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Extraction-spectrophotometric characterization of a ternary complex of iron(III) with 4-(2-pyridylazo)resorcinol (PAR) and 2,3,5-triphenyl-2H-tetrazolium chloride (TTC)

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Abstract

Complex formation and liquid-liquid extraction were studied in a system containing iron(III), 4-(2-pyridylazo)resorcinol (PAR), 2,3,5-triphenyl-2H-tetrazolium chloride (TTC), water, and chloroform. The optimum conditions for iron(III) extraction from water to chloroform as an ion-association complex, (TT⁺)[Fe³⁺(PAR)₂]⁻, were found: pH, concentration of the reagents and shaking time. The following key equilibrium constants were calculated: constant of association, constant of distribution and constant of extraction. Some analytical characteristics were estimated and the settings at which the extraction system doesn’t produce spectrophotometric signal were specified.

Introduction

Iron is the most abundant transition metal in the Earth’s crust. Being the most important metal in the history of mankind, it continues to be the backbone of modern economy, supported by copper, zinc, lead, cobalt, nickel, chromium, vanadium, indium, etc. It is known that iron and all the mentioned metals form intensively coloured ternary and multicomponent complexes with 4-(2-pyridylazo)-resorcinol (PAR) and bulky organic compounds, such as quaternary ammonium, arsonium and phosphonium salts, tetrazolium salts, diphenylguanidine, xylometazoline hydrochloride, nitron, etc. Some of these complexes are of analytical importance and can be used for sensitive and low-cost extraction-spectrophotometric metal (M) determination and speciation; M = Zn(II) [1] Co(II) [2], Cu(II) [3], Nb(V) [4], V(IV,IV) [5, 6], Cr(III) [7], etc. However, one of the typical problems arising during their application is the interference caused by Fe(II,III) in the sample [6-9]. There are several approaches to eliminate iron interference: a) separation; b) masking; and c) choice of suitable extraction-spectrophotometric conditions. In the light of the described situation, the present paper has two goals: 1) to find the optimum conditions for Fe(III) liquid-liquid extraction-spectrophotometric
determination with PAR and the most widely used tetrazolium salt: 2,3,5-triphenyltetrazolium chloride (TTC) [10]; 2) to find conditions at which Fe(III) doesn’t form extractable complexes with PAR and TTC; such information can be of help in the development of a simple iron interference-free method for M determination.

Experimental

Reagents and apparatus: Iron(III) standard solution (1 mg mL⁻¹) was prepared by the procedure [11]: Weigh out 8.6350 g of ferric alum, FeNH₄(SO₄)₂.12H₂O, dissolve it in water containing 5 mL of conc. H₂SO₄, and dilute to volume with water in a 1-litre standard flask. Working solutions (50 µg mL⁻¹) were obtained by suitable dilution of the stock solution with 0.01 mol L⁻¹ H₂SO₄. Aqueous solutions of the reagents were used: PAR from Sigma-Aldrich Chemie GMBH, Steinheim, Germany (2×10⁻³ mol L⁻¹) and TTC from Loba Feinchemie GMBH, Fischamend, Austria (3×10⁻³ mol L⁻¹). The chloroform was redistilled and used repeatedly. The acidity of the aqueous medium was set by the addition of buffer solution, prepared by mixing 2 mol L⁻¹ aqueous solutions of CH₃COOH and NH₄OH. The resulting pH was checked by HI 83140 pH meter (Italy). A Camspec M508 spectrophotometer (United Kingdom), equipped with 10 mm path-length cells, was employed for reading the absorbance.

Procedure for establishing the optimum conditions: Aliquots of Fe(III) solution, PAR solution (up to 2.0 mL), TTC solution (up to 2.5 mL) and buffer solution (3 mL; pH ranging from 3.4 to 9.1) were introduced into 125-mL separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 mL. Then 10 mL of chloroform were added and the funnels were shaken for a fixed time (up to 5.0 min). A portion of each organic extract was transferred through a filter paper into a cell and the absorbance was read against a blank.

Procedure for determining the constant of distribution: The distribution constant Kₐ was found from the ratio Kₐ = A₁/(A₃-A₁) where A₁ is the light absorbance obtained after a single extraction (at the optimum operating conditions; see Table 1) and A₃ is the absorbance obtained after triple extraction under the same conditions. The final volume of the measured solutions in both cases was 25 mL.

