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Inorganic chemistry**THE COMPOSITION AND ELECTRON SPECTRA OF AQUEOUS DISPERSIONS OF MANGANESE(II) CHLORIDE WITH CYSTEINE COMPLEXES****S.N.Osmanova¹, Corresponding Member of NAS of Azerbaijan A.A.Mejidov¹,
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Aqueous dispersions of manganese(II) chloride with cysteine complexes are studied by dynamic light scattering and UV/Vis spectroscopy. The composition and structure of molecular and supra-molecular complexes stabilized in these dispersions and the values of the hydrodynamic radius, diffusion coefficient, size distribution of the complexes as a function of pH, concentration and ratio of the components of the dispersions are determined.

Keywords: *manganese(II)chloride, cysteine, aqueous dispersions, dynamic light scattering*

Introduction

Over the past two decade the number of papers on the role of biogenic macro- and microelements in the biochemical processes has considerably increased. It is noted that the role of macro- and microelements markedly enhanced when used in combination with amino acids. Amino acids can act as chelating ligands of metals that allows to create on this basis, preparations that combine amino acids with microelements and ensure their efficient transportation inside the living environment. Among the trace elements manganese occupies a special place. Manganese is among the micronutrients that are needed for the development of living organisms, and therefore must be in a live environment in the required quantities. Manganese is actively involved in protein and carbohydrate metabolism, stimulates the activity of enzymes that affect the absorption of calcium and phosphorus [1-4].

Currently the actual scientific task is to ascertain the composition and structure of the compositions on the basis of macro, trace elements and amino acids at the molecular and supramolecular levels and their mechanism of action, finding ways to improve the effectiveness of these compositions.

The aim of the present work is to study of aqueous dispersions based on cysteine and manganese chloride, the structure and composition of the complexes formed in these disper-

sions by dynamic light scattering (DLS) and UV /Vis spectroscopic methods.

Experimental

Preparation of the solutions. For physical-chemical studies 4 types of solutions were prepared. *First solution.* Weighed sample of 0.162g $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 20 ml of distilled water. *Second solution.* 0.121g cysteine was dissolved in 20ml distilled water. *Third solution* was a mixture of solutions 1 and 2 (a total of 20 ml + 20 ml = 40 ml). The pH of this solution is equal to three- i.e. this solution is acidic. Next, the mixture was heated with vigorous stirring for 30 min at 60°C. After cooling the electron absorption spectra (EAS) in UV/Vis region and dynamic light scattering (DLS) spectra were taken off. *The fourth solution* is a solution 3, which treated with KOH solution to pH7. EAS and DLS spectra of this solution were taken off also. After addition of the KOH solution for 30 minutes, the solution became transparent with a bluish tinge. When storing the solution brightens and white crystals precipitate. The precipitate was a polycrystalline powder which was characterized by IR spectra. IR –spectra of powder cysteine and the powders obtained from the above aqueous solutions were recorded on a FTIR Alfa, Bruker, Germany spectrometer.

Particle size and size distribution in the aqueous dispersions was determined by dynamic light scattering using analyzer LB-550, Horiba. The method is based on measuring the average

diffusion rate of the dispersed particles by recording fluctuations in the intensity of the scattered light; measurement of the spectral density (the time correlation function) of the scattered light. This method allows to measure directly the diffusion coefficient of the particles dispersed in the liquid. Since the diffusion coefficient of the dispersed particles is uniquely associated with the particle size, essentially DLS is the method of measuring the size of such particles [5,6]. The used analyzer allows us to study the processes of formation, transformation, decay particles, aggregates, and complexes in the temperature range 278-343K. The interval for determination of the size of the particles of this device 0,001-6 mm. The power of the radiation source 5mW, wavelength - 650 nm. The used calculation program allows to obtain more accurate results for the mean particle size and size distribution. Electronic absorption spectra (EAS) of water solutions were recorded in the wavelength range of 190-1100 nm at room temperature in quartz cuvettes with 1 cm in width using a spectrophotometer Shimadzu1800. The same cuvette was used to determine particle size and size distribution in the prepared solutions using the above analyzer LB-550, Horiba.

