ISSN 2321-807X

DYNAMIC LIGHT SCATTERING BY NANO- AND MICRO-SIZED COMPLEXES IN THE SYSTEM K_2REBR_6/P-AMINOBENZOIC ACID/HBR/H_2O

S.N.Osmanova[1], U.A.Kerimova[1] , N.S.Osmanov[1], E.H.Ismailov[2], S.A.Suleymanova[2].

[1]Institute of Catalysis and Inorganic Chemistry named after acad. M.F.Nagiyev of Azerbaijan National Academy of Sciences.

113, H.Javid Ave., Baku - AZ1143, Azerbaijan.

e-mail: o.sevinc1985@rambler.ru

[2]Institute of Petrochemical Processes named after acad. Yu.G.Mamedaliyev of Azerbaijan National Academy of Sciences.

30, Khojali pr., Baku- AZ1025, Azerbaijan.

e-mail: etibar.ismailov@gmail.com

ABSTRACT

K_2ReBr_6/p-aminobenzoic acid/HBr/H_2O system using dynamic light scattering (DLS) and electronic absorption spectra (EAS) were studied. The formation of nano- and micro-sized complexes with hydrodynamic radius 0.001-2.8 µm within the temperature interval 293-333 K and as a function of concentration of hydrobromic acid and K_2ReBr_6/p-aminobenzoic acid ratio are shown.

Keywords

Potassium Hexabromorhenate(IV); p-aminobenzoic acid; Dynamic Light Scattering; Particle Size Distribution, Electron Absorption Spectra

Discipline And Sub-Disciplines

Inorganic chemistry

TYPE (METHOD/APPROACH)

Experimental and spectral analysis

INTRODUCTION

Amino acids are the most important bioligands, they are part of the peptides and proteins. The latter play a major role in all life processes. Amino acids (AA) are considered as model ligands in the evaluation and prediction of interactions of the "metal-protein." Therefore, the development of new methods for the synthesis of complex compounds with the AA various metal ions, the establishment of specific types of ligands in the coordination compounds and their influence on the chemical nature of the metal and ligand study of their structure and properties are the contribution of both the fundamental knowledge of the chemistry of complex compounds and in related to the regulation of biological processes by metal ions. New data on the nature of the coordination of AA can improve the accuracy of predictions about the structure of the compounds studied yet and provide additional opportunities to improve techniques of directed synthesis of complexes of a given composition and structure [1-3].

The purpose of the article is to study the interaction of K_2ReBr_6 salt with p-aminobenzoic acid (p-ABA) in hydrobromic acid medium and the effect of hydrobromic acid concentration on the complexation of p-ABA with K_2ReBr_6 based on dynamic light scattering (DLS) and electronic absorption spectroscopy (EAS) in the UV and visible region.

EXPERIMENTAL

The used reagents: HBr acid, grade " Pure " , the manufacturer ReaChem. , Russia, p- aminobenzoic acid, grade "Chemically pure" , the manufacturer ReaChem., Russia , $KReO_4$, grade "Chemically pure" , the manufacturer ReaChem., Russia, distilled water. K_2ReBr_6 obtained by a known method described in [K.B.Lebedev.Rhenium, Second Edition , State Sci.-Technical Publ. House , M. , 1963.208 p. (in Russian)] , by reduction of potassium perrhenate $KReO_4$ with excess amount of potassium iodide (KJ) in the medium 7M HBr hydrobromic acid :

$$2KReO_4 + 6KJ + 16HBr \rightarrow 2K_2ReBr_6 + 4KBr + 3I_2 + 8H_2O$$

Then obtained solution was allowed to air. A few hours later well formed K_2ReBr_6 crystals of dark red color are precipitated. In this reaction Re^{7+} reduced to Re^{4+}.

