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Macroscopic Thermodynamics of Solvation for Bulk and Nano Silver Chromate (SCr) in Mixed Acetonitrile (AN)–H_2O Solvents at Different Temperatures

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Abstract
The silver chromate was prepared by the double salt interaction between silver nitrate and potassium chromate (2 $AgNO_3$ +K_2CrO_4 = Ag_2CrO_4 + 2 KNO_3). The molar solubility for bulk (normal) and nano silver chromate (SCr) in different percntages of acetonitrile (AN) and water were measured at 298.15, 303.15, 308.15 and 313.15K. From the molar solubilities for bulk and nano (SCr), the macroscopic solvation parameters like, 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 bulk and nano (SCr). The macroscopic thermodynamics are greater for bulk than nano SCr.

1. Introduction

Silver chromate (Ag_2CrO_4) is a brown-red monoclinic crystal and is a chemical precursor to modern photography. It can be formed by combining silver nitrate ($AgNO_3$) and potassium chromate (K_2CrO_4) or sodium chromate (Na_2CrO_4). This reaction has been important in neuroscience, as it is used in the "Golgi method" of staining neurons for microscopy: the silver chromate produced precipitates inside neurons and makes their morphology visible [1,2] . Ag_2CrO_4 (SCr) can be used as cathode for lithium cells [3], solid electrolyte system involving CuI and Ag_2CrO_4 (SCr), and ion transport, electrical and electrochemical properties [4]. Silver iodide solid electrolytes, containing dichromate anion (AgI-$Ag_2Cr_2O_7$) behave as super-cooled liquids [5].

Our aim is to evaluate the thermodynamic parameters of bulk silver chromate and compare with that of nano (SCr).

2. Experimental

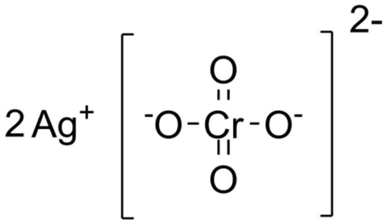
2.1. Materials

Silver nitrate is a versatile precursor to many other silver compounds, such as those used in photography. It is far less sensitive to light than the halides, molar mass is 169.87

and very soluble in water. From Al Nasr Co. was used. Potassium chromate, molar mass 194.19, very soluble in water and from Al Nasr chemicals Co. was used without purification. Acetonitrile (AN) of the type Adwic was used. It is used as a polar aprotic solvent in organic synthesis and in the purification of organic compounds.

2.2. Preparation of Bulk and Nano SCr

SCr of was prepared by reversible reaction between silver nitrate and potassium chromate in water .The insoluble SCr was separated by filtration ,washed with distilled water and dried .The nano SCr was prepared by ball - mill. The ball – mill was a Retsch MM 2000 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).



SCr structure

2.3. TEM Images

Fig. (1). all images measured by using JEOL HRTEM – JEM 2100 (JAPAN) show that TEM of SCr obtained in water are spheres with regular shapes in the form of big net forms. The particle sizes are in the range of 17 -38 nm. The nano particles gathered in big net forms ranging from 127 t0 138 nm.

