



INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

Thermodynamics of Solvation for Nano Copper Sulfate in Mixed DMF–H₂O Solvents at Different Temperatures

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Abstracts

The molar solubility for nano copper sulfate (CuSO₄) 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 CuSO₄ , 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 copper sulfate, free energy, enthalpy, entropy of solvation, mixed DMF – H₂O solvents.

Introduction

Copper sulfate pentahydrate is a fungicide. However, some fungi are capable of adapting to elevated levels of copper ions. Mixed with lime it is called Bordeaux mixture and used to control fungus on grapes, melons, and other berries. Copper ions are highly toxic to fish, so care must be taken with the dosage. Most species of algae can be controlled with very low concentrations of copper sulfate. Copper sulfate inhibits growth of bacteria [1]. Copper sulfate can cause cell death exposure to heavy metal toxic materials like copper sulfate results in two types of cell death : necrosis and apoptosis . The death of cell caused by necrosis result in swelling of cells and organelles , random disintegration of DNA , acute inflammation of cell cluster and secondary scarring . Apoptosis causes cancer and changes in hormone balance and hyperthermia. copper salts can form the two types of cell death [2].

Our purpose is to try to estimate different concentrations of nano copper sulfate to get rid from body and environment

Experimental

Materials

CuSO₄ from Al Nasr chemicals Co. was used without purification.

DMF of the type Adwic was used.

Preparation of nano CuSO₄

CuSO₄ of the type Adwic was milled by ball - mill. The ball – mill was a retsch MM2000 swing mill with 10 cm³ 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°C).

Preparation of saturated solutions and solubility measurement

The saturated solutions for nano CuSO₄ were prepared by dissolving suitable amount of solid material in closed test tubes containing DMF – H₂O solvents. The tubes were placed in water thermostat for a period of four days till equilibrium reached.

The solubility of CuSO₄ 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 CuSO₄ were calculated by subtracting the evaporated weights of samples minus that of empty beakers weight and calculation to changes to molar concentrations were done [22]. The same procedures were repeated at different temperatures.

Results and discussion

X-ray diffraction

The X-ray diffraction of nano copper sulfate in fig. (1) shows that it has about 100% of the structure is CuSO₄. The axial ratio of a : b : c is 0.519 : 1.000 : 0.5579 . The crystal system is triclinic – pinacoidal, the cell dimensions are : a = 6.12 , b = 10.7 , c = 5.97, z = 2 , v = 361.55, alpha =97.583 , beta = 107.167 and gamma = 77.55 . The forms are (0 2 1) (0 1 0) (1 3 0) (1 1 0) (1 1 1) (1 0 0) . The density calculated = 2.29 . The cleavage is { 1 1 0 } imperfect , { 1 1 0 } indistinct and

{ 1 1 1 } indistinct . The crystal size calculated by the sum of values in table (1) then take the mean value which equal 81.5 nm [9].

