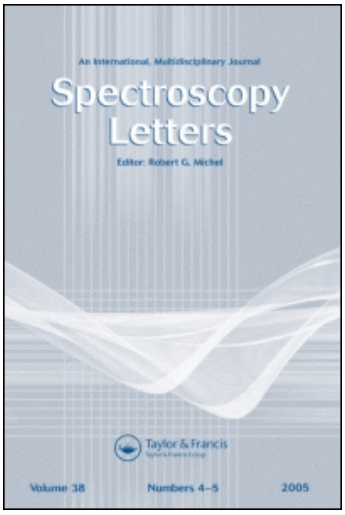

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UV-Visible Absorption Studies of Gossypol-Metal Cation Complexes in Acetonitrile Solution

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UV-VISIBLE ABSORPTION STUDIES OF GOSSYPOL-METAL CATION COMPLEXES IN ACETONITRILE SOLUTION

Key Words: Gossypol, gossypol-metal cation complexes, uv-visible absorption spectroscopy

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ABSTRACT

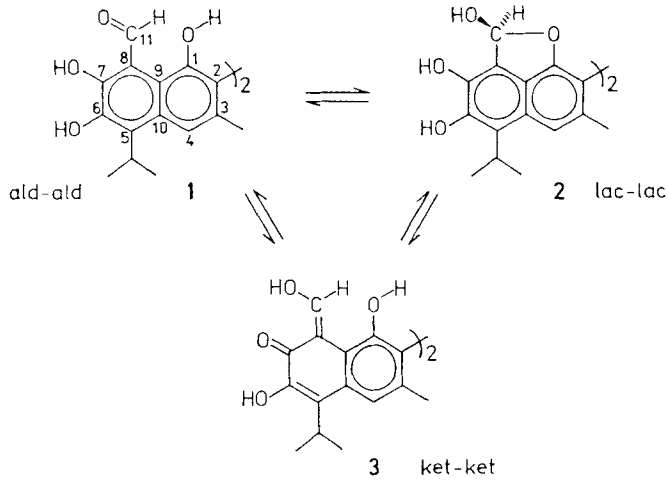
The systems of gossypol-metal cation in acetonitrile have been studied by UV-visible absorption spectroscopy. The formation of 1:1 complexes between gossypol and Be^{+2}, Cu^{+2}, Dy^{+3}, and Zn^{+2} has been proved and their formation constants, K, have been determined to be of an order of 10^4 M.

INTRODUCTION

Gossypol, 2,2′- bis (8 -formyl- 1,6,7- trihydroxy-5-isopropyl-3-methylnaphthalene), is a yellowish compound occuring in various parts of cotton plants [1]. The structure of gossypol has been confirmed by total

synthesis [2,3] and its physical and chemical properties have been described by Adams et al.[4]. Biological importance of gossypol, e.g. its contraceptive and toxic activities [4-6], was the reason for many recent extensive studies in solution [7-14].

Gossypol can occur in three symmetric tautomeric forms in solution[15]:



In nonpolar solvents it is present in aldehyde form, whereas in polar solvents the equilibrium between aldehyde and lactol tautomers depends on the nucleophilicity of the solvent used [9,10]. In alkaline solution of gossypol, ketol tautomer was found to be the main tautomeric form[16].

It was shown recently by means of FTIR spectroscopy that gossypol can form a 1:1 complex with Be^{+2} cation in acetonitrile[13]. With this complexation tautomeric form of gossypol is completely shifted from aldehyde to lactol form. In this paper the complexation of gossypol

with cations of various metals in acetonitrile is studied by UV-visible absorption spectroscopy.

EXPERIMENTAL

Yellow microcrystalline pure gossypol obtained from the Institute of Bioorganic Chemistry, Academy of Sciences of UzSSR, Tashkent, USSR, was recrystallized twice from hexane (m. p. 180 - 181 ^{0}C; Elemental Anal., calc. for $C_{30}H_{30}O_{8}$ (%): C,69.5; H,5.79; found: C, 69.3; H,5.74). The perchlorates of Mg^{+2}, Cu^{+2}, Na^{+}, Ni^{+2} and Dy^{+3} have been obtained and purified according to the known methods[17], whereas $Be(AuCl_4)_2$ as in ref. 13. Acetonitrile (spectra grade, Merck) stored over 3A molecular sieves was used without further purification.

UV-visible absorption spectra were recorded using Specord M-40 (Zeiss) and 8452A Diode Array (Hewlett Packard) spectrophotometers.

RESULTS AND DISCUSSION

UV-visible absorption spectra of gossypol (aldehyde tautomer) consists of three well separated bands, and they are well reproduced by semiempirical INDO/S CI calculations[14]. The position of absorption maxima and the values of molar absorption coefficients significantly depend on the solvent used and this can be explained by the way various solvents influence the aldehyde-lactol equilibrium[18].

