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SYNTHESIS AND STRUCTURE OF NEW COMPLEXES BASED ON SİLVER NANOPARTICLES, RHODAMINE REAGENT AND CETYLTRIMETHYLAMMONIUM BROMIDE

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The synthesis of new complexes based on silver nanoparticles (AgNPs), the rhodamine reagent (R6G), and cetyltrimethylammonium (CTAB) was carried out, and the optimal conditions for their production were determined. The interaction between rhodamine and Ag nanoparticles, as well as the nature of the synthesized complexes, was studied using infrared (IR) and ultraviolet (UV) spectroscopic analysis methods. The UV analysis revealed that the maximum absorption peaks of R6G are observed at wavelengths of 224 nm, 268 nm, and 304 nm, corresponding to the π-π transition of the C-C bond and the n-π* transition between the C=N groups. Due to the surface plasmon resonance of the binary complex, new peaks appear in the absorption spectra at wavelengths of 242 nm, 271 nm, and 308 nm. In the ternary complex, peaks in the absorption band are observed at wavelengths of 215 nm, 243 nm, and 278 nm. The spectroscopic properties of R6G and its binary and ternary complexes were further investigated through IR analysis. The aromatic C-H bonds of the phenyl group appear in the range of 3000-3100 cm^{-1}, while the C=C bonds of the phenyl group are found around 1500-1600 cm^{-1}. The carbonyl (C=O) bonds of the carbazide group are observed in the range of 1650-1700 cm^{-1}. Peaks associated with the N-H groups are found between 1400-1600 cm^{-1}. The interaction between rhodamine and AgNPs was assessed by analyzing the shifts and intensity changes in the IR absorption bands.*

Keywords: *silver, nanoparticle, CTAB, complex, reagent*

INTRODUCTION

Recent interest in the use of silver nanoparticles (AgNPs) in spectrophotometry as an alternative to classical spectrophotometric reagents is linked to the effect of surface plasmon resonance in nanoanalytical chemistry. The advantages of silver NPs as spectrophotometric reagents include relative ease of production, high molar absorption coefficients, and the ability to tune their spectral properties by changing the size, shape, and chemical environment of the nanoparticles [1-6]. The use of silver nanoparticles in spectrophotometry opens up new opportunities for the development of rapid and cost-effective methods for determining metal cations, anions, and organic compounds. Surface plasmon resonance (SPR) is a key property of AgNPs, providing them with unique optical characteristics [7-12]. The application of silver nanoparticles in spectrophotometric analysis relies on the strong dependence of the absorption maximum of the SPR band on the degree of aggregation of the nanoparticles in the presence of various analytes. Silver NPs are often used for the spectrophotometric determination of various organic compounds and metal ions, and in some cases, for the determination of anions. The nature of the stabilizer used during the synthesis significantly affects the properties of silver NPs as reagents for spectrophotometric analysis. The use of cationic stabilizers is particularly promising, as these cations can influence the formation of nanoparticles and their stability due to their high charge density. AgNPs exhibit specific bands in UV-Vis spectra (390-440 nm), depending on their size, shape, and dielectric medium. For this reason, pre-synthesized AgNPs are widely utilized for the spectrophotometric determination of metal cations, anions, and organic compounds in analytical chemistry. By varying the nature of the stabilizer and its amount in the reaction mixture, the size and charge of the nanoparticles can be controlled. Rhodamine B, a textile dye, is toxic to humans. When ingested with food, it can enter the body and cause oxidative stress in cells and tissues. Rhodamine and its derivatives are fluorescent probes that interact with all types of biomolecules. Their fluorescent properties arise from the presence of a planar, multi-ring aromatic xanthene core structure, which, in this case, features nitrogen atoms replacing oxygen in the outer parts. Rhodamines are synthetic dyes characterized by a general xanthene structure. They are known for their vivid colors and high fluorescence, making them widely used in biochemical studies, imaging, and labeling. In the presented article, the synthesis of new complexes based on silver nanoparticles (AgNPs), the rhodamine reagent (R6G), and cetyltrimethylammonium (CTAB) was conducted, and the optimal conditions for their preparation were determined. The structure of the obtained complexes was studied using IR and UV spectroscopy methods. The potential applications of the synthesized complexes in the determination of various ions in analytical chemistry were also investigated [13-18].