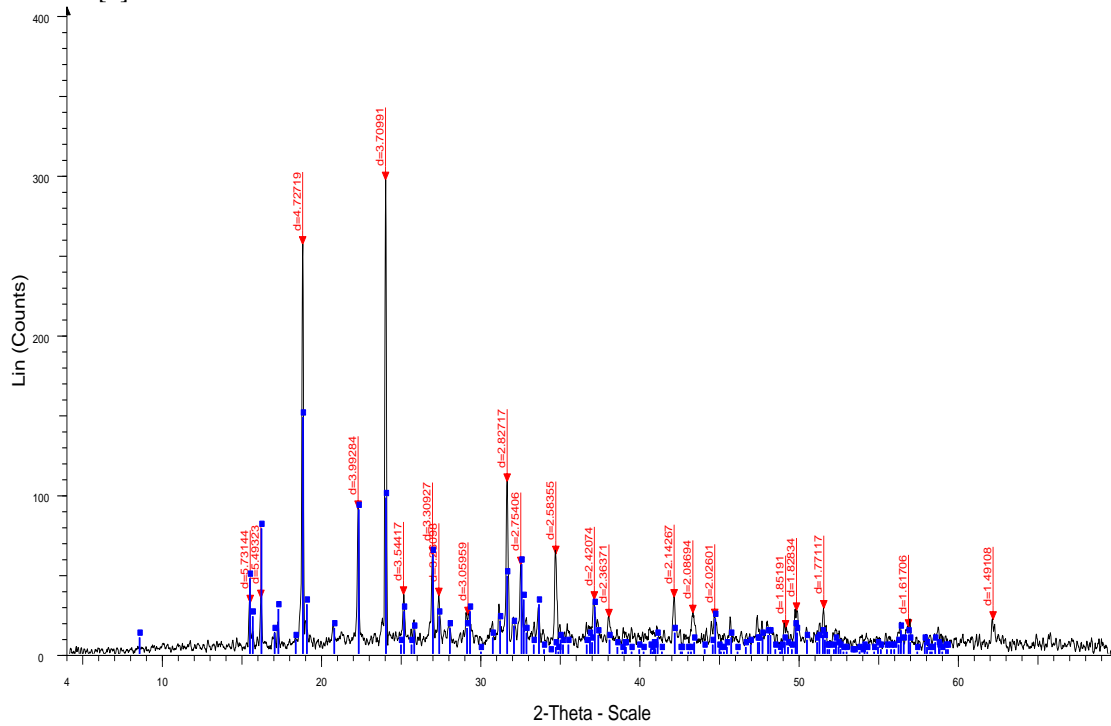


Figure (1) X-ray diffraction of nano copper sulfate

Table (1) : Crystal size of nano copper sulfate

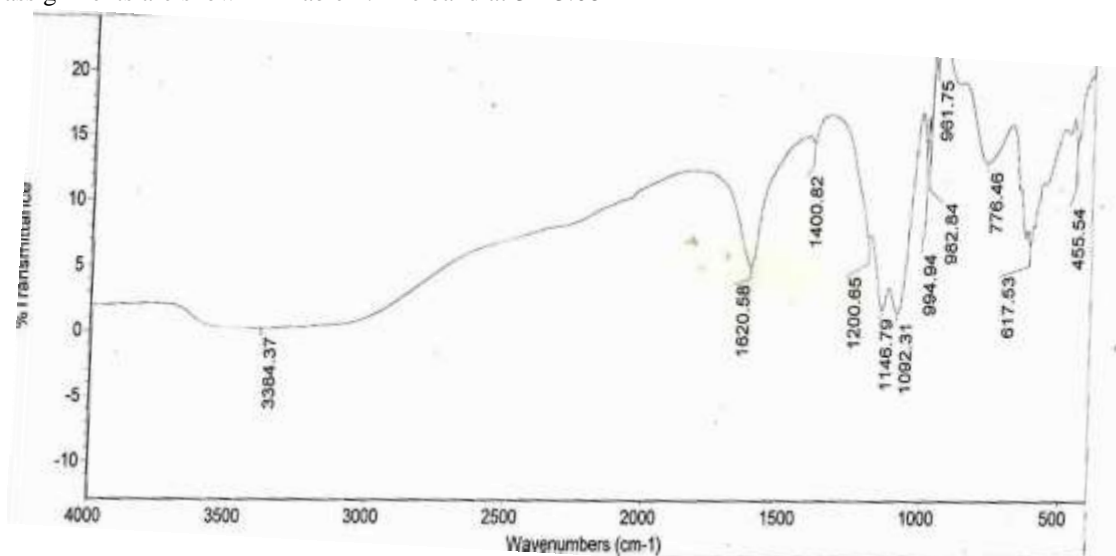
Position	Area	Cry Size L(nm)	Microstrain	RMS Strain(%)
15.40607	5.385739	82.1	0.1	0.1
16.11798	6.180037	83.1	0.1	0.1
18.73242	37.84529	138	0.1	0.1
22.22321	15.01088	107.8	0.1	0.1
23.96124	30.26251	276.4	0.1	0.1
24.98457	49.57445	3	0.1	0.1
26.89488	9.664896	123.1	0.1	0.1
27.30997	5.8606	94.7	0.1	0.1
29.14289	11.77607	23.9	0.1	0.1
31.09892	3.931239	100.7	0.1	0.1
31.59848	15.88331	172.8	0.1	0.1
32.46491	6.987636	144.6	0.1	0.1
32.73509	51.00416	3	0.1	0.1
34.66203	10.49391	138.4	0.1	0.1
37.05016	17.83103	15	0.1	0.1
40.28682	41.57317	3	0.1	0.1
42.11456	5.804527	106.8	0.1	0.1
43.29271	6.87026	55.6	0.1	0.1