In acetonitrile solution gossypol exists mainly in the aldehyde form with the longwavelength absorption band at about 370 nm. (The longwavelength absorption band of lactol form appears at about 320 nm[18].) Addition of metal cations (Me^{+n}) to this solution leads to the appearance of a new absorption band about 430 nm and the vanishing of the gossypol band at 370 nm with some isosbestic points. Typical changes in the absorption

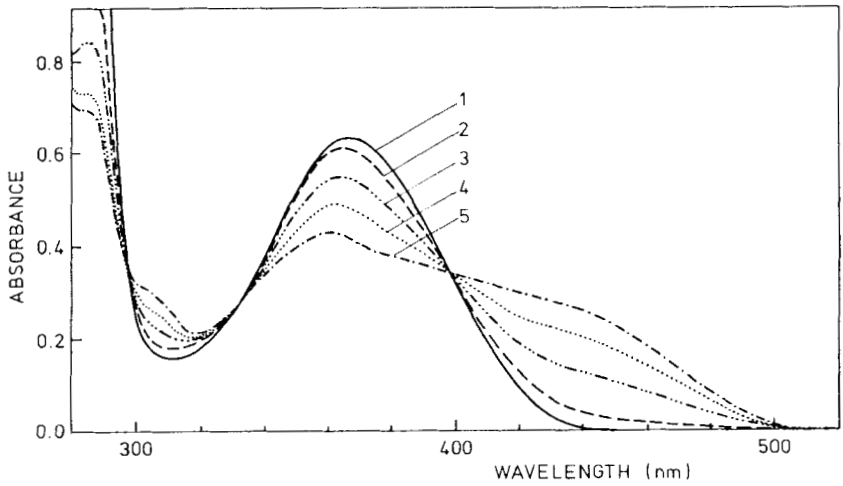


Fig.1. Changes in the absorption spectra of the gossypol-Cu^{+2} system in acetonitrile solution at room temperature. Concentration of gossypol equal to 4×10^{-5} M in each sample; 1: without $Cu(ClO_4)_2$; 2: 0.8×10^{-5}M $Cu(ClO_4)_2$; 3: 2.0×10^{-5}M $Cu(ClO_4)_2$; 4: 3.5×10^{-5}M $Cu(ClO_4)_2$; 5: 4.0×10^{-5}M $Cu(ClO_4)_2$.

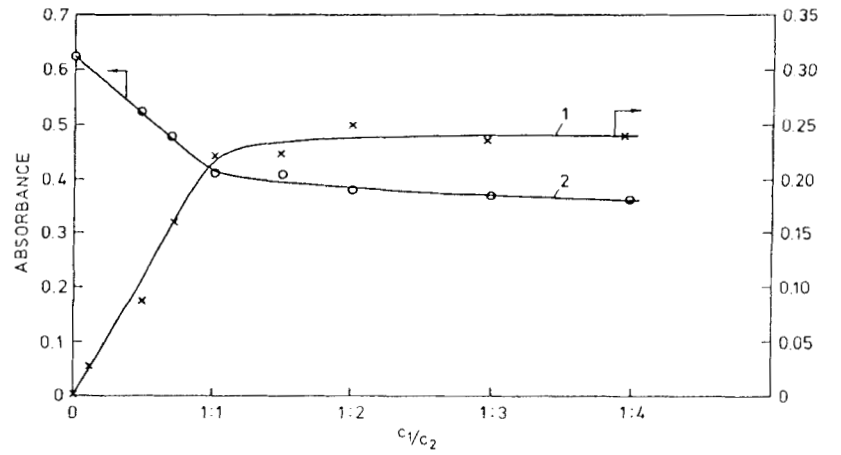


Fig.2. Absorbance at 450 nm (curve 1) and at 370 nm (curve 2) versus ratio of molar concentrations of gossypol and Cu^{+2} in acetonitrile.

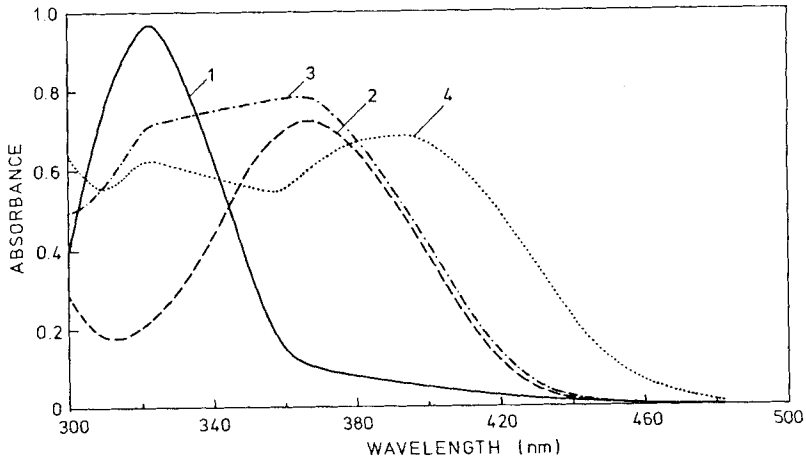


Fig.3. Absorption spectra of $Be(AuCl_4)_2$ (4.0×10^{-5} M) - curve 1; gossypol (4.0×10^{-5} M) - curve 2; calculated sum of spectra 1 and 2 - curve 3; observed spectrum of 1:1 gossypol- $Be(AuCl_4)_2$ system - curve 4 in acetonitrile.

spectra of gossypol in acetonitrile with the addition of copper(II) perchlorate are presented in Figure 1, and changes of absorbance at 450 nm and 370 nm in Figure 2.

