

Coordination Number and Gibbs Free Energy of Complexation for the Interaction of Nano CuSO_4 with Ammonia in Water from Distribution Measurements

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Coordination Number, Distribution Coefficient, Gibbs Free Energies of Complexation, Copper Sulfate, Ammonia

From the distribution constants of ammonia (ammonium hydroxide) in water and chloroform, the interaction solvation parameters with nano copper sulfate was studied at 29.15K.. The distribution constant K , coordination number for copper ammonia complex, equilibrium reaction constant K_{eq} and Gibbs free energies of solvation were evaluated for this reaction. All the data were done five times and compared with that by using normal copper sulfate. The aim of this work is to compare between the different solution behavior for nano CuSO_4 and normal one in copper ammonia complex formed in aqueous layer.

Introduction

The nature of copper-ammonia complexes in aqueous solutions is followed by the distribution coefficients of ammonia between aqueous copper sulfate solution and chloroform serves to indicate complex formation between CuSO_4 and ammonia. The deviation of ammonia concentration from its normal value for pure water and chloroform measures the extent of complexation between CuSO_4 and ammonia. Valuable calculations can be done on the use of distribution coefficient [1-11]. Tetramminecopper (II) sulfate is the inorganic compound with the formula $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_n]\text{SO}_4$ in solid state (Fig. 1). This dark blue solid is a metal complex with faint odor of ammonia. It is closely related to Schweizer's reagent, which is used for the production of cellulose fibers in the production of rayon. It is used to print fabrics, used as a pesticide and to make other copper compounds like copper nano-powder [11]. Our purpose is to compare the solid tetramminecopper (II) with the existence of this complex in solution.

Experimental

Preparation of nano copper sulfate: 1)

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was provided from Al Nasr chemicals Co., while nano CuSO_4 was prepared by ball milling using Retsch MM 2000 swing mill with 10 cm^3 stainless steel double walled tubes. Two balls stainless steel with diameter of 12 mm were used. Ball milling was performed at 20225Hz and shaking was done usually at room temperature for one hour, temperature did not rise above 30°C .

Tetraamminecopper (II) sulfate

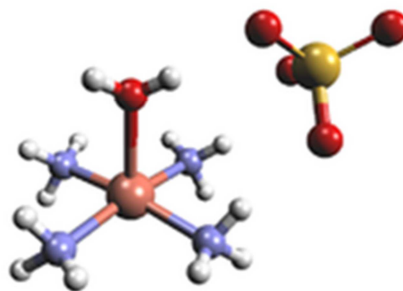
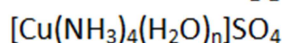


Fig. 1. Structure of solid tetramminecopper (II) sulfate complex.

2) Chemicals:

Chloroform and ammonia are provided from Al Gomheria chemical Co. and used without purification.

3) Transmission electron microscope:

The images for nano copper sulfate were measured by using JEOL HRTEM – JEM 2100 (JAPAN).

4) Preparation of solutions:

The solution prepared are, 1 M NH_4OH (checked by exact HCl), 0.2 N HCl (checked by standard sodium carbonate solution) and 0.1 M CuSO_4 nano and normal).

5) Procedure for experiment:

The following solutions were prepared in the three used bottles:

Table (1). Different bottles content.

Solution, ml	1	2	3
Distilled water	—	20	—
Ammonia	50	30	40
Chloroform	20	20	20
Copper sulfate	—	—	10

After shaking the three bottles well for about 40 minutes, the solutions were transferred to clean measuring cylinder and leaving for complete separation. We titrated 5 ml of the aqueous layer against 0.2 N HCl and the concentration of free ammonia in bottles 1 and 2 were evaluated. For the determination of the concentration of ammonia in the organic layer, 5ml of CHCl_3 layer was transferred to conical flask containing 50 ml distilled water and titration with 0.01 N HCl was carried out for the three bottles.

Results and Discussion

TEM Images for nano CuSO_4 :

The photogram from TEM is presented for nano CuSO_4 salt. The images in Fig. 2 show that the nano CuSO_4 is in the form of irregular spheres or deformed spheres, the images show also crystalline form as clear in the electron diffraction picture. The boundaries were seen and the size ranging from 20-40 nm.

Distribution coefficient evaluation:

Application of equation 1 was carried out for the evolution of distribution coefficient.

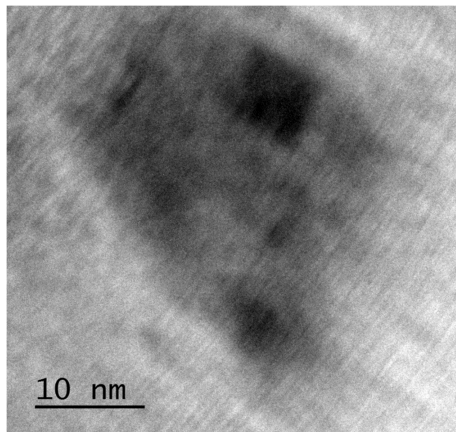
$$K = \text{Concentration of free ammonia in } \text{CHCl}_3 / \text{concentration of free ammonia in } \text{H}_2\text{O} \quad (1)$$

The mean value for the distribution coefficient (K mean) was estimated by taking the mean values for bottles 1 and 2.