Preparation of complexes. K_2ReBr_6 complexes with p- ABA were obtained at a ratio mol per mol (1:1, 1:2, 1:4, 1:8, 1:32) in HBr acid medium. K_2ReBr_6 powder in an amount of 0.744 grams was mixed well in a mortar p-ABA powder in an amount of 0.137 grams with the addition of 2-3 drops of HBr acid and heated at 45 C for 30 min. So, there was prepared K_2ReBr_6 with p- ABA (1:1). By the same way the other complexes were obtained. Then, before the DLS and ESP measurements the obtained complexes were transferred to a desiccator. Also before the DLS and EAS measurements solutions with the different concentration of these complexes were prepared. 10 mg of each complex dissolved in 10 ml of HBr acid solution and before the each next measurement the solution in cuvette was twice diluted. DLS measurements were carried out and EAS standard for spectrophotometric measurements and DLS with the same cuvette with the width of 1 cm. Spectrophotometric measurements were made with a UV/VIS spectrophotometer. Linear sizes of the complexes formed in solution, their size distribution were studied by dynamic light scattering method using an apparatus LB-550, Horiba. The essence of the method is to measure the time-dependent fluctuations in the intensity of the scattered light from the particles that are in a random Brownian motion in the liquid phase. In liquids with suspended fine particles of random Brownian motion of dispersed particles causes fluctuations in their local concentration. In turn, these fluctuations lead to local inhomogeneities of the refractive index of the medium and light is scattered by these irregularities. The fluctuations of the scattered light intensity fluctuations correspond to the local concentration of the dispersed particles and the diffusion coefficient is uniquely associated with the radius of the particle [4-6]. For spherical particles can be used the Stokes-Einstein formula: $D = k_B T / 6\pi\eta R$, where k_B - Boltzmann constant, T - absolute temperature, and η-viscosity of the solution in which particles with the radius R are suspended. Used analyzer allows to explore the processes of complex formation in the temperature range 278-343 K and particles diameter range 0,001-6 *µm*. The device provides automatic calculation of the backscattering by the Mie theory for spherical particles and irregular particles (needle-like) shape. Correct measurement results when analyzing the particle size distribution measurements confirmed the standard for calibration of the system. Light source - 650 nm, 5mW, diode laser.

Electronic absorption spectra (EAS) detected using a spectrophotometer UV/VIS, Specord, Germany in the wavelength range 200-800nm in a temperature range of 293-353 K. Alfa FT-IR (Bruker, Germany) spectrometer is used for measuring the infrared spectra of complexes at room temperature in the range 350-7800 cm^{-1} (wavenumber accuracy: 0.01 cm^{-1}).

RESULTS AND DISCUSSION

Figure 1, a,b shows the DLS spectra at 298 K of K_2ReBr_6/p-ABA complexes in aqueous HBr (7M) solutions with the ratio (mol to mol) 1:1 (a) and 1:4 (b). As shown from the fig. 1 at 298 K in the HBr/water solutions containing K_2ReBr_6 and p-ABA stabilized clusters with the sizes of hydrodynamic radius in the range 0.01-2,8 *µm*. The DLS picture changes over time after twice dilution of this solution with distilled water are shown in fig.2a-c.

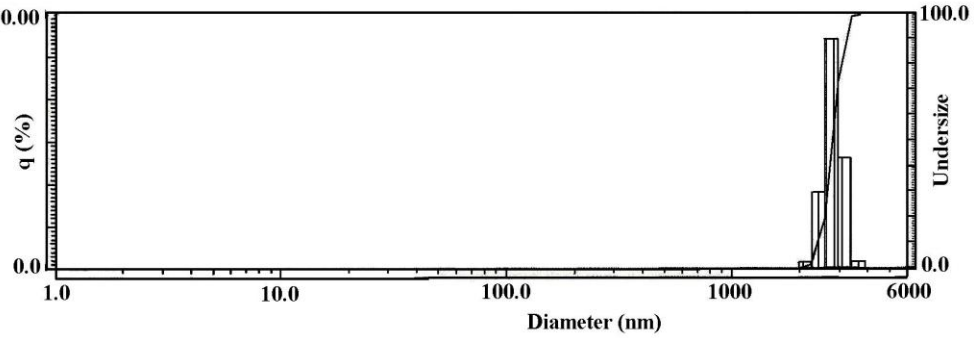

Figure 1,a.

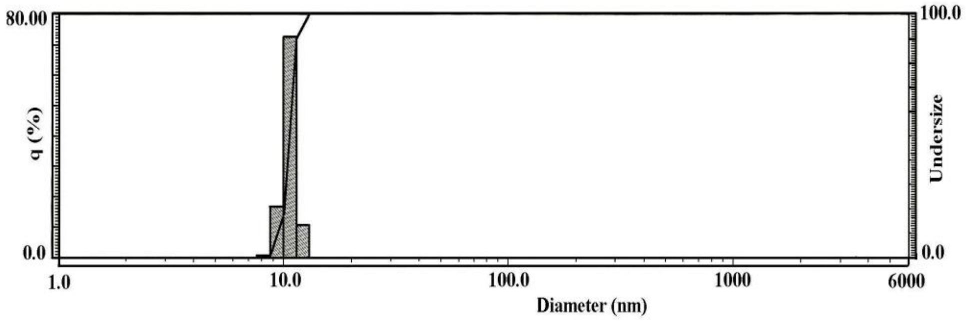

Figure 1,b.