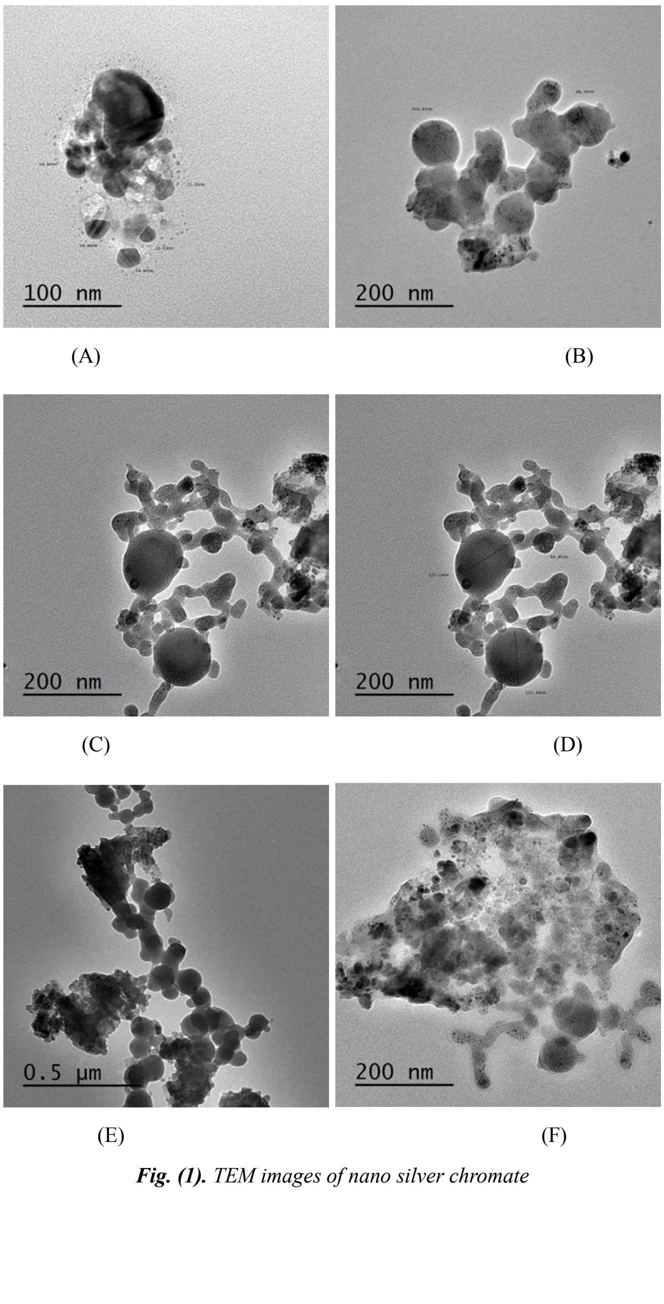
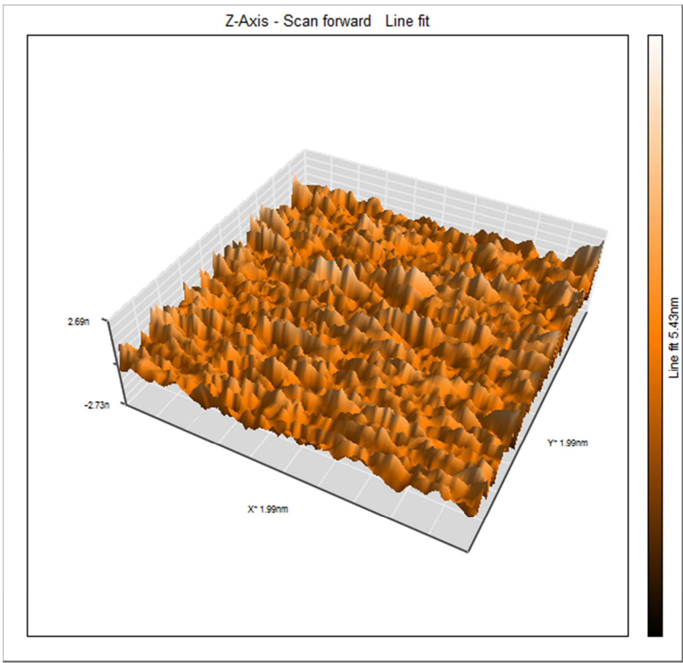