Results and Discussion

According to DLS data the aqueous compositions of manganese chloride and cysteine

are aqueous dispersions. After neutralization with KOH during the some time the precipitate as a white powder was formed. The IR spectra of this powder and cysteine powder are differ greatly. There are the intense bands at 1790 and 3374 cm^{-1} in the IR spectrum of cysteine, which belong to the stretching vibration of the carboxyl and amine groups, respectively. These bands in the IR spectrum of the complex are almost absent. Instead of these bands in the IR spectrum of the complex, the bands at 1582 and 3100 cm^{-1} are detected (Fig.1). Note that the band of medium intensity, which is characteristic for stretching vibrations of -SH group, in the spectrum of the free ligand appears at 2552 cm^{-1} . In the spectrum of the complex, this band appears at 2586 cm^{-1} . The intensity of this band is considerably lower than in the spectrum of the ligand, which apparently is due to the participation of -SH groups in the intra- and / or intermolecular hydrogen bonds [7-9]. Analysis of the infrared spectra shows that the precipitate obtained from the solution 3, by adding KOH, likely is the complex of chelate structure of cysteine with bivalent manganese. Note that the presence of two - the carboxyl and amine donor centers in the composition of this amino acid, makes possible the chelation during the reaction of cysteine with manganese ions.

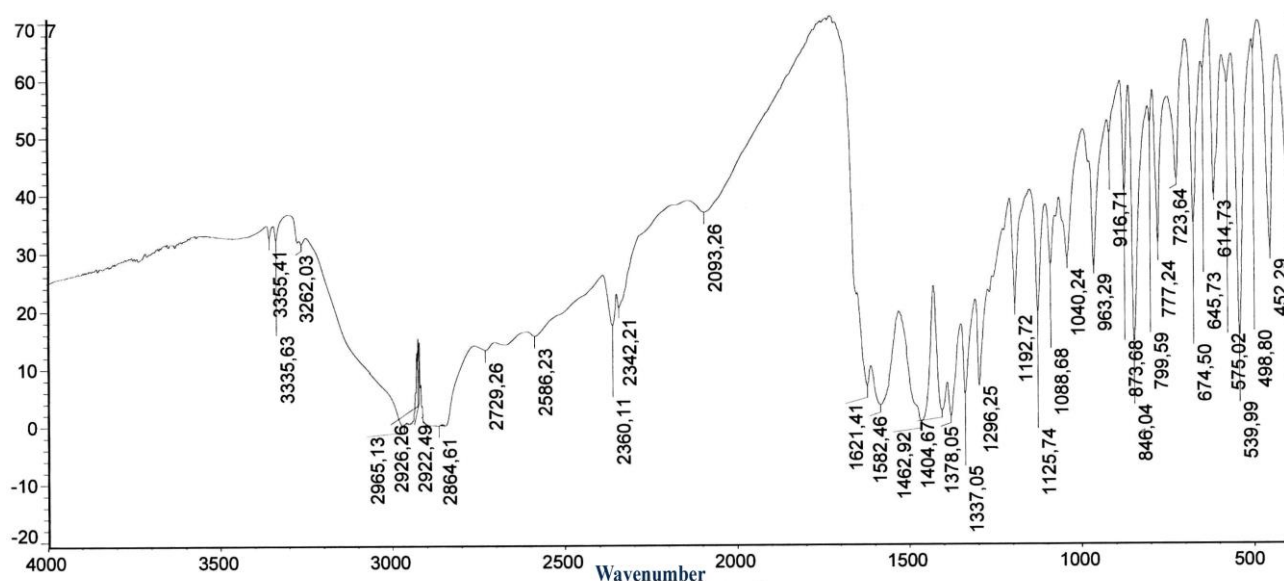


Fig. 1. IR spectra of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O} + \text{Cys} + \text{KOH}$ ($\text{MnCl}_2 \cdot 2\text{H}_2\text{O} / \text{Cys} = 1:1$) powder

In fig.2, a-b the electronic absorption spectra (EAS) of prepared aqueous solutions are given. As seen from the fig.2 in the EAS the absorption bands characteristic for complexes of amino acids with divalent manganese are detected [10]. The study of optical density of the solution as a function of concentration of metal ions allowed to conclude that the amino acid-metal stoichiometry in the complexes is equal to 2:1. The nature of coordination of the amino acids is strongly dependent on pH, because protons are able to compete with manganese ions for the coordination with ligand. [11,12]. Therefore, in an acidic medium, when the majority of the aforementioned groups is protonated, we have

the weak complexing between the amino acids and manganese ions.

The results of DLS measurements are shown in table and the DLS spectrum in fig.3. As seen from the data in table and fig.3.1 and fig.3.2, after adding of KOH to a solution, consisting of manganese chloride(II) and cysteine, the DLS parameters dramatically changed, there is a colloid having a particle size appreciably smaller than that before the introduction of the KOH into the solution. The observed phenomenon likely is due to the change in the composition and structure of supramolecular structures as a result of changes in the pH of the solution.

