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

KEYWORDS: Thermodynamics, molar solubility, Nano copper carbonate, free energy, enthalpy, entropy of solvation, mixed DMF – H_2O solvents

Mohamed N .H .Hamed	Esam A.Gomaa	Sameh G .Sanad
Faculty of Education , Chemistry Department , Ain Shams University, Roxy , Cairo , Egypt	Faculty of Science ,Chemistry Department , Mansoura University, Mansoura, Egypt.	Faculty of Education , Chemistry Department , Ain Shams University, Roxy , Cairo , Egypt

ABSTRACT *The molar solubility for Nano copper carbonate ($CuCO_3$) in different percentages of dimethyl formamide (DMF) and water were measured at 292.15, 303.15, 308.15 and 313.15 K. From the molar solubilities for Nano CuCO3, 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.*

1. Introduction:

Copper salts are fungicide [1]. Copper salts inhibit growth of bacteria [1]. Copper salts can cause cell death exposure to heavy metal toxic materials like copper carbonate results in two types of cell death: necrosis and apoptosis . The death of cell caused by necrosis result in swelling of cells and oganelles , 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.

2. Experimental

2.1. Materials

$CuCO_3$ from Al Nasr chemicals Co. was used without purification.

DMF of the type Adwic was used.

2.2. Preparation of Nano $CuCO_3$

$CuCO_3$ 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).

2.3. Preparation of saturated solutions and solubility measurement

The saturated solutions for Nano $CuCO_3$ 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 $CuCO_3$ 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 $CuCO_3$ 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.

3. Results and discussion

3.1. X-ray diffraction

The X-ray diffraction of Nano copper carbonate in Fig. (1) shows that it has about 100% of the structure is $Cu_3(SO_4)(OH)_4$. The axial ratio of a : b : c is 0.6872 : 1.0000 : 0.5029 . The crystal system is orthorhombic – dipyramidial , the cell dimensions are : a = 8.24 , b = 11.99 , c = 6.03, z = 4 , v = 595.75 .The forms are (1 1 1) (1 1 0) (0 1 1) . The density calculated = 3.95 . The cleavage is { 0 1 0 } perfect . The crystal size calculated by the sum of values in table (1) then take the mean value which equal 43.5 nm.

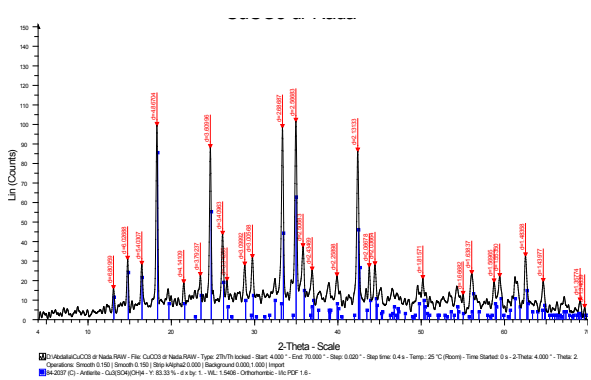

Figure (1) X-ray diffraction of Nano copper carbonate

Table (1) : Crystal size of Nano copper carbonate

Position	Area	Cry Size L(nm)	Micro-strain	RMS Strain(%)
12.98446	3.619637	52.4	0.1	0.1
14.66077	8.56753	48	0.1	0.1
16.37951	11.04145	28.7	0.1	0.1
18.1862	30.196	52.9	0.1	0.1

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22.187	40.26305	3	0.1	0.1
23.40171	3.664874	55.1	0.1	0.1
24.61558	25.11545	57.5	0.1	0.1
26.08845	14.94969	38.1	0.1	0.1
28.74913	3.160116	105.4	0.1	0.1
29.60889	59.00428	3	0.1	0.1
33.27458	36.35533	42.7	0.1	0.1
34.89013	37.19016	45.9	0.1	0.1
35.74474	13.27291	35.7	0.1	0.1
36.8161	7.339889	38.5	0.1	0.1
39.09718	41.08763	3	0.1	0.1
42.33716	28.80627	58.2	0.1	0.1
43.72855	3.846022	110.4	0.1	0.1
45.17757	44.14599	3	0.1	0.1
56.06878	10.16795	34.8	0.1	0.1
59.10224	19.26676	7.5	0.1	0.1
62.53589	12.12361	48.2	0.1	0.1
64.63181	4.821295	85.5	0.1	0.1

3.2. F.T.I.R Spectra

Fig. (2) shows FTIR spectra of $CuCO_3$ in reverse micelles. The IR spectrum in the range 400-3500 cm^{-1} show well pronounced broad intense peaks in case of $CuCO_3$. 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].