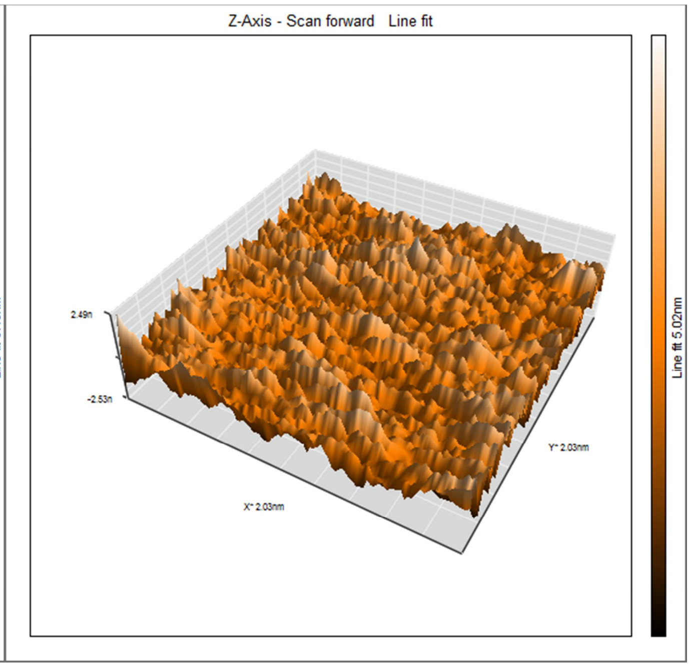
Fig. (1). *TEM images of nano silver chromate*

2.4. Atomic Force Microscope (AFM)

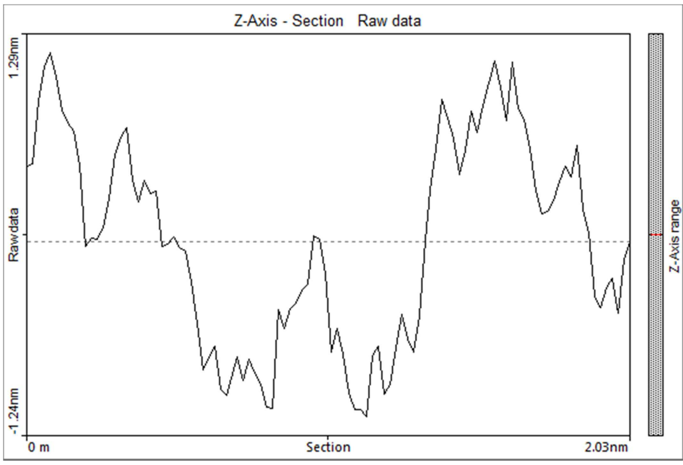
The images of atomic force microscope for nano sample SCr measured in Mansoura University Nanotechnology Center using Nanosurf Flex AFM , Switzerland apparatus are shown in Fig. (2). Image A for forward direction and B for backward direction. Similar trend seen. It is seen in Fig.(2) C ,the roughness with average in -1.24 nano meter to +1.29 nano meter of the surface. This surface of the nano CAc has the following properties which clear in Fig.(2) D for backward measuring : roughness average (R_a) 557.9 pico meter , root mean square (R_q) 647.45 pico meter, peak height (R_p) 1194 pico meter, the peak-valley height (R_y) -1.105 n m and valley depth (R_m) -20.01 pico meter. Approximate vales are obtained for forward measurements S values (Fig.2 E). All AFM images and roughness data proves the homogeneous surface of the nano prepared samples. The roughness parameters in back direction are seen in Fig 2(E). Fig. 2 (F) is the normal microscope picture of nano SCr using TUCSEN microscope with 1000 multiplication.



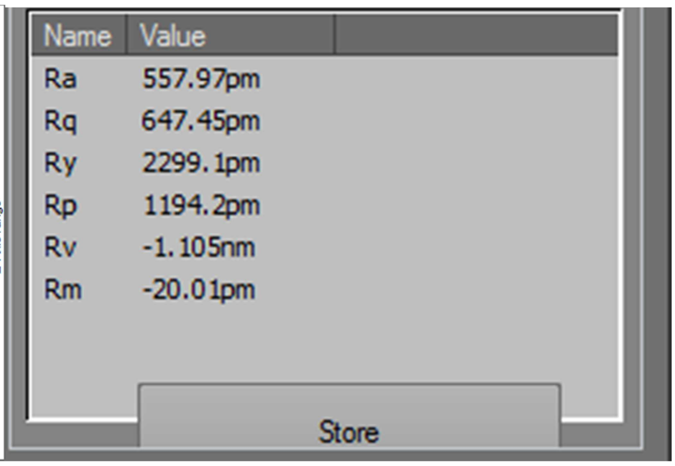
(A)