EXPERİMENTAL PART

MATERIAL AND METHODS

Silver nitrate $AgNO_3$ (PLC 141459), soluble starch ($C_6 H_{10} O_5$) n (PLC 121096), β-D glucose $C_6 H_{12} O_6$; sodium hydroxide NaOH (PLC 141687), CTAB (AB 117004) , Rhodamine B (CID 6694) were used as received

Synthesis of Ag nanoparticles.

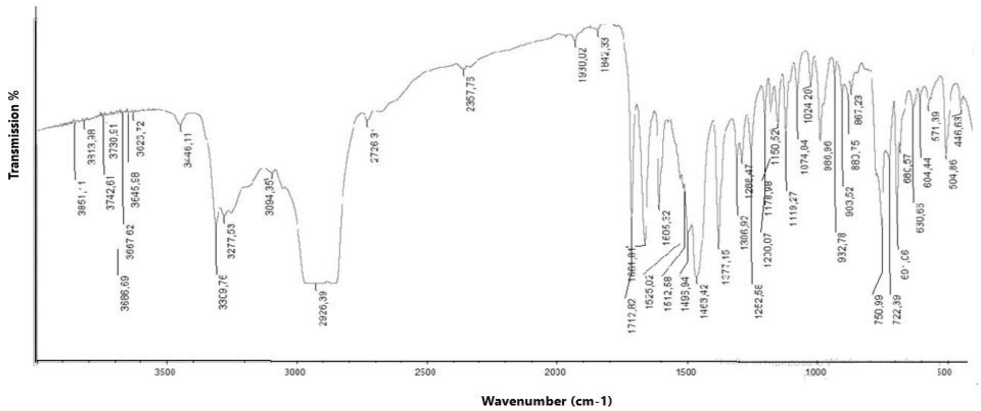
The synthesis and stabilization of silver nanoparticles (AgNPs) were carried out as follows: 150 mL of a 1% starch solution was added to 100 mL of a 0.01 M $AgNO_3$ solution. Next, 100 mL of a 0.2 M glucose solution was combined with 100 mL of a 0.07 M sodium hydroxide (NaOH) solution. The prepared NaOH and glucose solution was then added to the $AgNO_3$ and starch mixture and stirred for 30 minutes. The solution immediately turned dark brown, indicating the formation of a colloidal solution of Ag nanoparticles. To purify the Ag nanoparticles from extraneous and unreacted ions, they were separated using a 12,000 rpm R 5430 Eppendorf ultracentrifuge and washed several times with a mixture of water and ethanol. It is important to note that during the synthesis, dissolved starch acts as both a reducing agent and a stabilizer, NaOH serves as an accelerator, and glucose functions as a reducing agent.

Synthesis of the Ag+R6G+CTAB Complex

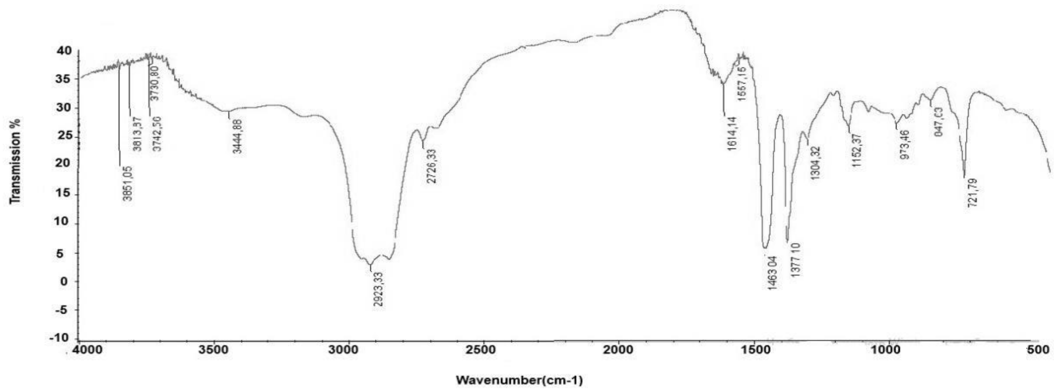
In this study, the synthesis of new complexes involving silver nanoparticles, the R6G reagent, and cetyltrimethylammonium bromide (CTAB) was conducted. First, a 10^{-3} M solution of the R6G reagent was prepared. Then, 10 mL of the 0.01 M silver nanoparticle solution was added to 50 mL of the 10^{-3} M R6G solution and mixed using a magnetic stirrer for 2 hours. During this process, the color of the solution changed from orange to red-purple, indicating the formation of a binary complex. To synthesize the ternary complex, an additional 10 mL of the 0.01 M silver nanoparticle solution was added to the 50 mL of the 10^{-3} M R6G solution and stirred for another 2 hours. After this period, 5 mL of a 0.5% 0.01 M CTAB solution was added, and stirring continued. At this stage, CTAB enhanced the stability of the complex by serving a stabilizing role in the formation of the silver nanoparticles-R6G complex. As a result, a ternary complex was obtained. Ultraviolet spectra were obtained at a wavelength of 200–900 nm at room temperature on a Specord 210 spectrophotometer. The IR spectra of the samples were measured on a Varian 3600 infrared spectrometer at a wavelength of 400-4000 cm-1 at room temperature.

