Extraction of Gallium(III) with a New Azo Dye in The Presence or Absence of Xylometazoline Hydrochloride

Petya V. Racheva,1,2 Nikolina P. Milcheva,1,2 Antoaneta D. Saravanska,1 Kiril B. Gavazov1,2,*

1 Department of Chemical Sciences, Medical University of Plovdiv, 120 Buxton Brothers St., Plovdiv 4004, Bulgaria
2 Research Institute at the Medical University of Plovdiv, 15A Vasil Aprilov Bld., Plovdiv, Bulgaria
* Corresponding author’s e-mail address: kgavazov@abv.bg

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Abstract: Complex formation between Ga(III) and 6-hexyl-4-(2-thiazolylazo)resorcinol (HTAR, H2L) was studied in a water-chloroform medium, in the presence or absence of xylometazoline hydrochloride (XMH). Optimum conditions for the extraction of Ga(III) were found. In the presence of XMH, the extracted ion-associate has the formula [(XMH+)[GaIIIL2–]], where HTAR is in its deprotonated form L2–. Some key extraction-spectrophotometric characteristics were determined: absorption maximum (521 nm), apparent molar absorptivity (5.8 × 104 dm3 mol–1 cm–1), limit of detection (18 ng cm–3), limit of quantitation (60 ng cm–3), extraction constant (LogK = 4.44), distribution ratio (LogD = 2.2) and fraction extracted (99.3 %). In the absence of XMH, the extracted chelate contains one deprotonated and one monoprotonated HTAR: [GaIII(HL–)(L2–)]. It has an absorption maximum at 523 nm and a shoulder at 580–590 nm. The pK a of HTAR (H2L ⇄ H+ + HL– equilibrium) was calculated (5.4) and the effect of foreign ions was studied.

Keywords: gallium, 6-hexyl-4-(2-thiazolylazo)resorcinol, xylometazoline hydrochloride, liquid-liquid extraction, ion-association, spectrophotometry.

INTRODUCTION

GALLIUM is a dispersed rare element in the Earth’s crust with an average content of about 17 ppm. It belongs to the p-block of the periodic table and is classified as a post-transition metal. Some peculiarities of gallium’s geochemical behavior are the reason for the lack of its own minerals in economically significant quantities.[1] This, along with gallium high tech and military applications, makes it a strategic metal.[2–4] Currently, gallium is difficult to be replaced by other materials[5] in most of its uses in microelectronics, optics, renewable energetics, data storage, low-freezing-point alloys, plutonium alloys and medicine. Therefore, the interest in its extraction, separation, recycling and determination is great.[6,6–12]

Gallium(III) forms intensely colored chelate species with azo dyes, such as 4-(2-pyridylazo)resorcinol (PAR) and 4-(2-thiazolylazo)resorcinol (TAR).[13–18] Cationic ion-association reagents have been used in our laboratory to improve the hydrophobicity and extraction characteristics of such chelates: tetrazolium salts,[19,20] nitron,[21] and xylometazoline hydrochloride (XMH).[22] Extraction systems containing both Ga(III) and 6-hexyl-4-(2-thiazolylazo)resorcinol (HTAR) have not been studied so far. The aim of this paper is to investigate the complex formation between Ga(III) and HTAR in water-chloroform medium in the presence or absence of XMH. The azo dye HTAR is both commercially available and poorly studied. It is part of a collection of rare and unique chemicals and can be considered a good candidate for complexation with gallium ions due to the presence of a favorable combination of donor atoms. In a previous work on vanadium(V) liquid-liquid extraction, we reported its advantages over well-known azo dyes in terms of hydrophobicity and color-forming properties.[23] The other reagent, XMH, has been used in medicine and analytical chemistry. Its cation (XMH+) has a dispersed positive charge[24] and tends to form ion-pairs with various complex anions.[22,23,25–27]
MATERIALS AND METHODS

