Cent. Eur. J. Chem. • 9(6) • 2011 • 1143-1149
DOI: 10.2478/s11532-011-0101-z

VERSITA

Central European Journal of **Chemistry**

Ternary ion-association complexes between the indium(III) – 4-(2-pyridylazo)resorcinol anionic chelate and some tetrazolium cations

Research Article

Galya K. Toncheva, Kiril B. Gavazov*, Vanya D. Lekova, Kirila T. Stojnova, Atanas N. Dimitrov

Department of General and Inorganic Chemistry, University of Plovdiv, 4000 Plovdiv, Bulgaria

Received 17 June 2011; Accepted 17 August 2011

Abstract: Complex formation and liquid-liquid extraction were studied in systems containing indium(III), 4-(2-pyridylazo)resorcinol (PAR), tetrazolium salt (TZS), water and chloroform. Two different TZS were used: 2,3,5-triphenyl-2H-tetrazolium chloride (TTC) and 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide (MTT). The optimum conditions for extraction of In(III) as a ternary complex, $(TT^+)[In(PAR)_2]$ or $(MTT^+)[In(PAR)_2]$, were found: pH, extraction time, concentration of PAR and concentration of TZS. The constants of extraction (K_{ex}), constants of association (β), constants of distribution (K_D) and recovery factors (R%) were determined. The apparent molar absorptivities in chloroform were calculated to be $\varepsilon'_{520}=6.6\times10^4$ L mol^{-1} cm^{-1} and $\varepsilon'_{515}=7.1\times10^4$ L mol^{-1} cm^{-1} for the systems with TTC (**I**) and MTT (**II**), respectively. Beer's law was obeyed for In(III) concentrations up to 3.4 μg mL^{-1} in both the cases. The limits of detection (LOD=0.07 μg mL^{-1} **I** and LOD=0.12 μg mL^{-1} **II**), limits of quantification (LOQ=0.24 μg mL^{-1} **I** and LOQ=0.41 μg mL^{-1} **II**) and Sandell's sensitivities (SS) were estimated as well.

Keywords: *Indium • Liquid-liquid extraction • Spectrophotometry • Triphenyltetrazolium • Thiazolyl Blue Tetrazolium*

1. Introduction

Indium is a post-transition metal of strategic importance. It has a broad spectrum of applications in high technology materials and products, such as liquid crystal displays and touchscreens, 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, resistant to atmospheric corrosion mirrors, dental alloys, rewritable CDs and DVDs, *etc*. As a low-melting metal (156.6°C) with a relatively low toxicity, indium could be used instead of some hazardous elements (Hg, Pb) in relays and solders. However, its high and fluctuating price is limiting these applications [1].

Indium is a very dispersed rare element in the Earth's crust (0.1 μg g^{-1}) [1,2]. Fewer than 10 indium minerals are known, such as dzhalindite ($In(OH)_3$), indite ($FeIn_2S_4$), roquesite ($CuInS_2$), laforetite ($AgInS_2$), and yanomamite ($InAsO_4$•$2H_2O$), but none of these occur in significant deposits [1,3]. That is why indium is commonly produced from residues generated during zinc-lead ore processing [1,4]. Other important sources of indium could be minerals containing tin, cuprum and iron (*e.g*. stannite, cassiterite, and chalcopyrite) [3,5]. There is an opinion based on the indium content in the aforementioned ore deposits and the supposed annual indium consumption will exhaust the world's indium reserves in several decades [6]. In order to ensure a long-term supply of indium, sufficient to meet increasing future demands, recycling [7-10] and new mining investments are required [8]. In relation to this is the importance of developing new reliable procedures for indium extraction and sensitive determination [11].

It is known that indium(III) forms intensively colored chelates with azocompounds, such as 2,2';3,4-tetrahydroxy-3',5'-disulphoazobenzene (Tetrahydroxyazon 2S) [12], 4-(2-pyridylazo)resorcinol (PAR) [13-20], bromo- and methyl- derivatives of PAR [20,21], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (BPDEAP) [22], 1-(2-pyridylazo)-2-naphthol (PAN) [16,20,23-26], 2-(2-pyridylazo)-1-naphthol-4-sulphonic acid (PAN-S) [27,28], 4-(2-quinolylazo)resorcinol (QAR)