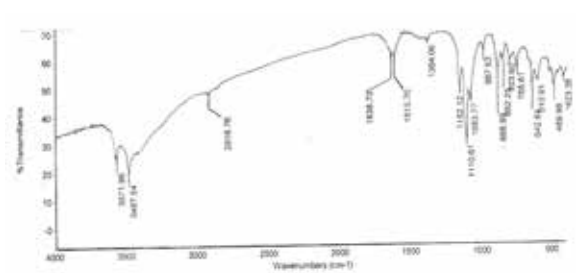
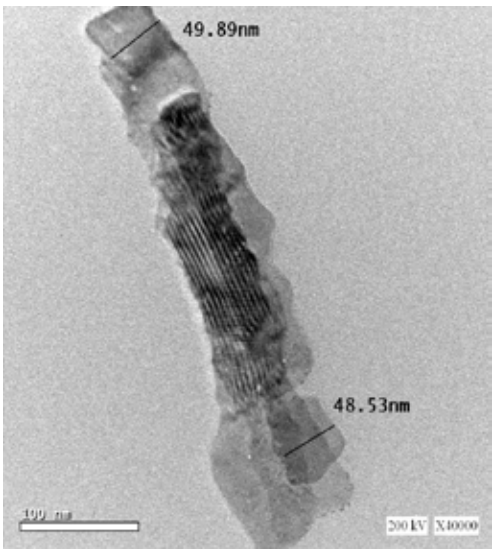


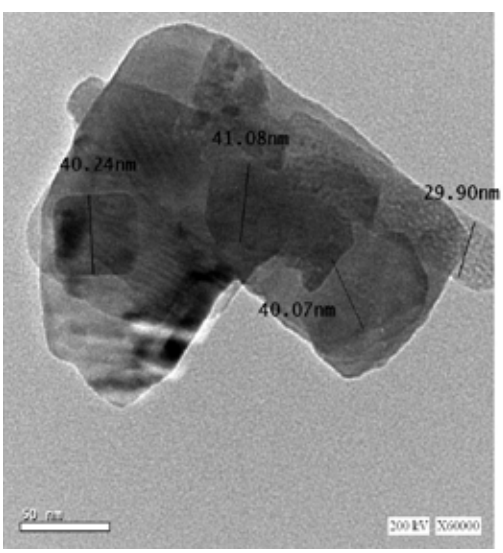
Figure (2) Fourier transform infra-red spectra of Nano **copper carbonate**

3.3. TEM Images

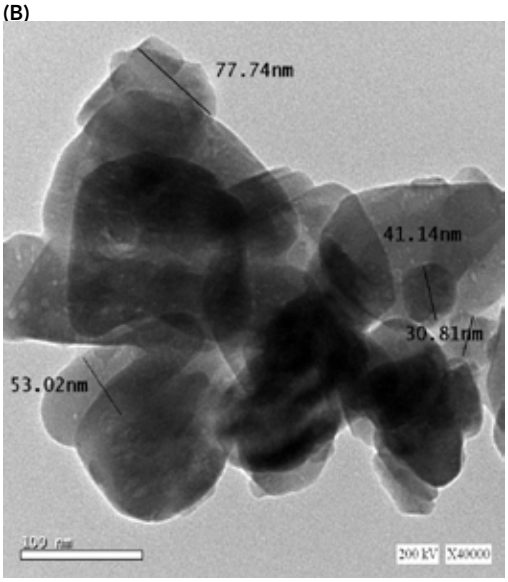
Fig. (**3**) shows that TEM images of $CuCO_3$ obtained in ethanol solution are cylinders with an average length of 3 µm and diameter in the range of 22 to 77 nm. The small sizes of Nano copper carbonate are aggregated to form higher sizes in the range from 48 to 77 nm.