44.6428	10.07519	23.4	0.1	0.1
45.62801	4.06546	34.8	0.1	0.1
47.61323	19.168	7.5	0.1	0.1
49.07954	2.20778	172.2	0.1	0.1
49.7793	5.860955	90.1	0.1	0.1
51.48527	39.93425	3	0.1	0.1
56.25219	3.557221	54.6	0.1	0.1
56.83303	7.093609	30.6	0.1	0.1
62.2483	8.784952	17	0.1	0.1
64.24262	0.570482	179	0.1	0.1

F.T.I.R Spectra

Fig. (2) shows FTIR spectra of CuSO_4 done by NICOLET IS10 apparatus was used by forming potassium bromide. The IR spectrum in the range $400\text{-}3500\text{ cm}^{-1}$ show well pronounced broad intense peaks in case of CuSO_4 . The observed IR bands and their assignments are shown in Table 2. The band at 3423.08

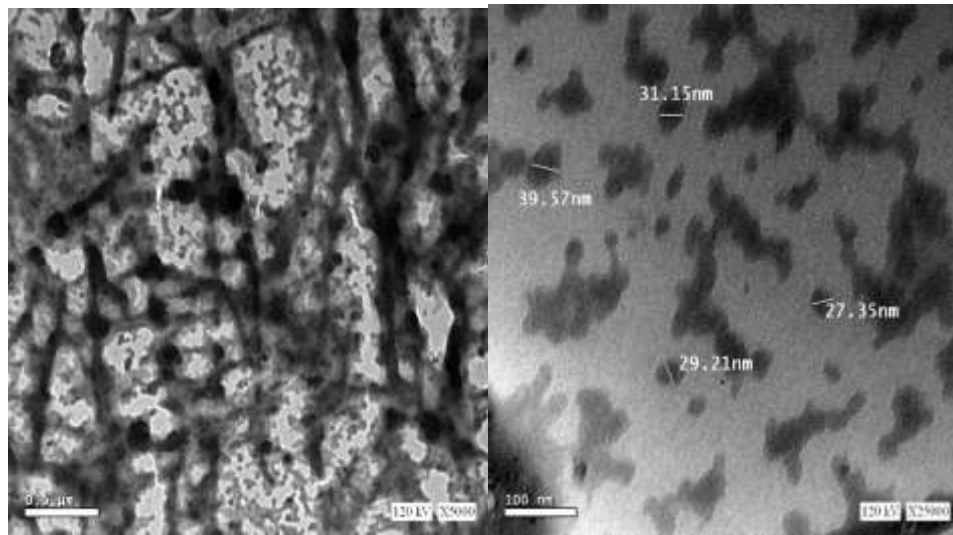
cm^{-1} correspond to H_2O bending, the band at 1620.74 cm^{-1} correspond to H_2O asymmetric stretching, the band at 1197.71 cm^{-1} correspond to SO_4 symmetric stretching, the band at 1147 cm^{-1} correspond to O-H bending and the band at 982.91 cm^{-1} correspond to SO_4 - non - degenerated mode.