Reagents and Apparatus
A stock Ga(III) solution was prepared by dissolving 0.1346 g of Ga₂O₃ (Koch-Light Laboratories Ltd., 99.99 %) in a hot conc. HCl solution (20 cm³). After cooling, the obtained solution was collected into a 100-cm³ calibrated flask and diluted to the mark with 6.5 mol dm⁻³ HCl.[19] The working solutions (1×10⁻⁴ mol dm⁻³) were prepared by appropriate dilution of the stock solution with water. The reagents, XMH (purity ≥ 99 %) and HTAR, were purchased from Merck. Aqueous solutions of XMH (2×10⁻² mol dm⁻³) and HTAR (2×10⁻³ mol dm⁻³) were used. To increase the solubility of HTAR in water, its solution was prepared by the addition of KOH.[23] The pH values of the aqueous phase were adjusted by using ammonium acetate buffer prepared by mixing 2.0 mol dm⁻³ solutions of acetic acid and ammonia. The pH was monitored by a WTW InoLab 720 pH-meter (Germany). Absorbance was measured using a Ultrospec3300 pro spectrophotometer (UK), equipped with 10-mm path-length cells. Distilled water was used in all experiments. The chloroform was purified by distillation and used repeatedly.

General Procedure for One-Factor-at-a-Time Optimization
Solutions of Ga(III), HTAR, buffer and XMH were pipetted into a separatory funnel. Water was added to the total volume of 10 cm³. Then chloroform (10 cm³) was buretted and the mixture was shaken for extraction. After a short wait for phase separation, a portion of the organic layer was transferred through a filter paper into the spectrophotometer cell. The absorbance was measured against chloroform or a blank prepared at the same time.

Procedure for Studying the Effect of Foreign Ions
The effect of foreign ions was studied under optimal conditions for Ga(III) extraction. For this purpose, a certain amount of the foreign ion solution was added into a separatory funnel containing 0.5 cm³ of 2×10⁻⁴ mol dm⁻³ Ga(III) solution. Then, 0.7 mL of 2×10⁻³ mol dm⁻³ HTAR solution, 3 cm³ buffer (pH 5.0) and 0.5 mL of 2×10⁻² mol dm⁻³ XMH solution were added. The resulting solution was diluted with water to 10 cm³ and shaken for 3 min with chloroform (10 cm³). After a short wait for phase separation, a portion of the organic layer was transferred through a filter paper into the spectrophotometer cell. The absorbance was measured at 521 nm against chloroform or a sample prepared simultaneously in the absence of a foreign ion.

Determination of the Distribution Ratio and Fraction Extracted
The distribution ratio (D) was found from the equation \( D = A_1 / (A_3 - A_1) \), where \( A_1 \) is the absorbance measured after a single extraction (under the optimal conditions, Table 1) and \( A_3 \) is the absorbance after a triple extraction under the same conditions.[28] The total volume in both cases (single and triple extraction) was 25 cm³. The fraction extracted (E) was calculated from the equation \( E / \% = 100 × D / (D + 1) \).

RESULTS AND DISCUSSION

Absorption Spectra
Spectra of chloroform extracts of Ga(III)–HTAR complexes in the absence (1) or presence (2, 3) of XMH are shown in Fig. 1. The spectrum 1 is characterized by a maximum at the optimum conditions in the presence of HTAR (1×10⁻³ mol dm⁻³) and XMH (2×10⁻² mol dm⁻³) solutions. The absorbance was measured against chloroform or a blank prepared at the same time.

