American Journal of Materials Research
2015; 2(1): 16-21
Published online February 20, 2015 (http://www.aascit.org/journal/ajmr)
ISSN: 2375-3919

AASCIT American Association for Science and Technology

Keywords
Thermodynamics,
Molar Solubility,
Nano and Bulk Lead Bromide,
Free Energy,
Enthalpy,
Entropy of Solvation,
Mixed DMF - H_2O Solvents

Received: January 23, 2015
Revised: February 12, 2015
Accepted: February 13, 2015

Thermodynamics of Solvation for Nano and Bulk Lead Bromide (LBr) in Mixed DMF–H_2O Solvents at Different Temperatures

Esam A. Gomaa*, Rania R. Zaky, Ahmed Fekri, Mohamed A. Abdel-Fattah

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

Email address
esam_1947@hotmail.com (E. A. Gomaa)

Citation
Esam A. Gomaa, Rania R. Zaky, Ahmed Fekri, Mohamed A. Abdel-Fattah. Thermodynamics of Solvation for Nano and Bulk Lead Bromide (LBr) in Mixed DMF-H_2O Solvents at Different Temperatures. *American Journal of Materials Research.* Vol. 2, No. 1, 2015, pp. 16-21.

Abstract
The molal solubility for nano and bulk (normal) lead bromide (LBr) in different percentages of dimethylformamide (DMF) and water were measured at 298.15, 303.15, 308.15 and 313.15K. From the molar solubilities for nano and bulk (LBr), 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 and compared for both nano and bulk (LBr).

1. Introduction

Lead bromide (LBr) was prevalent in the environment as the result of the use of leaded gasoline. Tetraethyl lead was once widely used to improve the combustion properties of gasoline. To prevent the resulting lead oxides from fouling the engine, gasoline was treated with an organobromine compound that converted lead oxides into the more volatile lead bromide, which was then exhausted from the engine into the environment. Like other compounds containing lead, lead dibromide is categorized as probably carcinogenic to humans (Category 2A), by the international agency for research on cancer (IARC). Its release into the environment as a product of leaded gasoline was highly controversial [1-3].

Our purpose is to estimate the solubilities of bulk lead bromide and compare with that of nano (LBr) to help in getting rid from environment.

2. Experimental

2.1. Materials

$PbBr_2$ (LBr) from Al Nasr chemicals Co. was used without purification.
DMF of the type Adwic was used.

2.2. Preparation of Nano LBr

$PbBr_2$ (LBr) was prepared 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 12 mm 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 bulk and nano LBr 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 LBr in each mixture was measured by taking 1 ml of each saturated solution and putting in small weighed beaker (10 ml) and evaporated under IR lamp till dryness and then weighted [4-25].

The molal solubilities for nano LBr were estimated by subtracting the evaporated weights of samples minus that of empty beakers weight and calculation of molal concentrations were done [25-50]. The same procedures were repeated at different temperatures.

3. Results and Discussion

3.1. X-ray Diffraction

The X-ray diffraction of nano LBr in Fig. (1) shows that it has about 50% of the structure is LBr. Orthorhombic crystals, dX by:1, WL:1.5406, I/Ic PDF 1.8.. The crystal size calculated by the sum of values in Table (1) then takes the mean value which equal 108.87 nm.