Table 1: Optimum extraction-spectrophotometric conditions and some analytical characteristics of the system of Fe(III), PAR, TTC, water and chloroform

<table>
<thead>
<tr>
<th>Optimum conditions for Fe(III) extraction</th>
<th>Analytical characteristics</th>
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<tbody>
<tr>
<td>Wavelength: 540 nm</td>
<td>Molar absorptivity: ε₅₄₀=4.7×10⁴ L mol⁻¹ cm⁻¹</td>
</tr>
<tr>
<td>pH: 6.8 (acetate buffer)</td>
<td>Sandell’s sensitivity: 1.12 ng cm⁻²</td>
</tr>
<tr>
<td>Cₚₐṛ: 3.0×10⁻⁴ mol L⁻¹</td>
<td>Range of linearity of the analytical curve: 0.25-1.5 µg mL⁻¹</td>
</tr>
<tr>
<td>Cₜₜᶜ: 6.0×10⁻⁴ mol L⁻¹</td>
<td>Limit of detection: 0.10 µg mL⁻¹</td>
</tr>
<tr>
<td>Shaking time: 2 min</td>
<td>Limit of quantification: 0.35 µg mL⁻¹</td>
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</table>
Results and discussion

Spectral characteristics: Spectra of the extracted ternary Fe-PAR-TTC complex and the blank are shown in Fig. 1. Two relatively sharp maxima are recorded at 500 and 540 nm (curve 1). The second one is more suitable for spectrophotometric measurements because the blank at 540 nm is close to zero (curve 2). It should be mentioned that there is no noticeable peak in the spectral region 700-720 nm; this fact could be regarded as evidence that iron saves its initial +3 oxidation state in the ternary complex [12-14].

Effect of pH: The effect of pH on the extraction of Fe(III) is shown in Fig. 2. The results showed that the optimum pH is 6.6-7.1. All further optimisation experiments were carried out at pH 6.8. The shape of the obtained pH curve is governed mainly by the following two factors: 1) protonated PAR and Fe-PAR species predominate at pH values lower than pH_{opt} [15, 16]; 2) hydrolysed Fe(III) species exert noticeable effects on the complex formation at pH values higher than pH_{opt} [15-17]. The left slope of the pH curve is steeper than the right one; obviously, the factor 1 is the most important for formation of the extractable ternary complex. It could be concluded from Fig. 2 that the PAR-TTC-water-chloroform extraction-chromogenic system produces very low analytical signal with Fe(III) at pH <5.5-5.0. This fact could be used for the development of a simple Fe(III) interference-free method for determination of various ions (e.g. V(V)).
Effect of reagents concentration: The effect of PAR and TTC concentrations on the absorbance is shown in Fig. 3. It could be estimated that 1 mL $2 \times 10^{-3}$ mol L$^{-1}$ PAR and 2 mL $3 \times 10^{-3}$ mol L$^{-1}$ TTC are sufficient for maximum Fe(III) extraction. The optimum TTC concentration (ca. $6 \times 10^{-3}$ mol L$^{-1}$) is relatively high. If the PAR-TTC-water-chloroform system is used for the extraction-spectrophotometric determination of other ions (not Fe(III)), the TTC concentration could be selected lower than $6 \times 10^{-3}$ mol L$^{-1}$; this can additionally reduce the potential Fe(III) interference.

![Fig. 3: Absorbance of the extracted ternary complex vs. concentration of the TTC (curve 1) and PAR (curve 2) plots. 1- $C_{Fe(III)} = 2.23 \times 10^{-5}$ mol L$^{-1}$, $C_{PAR} = 3.0 \times 10^{-4}$ mol L$^{-1}$, $\lambda = 540$ nm; 2- $C_{Fe(III)} = 2.23 \times 10^{-5}$ mol L$^{-1}$, $C_{TTC} = 3.0 \times 10^{-4}$ mol L$^{-1}$, $\lambda = 540$ nm.](image)

Effect of shaking time: The extraction equilibrium is reached for ca. 1 min. A longer shaking time (up to 5 min) had no effect on the absorbance values. In order to avoid accidental errors caused by the combination of short shaking times and different shaking rates, we extracted for 2 min in our further experiments.

Composition of the complex and suggested formula: The molar PAR-to-Fe(III) and TTC-to-Fe(III) ratios were determined on the basis of the saturation curves presented in Fig. 3. Two different methods were used: the mobile equilibrium method [18] (Fig. 4) and the straight-line method of Asmus [19]. The results of both methods showed that the extracted ternary complex has a composition of 1:2:1 (Fe:PAR:TTC). Having in mind the spectral properties described above, we suggest the following formula of the extracted ternary complex: $(TT^+)[Fe^{3+}(PAR)_2]^-$. In this formula PAR is in its deprotonated form (PAR$^2^-$) and iron ion saves its initial +3 oxidation state. It is important to stress on the last mentioned oxidation state because of the information [13]: in alkaline aqueous-alcoholic solutions [Fe$^{3+}$(PAR)$_2$]$^-$ species are transformed spontaneously to inert [Fe$^{2+}$(PAR)$_2$]$_2^-$ ones. The present results (Fe:TTC=1:1; a lack of absorbance in the spectral range 700-720 nm) and some previous observations on extraction systems containing tetrazolium salts [10] give us ground to suggest that TTC acts as a protector of Fe(III) in the ion-associate.
Table 2: Calculated values of Log $\beta$, Log $K_D$ and Log $K_{ex}$

