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Spectroscopic Study of 2,3-Bis(*p*-methoxybenzoyl)cyclopentadiene as Potential Iron(III)-Chelating Agent[1]

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Abstract—2,3-Bis(*p*-methoxybenzoyl)cyclopentadiene was studied as iron(III)-chelating agent. Its pK_a value was determined by spectrophotometry (pK_a = 8.27 ± 0.02 at 25 ± 0.1°C; λ = 421 nm). 2,3-Bis(*p*-methoxybenzoyl)cyclopentadiene reacts with Fe^{3+} ions in aqueous ethanol (1 : 1, by volume) to give a 2 : 1 ligand–metal complex. The effects of different factors on the complex formation were studied. The reaction of 2,3-bis(*p*-methoxybenzoyl)cyclopentadiene with Fe^{3+} ions can be used as an alternative method for spectrophotometric determination of iron(III) in a range of concentrations from 0.1 to 1 μg cm^{-3}, where the Beer law is fulfilled with a correlation coefficient of 0.9992. The results of spectrophotometric determination of iron(III) in geological materials (iron rock) showed very good agreement with those obtained by the atomic absorption measurements.

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2,3-Bis(*p*-methoxybenzoyl)cyclopentadiene belongs to the 1,2-diacylcyclopentadiene series [1–5] and exists exclusively in the enol form. Proton chemical shifts in the ^{1}H NMR spectra of these compounds suggest the presence of a very strong intramolecular hydrogen bond [4, 6, 7]. Gilli and Bertolasi [8] classified such compounds as γ-diketone enols which are potentially capable of forming complexes with metal ions. Linn and Sharkey [9] synthesized 2,3-dibenzoylcyclopentadiene in an inert atmosphere. However, any attempts to obtain sandwich-like complexes of iron with 2,3-dibenzoylcyclopentadiene were unsuccessful, which was attributed to π-electron delocalization in the cyclopentadiene ring [10]. Despite extensive studies on the complex formation with β-diketones [11, 12], to the best of our knowledge, no formation of complexes by this class of compounds has been reported.

Iron is the fourth most abundant element in the earth crust occurring in nearly all types of rocks and soil minerals as Fe^{2+} and/or Fe^{3+} [13]. As concerns its biological activity, iron is a highly versatile element serving as an active center of proteins responsible for oxygen and electron transfer in metal enzymes such as oxidases and dehydratases [14]. Highly sensitive methods for the determination of iron in environmental and biological samples have been developed. The oxidation state of iron in different samples is usually determined via complex formation with specific chelating agents, followed by spectroscopic measurements. Tiron (4,5-dihydroxybenzene-1,3-disulfonic acid) [15], 1-(2-pyridylazo)-2-naphthol (PAN) [16], dithiocarbonate [17], cupferron [18], 8-hydroxyquinoline [19], β-diketones [20], and many other chelating reagents were used for the determination of iron(III) after oxidation of iron(II). New chelating agents have been proposed for the determination of trace elements and preparation of chelating resins. Spectrophotometric [21, 22] or chemoluminescence detection [23, 24] and many other analytical methods have been developed for the determination of iron with high sensitivity.

In this paper we report on 2,3-bis(*p*-methoxybenzoyl)cyclopentadiene as a new ligand for spectrophotometric determination of Fe^{3+}. Bis(*p*-methoxybenzoyl)cyclopentadiene is poorly soluble in water but soluble in 50% aqueous ethanol. It is readily soluble in most organic solvents, such as acetone and benzene, as well as in aqueous alkali. The electronic absorption spectrum of bis(*p*-methoxybenzoyl)cyclopentadiene in 50% aqueous ethanol contains three main maxima at λ 421, 361, and 286.4 nm. The intensity of the first two maxima decreases as pH rises, and a new maxi-

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[1] The text was submitted by the authors in English.