TEM Images

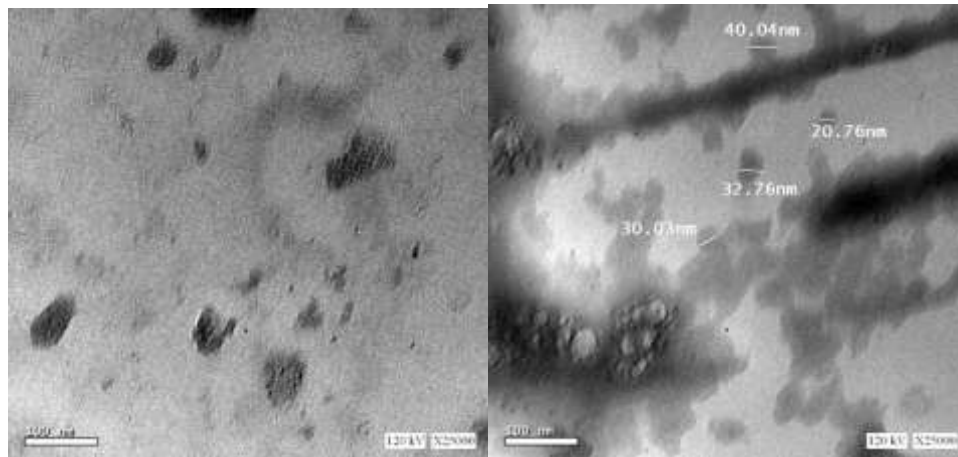
Fig. (3) in all images measured by using JEOL HRTEM – JEM 2100 (JAPAN) show that TEM of CuSO_4 obtained in ethanol are aggregated irregular spheres in the form of cylinders. The diameter in the range of $10,2\text{-}77.86\text{ nm}$. The small sizes in the range between 10.2 , 12.05 to 20.76 nm are collected to give sizes between

20.76 to 77.86 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 copper sulfate need controlling during the primary preparation of the samples.



(A)

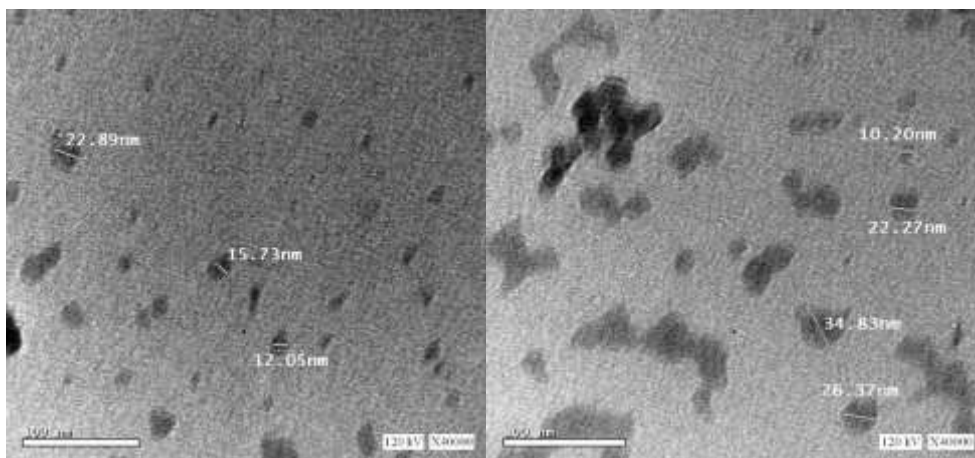
(B)



(C)

(D)

Fig.3 a : TEM for nano copper sulfate



(E)

(F)

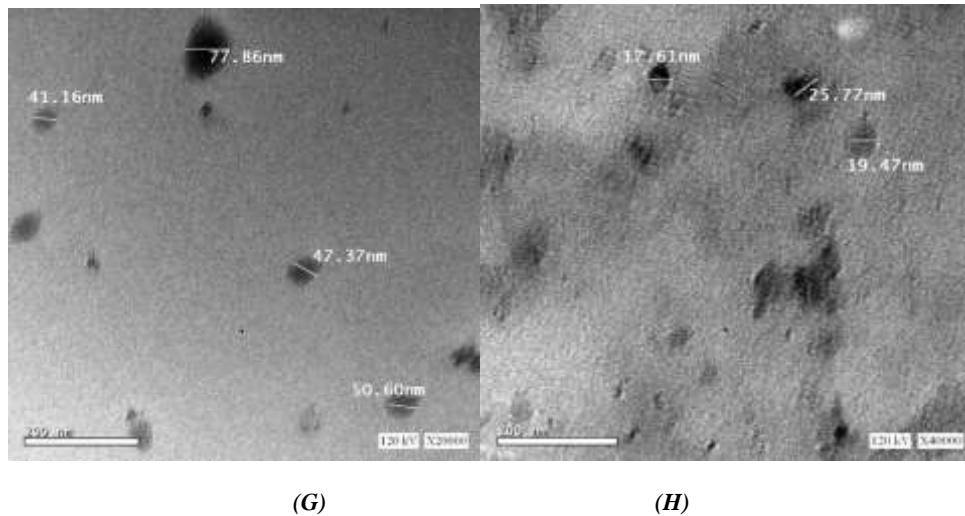


Fig.3 b : TEM for nano barium carbonate

Gibbs free energies of solvation

The molar solubility (S_M) for nano $CuSO_4$ 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 – Huckel equation (1) [25-32] and their values are given also in tables 3, 4, 5 and 6.