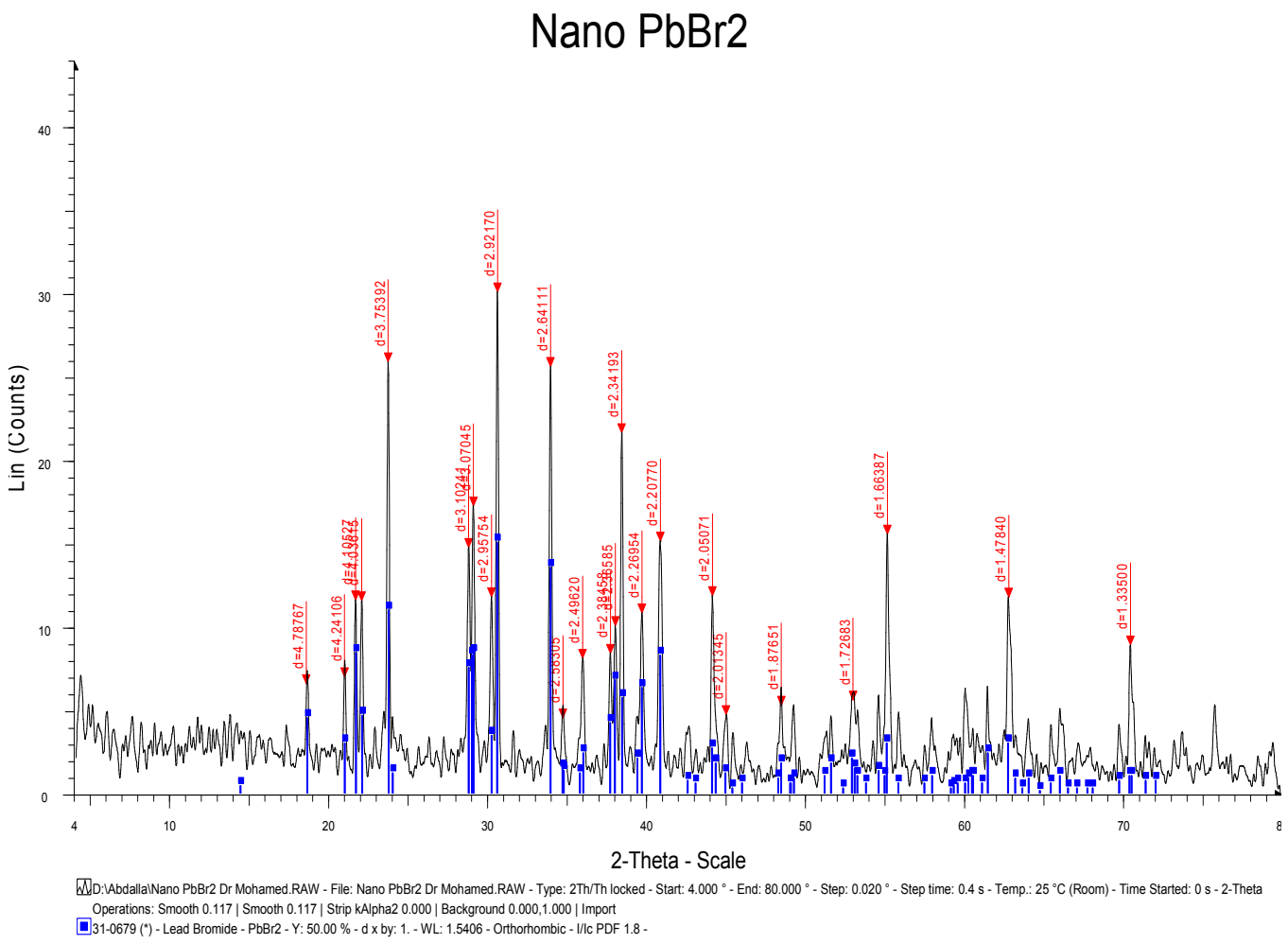

Fig. (1). *X-ray diffraction of nano lead bromide (LBr)*

Table (1). *Crystal size of nano lead bromide (LBr)*

Position	Area	Cry Size L(nm)	Microstrain	RMS Strain (%)
18.56827	1.089639	93.3	0.1	0.1
20.92567	0.975761	141.9	0.1	0.1
21.61718	1.584806	147.7	0.1	0.1
21.99808	1.73495	128.3	0.1	0.1
23.65776	5.197448	91.8	0.1	0.1
28.7312	3.220013	73.5	0.1	0.1
29.02948	3.555349	87.9	0.1	0.1