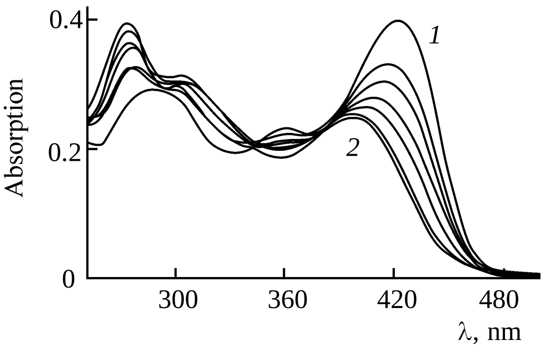

Fig. 1. Variation of the electronic absorption spectrum of 2,3-bis(*p*-methoxybenzoyl)cyclopentadiene (c = 2×10^{-5} M) in aqueous ethanol (1 : 1, by volume) vs. pH: (*1*) pH 5, (*2*) pH 10.

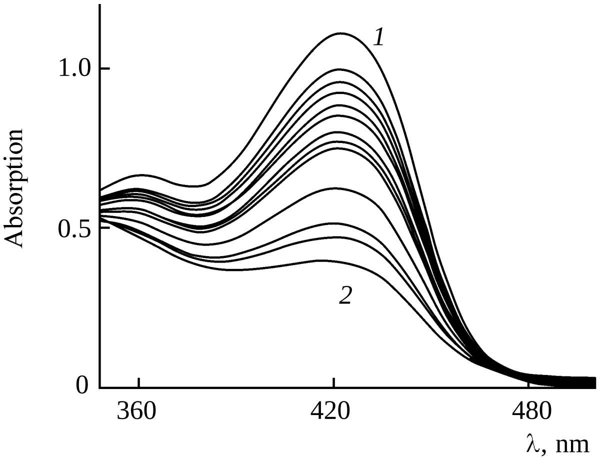

Fig. 2. Variation of the electronic absorption spectrum during complex formation of 2,3-bis(*p*-methoxybenzoyl)-cyclopentadiene (c = 2×10^{-5} M) with Fe^{3+} ions vs. concentration of the latter: (*1*) $c_{Fe^{3+}}$ = 0.1, (*2*) $c_{Fe^{3+}}$ = 1.5 μg ml^{-1}; pH 2.

mum appears in the UV region (λ 272.8 nm). The absorption curves of bis(*p*-methoxybenzoyl)cyclopentadiene in the pH range from 5.00 to 12.00 give an isosbestic point at λ 343 nm (Fig. 1), indicating acid–base equilibrium in solution. From the data obtained by spectrophotometric titration and the plot of absorbance versus pH, the pK_a value of this compound in 50% aqueous ethanol was estimated at 8.27 ± 0.02.

Bis(*p*-methoxybenzoyl)cyclopentadiene was quite stable in ethanol and aqueous ethanol on storage for over a month. The spectra of these solutions did not show any significant change.

Addition of Fe^{3+} to a solution of 2,3-bis(*p*-methoxybenzoyl)cyclopentadiene in aqueous ethanol (1 : 1, by volume) leads to lowering of the absorption intensity at λ 421 nm (Fig. 2). The conditions for effective complex formation we optimized by studying the effects of different factors, such as pH, reactant concentration, and ionic strength. The effect of pH was examined in the pH range 1–7; the required pH value was adjusted by adding $HClO_4$ or NaOH. The complexation starts at pH 1.0 and reaches its maximum at pH ~2.0, where the largest difference in the absorbances of the complex and the ligand is observed. A series of experiments was performed at pH ~2.0 to determine the stoichiometry of the interaction between 2,3-bis(*p*-methoxybenzoyl)cyclopentadiene and Fe^{3+} in solution. It was found that Fe^{3+} forms a 1 : 2 complex with the ligand. The effect of reactant concentration was studied in 0.1 M solutions of $NaClO_4$ (to maintain a constant ionic strength) containing 0.28 μg ml^{-1} of Fe^{3+}. The ligand concentration was varied in such a way that the ligand-to-metal ratios were within 1–10. The maximal difference in the absorbances of the ligand and the complex was observed at above 5-fold excess of the former. Further raising of the ligand-to-metal ratio almost did not affect the absorbance at λ 421 nm. Variation of the ionic strength through variation of the $NaClO_4$ concentration from 0.001 to 0.1 M did not cause appreciable change in the absorbance. We also examined the effect of foreign anions and cations on the complexation of iron(III) with bis(*p*-methoxybenzoyl)-cyclopentadiene. As tolerance limit we assumed that concentration of a foreign ion, which caused an error of no more than 5% in the determination of the analyte (see table). Among the examined foreign ions, only iodide (I^-) and hydrogen phosphate (HPO_4^{2-}) interfered significantly (>5%).