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

Where S_M is the molar solubility . The solubility product pK_{sp} was calculated by the use of equation (2) [30-35].

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

From the solubility products, Gibbs free energies of solvation ΔG_s were calculated by using equation (3) [36-38].

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

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 = $-\Delta H/2.303R$) [38] and their values given in table 7.

The entropies of solvation were calculated by use of Gibbs-Helmholtz equation (4) [29-733]
 $\Delta G_s = \Delta H_s - T\Delta S \dots \dots \dots (4)$

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 $CuSO_4$

The molar volumes (V_M) for nano $CuSO_4$ were obtained from density measurements. The V_M as calculated by dividing the molecular weight of $CuSO_4$ by exact solution densities and their values were given in table 8. The packing density (ρ) as explained by Kim [37-40] , the relation between Van der Waals volumes (V_W) and the molar volumes (V_M) for relatively large molecules was found to be constant [39] and equal to 0.661.

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

The electrostriction volumes (V_e) [36-40] which is the volume compressed by the solvent can be calculated by using equation (6) as follows:

$$V_e = V_W - V_M \dots \dots \dots (6)$$

All different volumes for nano $CuSO_4$ are presented in table 8 which reveals that the above results demonstrate that solubilities of nano $CuSO_4$ decrease by increase DMF percentages due to less solvation. This is supported by volume measurements.

Table (2): Assignment of IR Band Frequencies.

S. No.	Copper Sulfate	Assignments
1.	3423.08 cm ⁻¹	H ₂ O bending
2.	1620.74 cm ⁻¹	H ₂ O asymmetric stretching
3.	1197.71 cm ⁻¹	SO ₄ symmetric stretching
4.	1147.00 cm ⁻¹	O-H bending
5.	982.91 cm ⁻¹	SO ₄ - non - degenerated mode

Table (3): Molar solubility (S_M), log activity coefficient (γ_{\pm}), solubility product (pK_{sp}) and Gibbs free energies of solvation (ΔG_s) for nano CuSO₄ in mixed DMF -H₂O solvent at 292.15 K.

X _s	S _M (g.mol/1000g solvent)	Log γ_{\pm}	pK _{sp}	ΔG_s (kJ/mole)
0.1894	25.0620X10 ⁻³	-0.0801	3.3621	18.7979
0.2595	12.5310 X10 ⁻³	-0.0566	3.9172	21.9016
0.3528	11.9040 X10 ⁻³	-0.0552	3.9590	22.1353
0.4831	19.4320 X10 ⁻³	-0.0705	3.5639	19.9262
0.6774	33.8340 X10 ⁻³	-0.0931	3.1274	17.4857
1.0000	62.0290 X10 ⁻³	-0.0362	4.6545	26.0239

Table (4): Solvation parameters for nano CuSO₄ in mixed DMF -H₂O solvent at 303.15 K.

X _s	S _M (g.mol/1000g solvent)	Log γ_{\pm}	pK _{sp}	ΔG_s (kJ/mole)
0.1894	83.3320 X10 ⁻³	-0.1461	2.4505	14.2169
0.2595	49.4980 X10 ⁻³	-0.1126	2.8360	16.4535
0.3528	25.6890 X10 ⁻³	-0.0811	3.3427	19.3932
0.4831	35.7140 X10 ⁻³	-0.0956	3.0855	17.9010
0.6774	57.6430 X10 ⁻³	-0.0978	3.0511	17.7014
1.0000	16.9170 X10 ⁻³	-0.0658	3.6749	21.3205

Table (5): Solvation parameters for nano CuSO₄ in mixed DMF -H₂O solvent at 308.15 K.