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>Equilibrium constant</th>
<th>Value</th>
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<tbody>
<tr>
<td>Eq. 1</td>
<td>$\beta= [(TT^+)[Fe(PAR)_2]] / [TT^+][Fe(PAR)_2]$</td>
<td>Log $\beta=4.13\pm0.14^a$</td>
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<tr>
<td></td>
<td></td>
<td>Log $\beta=4.03\pm0.15^b$</td>
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<tr>
<td></td>
<td></td>
<td>Log $\beta=4.06\pm0.22^c$</td>
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<tr>
<td>Eq. 2</td>
<td>$K_D= [(TT^+)[Fe(PAR)<em>2]</em>{org} / [TT^+][Fe(PAR)<em>2]</em>{aq}$</td>
<td>Log $K_D=0.070\pm0.002$</td>
</tr>
<tr>
<td>Eq. 3</td>
<td>$K_{ex}= [(TT^+)[Fe(PAR)<em>2]</em>{org} / [TT^+][Fe(PAR)<em>2]</em>{aq}$</td>
<td>Log $K_{ex}=4.20\pm0.15^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Log $K_{ex}=4.10\pm0.15^e$</td>
</tr>
</tbody>
</table>

a – Calculated by the Holme-Langmyhr method
b – Calculated by the Harvey-Manning method
c – Calculated by the mobile equilibrium method
d – Calculated by the formula $K_{ex}=K_D\times\beta$, where $\beta$ is determined by the Holme-Langmyhr method
e – Calculated by the formula $K_{ex}=K_D\times\beta$, where $\beta$ is determined by the Harvey-Manning method

Equilibrium constants and recovery: Several equilibrium processes should be taken into account for the system of $[Fe(PAR)_2]$, $TT^+$, water and chloroform.

(i) Formation of a ion-associate complex in the aqueous phase:

$$TT^+ + [Fe(PAR)_2] \leftrightarrow (TT^+)[Fe(PAR)_2]$$

(ii) Distribution of the complex between the aqueous and the organic phase:

$$[TT^+][Fe(PAR)_2]_{aq} \leftrightarrow (TT^+)[Fe(PAR)_2]_{org}$$

(iii) Extraction from water into chloroform:

$$[Fe(PAR)_2]_{aq} + TT^+ \leftrightarrow (TT^+)[Fe(PAR)_2]_{org}$$

The equilibrium constants describing these equations and the obtained values are shown in Table 2. The association constant $\beta$ was determined by several independent methods: Holme-Langmyhr method [20], Harvey-Manning method [21] and mobile equilibrium method [18] (Fig. 4, straight line 2). The distribution constant $K_D$ was calculated from the absorption values obtained after single and triple extraction as described above. The extraction constant $K_{ex}$ was calculated by the formula $K_{ex}=K_D\times\beta$. All
experiments were performed at room temperature of ~22°C and the calculations were carried out at a probability of 95%.

Analytical characteristics: The dependence between the Fe(III) concentration and the light absorbance was studied at the optimum conditions (Table 1). A good linearity was observed in the concentration interval of 0.25–1.5 μg mL$^{-1}$ Fe(III) (r=0.9980). The obtained straight line equation was $y=0.9960x-0.1029$. The relatively high negative y-intercept value and the noticeable positive deviation from the Beer’s law at Fe(III) concentrations higher than 1.5 μg mL$^{-1}$ can be attributed to a process of dimerization in the organic phase, similar to that observed in the system of Fe(III), PAR, benzylidimethyltetradecylammonium chloride, water and chloroform [22]. Other important analytical characteristics of the studied in the present work system (molar absorptivity, Sandell’s sensitivity, limit of detection and limit of quantification) are included in Table 1.

Conclusions
Iron(III) forms a ternary complex with 4-(2-pyridylazo)resorcinol and 2,3,5-triphenyltetrazolium chloride. The complex could be regarded as an ion-associate between an intensively colored anion, [Fe(PAR)$_2$]$^-$, in which iron is +3 oxidation state, and a bulky hydrophobic cation (TT$^+$). The following equilibrium constants and analytical characteristics were determined: constant of extraction, constant of association, constant of distribution, molar absorptivity, Sandell’s sensitivity, limit of detection and limit of quantification. The optimum conditions for extraction-spectrophotometric determination of Fe(III) were found and several approaches were proposed for the elimination of potential Fe(III) interference when the couple PAR-TTC is used for determination of other ions.

Acknowledgments
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References