The calibration curve was plotted under the optimal conditions. The Beer law was fulfilled in the Fe^{3+} concentration range from 0.1 to 1 μg cm^{-3} (correlation coefficient r^2 = 0.9992, slope 2.45×10^4, intercept 0.0558); the detection limit was 0.06 μg ml^{-1} (n = 6); relative standard deviation 0.67% at $c_{Fe^{3+}}$ = 0.56 μg ml^{-1}.

The developed procedure was tested using geological materials. The results are given below [concentration of 2,3-bis(*p*-methoxybenzoyl)cyclopentadiene 5×10^{-5} M, 50% aqueous ethanol; E_R stands for relative error] in comparison with the data obtained by atomic absorption spectroscopy. The data obtained by the two methods are in excellent concordance.

	Iron ore	Bauxite
Spectrophotometry	73.84	33.07
Atomic absorption spectroscopy	73.14	32.68
E_R, %	0.95	1.18

Thus, bis(*p*-methoxybenzoyl)cyclopentadiene is a promising ligand for the spectrophotometric determination of iron(III) both in solution and in natural materials in the presence of various foreign salts.

EXPERIMENTAL

2,3-Bis(*p*-methoxybenzoyl)cyclopentadiene was prepared by the procedure described in [9] from lithium cyclopentadienide and *p*-methoxybenzoyl chloride under argon. The product was a yellow crystalline substance which recrystallized from acetic acid. Yield 65%, yellow needles, mp 157–158°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.91 s (6H), 6.49 t (1H, J = 3.6 Hz), 7.02 d (4H, J = 8.6 Hz), 7.28 d (2H, J = 3.6 Hz,), 7.84 d (4H, J = 8.6 Hz), 18.62 s (1H).

A stock solution of the ligand ($c = 10^{-3}$ M) was prepared by dissolving a known amount of 2,3-bis(*p*-methoxybenzoyl)cyclopentadiene in anhydrous ethanol and was diluted to a required working concentration. All reagents (from Merck) were of analytical grade and were used without additional purification. Solutions containing Fe^{3+} ions at different concentrations were prepared from a standard solution of $Fe(NO_3)_3$; pH was adjusted by adding $HClO_4$ or NaOH. Interference studies were performed using different salts, preferentially as chlorides (for cations) or sodium salts (for anions). Deionized water and pure ethanol were used to prepare solutions.

Spectrophotometric measurements were performed at 25.0°C on a Shimadzu-3100S spectrophotometer coupled with a Model 200-91027 color plotter. Samples were placed in quartz cells (1.00 cm path length) with a stopper. The atomic absorption spectra were measured on a Varian AA-20 instrument. The pH values were measured using a Metrohm-Herisau E-603 pH-meter, which was preliminarily calibrated against standard buffer solutions. All measurements were performed at 25°C in 50% aqueous ethanol (by volume). An AdvantechMillipore F2HN-6496SC system was used to obtain deionized water.