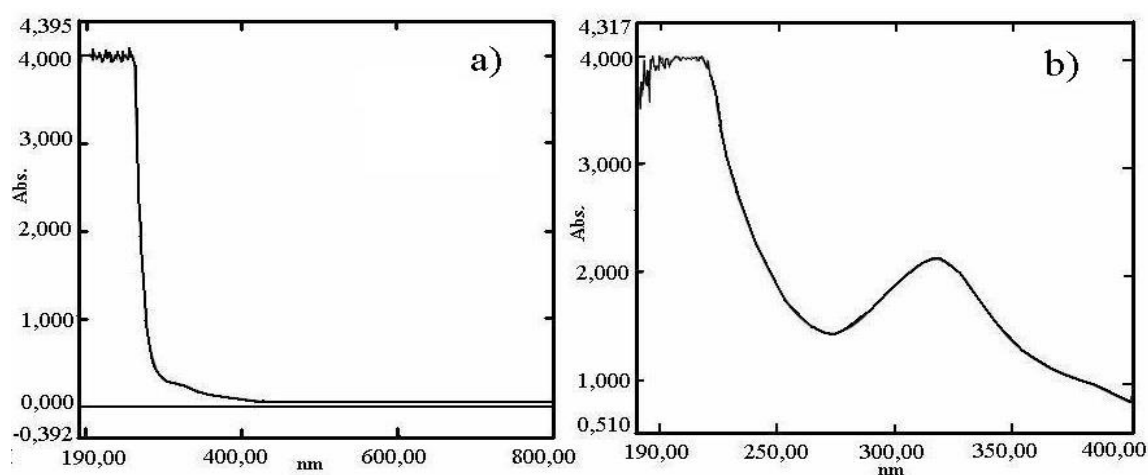


Fig. 2. UV/Vis. spectra of aqueous solutions of a) b) $\text{MnCl}_2 \cdot 2\text{H}_2\text{O} + \text{Cys} + \text{KOH}$ ($\text{MnCl}_2 \cdot 2\text{H}_2\text{O} / \text{Cys} = 1:1$)

Table

Values of the DLS parameters of investigated aqueous dispersions

№	Median, nm	Median (Diameter on %), nm			Mean, nm	Mode, nm	Span.	D, $\text{E}^{-11} \text{ m}^2/\text{s}$
		10%	50%	90%				
3.1	10.8	8.4	10.8	13.5	10.9	10.8	0.4727	4.0645
3.2	5.8	4.5	5.8	7.2	5.8	6.0	0.4780	3.8160

Here «Median» - average value of particle size, equal to 50% part of a total number of particles; «Mean» - arithmetic average value of distribution density determined according to the equation: arithmetic average = $\sum \{q(J) \times X(J)\} \div \sum \{q(J)\}$, where J: number of divisions, q (J): the value of the distribution density (%), X(J) - typical size (in microns) in «J» range of particle size; Mode - value of the particle size at the maximum of the distribution curve, Span - amplitude, D-diffusion coefficient.