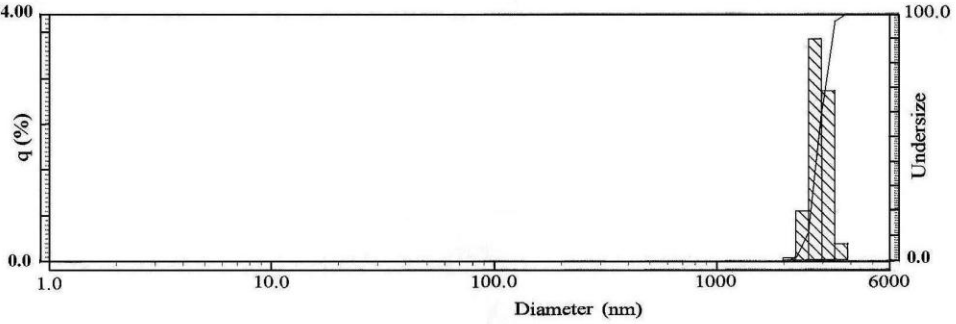

Figure 2,a.

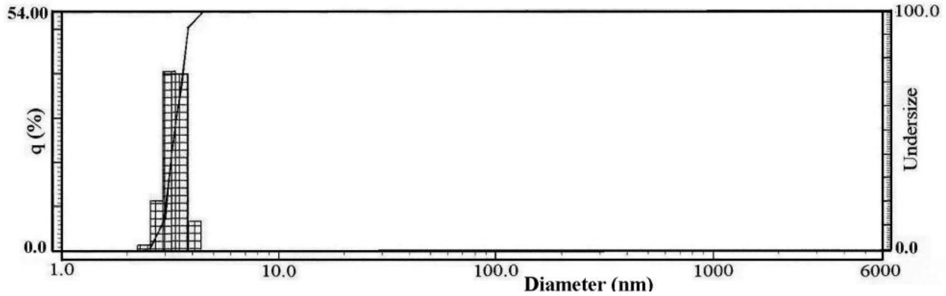

Figure 2,b

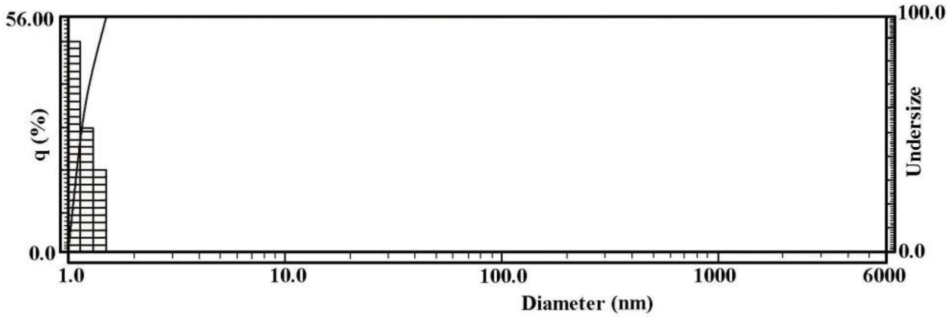

Figure 2,c.

Electronic absorption spectra of K_2ReBr_6 and products of its interaction with p-aminobenzoic acid in solutions of HBr found a wide range of absorption bands between 200-800nm (fig 3,4).

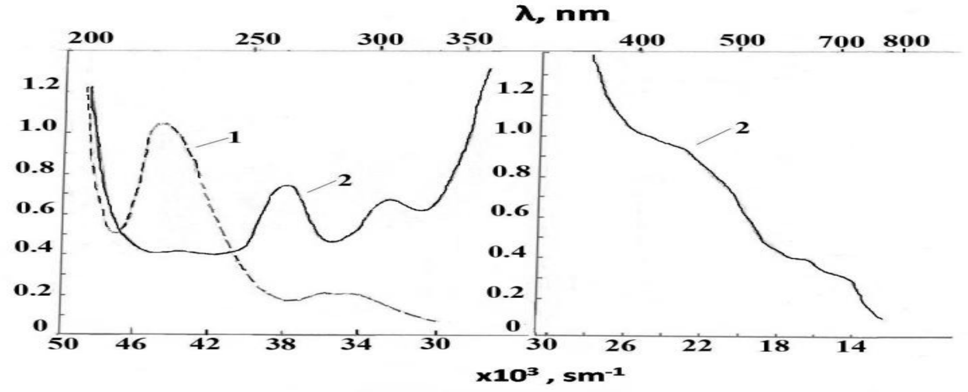

Figure 3.