RESULTS AND DISCUSSION

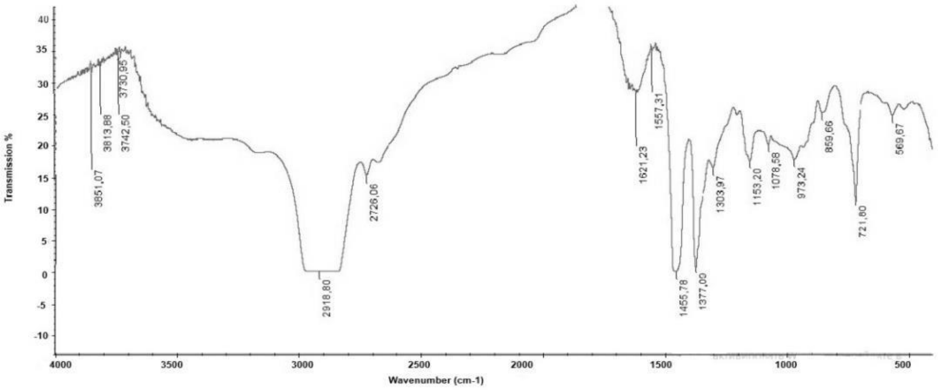
IR spectroscopy is one of the most widely used analytical methods for characterizing rhodamine and its metal complexes, providing valuable information about their molecular structure and interactions. The unique properties of these compounds allow for various scientific and industrial applications [19-20]. When a molecule absorbs IR radiation, the bonds within the molecule vibrate at characteristic frequencies. The resulting spectrum displays peaks that correspond to the functional groups and the overall molecular structure. Figure 1 shows the İR spectra of the Rhodamine reagent (a), the R+Ag binary complex (b), and the R+Ag+CTAB ternary complex (c). Rhodamine typically contains amine groups, which show N-H bonds in the range of 3300-3500 cm⁻¹. The carbonyl group (C=O) of rhodamine contributes to a strong absorption peak around 1650–1700 cm⁻¹, indicative of its ether or carbonyl functionality. The presence of aromatic rings is evidenced by C=C bonds, usually observed in the range of 1400-1600 cm⁻¹. Additionally, the IR spectrum of rhodamine features specific peaks between 600-1400 cm⁻¹ that confirm the presence of the xanthene structure. When rhodamine forms complexes with metals, noticeable shifts in the IR spectrum occur. Coordination with metals often affects the peaks associated with C=O and N-H bonds, highlighting the interactions between rhodamine and the metal ions.



a)



b)



c)

