Complex Formation in a Liquid-Liquid Extraction System Containing Indium(III), 4-(2-Pyridylazo) Resorcinol and Neotetrazolium Chloride

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Abstract

Complex formation and liquid-liquid extraction were studied in a system containing indium(III), 4-(2-pyridylazo) resorcinol (PAR), 3,3’-(4,4’-biphenylene) bis(2,5-diphenyl-2H-tetrazolium chloride) (Neotetrazolium chloride, NTC), water and chloroform. The optimum conditions for indium(III) extraction as an 1:2 ion-associate of the In(III)-PAR anionic chelate, \[\text{[In}^{3+}(\text{OH})_3(\text{PAR}^{2-})_2]^4^-\], and neotetrazolium cation (NT \(^2+\)) and were found: pH (8.0-8.5), shaking time (2 min), concentration of the reagents (\(C_{\text{PAR}}=C_{\text{NTC}}=4\times10^{-4}\) mol L\(^{-1}\)) and the sequence of their addition. The following key constants were calculated: constant of extraction (Log \(K_{\text{ex}}=9.60\pm0.06\)), constant of association (Log \(\beta=8.82\pm0.05\)) and constant of distribution (Log \(K_D=0.78\pm0.01\)). Some additional characteristics concerning the application of PAR and NTC for extractive-spectrophotometric determination of In(III) were estimated as well: absorption maximum (\(\lambda=515\) nm), apparent molar absorptivity (\(\varepsilon=7.0\times10^4\) L mol\(^{-1}\) cm\(^{-1}\)), recovery factor (R\%=85.0\pm0.1), limit of detection (LOD=0.10 µg cm\(^{-3}\)), limit of quantification (LOD=0.34 µg cm\(^{-3}\)) and Sandell’s sensitivity (SS=1.64 ng cm\(^{-2}\)). Beer’s law is obeyed for In(III) concentrations up to 2.9 µg mL\(^{-1}\) with a correlation coefficient of 0.9994.

Keywords: Indium, Ternary Complex, Solvent Extraction, Spectrophotometry, Azo Compound, Ditetrazolium Salt

1. Introduction

Indium is a post-transition metal of strategic importance for modern industry and science. Indium metal, its compounds and alloys are useful in the following high technology products and materials: liquid crystal displays and touch-screens, electroluminescent panels, thin film solar cells, cryogenic and ultra-high vacuum devices, high-speed transistors, light-emitted diodes and laser diodes, thermistors, solid-state batteries, nuclear reactor control rods, dental alloys, solders, special mirrors, re writable CDs and DVDs, etc. As a result, the indium usage for 2011 reached 1500 tonnes with bullish tendency (Mikolajczak & Jackson, 2011).

Unfortunately, the heightened indium demand cannot be easily met by the known natural resources due to the following reasons:

1. **a)** Indium is a dispersed rare element in the Earth’s crust (0.1 µg g\(^{-1}\)) (Alfantazi & Moskalyk, 2003 and Chatterjee, 2007). Fewer than 10 indium minerals are known, such as dzhalindite, indite, roquesite, laforetite, and yanomamite, but none of these occur in significant deposits (Fedorov & Akchurin, 2000 and Wood & Samson, 2006). In fact, indium is a by-product of base metals (Zn, Pb, Sn, Cu, Fe) production (Fedorov & Akchurin, 2000; Alfantazi & Moskalyk, 2003; Wood & Samson, 2006; Poledniok & Buhl, 2006 and Gupta et al, 2007).

**b)** The total known indium reserves (proven and probable, measured and indicated, and inferred) are estimated to be only about 49,000 tonnes (Mikolajczak & Jackson, 2011). That is why indium is regarded as a semiprecious non-ferrous metal (Alfantazi & Moskalyk, 2003) and its high...
and increasing price (Mikolajczak & Jackson, 2011) is evidence that controvert to the attempts of some industrial circles to belittle the problem with indium shortage and corresponding ecological complications arising from the need to process low grade ores.

In order to ensure indium long-term supply, new mining investments and appropriate recycling procedures are required (Paiva, 2001; Gupta et al, 2007; Reller et al, 2009; Vang et al, 2010 and Mikolajczak & Jackson, 2011). In relation to this is the importance of studying new compounds, which are prospective for the development of reliable methods of extraction, separation and sensitive determination of this key element.

It is known that indium (III) forms intensively coloured anionic chelates with 4-(2-pyridylazo)resorcinol (PAR), which can readily associate with bulky cations, deriving from monotetrazolium halides, such as 2,3,5-triphenyl-2H-tetrazolium chloride and 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide. The formed ion-association complexes are slightly soluble in water and easily extracted in organic solvents (Toncheva et al, 2011).