(A)



(B)



(C)

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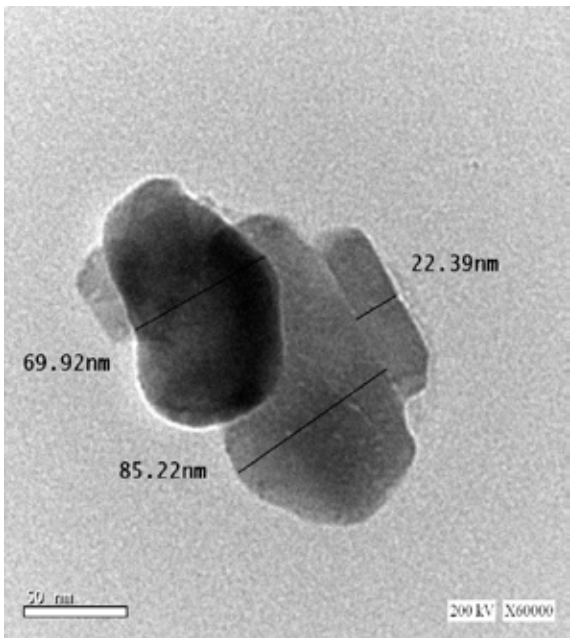

(D)

3.4. Gibbs free energies of solvation

The molar solubility (S_M) for Nano $CuCO_3$ 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) [41-62] and their values are given also in Tables 3, 4, 5 and 6.

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

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

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

From the solubility products, Gibbs free energies of solvation ΔG_s were calculated by using equation (3) [56-62].

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

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.

3.5. Enthalpies and entropies of solvation

From the linear plots of log K_{sp} vs 1/T of Nano $CuCO_3$, the enthalpies were calculated from the slopes (slopes = $-\Delta H/2.303R$) [62] and their values given in Table 7.

The entropies of solvation were calculated by use of Gibbs-Helmholtz equation (4) [60-62]

$$\Delta G_s = \Delta H_s - T\Delta S \quad \text{.....(4)}$$

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.

3.6. Different volumes of Nano $CuCO_3$

The molar volumes (V_M) for Nano $CuCO_3$ were obtained from density measurements. The V_M as calculated by dividing the molecular weight of $CuCO_3$ by exact solution densities and their values were given in table 8. The packing density (ρ) as explained by Kim [52-62] , 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.

$$\rho = V_W / V_M = 0.661 \pm 0.017 \quad \text{.....(5)}$$

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

$$V_e = V_W - V_M \quad \text{.....(6)}$$

All different volumes for Nano $CuCO_3$ are presented in Table 8 which reveals that the above results demonstrate that solubilities of Nano $CuCO_3$ decrease by increase DMF percentages due to less solvation. This is supported by volume measurements.

Table (2): Assignment of IR Band Frequencies.

S. No.	Copper 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 $CuCO_3$ in mixed DMF –H_2O solvent at 292.15K

X_s	S_M	log $\gamma_{\pm}$	pK_{sp}	ΔG kj/ mole
0.1894	3.2388 x10^{-3}	-0.0288	5.0360	27.5514
0.2595	4.7863 x10^{-3}	-0.0350	4.7100	25.7679
0.3528	5.6751 x10^{-3}	-0.0382	4.5684	24.9932
0.4831	8.1096 x10^{-3}	-0.0455	4.2730	23.3772
0.6774	11.336 x10^{-3}	-0.0539	3.9988	21.8770
1.0000	7.2874 x10^{-3}	-0.0432	4.3612	23.8596

Table (4) : Solvation parameters for Nano $CuCO_3$ in mixed DMF –H_2O solvent at 303.15 K

X_s	S_M	log $\gamma_{\pm}$	pK_{sp}	ΔG kj/ mole
0.1894	6.1659 x10^{-3}	-0.0397	4.4994	25.5426
0.2595	7.2878 x10^{-3}	-0.0432	4.3612	24.7581
0.3528	7.7624 x10^{-3}	-0.0446	4.3091	24.4627
0.4831	8.7096 x10^{-3}	-0.0472	4.2144	23.9247
0.6774	9.7185 x10^{-3}	-0.0499	4.1246	23.4149
1.0000	9.7185 x10^{-3}	-0.0499	4.1246	23.4149