Figure 1. Absorption spectra of complexes against blanks (1–3; \( c_{Ga} = 1 × 10^{-3} \) mol dm⁻³, \( t_{ex} = 3 \) min) and corresponding blanks against chloroform (1‘–3’).

| Parameter                      | Optimization range | Optimal value |
|--------------------------------|--------------------|---------------|
| Wavelength, nm                 | Visible range      | 521           |
| pH                             | 3.67–9.15          | 5.0           |
| Concentration of HTAR, mol dm⁻³| (0.14–2.0) × 10⁻⁴  | 1.4 × 10⁻⁴    |
| Concentration of XMH, mol dm⁻³ | (0–2.0)×10⁻³        | 1.0 × 10⁻³    |
| Extraction time, seconds       | 15–240             | 180           |

* The optimization was performed at room temperature (22 °C), equal volumes of the two phases (10 cm³) and \( c_{Ga} = 1 × 10^{-3} \).
XMH (3) appears at 521 nm and the shoulder at 580–590 nm is missing. This shoulder is observed only in the absence of XMH.

**Effect of pH**

The effect of pH is shown in Fig. 2. All experiments were performed in the presence of 3 cm$^3$ of ammonia-acetate buffer. The maximum of series 1, obtained in the absence of XMH, lies at pH 6.4, and the curve is symmetrical (bell-shaped). The absorbance profile in the presence of XMH (2) is more complex. With an increase in pH from 3.5 to 5.0, the absorbance increases almost linearly. The maximum (pH 5.04) is followed by a section (pH 5.7–7.9) where the absorption remains practically constant. A sharp decrease follows at higher pH values, most likely due to the formation of hydrolysis products.[29]

Series 3 shows the increase in absorbance of the blank (HTAR-XMH) with increasing pH. It allows to calculate the dissociation constant $K_a$, which characterizes the loss of the proton of the OH group in the p-position relative to the azo group (Fig. 3).

![Figure 3. Equilibrium between the two forms of HTAR (H$_2$L and HL$^-$).](image)

One can estimate from Fig. 2 (series 3) that the $pK_a$ of HTAR is ca 5.4. This $pK_a$ value is close to those for other reagents of the same class[30–33] and is expected to decrease at higher XMH concentrations.[33] At pH > 5.4, HTAR predominantly exists in its monoprotonated anionic form (HL$^-$), which is able to associate with XMH$^+$ to form an electro-neutral, well extractable ion-pair. The formula of this ion-pair is most likely (XMH$^+$)(HL$^-$), which is in agreement with previous studies of similar compounds.[34,35] Its absorption maximum is determined by the anionic moiety and is located at 454 nm (in chloroform).

**EFFECT OF REAGENTS’ CONCENTRATION, MOLAR RATIOS, FORMULAE AND EQUATIONS**

The effect of HTAR concentration on absorbance in the absence and presence of XMH is shown in Fig. 4, series 1 and 2, respectively. The effect of $c_{HTAR}$ at the optimum pH and $c_{HTAR}$ is shown in Fig. 5.

![Figure 4. Effect of HTAR concentration in the absence (1) or presence (2) of XMH.](image)

![Figure 5. Effect of XMH concentration on the absorbance.](image)
The experimental data in Fig. 4 were processed by two methods\(^{[36,37]}\) to find the HTAR-to-Ga molar ratio in the extracted species. The results (Figs. 6 and 7) show that this ratio is 2 : 1 regardless of whether XMH is present or absent. The complex obtained in the absence of XMH most probably contains one deprotonated (L\(^2^-\)) and one monoprotonated ligand (HL\(^-\)) as shown in Eq. (1).

\[
2 \text{H}_2\text{L}(aq) + \text{Ga}^{III}(aq) \rightleftharpoons [\text{Ga}^{III}(\text{HL})\text{L}]^0(\text{org}) + 3 \text{H}^+(aq) \quad (1)
\]

The molar XMH-to-Ga ratio in the ternary complex is 1:1 (Figs. 6 and 7c). Hence, its composition is \(n_{\text{Ga}} : n_{\text{HTAR}} : n_{\text{XMH}} = 1 : 2 : 1\). Under the optimal conditions, it is formed according to Eq. (2).