In the present paper we investigated the complex formation in a liquid-liquid extraction system containing indium (III), 4-(2-pyridylazo)resorcinol (PAR) and a ditetrazolium salt 3,3’-(4,4’-biphenylene) bis (2,5-diphenyl-2H-tetrazolium chloride) (Neotetrazolium Chloride, NTC). NTC, alone or in combination with other reagents (e.g., PAR, 4-(2-thiazolylazo) resorcinol, catechol, 4-nitrocatechol, pyrogallol, KSCN, etc.), has been used for extraction and spectrophotometric determination of many metal ions (Alexandrov & Kamburova, 1985; Alexandrov & Simeonova, 1985; Singh & Kumar, 1985; Singh et al, 1985; Simeonova et al, 1995; Kamburova, 1997; Gavazov et al, 1998; Gavazov et al, 2000; 2007; Genç et al, 2010 and Gavazov & Racheva, 2011).

Structural formulae of the reagents used in the present study are shown in Figure 1.

2. Experimental Procedure

2.1. Reagents and Apparatus

The stock indium(III) solution (100 mL) was prepared by mixing anhydrous InCl₃ from Alfa Aesar (99.99% metal basis; ca. 0.2000 g), 5 mL 1:1 HCl and distilled water. Working solutions (C_{In(III)}=1x10^{-4} mol L⁻¹) were prepared by diluting appropriate volumes of the stock solution (Toncheva et al, 2011). Aqueous 2.0 × 10⁻³ mol L⁻¹ solutions of the reagents PAR and NTC (both from Fluka AG) were used. The organic solvent was chloroform (redistilled). The acidity of the aqueous medium was set by the addition of buffer solution, prepared by mixing 2.0 mol L⁻¹ aqueous solutions of CH₃COOH and NH₄OH and 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.

![4-(2-pyridylazo) Resorcinol(PAR)](image)

![3,3’-(4,4’-biphenylene)bis(2,5-diphenyl-2H-tetrazolium chloride) (Neotetrazolium chloride, NTC)](image)

Figure 1. Reagents in the Present Study

2.2. Procedure for Establishing the Optimum Operating Conditions

Aliquots of In(III) solution, PAR solution (up to 3.0 mL), NTC solution (up to 2.1 mL) and buffer solution (1.5-5 mL; pH ranging from 6 to 9.8) 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 was added and the funnels were shaken for a defined period of time (10 sec-6 min). A portion of the organic extract was filtered through a filter paper into a cell and the absorbance was read against a blank.
2.3. Procedure for Determination of the Distribution Constant

The distribution constant $K_D$ was found from the ratio $K_D = A_1/(A_3-A_1)$ where $A_1$ is the light absorbance obtained after a single extraction (at the optimum operating conditions, Table 1) and $A_3$ is the absorbance obtained after a triple extraction under the same conditions. The single extraction and the first stage of the triple extraction were performed with 10 mL chloroform. The organic layers were transferred into 25 mL calibrated flasks and the flask for the single extraction was brought to volume with chloroform. The second stage of the triple extraction was performed by adding a 7 mL portion of chloroform to the aqueous phase, which remained after the first stage. The third stage was performed in the same manner. The two successive organic layers were transferred to the flask containing the organic layer obtained after the first stage. The volume was brought to the mark with chloroform and shaken for homogenization. Absorbencies $A_1$ and $A_3$ were measured against a blank (Toncheva et al, 2011 and Stoynova et al, 2012).

Table 1. Optimum Conditions and Analytical Characteristics of the In(III)-PAR-NTC-Water-Chloroform System

<table>
<thead>
<tr>
<th>Optimum Conditions</th>
<th>Analytical Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength: 515 nm</td>
<td>Apparent molar absorptivity: $\varepsilon = 7.0 \times 10^4$ L mol$^{-1}$ cm$^{-1}$</td>
</tr>
<tr>
<td>pH: 8.0-8.5 (acetate buffer)</td>
<td>Beer’s law range: up to 2.9 $\mu$g mL$^{-1}$</td>
</tr>
<tr>
<td>$C_{\text{PAR}}$: $4.0 \times 10^{-4}$ mol L$^{-1}$</td>
<td>Limit of detection: 0.10 $\mu$g mL$^{-1}$</td>
</tr>
<tr>
<td>$C_{\text{NTC}}$: $4.0 \times 10^{-4}$ mol L$^{-1}$</td>
<td>Limit of quantification: 0.34 $\mu$g mL$^{-1}$</td>
</tr>
<tr>
<td>Shaking time: 2-3 min</td>
<td>Sandell’s sensitivity: 1.64 ng cm$^{-2}$</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Absorption Spectra

Spectra of the ternary In(III)-PAR-NTC complex and the blank in chloroform are shown in Figure 2. The main absorption maximum of the complex is recorded at 515 nm. It is shifted to 5 nm as compared to the maximum of the binary complex in aqueous medium (510 nm; pH=8.0-8.5) and that of the 2,3,5-triphenyl-2H-tetrazolium (TT$^+$) ion-association complex (TT$^+$)[In$^{3+}$(PAR$^{2-}$)$_2$] in chloroform (520 nm) (Toncheva et al, 2011).