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Table (5) : Solvation parameters for Nano $CuCO_3$ in mixed DMF –H_2O solvent at 308.15 K

X_s	S_M	log $\gamma_\pm$	pK_{sp}	ΔG kj/mole
0.1894	2.3003 x10^{-3}	-0.0430	4.3680	25.2059
0.2595	2.9000 x10^{-3}	-0.0472	4.2164	24.3311
0.3528	3.8018 x10^{-3}	-0.0495	4.1390	23.8845
0.4831	5.1286 x10^{-3}	-0.0548	3.9696	22.9065
0.6774	6.4565 x10^{-3}	-0.0683	3.6166	20.8699
1.0000	6.7608 x10^{-3}	-0.0608	3.8036	21.9488

Table (6) : Solvation parameters for Nano $CuCO_3$ in mixed DMF –H_2O solvent at 313.15 K

X_s	S_M	log $\gamma_\pm$	pK_{sp}	ΔG kj/mole
0.1894	8.7096 x10^{-3}	-0.0472	4.2144	24.7140
0.2595	0.0105 x10^{-3}	-0.0517	4.0710	23.8731
0.3528	0.01202x10^{-3}	-0.0555	3.9510	23.1694
0.4831	1.2000 x10^{-3}	-0.0615	3.7830	22.1842
0.6774	1.6003 x10^{-3}	-0.0683	3.6166	21.2084
1.0000	2.7002 x10^{-3}	-0.0715	3.5430	20.7766

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

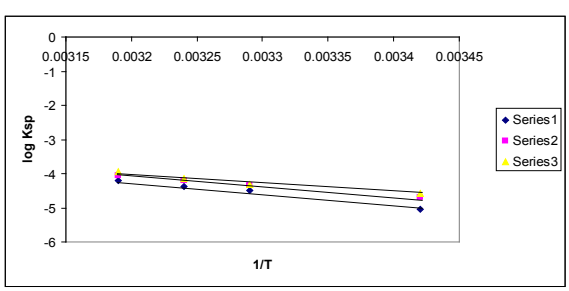

Figure (4) shows the relation between log K_{sp} and 1/T for different concentrations of DMF and water where :
Series 1 : 50% DMF – 50% H_2O
Series 2 : 60% DMF – 40% H_2O
Series 3 : 70% DMF – 30% H_2O

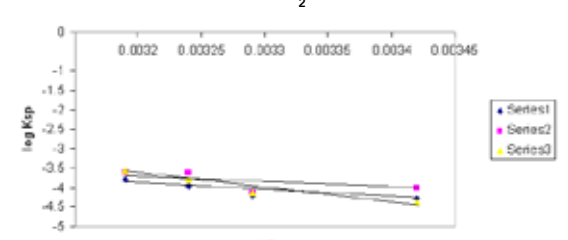

Figure (5) shows the relation between log K_{sp} and 1/T for different concentrations of DMF and water where :
Series 1 : 80% DMF – 20% H_2O
Series 2 : 90% DMF – 10% H_2O
Series 3 : 100% DMF –0% H_2O

Table (7) : Enthalpies and entropies of solvation for Nano $CuCO_3$ in mixed DMF –H_2O solvent at 313.15 K

X_s	ΔH kJ/mole	TΔS
0.1894	58.7917	34.0777
0.2595	55.6531	31.7800
0.3528	71.9586	48.7892
0.4831	40.7721	18.5879
0.6774	31.8022	10.5938
1.0000	99.7469	78.9703