X _s	S _M (g.mol/1000g solvent)	Log γ_{\pm}	pK _{sp}	ΔG_s (kJ/mole)
0.1894	70.8010 X10 ⁻³	-0.1346	2.5691	15.1508
0.2595	58.8960 X10 ⁻³	-0.1600	2.3204	13.6842
0.3528	79.5730 X10 ⁻³	-0.1427	2.4838	14.6478
0.4831	35.7140 X10 ⁻³	-0.0956	3.0855	18.1962
0.6774	31.9540 X10 ⁻³	-0.0904	3.1717	18.7046
1.0000	55.1370 X10 ⁻³	-0.1188	2.7547	16.2454

Table (6): Solvation parameters for nano CuSO₄ in mixed DMF -H₂O solvent at 313.15 K.

X _s	S _M (g.mol/1000g solvent)	Log γ_{\pm}	pK _{sp}	ΔG_s (kJ/mole)
0.1894	89.5980 X10 ⁻³	-0.1515	2.3984	14.3737
0.2595	30.7010 X10 ⁻³	-0.1599	1.6817	10.0785
0.3528	34.4610X10 ⁻³	-0.1539	1.8131	10.8659
0.4831	39.9670 X10 ⁻³	-0.1011	2.9987	17.9713
0.6774	47.6180 X10 ⁻³	-0.1104	2.8652	17.1712
1.0000	30.0750 X10 ⁻³	-0.1600	1.6803	10.0701

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

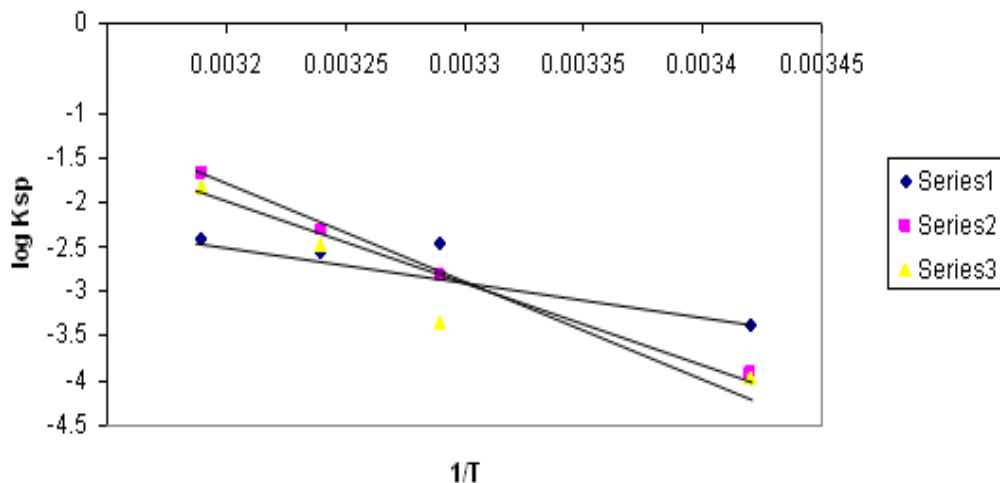


Figure (4) shows the relation between $\log K_{sp}$ and $1/T$ for different concentrations of DMF and water where:
 Series 1 : 50% DMF – 50% H_2O
 Series 2 : 60% DMF – 40% H_2O
 Series 3 : 70% DMF – 30% H_2O