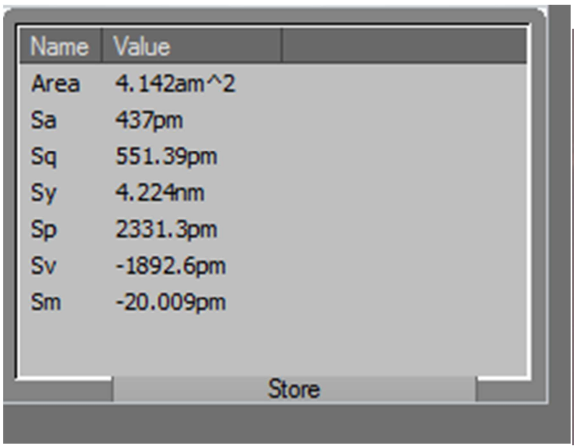
(B)



(C)



(D)



(E)

(F)

Fig. (2). *AFM for nano silver chromate (SCr)*

2.5. Preparation of Saturated Solutions and Solubility Measurement

The saturated solutions for bulk and nano SCr were prepared by dissolving suitable amount of solid material in closed test tubes containing ethanol (EtOH) – H_2O (W) solvents. The tubes were placed in water thermostat for a period of four days till equilibrium reached.

The solubility of SCr 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 [3- 35].

The molar solubilities for bulk and nano SCr 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. The experimental data was shown in Tables 1 and 5 for bulk and nano SCr from the mean values of three measurements.

3. Results and Discussion

3.1. Macroscopic Gibbs Free Energies of Solvation

The molar solubility (S) for nano SCr in mixed EtOH – H_2O solvents were measured at 298.15 , 303.15 , 308.15 and 313.15 K, gravimetrically by taking mean value for three reading for each solution. The S values are listed in tables 3, 4, 5 and 6 at different temperatures. More accurate solubility in AN was obtained than in literature $1.573x10^{-4}$ mole/L [30], because of multiple purification of SCr. by distilled water. The activity coefficients were calculated by the use of Debye – Hückel equation (1) [25-32].

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

Where S is the molar 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, the macroscopic Gibbs free energies of solvation (total free energy) ΔG_s were calculated by using equation (3) [36-38].

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

All the data tabulated in Tables 3 and 4 for bulk and nano SCr. The data reveal that Gibbs free energies of solvation increase in positivity by increasing the mole fraction of AN in the (AN-H_2O) mixtures. This may be due to the more solvation by increasing mole fraction of AN.

3.2. Macroscopic Enthalpies and Entropies of Solvation

From the linear plots of log K_{sp} vs 1/T of bulk and nano SCr the macroscopic enthalpies (total enthalpies) were calculated from the slopes (slopes = -ΔH/2.303R) [38] and their values given in Tables 4 and 8 for bulk and nano SCr.

The Macroscopic entropies (total entropies) of solvation were calculated by use of Gibbs-Helmholtz equation (4) [29-79].

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

Their values were also shown in Tables 4 and 8 for both bulk and nano SCr at all the used temperatures and at volume ethanol –water percentages of 20,40,60 80 and100%. More endothermic character (i.e.–ΔH) could be obtained by adding more AN and less positive entropies favor, less solvation behavior.

Table (1). *Molar solubilities (S) for bulk silver chromate (SCr) in mixed AN-H_2O(W) solvents at different temperatures (298.15, 303.15, 308.15 and 313.15K).*

AN %	X_s	298.15K	303.15K	308.15K	313.15K
20	0.0788	0.00107	0.0031	0.0034	0.0145
40	0.1857	0.00126	0.0085	0.0044	0.0161
60	0.3391	0.00883	0.0085	0.0056	0.017
80	0.5777	0.01075	0.0042	0.0055	0.018
100	1	0.00738	0.0019	0.0054	0.0132

Table (2). *Solubility products for bulk silver chromate (SCr) in mixed AN-H_2O(W) solvents at different temperatures (298.15.303.15,308.15 and 313.15K).*

AN %	X_s	298.15K	303.15K	308.15K	313.15K
20	0.0788	5.6930	7.1662	7.0459	5.3250
40	0.1857	8.2716	5.9869	6.7498	5.2363
60	0.3391	6.0005	6.0337	6.5148	5.2276
80	0.5777	5.8871	6.937	6.6002	5.2831
100	1	6.6207	8.0109	6.8971	5.9844