Position	Area	Cry Size L(nm)	Microstrain	RMS Strain (%)
30.166	2.138264	104.7	0.1	0.1
30.54546	5.303619	150.1	0.1	0.1
33.8914	5.350121	114.3	0.1	0.1
35.91831	1.514265	111.2	0.1	0.1
37.94365	2.218099	65.8	0.1	0.1
38.38776	3.597116	161	0.1	0.1
39.63743	2.759124	71.2	0.1	0.1
40.80993	3.834736	97.6	0.1	0.1
44.1157	2.597793	98.9	0.1	0.1
44.94201	0.530393	191.6	0.1	0.1
55.11986	4.120582	86.7	0.1	0.1
62.78011	4.512664	51.1	0.1	0.1

3.2. TEM Images

Fig. (2) in all images measured by using JEOL HRTEM – JEM 2100 (JAPAN) show that TEM of LBr obtained in water are clear rods with regular shape in the form of big cylinders. The diameters in the range of 32 -54.59 nm. The nano particles gathered in cylinders ranging from 200 t0 350 nm lengths as proved from x-ray diffraction pictures and TEM images. Electron diffraction Fig. 3D proves the crystalline form of the prepared nano lead bromide LBr.

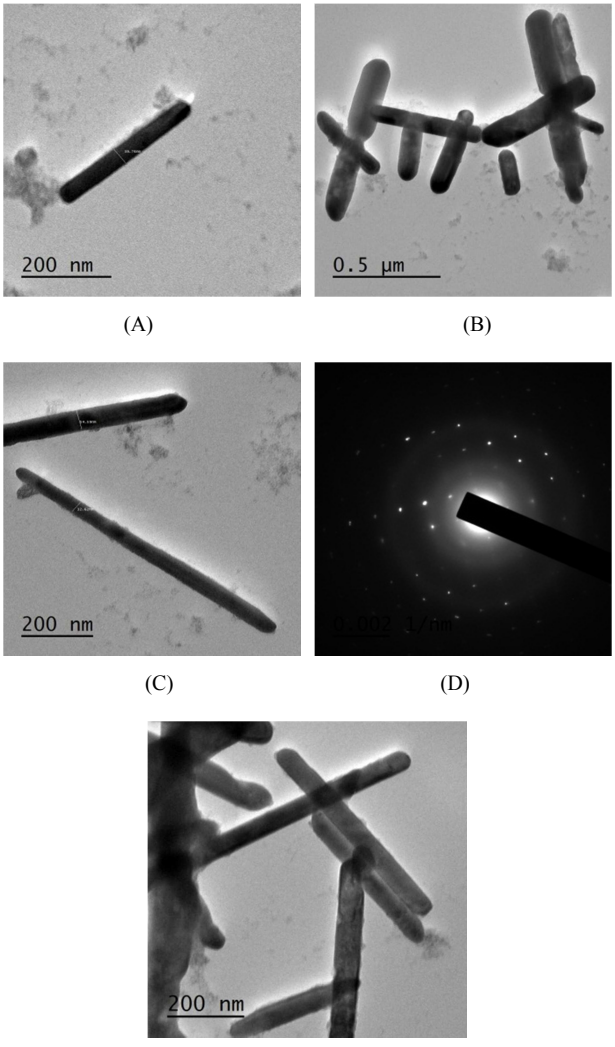

Fig. (2). *TEM for nano lead bromide*

3.3. Gibbs Free Energies of Solvation

The molal solubility (S_M) for nano LBr in mixed DMF – H_2O solvents were measured at 298.15, 303.15, 308.15 and 313.15 K, gravimetrically by taking mean value for three readings for each solution. The S_M values are listed in Tables and 5 for nano and bulk LBr at different temperatures. The activity coefficients were calculated by the use of Debye – Hückel equation (1) [6-32] and their values are given also in Fig. (3) & (4) for nano and bulk LBr in mixed solvents used and at all temperatures.

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

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

$$pK_{sp} = -\log (4S^3 + 4 \log \gamma_{\pm}^3) \quad (2)$$

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

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

All the data are for molal solubilities and free energies of solvation are tabulated in Tables 2, 3 for nano 4 ,5 and for bulk CS. These 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.