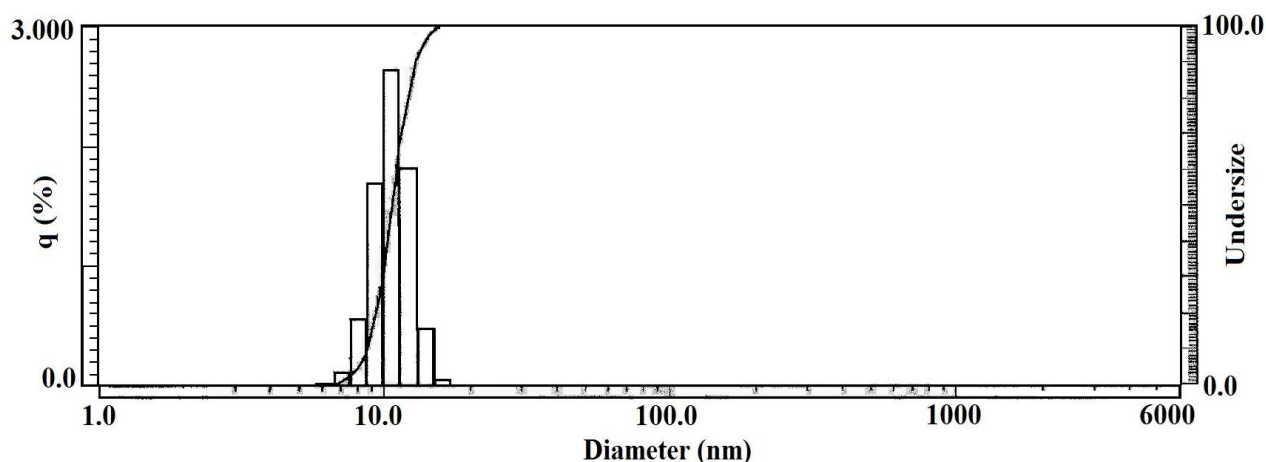


Fig. 3.1. DLS histogram of aqueous solution of cysteine

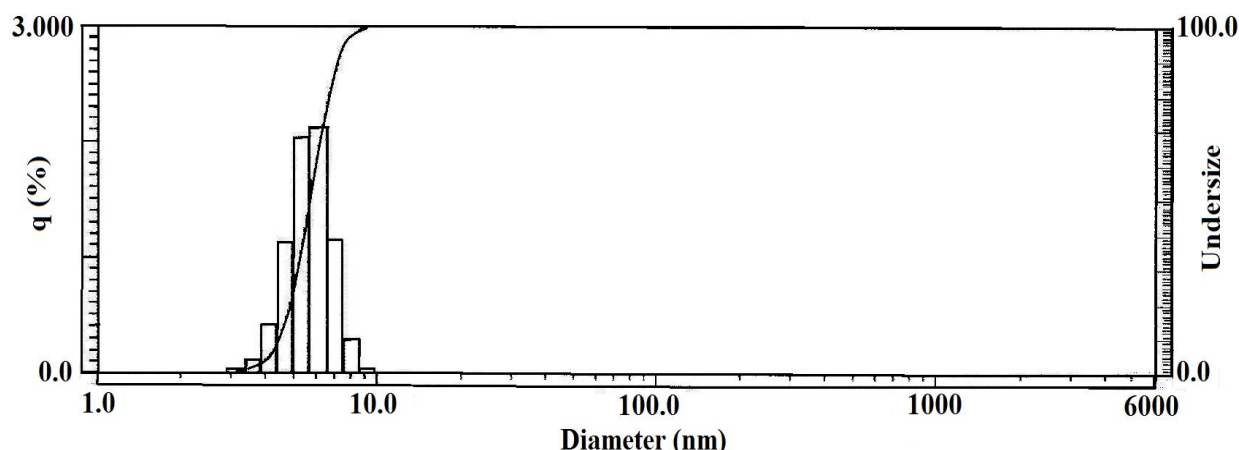


Fig. 3.2. DLS histogram of aqueous dispersion $\text{MnCl}_2 \cdot 2\text{H}_2\text{O} + \text{Cys} + \text{KOH}$, ($\text{MnCl}_2 \cdot 2\text{H}_2\text{O}/\text{Cys} = 1:1$)

Conclusion

These techniques have allowed to establish the formation of complexes of the ion manganese(II) with cysteine and determine the values of the diffusion coefficient, the hydrodynamic radius of supramolecular structures, their size distribution. Analysis of the dependence of the change in optical density of the solution on the concentration of metal ions led to the conclusion on the formation of complexes of amino acid-metal stoichiometry of 2: 1. DLS data showed that aqueous solutions of cysteine with manganese chloride contain supramolecular structure with the values of the diffusion coefficient $(3.82\text{--}4.06) \cdot 10^{-11} \text{ (m}^2/\text{s)}$ and the average size of the hydrodynamic radius of 5.8 nm constituting likely cluster complexes aqueous manganese chloride with cysteine.

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MANQAN(II) XLORİDİN SİSTEİNLƏ KOMPLEKSLƏRİNİN SU DİSPERSİYALARININ TƏRKİBİ VƏ ELEKTRON SPEKTRLƏRİ

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Manqan(II) xloridin sisteinlə komplekslərinin su dispersiyaları işıq dinamik səpilməsi və ultrabənövşəyi görünən sahə spektroskopiyası metodları ilə tədqiq edilmişdir. Bu dispersiyalarda stabilləşən molekulyar və supra-molekulyar komplekslərin tərkibi və quruluşu, hidrodinamik radiusunun, diffuziya əmsalının qiymətləri, ölçülərinə görə paylanması maye mühitin pH-dan, qatılığından və komponentlərinin nisbətindən asılı olaraq müəyyən edilmişdir.

Açar sözlər: su dispersiyaları, manqan(II) xlorid, sistein, işıq dinamik səpilməsi, ultrabənövşəyi/görünən sahə spektroskopiyası

СОСТАВ И ЭЛЕКТРОННЫЕ СПЕКТРЫ ПОГЛОЩЕНИЯ ВОДНЫХ ДИСПЕРСИЙ КОМПЛЕКСОВ ХЛОРИДА МАРГАНЦА(II) С ЦИСТЕИНОМ

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Исследованы водные дисперсии комплексов хлорида марганца(II) с цистеином методами динамического рассеяния света и УФ/Вид спектроскопии. Определены состав и строение стабилизирующихся в этих дисперсиях молекулярных и надмолекулярных структур, значения гидродинамического радиуса, коэффициента диффузии, распределение по размерам последних в зависимости от pH, концентрации и соотношения компонент жидкой среды.

Ключевые слова: водные дисперсии, хлорид марганца(II), цистеин, динамическое рассеяние света, УФ/Вид спектроскопия