Table (3). *Macroscopic Gibbs free energies for bulk silver chromate (SCr) in mixed AN-H_2O(W) solvents at different temperatures in kJ/mole.*

AN-W %	X_s	298.15K	303.15K	308.15K	313.15K
20	0.0788	32.500	41.596	41.572	31.928
40	0.1857	47.221	34.75	39.825	31.396
60	0.3391	34.255	35.022	38.439	31.344
80	0.5777	33.608	40.266	38.942	31.677
100	1	37.796	46.499	40.694	35.882

Table (4). *Macroscopic enthalpies and entropies for bulk silver chromate (SCr) in mixed AN-H_2O (W) solvents at different temperatures (298.15.303.15, 308.15 and 313.15K). in kJ/mole*

AN-W %	X_s	ΔH	298.15K	303.15K	308.15K	313.15K
20	0.0788	10.807	0.0269	0.0077	0.0085	0.0362
40	0.1857	6.872	0.0032	0.0213	0.011	0.0402
60	0.3391	21.332	0.0221	0.0213	0.0139	0.0425
80	0.5777	11.948	0.0269	0.0104	0.0139	0.0451
100	1	102.973	0.0184	0.0049	0.0136	0.0330

Table (5). *Molar solubilities (S) for nano silver chromate (SCr) in mixed AN-H_2O solvents at different temperatures.*

AN-W %	X_s	298.15K	303.15K	308.15K	313.15K
20	0.0788	0.0034	0.0095	0.0037	0.0135
40	0.1857	0.0063	0.0028	0.0019	0.0142
60	0.3391	0.0046	0.0128	0.0029	0.0121
80	0.5777	0.0049	0.0135	0.0024	0.0108
100	1	0.005	0.0085	0.0012	0.0116

Table (6). *Solubility products solubilities for nano silver chromate (SCr) in mixed AN-H_2O solvents at different temperatures.*

AN-W %	X_s	298.15K	303.15K	308.15K	313.15k
20	0.0788	7.0573	5.8253	6.9413	5.4014
40	0.1857	6.3444	7.2832	7.7679	5.3797
60	0.3391	6.7569	5.5735	7.2628	5.6120
80	0.5777	6.7713	5.6232	7.5528	5.8494
100	1	7.006	6.4551	8.5738	6.1080

Table (7). *Macroscopic Gibbs free energies for nano silver chromate (SCr) in mixed AN-H_2O solvents at different temperatures in kJ/mole.*

AN-W %	X_s	298.15K	303.15K	308.15K	313.15K
20	0.0788	40.288	33.813	40.955	32.386
40	0.1857	36.218	42.275	45.832	32.256
60	0.3391	38.573	32.351	42.852	33.649
80	0.5777	38.655	32.64	44.563	35.072
100	1	39.995	37.468	50.587	36.623

Table (8). *Macroscopic enthalpies and entropies (T Δ S) for nano silver chromate (SCr) in mixed AN- H_2O solvents at different temperatures (298.15.303.15, 308.15 and 313.15K) . In kJ/mole.*

AN-W %	X_s	ΔH	298.15K	303.15K	308.15K	313.15K
20	0.0788	10.807	-29.481	-23.006	-30.148	-21.579
40	0.1857	6.872	-29.346	-35.403	-38.960	-25.384
60	0.3391	21.332	-17.242	-11.020	-21.520	-12.318
80	0.5777	11.948	-26.708	-20.692	-32.615	-23.124
100	1	22.973	-17.022	-14.495	-27.614	-13.650

4. Conclusion

All the macroscopic thermodynamic parameters are greater for bulk than nano SCr, indicating the possibility for more gathering for nano salt in solid state than the bulk one in the used solvent mixtures. The solubilties for both bulk and nano SCr were measured in mixed AN-H_2O solvents. Study the solvation thermodynamic parameters help to understand their behaviour .Comparison between bulk and nano SCr needed to help their uses and application study.

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