3.4. Enthalpies and Entropies of Solvation

From the linear plots of log K_{sp} vs 1/T of nano and bulk LBr, the enthalpies were calculated from the slopes (slopes = $-\Delta H/2.303R$) [38] and their values are given in Tables (4), (60 for nano and bulk LBr.

The entropies of solvation were calculated by use of Gibbs-Helmholtz equation (4) [29-75]

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

Their values were also shown in Tables 4,7 for nano and bulk CS. More exothermic character (i.e. $-\Delta H$) could be obtained by adding more DMF and more negative entropies favor, less solvation behavior.

3.5. Different Volumes of Nano and Bulk LBr

The molar volumes (V_M) for nano and bulk LBr were obtained from density measurements. The V_M as calculated by dividing the molecular weight of LBr by exact solution densities. The packing density (ρ) as explained by Kim [49, 50] , the relation between Van der Waals volumes (V_W) and the molar volumes (V_M) for relatively large molecules was found to be constant [49] and equal to 0.661.

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

The electrostriction volumes (V_e) [40-79] which is the volume compressed by the solvent can be calculated by using equation (6) as follows:

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

All different volumes for nano and bulk LBr are presented in Table 8 and 9 which reveals that the above results demonstrate that smaller volumes for nano LBr than bulk one. Most of volumes increase by increase DMF percentages especially in case of using nano CS due to more solvation.

Table (2). *Molal solubility (S_M) nano LBr in mixed DMF –H_2O solvents at different temperatures.*

DMF vol. %	X_s	S in (g. mole / 1000 g. solvent)			
		298.15K	303.15K	308.15K	313.15K
0	0	0.03443	0.03612	0.03755	0.04037
10	0.02528	0.03694	0.03891	0.04035	0.0451
20	0.05514	0.03645	0.03623	0.03711	0.04215
30	0.09095	0.04091	0.04070	0.04655	0.04197
40	0.13468	0.03248	0.04328	0.04445	0.07197

Table (3). *Solvation Gibbs free energies for nano LBr in mixed DMF –H_2O solvents at different temperatures in (kJ mol^{-1}).*

DMF vol. %	X_s	ΔG_s in (kJ mol^{-1})			
		298.15 K	303.15 K	308.15 K	313.15 K
0	0	30.0791	30.4244	30.818	31.0442
10	0.02528	29.8995	30.2287	30.6278	30.6857
20	0.05514	30.1116	30.7517	31.1754	31.2034
30	0.09095	29.8086	30.4492	30.3687	31.4705
40	0.13468	31.1251	30.4228	30.9473	29.403

Table (4). *Solvation enthalpies and entropies for nano LBr in mixed DMF –H_2O solvents at different temperatures in (kJ mol^{-1}).*

DMF vol. %	X_s	Δ H (kJ mol^{-1})	TΔ S 298.15K	TΔ S 303.15K	TΔ S 308.15K	TΔ S 313.15K
0	0	10.437	-19.643	-19.988	-20.381	-20.608
10	0.02528	13.391	-16.509	-16.838	-17.237	-17.295
20	0.05514	7.949	-22.162	-22.802	-23.226	-23.254
30	0.09095	0.715	-29.093	-29.734	-29.653	-30.755
40	0.13468	58.515	27.390	28.092	27.568	29.112

Table (5). *Molal solubilities for bulk LBr in mixed DMF –H_2O solvents at different temperatures.*

X_s DMF	S in (g. mole / 1000 g. solvent)			
	298.15K	303.15K	308.15K	313.15K
0	0.0372	0.0358	0.037	0.0412
0.02528	0.0358	0.0364	0.0379	0.0426
0.05514	0.0441	0.0392	0.0448	0.0466
0.09095	0.0461	0.0415	0.049	0.0500
0.13468	0.0449	0.0413	0.0425	0.0686

Table (6). *Gibbs free energies change of solvation (ΔG_s) for bulk lead bromide LBr in (DMF–H_2O) mixed solvents at different temperatures in (kJ mol^{-1}).*