3.2. Effect of pH

Buffer solutions prepared from acetic acid and ammonium hydroxide with concentration of 2 mol L$^{-1}$ were applied to control the pH. The use of 1.5-2.5 mL of the buffer solution per 10 mL (final aqueous solution) was found to give a constant absorbance. The effect of pH on the extraction is represented in Figure 3. It could be seen that ternary complex is extracted in a great extent at pH values between 7.5 and 9. All further experiments were performed with 2 mL buffer solutions with pH ranging between 8.0 and 8.5.

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3.3. Effect of Reagents Concentrations and Order of Their Addition

A red colour is developed immediately after the mixing of In(III) and PAR solutions. For up to 2.9 µg mL\(^{-1}\) of In(III), the optimum concentration of both reagents i.e. PAR and NTC, was 4.0×10\(^{-4}\) mol L\(^{-1}\) (Figure 4). Under the optimum conditions, the colouration of the organic extract remains constant for at least an hour at room temperature. It was found that the order of reagents addition is also of importance for good colour development. The correct order is given in Section 2.3: In(III), PAR, NTC and buffer.

3.4. Effect of Shaking Time

Further optimization of the extraction process was performed by testing different shaking times (from 10-360 seconds). It was found that the absorbance is maximum and constant for the interval between 90 and 360 seconds. Hence, we extracted for 2-3 min (120-180 seconds) in our further experiments.

3.5. Composition of the Complex

The molar PAR-to-In(III) and NTC-to-In(III) ratios were determined by the mobile equilibrium method (Zhiming et al, 1997) (Figure 5) and the method of Asmus (1960) (Figures 6 and 7). The results showed that a ternary complex with a ratio of 1:2:2 (In:PAR:NTC) is extracted into organic phase.

3.6. Complex Formation Scheme

The obtained in Section 3.5 results showed that the complex formation scheme differs from that reported in our previous investigations on the In(III)-PAR-MTS-water-chloroform system (Toncheva et al, 2011) where MTS is a monotetrazolium salt. Most probably, the difference (Table 2) could be attributed to the bulkiness of
ditetrazolium cations, NT<sup>2-</sup>, which envelop hydrolyzed anionic chelate, stabilizing it and improving its hydrophobicity. One can obtain a similar difference comparing ternary vanadium(IV)-PAR complexes with monotetrazolium and ditetrazolium cations: ditetrazolium cations (in contrast to monotrazolium ones) are prone to stabilize hydrolyzed species with a high negative charge (Genç et al, 2010).

3.7. Equilibrium Constants and Recovery

The equilibrium constants required for quantitative assessment of the extraction system are shown in Table 3. The association constant β, characterizing Equation 3' in Table 3, was calculated by several methods: Holme-Langmyhr method (1966), Harvey-Manning method (1950), mobile equilibrium method (Zhiming et al, 1997) and Komar-Tolmachev method (Bulatov & Kalinkin, 1986). The distribution constant KD was calculated from the absorption values obtained after single and triple extraction as described in Section 2.3. The extraction constant, characterizing the entire extraction process, was calculated by the dependence KD = Kex × β (Alexandrov et al, 1976). The recovery factor R was estimated by the formula R% = KD×100 / (KD + 1). The following value was obtained: R = 85.0 ± 0.1 %, it is slightly higher than these obtained for similar systems with monotetrazolium salts (Toncheva et al, 2011).

3.8. Molar Absorptivity, Beer’s Law and other Analytical Characteristics

The Komar-Tolmachev method also allows calculating the true molar absorptivities (ε) of the complexes (Figure 8). The obtained value, ε = (7.5 ± 0.7)×10<sup>3</sup> L mol<sup>-1</sup> cm<sup>-1</sup>, agrees well with that obtained from Beer’s law (ε') (Table 1) and this is an indication for absence of serious side-reactions (Bulatov & Kalinkin, 1986). Beer’s law, checked at optimum conditions (Table 1), was valid up to 2.9 µg mL<sup>-1</sup> of In(III). A straight-line with equation y=0.631x+0.0126 and a correlation coefficient of 0.9994 was obtained. Sandell’s sensitivity was estimated to be 1.64 ng cm<sup>-2</sup>. The limits of detection (LOD) and quantification (LOQ) were calculated as 3 times and 10 times standard deviation of the intercept divided by the slope: LOD = 0.10 µg cm<sup>-2</sup> and LOQ = 0.34 µg cm<sup>-2</sup>.