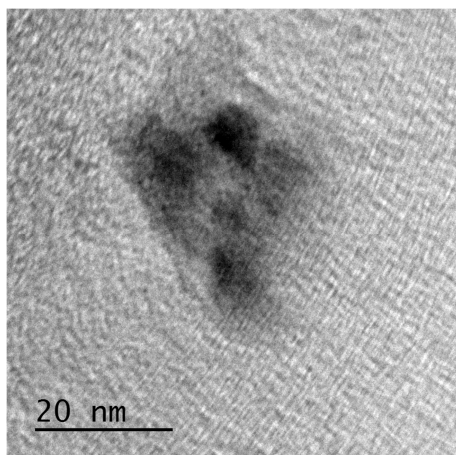
In bottle 3 (in the presence of nano copper sulfate) the concentration of free ammonia in chloroform layer C org is calculated.

Concentration of free ammonia in aqueous layer (C_{aq. free}) is determined from equation (2):

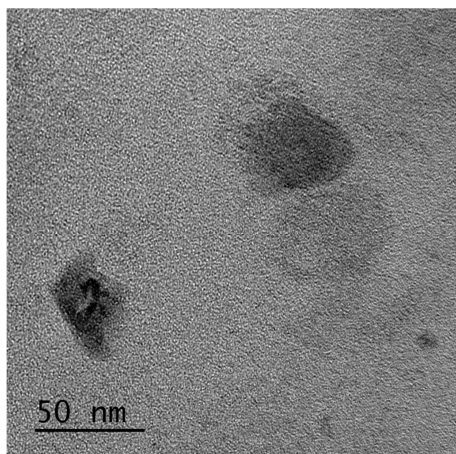
$$C_{aq. free} = C_{org. free} / K_{mean} \quad (2)$$



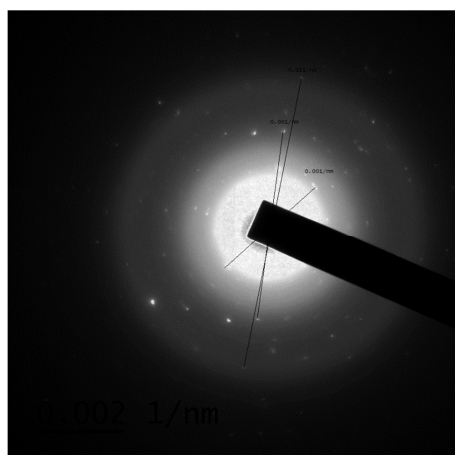
(a)



(b)



(c)



(d)

Fig. 2. TEM images for nano CuSO_4 , a, b, c photos and d is the electron diffraction image.

The total concentration of $[\text{NH}_3]$ is determined by:

$$[\text{NH}_3] = \text{Corg, free} + \text{Caq, free} + \text{Caq, complexed (x)} \quad (3)$$

Where x equal to the concentration of the complexed ammonia with Cu^{2+} ions. Therefore the coordination number is obtained by dividing x by 0.1.

All the above steps were done five times on using nano and normal CuSO_4 and the mean values were taken from the concentration of the complexed ammonia which equal the concentration also of CuSO_4 coordinated, then the equilibrium constant for complex formation was estimated by applying equation (4):

$$K_{\text{eq}} = [\text{Cu}^{2+}][\text{NH}_3^+]/[\text{CuSO}_4] \quad (4)$$

The Gibbs free energies for complexation were calculated following equation (5) [12-27].

$$\Delta G = -RT \ln K_{\text{eq}} \quad (5)$$

The calculated values are presented in Table (2).

It was observed that the coordination copper ammonia complexes are smaller in case of using nano copper sulfate solution than the normal one. This can be explained as the size became smaller in case of nano salt then little places were available for ammonia to bind with the metal ion. Also the equilibrium constant is bigger in the case of using normal salt than nano ones which gave more negative free energies of complexation at 292.15K. More spontaneous process for normal salt was found.

Table (2). Coordination number and Gibbs free energies of complexation for copper –ammonia complex.

	Nano CuSO_4	Normal CuSO_4
K_{mean} (distribution constant)	0.0558	0.0451
Coordination number	$2.58 = 3$	$4.90 = 5$
K_{eq} (equilibrium constant)	0.6671	2.438
ΔG (Gibbs free energy of complexation) in k J/mole	0.9480	-2.087

Conclusion

It was concluded experimentally that all distribution data, the coordination, equilibrium constant, coordination number and Gibbs free energy of complexation for the interaction of both nano and normal CuSO_4 with a ammonia favor bigger results for normal than nano salts. It was found that the coordination numbers for the interaction of copper sulfate with ammonia is greater in solution phase than forming solid complex. Also the coordination numbers on using nano copper sulfate are smaller than that of using normal copper sulfate after interaction with ammonia in aqueous phase. Discussing the difference in behavior between nano and normal salt in different solvents is promising study need applications. ■



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