X_s DMF	ΔG_s in (kJ mol^{-1})			
	298.15K	303.1 K	308.15K	313.15K
0	29.694	30.424	30.847	30.915
0.02528	30.000	30.487	30.886	30.915
0.05514	29.357	30.331	30.348	30.689
0.09095	29.318	30.310	30.195	30.631
0.13468	29.731	30.666	31.103	29.562

Table (7). *Enthalpy change (ΔH) and entropy change (TΔ S) of solvation for bulk lead bromide (LBr) in (DMF–H_2O) mixed solvents at different temperatures in (kJ mol^{-1}).*

X_s DMF	Δ H (kJ mol^{-1})	TΔ S 298.15K	TΔ S 303.15K	TΔ S 308.15K	TΔ S 313.15K
0	5.209	-24.485	-25.215	-25.639	-25.707
0.02528	11.166	-18.834	-19.321	-19.720	-19.749
0.05514	5.394	-23.963	-24.937	-24.954	-25.295
0.09095	6.492	-22.825	-23.817	-23.702	-24.139
0.13468	29.703	-0.028	-0.963	-1.400	0.141

Table (8). *Molar volume (V), Van der Waals volume (V_w), electrostriction volume (V_e) and solvated radii (r_o) of nano lead bromide (LBr) in different (DMF-H_2O) mixed solvents at 298.15K ($cm^3 mole^{-1}$).*

DMF vol. %	V	V_w	V_e	r_o (A°)
0	354.325	233.490	-119.75	4.3897
10	354.325	233.514	-119.76	4.3897
20	364.567	240.752	-123.47	4.4316
30	367.01	242.468	-124.35	4.4414
40	370.082	244.589	-125.44	4.4538

Table (9). *Molar volume (V), Van der Waals volume(V_w), electrostriction volume (V_e) and Solvated radii (r_o)of bulk lead bromide (LBr) in different (DMF-H_2O) mixed solvents at 298.15K ($cm^3 mole^{-1}$)..*

DMF vol. %	V	V_w	V_e	r_o (A°)
0	364.35	240.65	-123.42	4.4307
10	367.67	242.99	-124.62	4.4441
20	331.33	217.46	-111.53	4.2926
30	354.36	233.63	-119.82	4.3898
40	358.86	236.73	-121.41	4.4083

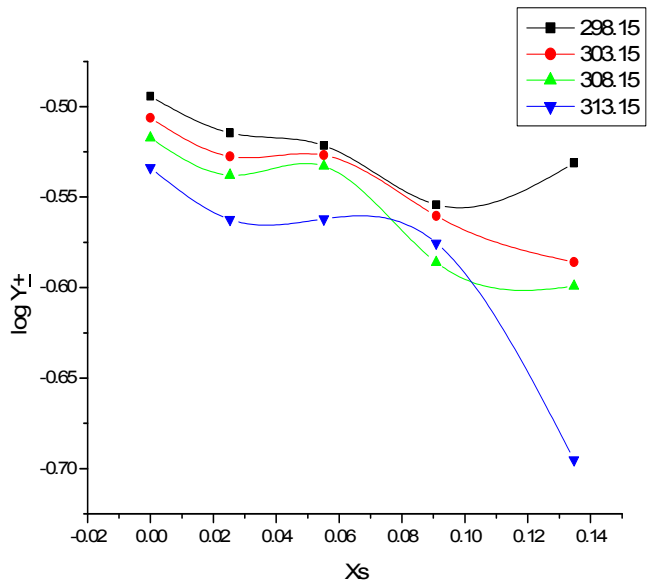

Fig. (3). *Relation between the activity coefficient ($\gamma_{\pm}$) of nano lead bromide (LBr) and the mole fraction of DMF (X_s) in (DMF–H_2O) mixed solvents at different temperatures.*

