{-3}$	-0.0441	4.3265	25.5149
0.2595	$9.1210 X10^{-3}$	-0.0483	4.1765	24.6303
0.3528	$6.5870 X10^{-3}$	-0.0411	4.4448	26.2126
0.4831	$10.6410 X10^{-3}$	-0.0522	4.0504	23.8866
0.6774	$9.1210 X10^{-3}$	-0.0483	4.1477	24.4605
1.0000	$7.6010 X10^{-3}$	-0.0441	4.3265	25.5149

Table (6): Solvation parameters for nano $BaCO_3$ in mixed DMF –H_2O solvent at 313.15 K.

X_s	S_M (g.mol/1000g solvent)	log $\gamma_{\pm}$	pK_{sp}	ΔG_s (kJ/mole)
0.1894	$8.6140 X10^{-3}$	-0.0470	4.2236	25.3122
0.2595	$10.6410 X10^{-3}$	-0.0522	4.0504	24.2742
0.3528	$8.6140X10^{-3}$	-0.0470	4.2236	25.3122
0.4831	$14.1880 X10^{-3}$	-0.0603	3.8168	22.8742
0.6774	$11.1480 X10^{-3}$	-0.0534	4.0124	24.0465
1.0000	$9.1210 X10^{-3}$	-0.0483	4.1765	25.0299

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

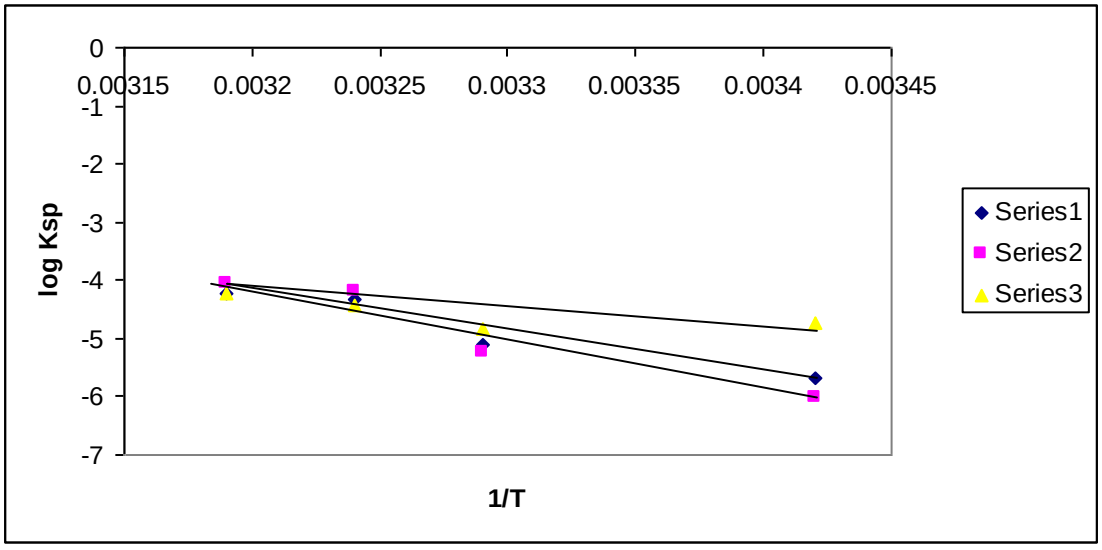

Figure (4) : The relation between log K_{sp} and 1/T for different concentrations of DMF and water where :
Series 1 : 50% DMF – 50% H_2O
Series 2 : 60% DMF – 40% H_2O
Series 3 : 70% DMF – 30% H_2O