As it has been recently shown by FTIR studies[13] the addition of $Be(AuCl_4)_2$ to the gossypol in acetonitrile solution leads to the formation of 1:1 complex between gossypol and Be^{+2} ion. Figure 3 shows the formation of this complex studied by means of UV-visible absorption spectroscopy. Similar results to those presented in Figures 1-3 were also obtained for $Dy(ClO_4)_3$, $Zn(CH_3COO)_2$. The addition of perchlorates of Na^+, Mg^{+2} and Ni^{+2} to gossypol solution did not lead to the formation of a new longwavelength band that could be attributed to the complex formation.

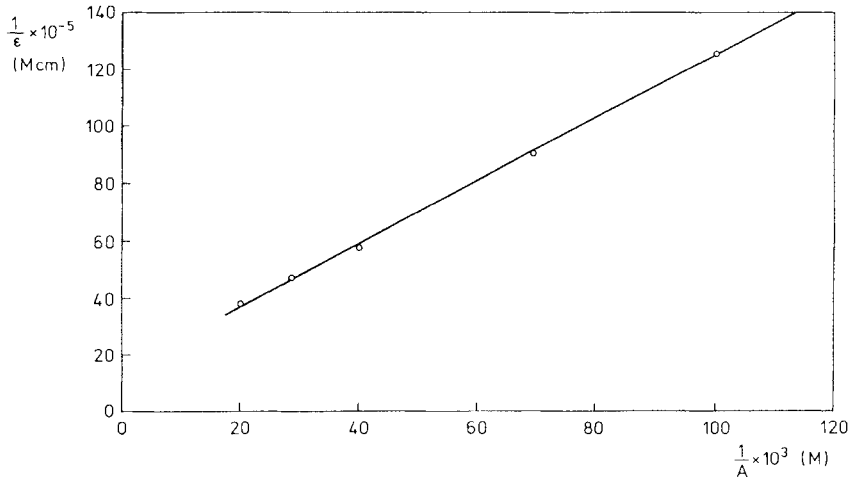


Fig.4. Dependence of $1/\varepsilon$ versus $1/[A]$ according to eq. (1) for the gossypol-$Be(AuCl_4)_2$ system in acetonitrile.

The influence of Cu^{+2} ions on the absorption spectra of gossypol (Figs.1 and 2) can be explained by the formation of a 1:1 complex between gossypol and copper cation. The decrease of the aldehyde tautomer absorption (at 370 nm) with addition of Me^{+n} ions as well as the results of FTIR studies obtained for Be^{+2} ions[13] suggest the presence of lactol tautomer in the gossypol-Me^{+n} complexes in acetonitrile.

The observed typical changes in the absorption spectra (Figs 1-3) confirm the formation of a 1:1 gossypol-Me^{+n} complex. Taking this fact into regard and making use of Eq. (1)[19] the formation constants (K) of the gossypol-Me^{+n} complexes can be determined:

$$\frac{1}{\varepsilon} = \frac{1}{K\,\varepsilon_c}\,\frac{1}{[A]} + \frac{1}{\varepsilon_c} \qquad (1)$$

where [A] is the molar concentration of Me^{+n} ,

TABLE 1

Formation Constants of the Gossypol-Me^{+n} Complexes in Acetonitrile at Room Temperature

Complex	$K \times 10^{-4}$ (M)
Gossypol- Be^{+2}	3.1 ± 0.3
Gossypol- Cu^{+2}	1.5 ± 0.2
Gossypol- Dy^{+3}	3.5 ± 0.9

ε=A/[Goss], A is the absorbance of gossypol-Me^{+n} system at 450 nm (l = 1 cm), ε_c is the molar absorption coefficient of the complex at 450 nm.

The typical results obtained for the gossypol-Be^{+2} complex are presented in Fig.4 and all data are summarized in Table 1.

The formation constants are in the range of 10^4 M for all complexes studied. They are similar to the values of formation constant for the acetylacetone-lanthanide(III) cation complexes in acetonitrile[20]. In the case of gossypol-$Zn(CH_3COO)_2$ system the UV-visible absorption spectra are more complex and show the presence of two longwavelength bands that can be attributed to two various complexes. Further IR and NMR studies on the nature of gossypol-Me^{+n} complexes in acetonitrile are in progress and will be presented in the paper to follow.

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