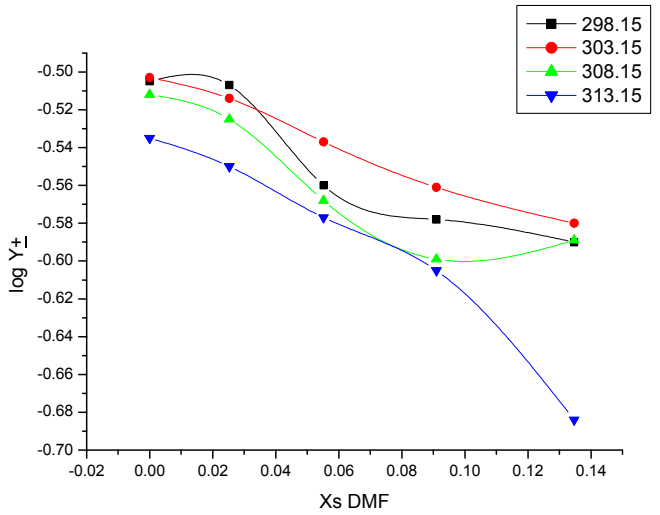

Fig. (4). *Relation between the activity coefficient ($\gamma_{\pm}$) of bulk lead bromide (LBr) and the mole fraction of DMF (X_s) in (DMF–H_2O) mixed solvents at different temperatures.*

4. Conclusion

The solubilties for both nano and bulk LBr were measured in mixed DMF-H_2O solvents. Study the solvation thermodynamic parameters help to understand their behaviour .Comparison between nano and bulk LBr needed to facilitative its uses and its environment study.

References

[1] A. F. Hollemanm, E. Wiberg, Inorganic Chemistry. San Diego: Academic Press. ISBN 0-12-352651-5, (2001).

[2] David A. Wright and Pamela Welbourn, Environmenal toxicology, Cambridge University Press, UK (2002).

[3] Lide, David R., ed. (2006). *CRC Handbook of Chemistry and Physics* (87th ed.). Boca Raton, FL: CRC Press. ISBN 0-8493-0487-3.

[4] Michael J. Dagani, Henry J. Barda, Theodore J. Benya, David C. Sanders "Bromine Compounds" in Ullmann's Encyclopedia of Industrial Chemistry" Wiley-VCH, Weinheim, 2000. doi:10.1002/14356007.

[5] Greenwood, Norman N.; Earnshaw, Alan (1997). *Chemistry of the Elements* (2nd ed.). Butterworth-Heinemann. ISBN 0080379419.

[6] S. Budavari (Ed.), The Merck Index: An Encyclopedia of Chemicals, Drugs and Biologicals, 12th ed., Merck Co. Inc., Whitehouse Station, NJ, 1996.

[7] A.E. Williams, in: H.F. Mark, D.F. Othmer, C.G. Overberger, G.T. Seaborg (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, vol. 3, 3rd ed., Wiley, New York, 1978, pp. 778–792.

[8] J. L. Opgrande, C. J. Dobratz, E. E. Brown, J. C. Liang, G. S. Conn, J. Wirth, J. Shelton, in: J. I. Kroschwitz, M. Howe-Grant (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, vol. 4, 4th ed., Wiley, New York, 1992, pp. 103–115.

[9] C.M. Park, R.J. Shechan, in: B. Elvers, S. Hawkins, G. Schultz (Eds.), Ullmann's Encyclopedia of Industrial Chemistry, vol. 18, fifth rev. ed, Basel, 1991, pp. 991–1043.

[10] D. E. Read, C. B. Purves, J. Am. Chem. Soc. 74 (1952) 116–119.

[11] E. E. Schrier, M. Pottle, H.A. Scheraga, J. Am. Chem. Soc. 86 (1964) 3444–3449.

[12] E. Suzuki, Y. Taniguchi, T. Watanabe, J. Phys. Chem. 77 (1973) 1918–1922.

[13] K. Yamamoto, N. Nishi, J. Am. Chem. Soc. 112 (1990) 549–558.

[14] P. Debye, E. Hückel, Z. Phys. 24 (1923)185, 305.