* *E-mail: kgavazov@abv.bg*

[29], 4-(2-thiazolylazo)resorcinol (TAR) [30], 2-(2-Thiazolylazo)-*p*-cresol (TAC) [31], 1-(2-thiazolylazo)-2-naphthol-3,6-disulphonic acid (TAN-diS) [32], Gallion [33], Lumogallion [34], Eriochrome Black T [35], Sulfarsazene (SAA) [36], Thorin [37], hydroxynaphtoic acid azodyes [38]. The following auxiliary reagents have been used to improve the chromophore and extraction properties of the complexes with some of the mentioned azodyes: Aliquat 336S [14], monocarboxylic acids [15,34], antipyrine [16], diphenylguanidine [35], N-p-chlorophenyl-2-furohydroxamic acid [19], cetylpyridinium chloride (CPC) [22], cetyltrimethylammonium bromide (CTMB) [23,25], cetyldimethylbenzylammonium chloride (CDMBAC) [39]. Extraction systems containing both indium(III) and tetrazolium salt (TZS) have not been investigated so far. The present paper aims at studying the complex formation and liquid-liquid extraction (LLE) of In(III) with the couple PAR+TZS [40-42]. Two commercially available TZSs were used (Table 1). The cations of these TZSs are known to form hydrophobic and analytically important ion-association complexes with many anionic species [43-47].

2. Experimental procedure

2.1. Reagents and apparatus

The stock indium(III) solution (100 mL) was prepared by mixing anhydrous $InCl_3$ from Alfa Aesar (99.99% metal basis; *ca.* 0.2000 g), 5 mL 1:1 HCl and distilled water. Working solutions ($C_{In(III)}$=1×10^{-4} mol L^{-1}) were prepared by diluting appropriate volumes of the stock solution. Aqueous 2×10^{-3} mol L^{-1} or 3×10^{-3} mol L^{-1} solutions of the reagents PAR (Fluka AG), TTC (Loba Feinchemie) and MTT (Merck) 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 mol L^{-1} aqueous solutions of CH_3COOH and NH_4OH and the resulting pH was checked by HI 83140 pH meter (Italy). A Camspec M508 spectrophotometer (United Kingdom), equipped with 5 and 10 mm path-length cells, was employed for reading the absorbance.

2.2. Procedure for establishing the optimum operating conditions

Aliquots of In(III) solution, PAR solution (up to 3 mL), TZS solution (up to 3.0 mL) and buffer solution (2 mL; pH ranging from 5.9 to 10.2) 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 0.5-5.0 min. A portion of the organic extract was filtered through filter paper into a cell and the absorbance was read against a blank.

2.3. Procedure for determination of the distribution constants

The distribution constants 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 – see Table 2) 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

Table 1. Tetrazolium salts (TZS) in the present study.

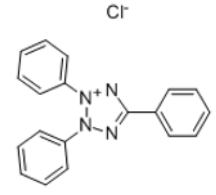
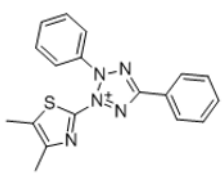
Formulae	Name	Abbreviation
	2,3,5-triphenyl-2H-tetrazolium chloride	TTC
	3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide (Thiazolyl Blue Tetrazolium).	MTT

Table 2. Optimum operating conditions.

Extraction system	Extraction time [min]	pH	C_{PAR} [mol L^{-1}]	C_{TZS} [mol L^{-1}]	λ_{max} [nm]
In(III)-PAR-TTC-H_2O-chloroform	3	7.8-8.4	4.0×10^{-4}	8.0×10^{-4}	520
In(III)-PAR-MTT-H_2O-chloroform	3	7.9-8.4	6.0×10^{-4}	6.0×10^{-4}	515

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.

3. Results and discussion

3.1. Spectral characteristics and optimum operating conditions

The spectra of the complexes and blank samples are shown in Fig. 1. The maxima in chloroform are recorded at 520 nm for the ternary compound with TTC (curve 1) and at 515 nm for the ternary compound with MTT (curve 2). These maxima are shifted to 5-10 nm as compared to the maximum of the binary In(III)-PAR chelate (curve 3, λ_{max}=510 nm). The observed bathochromic effects are small and give us grounds to suggest the formation of ternary ion-association complexes. It could be judged from Fig. 1 that the absorbencies of both the ternary complexes are significantly higher than those of the binary In(III)-PAR complex in aqueous medium. The ternary complex with MTT has higher molar absorptivity at the optimum operating concentrations (Table 2, Fig. 1). An advantage of the system containing TTC is the lowest absorbance of the blank (Fig. 1, curve 1'). The effect of pH on the extraction of the complexes is represented on Fig. 2.