Fig. 1. IR spectra of R (a), Ag+R6G (b) and Ag+R6G+CTAB (c) complexes

Figure 2 shows the UV spectrum of binary and ternary complexes formed by silver nanoparticles, rhodamine, and CTAB. As observed in Figure 2, the absorption band of the rhodamine reagent in the ultraviolet region lies within the range of 250-350 nm, with maxima at 224 nm, 268 nm, and 304 nm, corresponding to the π-π* transition of the C-C bond and the n-π* transition of the C=N groups. Upon adding silver nanoparticles at a concentration of 0.01 M to rhodamine, a bathochromic shift occurs, resulting in new peaks at 242 nm, 271 nm, and 308 nm in the absorption curves of the binary complex. This shift is attributed to surface plasmon resonance, and the color changes from orange to violet. The appearance of new peaks at longer wavelengths is due to the aggregation of Ag nanoparticles. When CTAB is added as a stabilizer to the binary complex, certain shifts in the spectrum occur, resulting in the formation of a ternary complex. The absorption peaks of the Ag-R6G-CTAB ternary complex shift to wavelengths of 215 nm, 243 nm, and 278 nm, respectively. These shifts are attributed to quantum size effects. The formation of complexes with the rhodamine reagent through the coating of Ag nanoparticles with the surfactant explains the new peaks in the absorption band due to surface plasmon resonance and the change of color from orange to dark purple due to nanoparticle aggregation. These color changes indicate the reduction of Ag+ ions to Ag0. During this aggregation, a hypochromic shift occurs in the binary complex. In Figure 2, the shift in the spectrum of silver nanoparticles compared to the spectra of the reagents and complexes is related to the magnitude of the plasmon frequency of silver. As indicated in Figure 2, the plasmon frequency of silver nanoparticles is greater than that of the complexes.

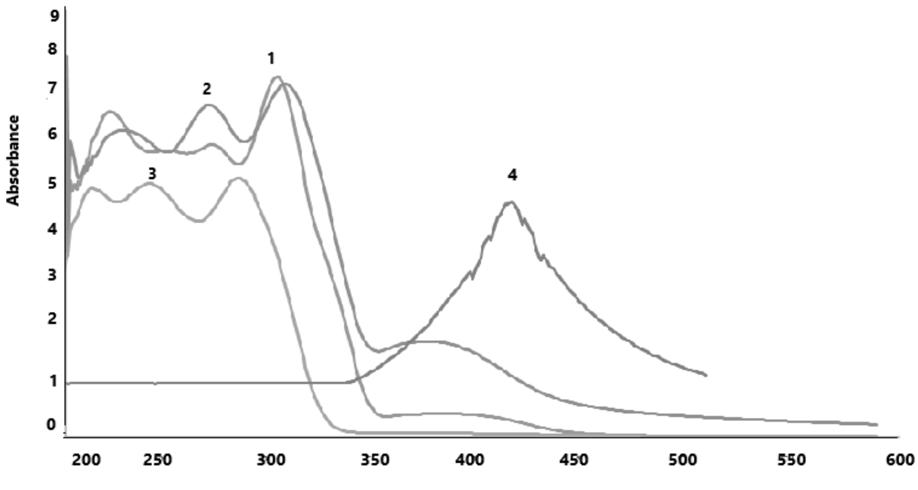


Fig. 2. UV spectra of R (1), Ag+R6G (2), Ag+R6G+CTAB (3) complexes and silver nanoparticles

CONCLUSION

In the presented work, the synthesis of new complexes based on silver nanoparticles, rhodamine, and cetyltrimethylammonium (CTAB) was carried out, and the optimal conditions for their synthesis were determined. The synthesized complexes were studied using IR and UV spectroscopy. The UV analysis revealed the formation of new maximum peaks at wavelengths of 242 nm, 271 nm, and 308 nm in the absorption curves associated with the surface plasmon resonance of the binary complex formed as a result of adding silver nanoparticles to the rhodamine reagent. For the ternary complex formed by adding CTAB as a stabilizer to the Ag-rhodamine complex, the absorption peaks shifted to 215 nm, 243 nm, and 278 nm, respectively. The IR spectrum of rhodamine showed the presence of N-H bonds in the range of 3300-3500 cm^{-1}, a carbonyl group (C=O) around 1650-1700 cm^{-1}, and aromatic rings in the range of 1400-1600 cm^{-1}. It also confirmed the presence of C=C bonds, providing detailed information about its chemical composition. In particular, specific peaks indicating the presence of the xanthene structure in the range of 600-1400 cm^{-1} further confirmed the chemical properties of rhodamine.