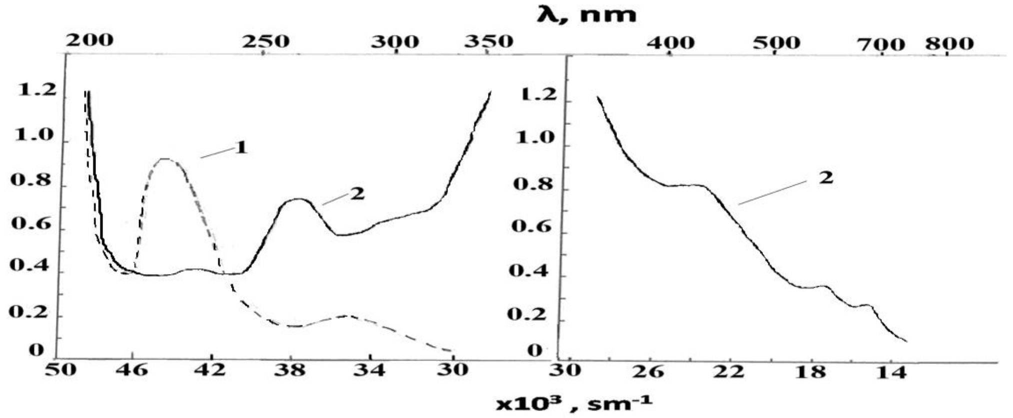

Figure 4.

The spectra marked as 1 in fig. 3 and 4 belong to HBr solutions of p-ABA. The spectra marked as 2 belong to HBr solutions of K_2ReBr_6/p-ABA complex with the ratio (mol/mol): amino acid / rhenium salt = 1:1 before dilution (fig.3) and after dissolution with 7M HBr acid of precipitate formed in diluted solution (fig.4). These spectra are typical for Re^{4+} complexes with chromophore $[ReBr_6]^{2-}$, and Re^{5+} with chromophore $[ReOBr_5]^{2-}$ with octahedral structure of the local environment of the rhenium ion [7,8]. Note that these spectra are obtained by dissolution of ReO_2 in concentrated HBr in air, the detected spectra in the wavelength range 240 - 800 nm in this case are likely attributed to pentavalent oksobromid rhenium complex $[ReOBr_5]^{2-}$. Noticeable changes appear in the range of absorption band at 420 nm when ReO_2 powder is dissolved in hydrobromic acid at a concentration of less than 7M, that probably due to the formation of hydrated oksobromide rhenium (V) complexes.

Thus, the presented results of this study show the complicated nature of complex formation in the system K_2ReBr_6/p-ABA/HBr as a function of HBr acid concentration. The formation and coexistence of nano- and micro-sized complexes with a hydrodynamic radius in the range of 0.001-2.8 microns and a different composition in these solutions are due to their dependence on the concentration of hydrobromic acid.

Role of HBr acid concentration. The concentration of hydrobromic acid significantly affects on complexation of K_2ReBr_6 with p-ABA. At lower concentrations of HBr acid 4 mol/l (4M HBr) we have the gradual hydrolysis of the obtained complex, i.e. the replacing of Br-ions by hydroxyl groups which is accompanied in further with the destruction of the complex obtained by the scheme:

$$[\text{p-ABAH}]_2[ReBr_6] + HOH \rightarrow [\text{p-ABAH}]_2[ReBr_5(OH)] \rightarrow \ldots \downarrow ReO_2$$

Visually the precipitation of ReO_2 as a dark blue, almost black powder is observed. Note that the HBr acid in the reaction plays the role of a protonating agent of p-aminobenzoic acid according to the scheme:

$$HCOOC_6H_4NH_2 + HBr \rightarrow HCOOC_6H_4NH_3^+Br^-$$

The obtained "onium" ion of p-amino benzoic acid is included in the outer sphere of the complex. The reaction proceeds with a reduction of Re^{6+} to Re^{4+} ions, but with the conservation of the number of bromide ions in the inner sphere $[ReBr_6]^{2-}$.

$$K_2ReBr_6 + HCOOC_6H_4NH_2 + 2HBr \rightarrow [HCOOC_6H_4NH_3^+]_2[ReBr_6]^{2-} + 2KBr$$

The resulting complex is characterized by IR spectra. A characteristic absorption band of carboxyl groups in the above complex appears at 1725 cm^{-1}. The free ligand in the IR spectra of this band appears at 1620 cm^{-1}. This indicates that in the resulting complex the carboxyl group is not involved in complexation directly through this group.