4. Conclusion

Indium (III) forms well chloroform-extractable ternary ion-association complex, (NT<sup>2-</sup>)<sub>2</sub>[In(OH)₃(PAR)]<sup>2+</sup>, with 4-(2-pyridylazo)resorcinol and Neotetrazolium chloride. The anionic part of the complex ensures intensive red colouration, and the hydrophobicity of the cationic part, in its turn, guarantees the poor solubility in water. The following equilibrium constants and analytical parameters are calculated i.e. constant of extraction (Kex), constant of association (β), constant of distribution (KD), recovery factor (R%), apparent molar absorptivity (ε'), true molar absorption coefficient (ε'), apparent molar absorptivity factor (ε''), apparent molar absorptivity factor (ε''), apparent molar absorptivity factor (ε'''', true molar absorption coefficient (ε''')).

Table 2. Complex Formation Schemes in Systems Containing In(III), PAR (H₃L⁺ or HL⁻ in Acidic or Neutral Medium Respectively), Ditetrazolium Salt (NTC) or Monotetrazolium salt (MTS)

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<td>[In(HL)]&lt;sup&gt;+&lt;/sup&gt; + HL⁻ + 5OH⁻ ⇌ [In(OH)₂L₂]&lt;sup&gt;-&lt;/sup&gt; + 2H₂O + 2NT&lt;sup&gt;2-&lt;/sup&gt; (2')</td>
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</tr>
<tr>
<td>[In(HL)]&lt;sup&gt;+&lt;/sup&gt; + HL⁻ + 5OH⁻ ⇌ [In(OH)₂L₂]&lt;sup&gt;-&lt;/sup&gt; + 2H₂O + 2NT&lt;sup&gt;2-&lt;/sup&gt; (2')</td>
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<tr>
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<td>[InL₂]⁻ + MT&lt;sup&gt;+&lt;/sup&gt; ⇌ (MT)[InL₂] (3')</td>
</tr>
</tbody>
</table>

a – Before Buffering
b – After Buffering
absorptivity (ε), limit of detection (LOD), limit of quantification (LOQ) and Sandell’s sensitivity (SS). The obtained has been checked by independent methods and similar values of some of the above mentioned characteristics are the good evidence of correctness of the performed experiments and suggested reaction scheme.

Table 3. Equilibrium Constants for the In(III)-PAR-NTC-Water-Chloroform System (P = 95%)

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>Equilibrium Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation 3’ from Table 2:</td>
<td>β = [(NT)$_2$[In(OH)$<em>3$(PAR)$<em>2$]$</em>{aq}$/ [NT$^{2+}$]$^{2}</em>{aq}$ × [[In(OH)$_3$(PAR)$<em>2$]]$</em>{aq}$</td>
<td>Log β = 8.82 ± 0.05$^a$</td>
</tr>
<tr>
<td>[][(NT)$_2$[In(OH)$_3$(PAR)$<em>2$]$</em>{aq}$/ [(NT)$_2$[In(OH)$_3$(PAR)$<em>2$]]$</em>{aq}$</td>
<td>K_D = [(NT)$_2$[In(OH)$_3$(PAR)$<em>2$]$</em>{aq}$/ [(NT)$_2$[In(OH)$_3$(PAR)$<em>2$]]$</em>{aq}$</td>
<td>Log K_D = 0.78 ± 0.01</td>
</tr>
<tr>
<td>[][(NT)$_2$[In(OH)$<em>3$(PAR)$<em>2$]$</em>{org}$/ [NT$^{2+}$]$^{2}</em>{aq}$ × [[In(OH)$_3$(PAR)$<em>2$]]$</em>{aq}$</td>
<td>K_ex = [(NT)$_2$[In(OH)$_3$(PAR)$<em>2$]$</em>{org}$/ [(NT)$_2$[In(OH)$_3$(PAR)$<em>2$]]$</em>{aq}$</td>
<td>Log K_ex = 9.60 ± 0.06$^e$</td>
</tr>
</tbody>
</table>

a – Calculated by the Harvey-Manning method (1950);
$b$ – Calculated by the Holme-Langmuir method (1966);
$c$ – Calculated by the Mobile equilibrium method (Zhiming et al, 1997);
d – Calculated by the Komar-Tolmachev method (Bulatov & Kalinkin, 1986);
e – Calculated by the equation Log K_ex = Log β + Log K_D, where β is obtained by the Harvey-Manning method.

Acknowledgments

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References


Figure 8. Determination of the Constant of Association (β) and True Molar Absorptivity (ε) by the Method of Komar-Tolmachev. n=2, C$_{PAR}$ = 4.0 × 10$^{-4}$ mol L$^{-1}$, pH=8.5