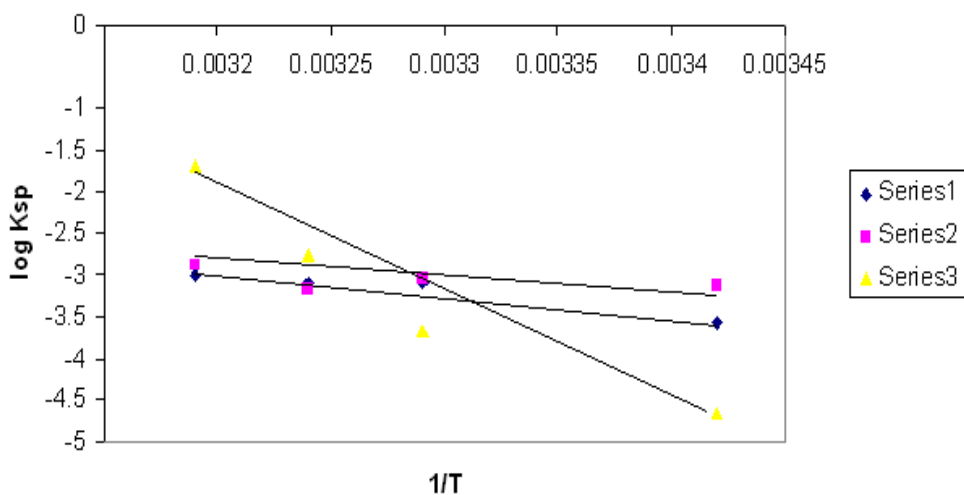


Figure (5) shows the relation between $\log K_{sp}$ and $1/T$ for different concentrations of DMF and water where :
 Series 1 : 80% DMF – 20% H_2O
 Series 2 : 90% DMF – 10% H_2O
 Series 3 : 100% DMF – 0% H_2O

Table (7): Enthalpies and entropies of solvation for nano $CuSO_4$ in mixed DMF – H_2O solvent at 313.15 K.

X_s	ΔH kJ/mole	$T\Delta S$
0.1894	80.1879	65.8142
0.2595	186.0123	175.9338
0.3528	178.5569	167.6909
0.4831	47.0294	29.0581
0.6774	21.8172	4.6460
1.0000	144.2116	134.1415

Table (8): The different volumes for nano CuSO₄ at 292.15, 303.15, 308.15 and 313.15 K.

Temperature	Concentration	V _M	V _w	V _e
292.15 K ⁰	100 % DMF	18.8126	12.4351	-6.3775
	90 % DMF	19.0193	12.5717	-6.4476
	80 % DMF	18.6172	12.3059	-6.3113
	70 % DMF	19.2952	12.7541	-6.5411
	60 % DMF	18.9011	12.4936	-6.4075
	50 % DMF	18.1211	11.9780	-6.1431
303.15 K ⁰	100 % DMF	18.6536	12.3300	-6.3236
	90 % DMF	19.1889	12.6838	-6.5051
	80 % DMF	19.4031	12.8254	-6.5777
	70 % DMF	18.8092	12.4329	-6.3763
	60 % DMF	19.2344	12.7139	-6.5205
	50 % DMF	18.4980	12.2271	-6.2709
308.15 K ⁰	100 % DMF	18.9949	12.5556	-6.4393
	90 % DMF	19.0798	12.6117	-6.4681
	80 % DMF	18.9672	12.5373	-6.4299
	70 % DMF	18.9328	12.5145	-6.4183
	60 % DMF	18.5639	12.2707	-6.2932
	50 % DMF	18.6262	12.3119	-6.3143
313.15 K ⁰	100 % DMF	18.5738	12.2773	-6.2965
	90 % DMF	18.7061	12.3647	-6.3414
	80 % DMF	19.1597	12.6645	-6.4952
	70 % DMF	18.2576	12.0683	-6.1893
	60 % DMF	18.2138	12.0393	-6.1745
	50 % DMF	18.1787	12.0161	-6.1626