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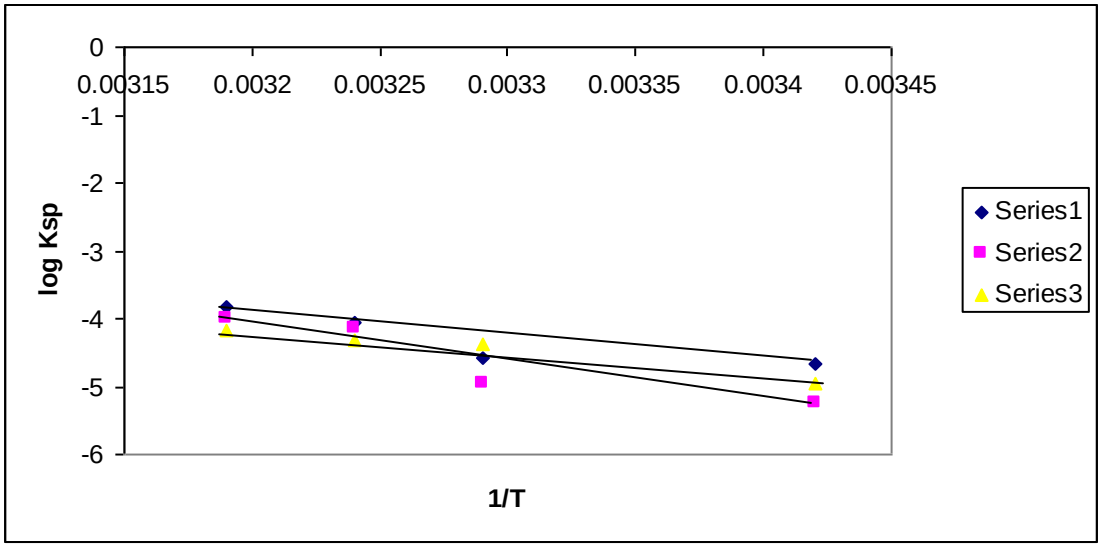

Figure (5) : The relation between log K_{sp} and 1/T for different concentrations of DMF and water where :
Series 1 : 80% DMF – 20% H_2O
Series 2 : 90% DMF – 10% H_2O
Series 3 : 100% DMF –0% H_2O

Table (7): Enthalpies and entropies of solvation for nano $BaCO_3$ in mixed DMF –H_2O solvent at 313.15 K.

X_s	ΔH_s (kJ/mole)	$T\Delta S$
0.1894	120.8269	95.5147
0.2595	163.9704	139.6962
0.3528	43.8258	18.5136
0.4831	89.4124	66.5382
0.6774	102.3713	78.3248
1.0000	65.2354	40.2055

Table (8): The different volumes for nano $BaCO_3$ at 292.15, 303.15, 308.15 and 313.15 K.

Temperature	Concentration	V_M	V_W	V_e
292.15 K	100 % DMF	20.9761	13.8652	-7.1109
	90 % DMF	20.8443	13.7780	-7.0662
	80 % DMF	21.1682	13.9921	-7.1760
	70 % DMF	21.6732	14.3260	-7.3472
	60 % DMF	20.7975	13.7471	-7.0504
	50 % DMF	21.0783	13.9328	-7.1455
303.15 K	100 % DMF	21.3427	14.1075	-7.2352
	90 % DMF	21.4746	14.1947	-7.2799
	80 % DMF	21.3781	14.1309	-7.2472
	70 % DMF	21.1134	13.5960	-7.1574
	60 % DMF	21.0609	13.9213	-7.1396
	50 % DMF	21.0997	13.9469	-7.1528
308.15 K	100 % DMF	21.4575	14.1834	-7.2741
	90 % DMF	21.4505	14.1788	-7.2717
	80 % DMF	21.1238	13.9628	-7.1610
	70 % DMF	21.6686	14.3229	-7.3457
	60 % DMF	20.9850	13.8711	-7.1139
	50 % DMF	20.5249	13.5670	-6.9579
313.15 K	100 % DMF	21.1907	14.0071	-7.1836

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	90 % DMF	20.9032	13.8170	-7.0862
	80 % DMF	21.2473	14.0445	-7.2028
	70 % DMF	21.1170	13.9583	-7.1587
	60 % DMF	21.0783	13.9328	-7.1455
	50 % DMF	20.6245	13.6328	-6.9917

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