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GÜMÜŞ NANOHİSSƏCİKLƏRİ, RODAMİN REAGENTİ VƏ SETİLTRİMETİLAMMONİUM BROMİD ƏSASINDA YENİ KOMPLEKSLƏRİN SİNTEZİ VƏ QURULUŞU

A.A. İmaməliyeva, F.V. Hacıyeva, F.M. Çıraqov

Təqdim olunan işdə gümüş nanohissəcikləri (AgNP), rodamin reagenti (R6G) və setiltrimetilammonium(STABr) əsasında yeni komplekslərin sintezi həyata keçirilmiş və alınmanın optimal şəraitləri müəyyən edilmişdir. Rodamin Ag nanohissəcikləri ilə qarşılıqlı əlaqəsi,sintez edilmiş komplekslərin təbiəti infraqırmızı (İQ) və ultrabənövşəyi (UB) spektroskopiya analiz metodları ilə tədqiq edilmişdir. UB analizlərdən aydın olmuşdur ki, R reagentinin maksimum pikləri C-C rabitəsinin π-π * keçidinə və C=N qrupları arasındakı n-π* keçidinə uyğun olaraq 224 nm, 268 nm, 304 nm dalğa uzunluğunda müşahidə olunur. İkili kompleksin səthi plazmon rezonans hesabına absorbsiya əyrilərində 242 nm, 271 nm, 308 nm dalğa uzunluğunda yeni piklərin yaranması ilə nəticələnir. Üçlü kompleksin udma zolağındakı piklər 215 nm, 243 nm və 278 nm dalğa uzunluğunda müşahidə olunur. İQ analizlərdən R6G-nin və ikili, üçlü komplekslərinin spektroskopik xüsusiyyətlərini araşdırılmışdır. Fenil qrupunun aromatik C-H rabitələri 3000-3100 sm^{-1}-də, fenil qrupundakı C=C rabitələri təxminən 1500-1600 sm^{-1}, karbazid qrupunun karbonil (C=O) rabitəsinin pikləri 1650-1700 sm^{-1} diapazonda yaranır. N-H qrupları arasındakı pikləri təxminən 1400-1600 sm^{-1}-də özünü göstərir. İQ spektroskopiya udma zolaqlarında sürüşmələri və intensivlik dəyişikliklərini təhlil edərək, rodaminin AgNP-lərlə qarşılıqlı əlaqəsi araşdırılmışdır.

Açar sözlər: *gümüş, nanohissəcik, STAB, kompleks, reagent*

СИНТЕЗ И СТРУКТУРА НОВЫХ КОМПЛЕКСОВ НА ОСНОВЕ НАНОЧАСТИЦ СЕРЕБРА, РОДАМИНОВОГО РЕАГЕНТА И БРОМИДА ЦЕТИЛТРИМЕТИЛАММОНИЯ

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Проведен синтез новых комплексов на основе наночастиц серебра (AgNP), родаминового реагента (R6G) и цетилтриметиламмония (CTAB) и определены оптимальные условия их получения. Взаимодействие родамина и наночастиц Ag, а также природа синтезированных комплексов изучены с использованием методов инфракрасного (ИК) и ультрафиолетового (УФ) спектроскопического анализа. УФ-анализ показал, что максимальные пики поглощения R6G наблюдаются на длинах волн 224 нм, 268 нм и 304 нм, что соответствует π-π*-переходу связи C-C и n-π*-переходу между группами C=N. Вследствие поверхностного плазмонного резонанса бинарного комплекса в спектрах поглощения появляются новые пики на длинах волн 242 нм, 271 нм и 308 нм. В тройном комплексе пики в полосе поглощения наблюдаются при длинах волн 215 нм, 243 нм и 278 нм. Спектроскопические свойства R6G и его бинарных и тройных комплексов были дополнительно исследованы с помощью ИК-анализа. Ароматические связи C-H фенильной группы появляются в диапазоне 3000-3100 $см^{-1}$, в то время как связи C=C фенильной группы находятся около 1500-1600 $см^{-1}$. Карбонильные (C=O) связи карбазидной группы наблюдаются в диапазоне 1650-1700 $см^{-1}$. Пики, связанные с группами N-H, находятся между 1400-1600 $см^{-1}$. Взаимодействие между родамином и AgNP оценивалось путем анализа сдвигов и изменений интенсивности в полосах поглощения ИК.

Ключевые слова: *серебро, наночастица, CTAB, комплекс, реагент*