Table (8) : The different volumes for Nano $CuCO_3$ 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	13.8640	9.1641	-4.6999
	90 % DMF	13.6247	9.0059	-4.6188
	80 % DMF	13.4228	8.8724	-4.5504
	70 % DMF	13.2083	8.7306	-4.4777
	60 % DMF	13.2498	8.7581	-4.4917
	50 % DMF	13.1020	8.6604	-4.4416
303.15 K^0	100 % DMF	13.2238	8.7409	-4.4829
	90 % DMF	13.3062	8.7953	-4.45109
	80 % DMF	13.6091	8.9956	-4.6135
	70 % DMF	13.7501	9.0888	-4.6613
	60 % DMF	13.1363	8.6831	-4.4532
	50 % DMF	13.4612	8.8978	-4.5634
308.15 K^0	100 % DMF	13.0787	8.6450	-4.4337
	90 % DMF	13.5862	8.9805	-4.6057
	80 % DMF	13.3950	8.8541	-4.5409
	70 % DMF	13.3801	8.8442	-4.5359
	60 % DMF	13.1876	8.7170	-4.4706
	50 % DMF	12.9852	8.5832	-4.4020
313.15 K^0	100 % DMF	15.2408	10.0742	-5.1666
	90 % DMF	15.2381	10.0724	-5.1657
	80 % DMF	13.5479	8.9552	-4.5927
	70 % DMF	13.1231	8.6744	-4.4487
	60 % DMF	13.0440	8.6221	-4.4219
	50 % DMF	13.0939	8.6551	-4.4388