[15] Esam A. Gomaa and R. M. Galal, Basic Sciences of Medicine, 1(2), (2012), 1-5.

[16] Esam A. Gomaa, Physics and Chemistry of Liquids, 50(2012)279-283.

[17] Esam A. Gomaa, International Journal of Materials and Chemisty, 2(1), (2012)16-18.

[18] Esam A. Gomaa, American Journal of Environmental Engineering, 2(3), (2012)54-57.

[19] Esam A. Gomaa. American Journal of Polymer Science, 2(3), (2012), 35-38.

[20] Esam A.Gomaa. Eur. Chem. Bull., 1(2013) 259-261.

[21] Esam A.Gomaa, Elsayed abou Elleef and E.A.Mahmoud , Eur . Chem. Bull, 2(2013), 732-735.

[22] Esam A Gomaa and Elsayed M.Abou Elleef, American Chemical Science Journal, 3(2013) , 489-499.

[23] Esam A. Gomaa, Elsayed M. Abou Elleef, Science and Technology, 3(2013)118-122.

[24] Esam A Gomaa and M. G. Abdel Razek, International Research Journal of Pure and Applied Chemistry, 3 (2013)320-329

[25] Esam A. Goma, International Journal of Theoretical and Mathematical Physcics, 3(2013)151-154.

[26] Esam A. Gomaa and B. A. Al Jahadali, Education., 2(3),(2012)37-40.

[27] Esam A Gomaa, American Journal of Biochemistry, 2(3), 92012),25-28.

[28] Esam A. Gomaa, Food and Public Health, 2(3), 2012, 65-68.

[29] Esam A. Gomaa, Global Advanced Research Journal of Chemistry and Material Science, 1(2012)35-38.

[30] Esam A. Gomaa, Frontiers in Science, 2(2012)24-27.

[31] Esam A Gomaa, Elsayed M. Abou Elleef, E. T. Helmy and Sh. M. Defrawy, Southern Journal of Chemistry, 21(2013)1-10.

[32] E. A. Gomaa, K. M. Ibrahim, N. M. Hassan, Frontiers in Science,2(2012) 76-85.

[33] E. A. Gomaa, K. M. Ibrahim and N. M. Hassan, The International Journal of Engineering and Science (IJES), 3 (20144) 44-51.

[34] E A. Gomaa, H. M. Abu El-Nader and Sh. E. Rashed, The International Journal of Engineering and Science (IJES), 3(2014) 64-73.

[35] E. A. Gomaa, K. M. Ibrahim and N. M. Hassan, Research and Reviews: Journal of Chemistry, 3(2014) 47-55.

[36] Esam A. Gomaa and Elsayed M. Abou Elleef, Thermal and Power engineering, 3 (2014), 222-226.

[37] Esam A Gomaa, Elsayed M. Abou Elleef, Elsayed T. Helmy , Research and reviews: Journal of Chemistry, 3(2014)22-27.

[38] Esam A. Gomaa,.Science and Technology,3(2013)123-126.

[39] E. A. Gomaa, Research and Reviews: Journal of Chemistry, 3(2014),28-37.

[40] E. A. Gomaa, A. H. El-Askalany and M. N. H. Moussa, Rev. Roum. Chim, 32 (1987)243.

[41] Esam A Gomaa, Thermochimica Acta, 128 (1988) 99.

[42] E. A. Gomaa, Indian J. of Tech., 24 (1986) 725.

[43] Esam A. Gomaa, Thermochimica Acta, 142 (1989) 19.

[44] Esam A. Gomaa, Croatica Chimica Acta, 62 (1989) 475.

[45] Esam A. Gomaa, Thermochimica Acta, 147 (1989) 313.

[46] E. A. Gomaa, A. M. Shallapy and M. N. H. Moussa, J. Indian Chem. Soc., 68(1991)339.

[47] E. A. Gomaa, A. M. Shallapy and M. N. H. Moussa, Asian J. of Chem., 4(1992)518.