CONCLUSION

The used technique and their experimental possibilities allow to evaluate the linear sizes of the particles in the system K_2ReBr_6 / p-aminobenzoic acid/HBr/H2O and to record electronic state for this solution practically in the same conditions of measurements. How to correlate DLS and EAS measurements? It is obviously the particle size and electronic state characteristics of the system are linked. Electronic state of a particle depends of course on the size of the particle. It also depends on the particle shape, composition, etc.. Are the observed DLS and EAS spectra belong to the same structure? The answer to this question requires additional theoretical and experimental researches. The aim of this work primarily is to present experimental results that may be further examined in this direction. Concerning of this case we have very interesting perspective to combine electronic and dimensional characteristics of supramolecular structures, clusters of large molecules, etc. For the same solution in the same cuvette with a thickness of 1 cm were recorded as DLS and EAS spectra. By DLS we obtain the linear dimensions of complex, its adducts, clusters, aggregates, if they are existence in the solution and their sizes are in the range of 1 nm to 6 microns. In EAS we were recorded electronic transitions for solutions of these complexes. As can be seen electronic and dynamic light spectra are very sensitive to any changes in the system based on the p-ABA and Re salt.

Figure captions.

Figure 1, a, b. DLS picture at 298 K when HBr solutions of K_2ReBr_6 aminobenzoic acid complexes with a ratio (mol/mol) of the amino acid / salt of rhenium: a) 1:1, b)1:4.

Figure 2, a-c. DLS picture of 1 mg K_2ReBr_6/aminobenzoic acid complexes with ratio (mol/mol): amino acid / rhenium salt = 1:1 in 10 ml of 7M HBr solution at 298 K after twice dilution with distilled water over the time: a) 2, b) 20, c) 30 min.

Figure 3. EAS spectra of : 1–p-ABA/HBr and 2 - K_2ReBr_6/aminobenzoic acid / HBr solutions with ratio (mol/mol): amino acid / rhenium salt = 1:1 at 298K.

Figure 4. EAS spectra of dissolved in powder ReO_2 in 7M HBr acid precipitated from the twice diluted with distilled water of the initial HBr solutions of: 1 –p-ABA and 2 - K_2ReBr_6/aminobenzoic acid mix with ratio (mol/mol): amino acid / rhenium salt = 1:1 at 298 K.

REFERENCES

1. Panyushkin V.T., Bukov N.N., Bolotin S.N., Volinkin V.A. The coordination chemistry of natural amino acids. Moscow: Nauka, (Russia). 2007. p.247.

2. Golovniov N.N., Novikova G.V. and others. Synthesis of compounds of elements with d-amino acids //Herald KSU. Natural Sciences, Krasnoyarsk State University,Russia, 2006, № 2 - p.38-44.

3. Kerimova U.A., Osmanov N.S., Akhmedov M.M., Khudaverdiyev R.A, Abbasov J.A "Synthesis and properties of complexes of rhenium(IV) with aminoacetic acid. "// Chemical problems (Azerbaijan), 2008, №2, p.277

4. Berne, B.J.; Pecora, R. Dynamic Light Scattering with applications to Chemistry, Biochemistry and Physics, Courier Dover Publications, 2000, 377 ps.

5. Fröba A.P., Leipertz A. Diffusion Measurements in Fluids by Dynamic Light Scattering// Diffusion Fundamentals, 2005, 2, 63.1 - 63.25

6. Dynamic Light Scattering Particle Size Analyzer LB-550, Instruction Manual, HORIBA, March 2009, 195 ps.

7. Rulfs C.L., Meyer R.J.. Rhenium(IV) Compounds: Synthesis aand Properties. J.Amer.Chem.Soc.,v.77, N17, pp. 4505-4507,1955.

8. Lever A.B.P. Inorganic Electronic Spectroscopy (Second Edition), Elsevier Science Pullishers B.V.1984, 944 ps.