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REFERENCE

1. David A. Wright and Pamela Welbourn , Cambridge Environmental Chemistry Series 111 , Cambridge University press , Cambridge UK (2002) . | 2. Fangzhi Huanga, Yuhua Shena, Anjian Xiea, , Li Zhangb, Wanghua Xuc, Shikuo Lia and Wensheng Lua., Reactive & Functional polymers 69 (2009) 843-850 | 3. JN Park , B Koo , KY Yoon . J Am Chem Soc 2005; 127: 8433. | 4. DE Zhang, XJ Zhang, Ni XM, HG Zheng, DD Yang . J Magn Mater 2005; 292: 79. | 5. BY Xia, PD Yang, YG Sun. Adv Mater 2003; 15: 353. | 6. X Duan, Y Huang, Y Cui, J Wang, CM Lieber. Nature 2001; 409: 66. | 7. YH Li, VP Kotzeva, DJ Fray. Mater Lett 2006; 60: 2743. | 8. WJ Liu, WD He, ZC Zhang, J Cryst Growth 2006; 290: 592. Yizahak Marcus, Pure and Applied Chem. , 62 (1990) 2069-2076 | 9. L Chen, Y Shen, A Xie, J Zhu, Z Wu, L Yang. Cryst Res Technol 2007; 42: 886. | 10. Esam A. Gmoaa , Thermochim Acta , 91 (1985) 251 | 11. El sayed M. Abou elleef and Esam A . Gomaa , international Journal of Engineering and innovative Techno;ogh, 2(2013) 308-313 | 12. Esam A. Gmoaa , American Iournal of systems sciences, 3 (1) (2014) 12-17 | 13. A.A. El-Khouly , E.A.Gomaa and S.M.Abou Elleef , Bulletin of Electrochemistry , 19 (4) (2003) 153 – 164 | 14. Esam A. Gomaa , Thermochim . Acta ,156 (1989) 91-99 | 15. Cleophase N goie Mpinga , Master of Technology , Faculity of Engineering , cape peninsula university of technology (2009) | 16. P. Carreras , A. Antony , F.Rojas , J.Bertmous , thin solid film , 520 (2011) 1223. | 17. E.A.Gomaa,A.H.El-Askalany and M.N.H.Moussa, Rev.Roum. Chim, 32 (1987)243. | 18. Esam A Gomaa, Thermochimica Acta,128(1988)99. | 19. E.A.Gomaa, Indian J.of Tech.,24(1986)725. | 20. Esam A.Gomaa,Thermochimica Acta ,142(1989)19. | 21. Esam A. Gomaa,Croatica Chimica Acta ,62(1989)475. | 22. Esam A. Gomaa, Thermochimica Acta,147(1989)313. | | 23. Esam A.Gomaa, International Journal of Theoretical and Mathematical Physcics, 3(2013)151-154. | 24. Esam A.Gomaa and B.A.Al Jahadali, Education., 2(3),(2012)37-40. | 25. P. Debye, H. Hückel, Phys. Z. 24, 305 (1923). | 26. Esam A Gomaa , American Journal of Biochemistry, 2(3), (2012),25-28. | 27. Esam A. Gomaa , Food and Public Health, 2(3),2012, 65-68. | 28. Esam A.Gomaa , Global Advanced Research Journal of Chemistry and Material Science, 1(2012)35-38. | 29. Esam A.Gomaa, Frontiers in Science, 2(2012)24-27. | 30. E.A.Gomaa,M.A.Mousa and A.A.El-Khouly,Thermochimica Acta,86 (1985)351. | 31. E.A.Gomaa,M.A.Mousa and A.A.El-Khouly,Thermochimica Acta ,89(1985)133. | 32. Esam A.Gomaa, Thermochimica Acta,91(1985)235. | 33. Esam A.Gomaa,Thermochimica acta,128(1988)287. | 34. Esam A.Gomaa,Thermochimica Acta,140(1989)7. | 35. Esam A.Gomaa, Bull.Soc.Chim.Fr. 5 (1989)620. | 36. Esam A.Gomaa , Bull.Soc.Chim.Fr., 5(1989)623. | 37. Esam A Gomaa , Thermochimica acta,152(1989)371. | 38. Esam A.Gomaa , Thermochimica Acta,156(1989)91. | 39. I.S.Shehatta ,A.H.El-Askalany and E.A.Gomaa , Thermochimica Acta, 219(1993)65. | 40. A.A. El-Khouly, E.A. Gomaa, and S. Abou-El-Leef, Bull. Electrochem 19, 153 (2003). | 41. M.A.Hamada, E.A.Gomaa and N.A.El-Shishtawi,International Journal of Optoelectronic enegineering, 1(2012)1-3. | 42. A.A.El-Khouly ,E.A.Gomaa and S.E.Salem, Southern Brazilian Journal of Chemistry ,vol.20 (2012)43-50. | 43. E.A.Gomaa and B.A.M.Al –Jahdali,American Journal of Environmrntal Engineering,2(2012)6-12. | 44. Esam A .Gomaa,Analele Uni.din Bucuresti-Chimie,vol.19 no1 ,pag.45-48(2010). | 45. D.J.G. Ives, Chemical Thermodynamics, University Chemistry, Maconald Technical and Scientific, 1971. | 46. R.E. Dickenson, I. Geis, W.A. Benjamin Chemistry, Matter, and the Universe, Inc. (USA), 1976. | 47. S.L. Oswal, J.S. Desai, S.P. Ijardar, and D.M. Jain, J. Mol. Liquids 144, 108 (2009). | 48. D. Bobicz, W. Grzybkowski, and A. Lwandowski, J. Mol. Liquids 105, 93 (2003). | 49. Kim, J.I., J. Physic. Chem., 82 , 191 (1978). | 50. J. Padova, and I.Abrahamer, J. Phys. Chem., 71, 2112 (1967). | 51. G. Schwitzgebel, and Z. Barthel, Physic. Chem., N.F; 68, 79 (1967). | 52. R.E. Verwall and B.E.Conway, J. Phys. Chem., 70, 3961 (1966). | 53. F.J. Millero, , J. Phys. Chem., 72,4589 (1968). | 54. J.I. Kim, A. Cecal, H.J. Born, and E.A. Gomaa, Z. Physik Chemic, Neue Folge 110, 209(1978). | 55. J.I.Kim and E.A.Gomaa, Bull.Soci. Chim.Belg.,90(1981)391. | 56. E.J .King, J. Phys. Chem., 73, 1220 (1969). | 57. F.C.Schmidt, W.E. Hoffmann and Proc. Schaap. Indiana, Acta, Sci., 72,127 (1962). | 58. R.Gopal, and M.A. Siddiqui, J. Phys. Chem., 73, 3390 (1969). | 59. Y. Marcus. The Properties of Solvents (Wiley, London, 1998). | 60. E.A.Gomaa,M.A.Hamada and R.Galal,Avances en Quimica,5(2),117-121(2010). | 61. Nagah A.El-Shishtawi , Maany A. Hamada and Esam A.Gomaa, Physical Chemistry,1(1),(2011,14-16. | 62. E.A.Gomaa and B.A.M.Al Jahdali , American Journal of Condenesed Matter Physics, 2(1),(2012),16-21. |