[48] H.M. Abu El-Nader and E. A. Gomaa, Mansoura Science Bulletin. (A Chem.) Vol .23 (1) July 1996.

[49] J. I. Kim, A. Cecal, H. J. Born, and E. A. Gomaa, Z. Physik Chemic, Neue Folge 110, 209 (1978).

[50] J. I. Kim and E. A. Gomaa, Bull. Soci. Chim. Belg., 90 (1981) 391.

[51] E. A. Gomaa, A. A. El-Khouly and M. A. Mousa, Indian Journal of Chemistry, 23 ((1984) 1033.

[52] E. A. Gomaa, M. A. Mousa and A. A. El-Khouly, Thermochimica Acta, 86 (1985) 351.

[53] E. A. Gomaa, M. A. Mousa and A. A. El-Khouly, Thermochimica Acta, 89 (1985) 133.

[54] Esam A.Gomaa, Thermochimica Acta, 91 (1985) 235.

[55] Esam A. Gomaa, Thermochimica acta, 128 (1988) 287.

[56] Esam A. Gomaa, Thermochimica Acta, 140 (1989) 7.

[57] Esam A. Gomaa, Bull. Soc. Chim. Fr. 5 (1989) 620.

[58] Esam A. Gomaa, Bull. Soc. Chim. Fr., 5 (1989) 623.

[59] Esam A. Gomaa, Thermochimica acta, 152 (1989) 371.

[60] Esam A. Gomaa, Thermochimica Acta, 156 (1989) 91.

[61] I. S. Shehatta, A. H. El-Askalany and E. A. Gomaa, Thermochimica Acta, 219(1993)65.

[62] E. A. Gomaa and G. Begheit, Asian Journal of Chemistry, 2(1990)444.

[63] A. A. El-Khouly, E. A. Gomaa, and S. Abou-El-Leef, Bull. Electrochem 19, 153 (2003).

[64] A. A. El-Khouly, E. A. Gomaa, and S. Abou El-Leef, Bull. Electrochem 19, 193 (2003).

[65] M. A. Hamada, E. A. Gomaa and N. A. El-Shishtawi, International Journal of Optoelectronic Enegineering, 1(2012)1-3.

[66] Kamal M. Ibrahim, Esam A. Gomaa, Rania R. Zaky and M. N. Abdel El-Hady, American Journal of Chemistry, 2(2012) 23-26.

[67] A. A. El-Khouly, E. A. Gomaa and S. E. Salem, Southern Brazilian Journal of Chemistry, vol. 20 (2012) 43-50.

[68] E. A. Gomaa and B. A. M. Al –Jahdali, American Journal of Environmrntal Engineering, 2(2012) 6-12.

[69] S. L. Oswal, J. S. Desai, S. P. Ijardar, and D. M. Jain, J. Mol. Liquids 144, 108 (2009).

[70] D. Bobicz, W. Grzybkowski, and A. Lwandowski, J. Mol. Liquids 105, 93 (2003).

[71] Y. Marcus. The Properties of Solvents (Wiley, London, 1998).

[72] E. A. Gomaa, A. H. El-Askalany, M. N. H. Moussa, Asian Journal of Chemistry,4(1992)553.

[73] Esam A. Gomaa, Rev. Roum. de Chimie,36(1991)11.

[74] Esam A. Gomaa, Journal of King Saud University, 3(1), 1991, 1411.

[75] Esam A. Gomaa, Oriental Journal of Chemistry, 6(1990)12.

[76] E. A. Gomaa, M. A. Hamada and R. Galal, Avances en Quimica, 5(2), 117-121(2010).

[77] Esam a. Gomaa, Analele Uni. din Bucuresti-Chimie, vol.19 no1, pag.45-48(2010).

[78] Nagah A. El-Shishtawi, Maany A. Hamada and Esam A. Gomaa, Physical Chemistry, 1(1), (2011), 14-16.

[79] E. A. Gomaa and B. A. M. Al Jahdali, American Journal of Condenesed Matter Physics, 2(1),(2012),16-21.