\[
\text{Ga}^{III}(aq) + 2 \text{H}_2\text{L}(aq) + \text{XMH}^{+}(aq) \rightleftharpoons (\text{XMH})[\text{Ga}^{III}\text{L}_2]^0(\text{org}) + 4 \text{H}^+(aq) \quad (2)
\]

The correctness of the proposed formulas and equations is confirmed by the following facts:
- The ternary complex is more intensely colored than [GaL(HL)]. This is an indication that it does not contain protonated ligands.
- The shoulder in the long-wavelength part of the spectrum of the binary complex can be attributed to the presence of the ligand in two different protonation states, HL\(^-\) and L\(^2^-\) (as shown for transition metal complexes with azo dyes).\(^{[32,38]}\)

**Extraction Characteristics**

The conditional equilibrium constant characterizing Eq. (2) was calculated by the mobile equilibrium method\(^{[36]}\) (Fig. 6, straight line 2) and the Holme-Langmyr method.
The obtained values are given in Table 2, along with the values for fraction extracted (F) and distribution ratio (D). For comparison, in Table 2 are included data for similar systems involving XMH and other azo dyes: 4-(2-thiazolylazo)resorcinol (TAR) and 4-(2-pirydylazo)resorcinol (PAR). Obviously, HTAR has better extraction ability than TAR and PAR. This can be attributed to its higher hydrophobicity.

### Beer’s Law and Analytical Characteristics

The relationship between concentration of Ga(III) and absorbance of the extract was studied under the optimal conditions (Table 1). A good linearity was obtained in the range of 0.06–0.84 μg cm⁻³ (R² = 0.9992, N = 6). The linear regression equation was A = 0.833 y + 0.0003, where A is the absorbance and y is the Ga(III) concentration (μg cm⁻³). The standard deviations of the slope and intercept were 0.011 and 0.005, respectively. The limits of detection (LOD) and quantitation (LOQ) were calculated in two ways: 3- and 10-times standard deviation of the intercept divided by the slope and 3- and 10-times standard deviation of the blank divided by the slope. The obtained values practically coincided: LOD = 18 ng cm⁻³ and LOQ = 60 ng cm⁻³.

The molar absorptivity (ε) and Sandell’s sensitivity (S) at λ_max = 521 nm were calculated as well: $\epsilon = 5.8 \times 10^4$ dm³ mol⁻¹ cm⁻¹ and $S = 1.2 \times 10^3$ μg cm⁻².

### Effect of Foreign Ions

The effect of foreign ions is summarized in Table 3. The most significant interferences were caused by Co(II), Cu(II), Fe(III), Ni(II) and V(V) which form intensively colored complexes, were found: [Ga(II)] and [XMH][Ga₂]. The first one contains one monoprotonated and one deprotonated HTAR. It is extracted at a maximum extent at pH 6.4. The extraction characteristics are better in the presence of XMH and the molar absorptivity is higher. Under the optimal working conditions (pH = 5.0, $c_{Ga^3+} = 10^{-4}$ mol dm⁻³).

### CONCLUSIONS

The present work shed light on the complex formation between Ga(III) and HTAR in the presence or absence of XMH. The conditions of formation of two electronneutral complexes, were found: [Ga(II)] and [XMH][Ga₂]. The first one contains one monoprotonated and one deprotonated HTAR. It is extracted at a maximum extent at pH 6.4. The extraction characteristics are better in the presence of XMH and the molar absorptivity is higher. Under the optimal working conditions (pH = 5.0, $c_{Ga^3+} = 1.4 \times 10^{-4}$ mol dm⁻³, Hydrolysis).
\( \text{CA}_{\text{GAL}} = 1.0 \times 10^{-3} \) mol dm\(^{-3} \), \( t = 3 \) min), Ga\(^{3+} \) is extracted quantitatively. The obtained values of \( K_{\text{ex}} \), \( D \) and \( E \% \) are higher in comparison to those achieved with similar azo dyes.

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