References

- Holleman . A . F . Wiberg , E . Inorganic chemistry . San Diego : Academic Press . ISBN 0-12-352651-5 , (2001).
- David A . Wright and Pamela Welbourn , Environmental toxicology , Cambridge University Press , UK (2002).
- Park JN, Koo B, Yoon KY, et al. Generalized synthesis of metal phosphide nanorods via thermal decomposition of continuously delivered metal-phosphine complexes using a syringe pump. J Am Chem Soc 2005; 127: 8433.
- Zhang DE, Zhang XJ, Ni XM, Zheng HG, Yang DD. Synthesis and characterization of NiFe₂O₄ magnetic nanorods via a PEG-assisted route. J Magn Mater 2005; 292: 79.
- Xia BY, Yang PD, Sun YG, et al. One-dimensional nanostructures: Synthesis, characterization, and applications. Adv Mater 2003; 15: 353.
- Duan X, Huang Y, Cui Y, Wang J, Lieber CM. Indium phosphide nanowires as building blocks for nanoscale electronic and optoelectronic devices. Nature 2001; 409: 66.
- Li YH, Kotzeva VP, Fray DJ. Electrochemical performance of CdS nanomaterials synthesized by microemulsion techniques. Mater Lett 2006; 60: 2743.
- Liu WJ, He WD, Zhang ZC, et al. Fabrication of CdS nanorods in inverse microemulsion using HEC as a template by a convenient-irradiation technique. J Cryst Growth 2006; 290: 592. Yizahak Marcus, pure and applied chem. , 62 (1990) 2069-2076
- Chen L, Shen Y, Xie A, Zhu J, Wu Z, Yang L. Nanosized barium carbonate particles stabilized by cetyltrimethylammonium bromide at the water/hexamethylene interface. Cryst Res Technol 2007; 42: 886.
- Esam A. Gmoaa , Thermochim Acta , 91 (1985) 251
- El Sayed M. Abou elleef and Esam A . Gomaa , international Journal of Engineering and innovative Techno;ogh, 2(2013) 308-313
- Esam A. Gmoaa , American Journal of systems sciences, 3 (1) (2014) 12-17
- A.A. El-Khouly , E.A.Gomaa and S.M.Abou Elleef , Bulletin of Electrochemistry , 19 (4) (2003) 153 – 164
- Esam A. Gomaa , Thermochim . Acta ,156 (1989) 91-99
- E. A. Gomaa & B.M.Al-Jahda;I , American Journal of fluid Dynamics 0.1 (2011) 4.

16. Esam A. Gomaa , Science and Technology , 1 (2011) 1-2
17. Esam A.Gomaa, American Journal of Environmental Engineering, 2(3) , (2012)54-57.
18. Esam A.Gomaa . American Journal of Polymer Science, 2(3) , (2012),35-38.
19. Esam A.Gomaa. Eur. Chem. Bull., 1(2013) 259-261.
20. Esam A.Gomaa, Elsayed abou Elleef and E.A.Mahmoud , Eur . Chem. Bull, 2(2013),732-735.
21. Esam A Gomaa and Elsayed M.Abou Elleef , American Chemical Science Journal , 3(2013) , 489-499.
22. Esam A. Gomaa , Elsayed M.Abou Elleef, Science and Technology, 3(2013)118-122.
23. Cleophas N goie Mpinga , Master of Technology , Faculty of Engineering , cape peninsula university of technology (2009)
24. P. Carreras , A. Antony , F.Rojas , J.Bertmous , thin solid film , 520 (2011) 1223.
25. D.J.G. Ives, Chemical Thermodynamics, University Chemistry, Maconald Technical and Scientific, 1971.
26. R.E. Dickenson, I. Geis, W.A. Benjamin Chemistry, Matter, and the Universe, Inc. (USA), 1976.
27. S.L. Oswal, J.S. Desai, S.P. Ijardar, and D.M. Jain, J. Mol. Liquids 144, 108 (2009).
28. D. Bobicz, W. Grzybkowski, and A. Lwandowski, J. Mol. Liquids 105, 93 (2003).
29. Kim, J.I., J. Physic. Chem., 82 , 191 (1978).
30. J. Padova, and I.Abrahamer, J. Phys. Chem., 71, 2112 (1967).
31. G. Schwitzgebel, and Z. Barthel, Physic. Chem., N.F; 68, 79 (1967).
32. R.E. Verwall and B.E.Conway, J. Phys. Chem., 70, 3961 (1966).
33. F.J. Millero, , J. Phys. Chem., 72,4589 (1968).
34. J.I. Kim, A. Cecal, H.J. Born, and E.A. Gomaa, Z. Physik Chemic, Neue Folge 110, 209(1978).
35. J.I.Kim and E.A.Gomaa, Bull.Soci.Chim.Belg.,90(1981)391.
36. E.J .King, J. Phys. Chem., 73, 1220 (1969).
37. F.C.Schmidt, W.E. Hoffmann and Proc. Schaap. Indiana, Acta, Sci., 72,127 (1962).
38. R.Gopal, and M.A. Siddiqui, J. Phys. Chem., 73, 3390 (1969).
39. Y. Marcus. The Properties of Solvents (Wiley, London, 1998).
40. E.A.Gomaa,M.A.Hamada and R.Galal,Avances en Quimica,5(2),117-121(2010).