Spectrophotometric analysis of ligand solutions ($c = 2 \times 10^{-5}$ M) in aqueous ethanol at different pH values was performed in the λ range from 250 to 500 nm at 25 ± 0.1°C. The required acidity (basicity) was adjusted by adding appropriate amount of $HClO_4$ or NaOH. The electrodes were calibrated in 50% ethanol in the acidic and basic ranges as described in [25, 26]. The reported pH values are referred to the suitable solvent scale.

Determination of pK_a. A stock solution of bis(*p*-methoxybenzoyl)cyclopentadiene in aqueous ethanol (1 : 1, by volume) was prepared with a concentration of 10^{-4} M. A 2.5-ml portion of that solution was transferred into a 5-ml volumetric flask, and the volume was adjusted to 5 ml by adding a 0.1 M solution of $HClO_4$ in 50% ethanol (acidic solution) or a 0.1 M solution of NaOH in 50% ethanol. The overall concentration of the ligand in the acidic (HA) and anionic forms (A^-) was calculated. Four series of acidic and basic solutions with different concentrations in the range $(0.5–2) \pm 10^{-5}$ M were thus prepared, and the optical density of each solution was measured at λ 421 nm. The absorption maxima (λ_{max}) of HA and A^- are located at λ 421.8 and 395.6 nm, respectively (molar absorption coefficients ε = 20 870 and 12 700 l mol^{-1} cm^{-1}, respectively). The pK_a value was determined from the sigmoid dependence of the absorbance at λ 421 nm versus pH [$\log(a_{A^-}/a_{HA}) = -1.0149 + 8.3927$; $r^2 = 0.9971$; a_{A^-} and a_{HA} are the activities of the corresponding forms].

Effect of foreign ions on the spectrophotometric determination of Fe^{3+} (c = 1 μg cm^{-3}) via complex formation with 2,3-bis(*p*-methoxybenzoyl)cyclopentadiene ($c = 5 \times 10^{-5}$ M) at pH 2

Foreign ion	Molar ratio to Fe^{3+}	Foreign ion	Molar ratio to Fe^{3+}
Na(I), K(I)	>1000	Cl^-, Br^-, NO_3^-	3 100
Ca(II), Mg(II), Ba(II)	100	CH_3COO^-, ClO_4^-	>1000
Al(III)	50	SO_4^{2-}	10
Cr(III)	10		

Determination of iron(III) ions. A 2.5-ml portion of an acidic Fe^{3+} solution containing 0.2 mol l^{-1} of $NaClO_4$ was transferred into a 5-ml volumetric flask, 2.5 ml of a solution of 2,3-bis(*p*-methoxybenzoyl)-cyclopentadieea ($c = 10^{-3}$ M) was added, pH was adjusted to 2 by adding a 0.3 M solution of $HClO_4$, and the volume was adjusted to 5 ml by adding deionized water. When the complex formation was complete, the optical density at λ 421 nm was measured against a blank solution prepared in a similar way.

Determination of the stoichiometry of the iron(III)–2,3-bis(*p*-methoxybenzoyl)cyclopentadiene complex. A series of solutions with a constant Fe^{3+} concentration and increasing concentration of the ligand was prepared, and the optical density of each solution at λ 421 nm was measured. The optical densities thus obtained were plotted against the ligand–metal molar ratio. The results showed a stoichiometry pf 2 : 1 (ligand–iron) for the complex.

Determination of iron(III) in geological samples. A 0.1-g portion of iron rock (Standard Reference

Material: Dominican Bauxite or Iron ore) was placed in a beaker and treated with concentrated perchloric acid (30 ml) and hydrochloric acid (50 ml) on heating and stirring for complete dissolution until gaseous HCl no longer evolved; during this procedure, water was added to maintain the volume. The resulting chloride-free solution was transferred into a 500-ml volumetric flask, and the volume was adjusted with deionized water. The concentration of iron(III) was determined as described above. The procedure was repeated four times for each sample, and the average value was calculated.

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