3.2. Composition of the complexes and reaction scheme

The molar PAR-to-In(III) and TZS-to-In(III) ratios in the ternary complexes were determined by the equilibrium shift method [48] (Fig. 3), the method of Asmus [48] (Table 3) and the method of continuous variations [48] (Fig. 4). The results (PAR:In=2:1 and TZS:In=1:1) and literature data about the state of PAR [26], In(III) [49] and In(III)-PAR chelate [15,18] before and after buffering (equation 1 and equations 2,3 respectively) suggest that the ion-associate formation could be represented as shown in Scheme 1.

3.3. Equilibrium constants

Several processes should be taken into account for the system of $[InL_2]^-$, TZ^+ (TT^+ or MTT^+), water and chloroform:

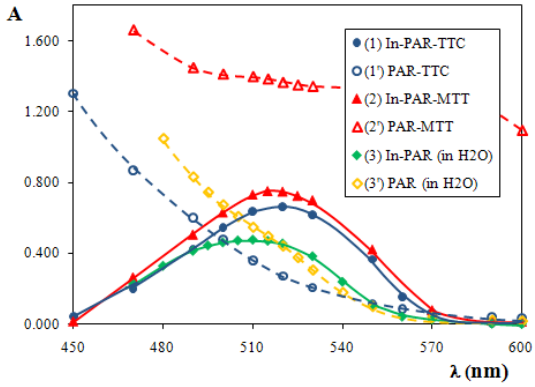


Figure 1. Absorption spectra of the ternary complexes (curves 1 and 2), binary In-PAR complex (curve 3) and blank samples (curves 1', 2' and 3'). $C_{In(III)}$= 1×10^{-5} mol L^{-1}; C_{PAR}=4.0×10^{-4} mol L^{-1} (curves 1, 1', 3 and 3') or C_{PAR}=6.0×10^{-4} mol L^{-1} (curves 2 and 2'), C_{TTC}=8.0×10^{-4} mol L^{-1}; C_{MTT}=6.0×10^{-4} mol L^{-1}, pH=8.1: (1) – In(III)-PAR-TTC in chloroform; (1') – PAR-TTC in chloroform; (2) – In(III)-PAR-MTT in chloroform; (2') – PAR-MTT in chloroform; (3) – In(III)-PAR in water; (3') – PAR in water.

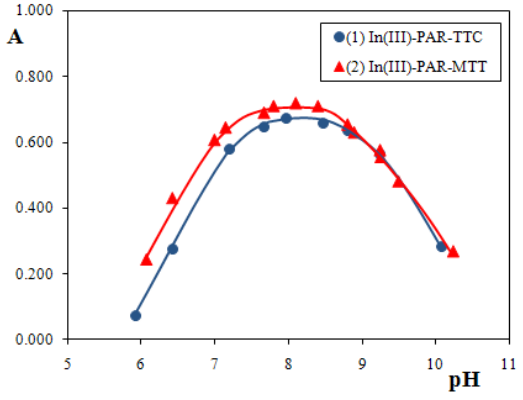


Figure 2. Absorbance of In(III)-PAR-TS complexes in chloroform vs. pH of the aqueous phase plots. (1) – $C_{In(III)}$= 1×10^{-5} mol L^{-1}, C_{PAR}=4.0×10^{-4} mol L^{-1}, C_{TTC}=8.0×10^{-4} mol L^{-1}; (2) – $C_{In(III)}$=1×10^{-5} mol L^{-1}, C_{PAR}= C_{MTT}=6.0×10^{-4} mol L^{-1}

(i) Formation of ion-associate complexes in the aqueous phase according to Eq. 3 with equilibrium constants $\beta=[(TZ)[InL_2]] / [TZ^+] \times [[InL_2]^-]$.

(ii) Distribution of the complexes between the aqueous and the organic phase $\{(TZ)[InL_2]\}_{aq} \leftrightarrow \{(TZ)[InL_2]\}_{org}$ with distribution constants $K_D=[(TZ)[InL_2]]_{org} / [(TZ)[InL_2]]_{ag}$.

Table 3. Determination of the PAR-to-In(III) and TZS-to-In(III) molar ratios (n and m, respectively) by the method of Asmus [48]. $C_{In(III)}=1\times10^{-5}$ mol L^{-1}, pH=8.1.

Extraction system	Correlation coefficient squired values (CC^2) corresponding to molar ratios 1, 2 and 3	
	PAR:In(III)	TZS:In(III)
In(III)-PAR-TTC	$CC^2=0.9533^a$ (n=1) $CC^2=0.9982^a$ (n=2) $CC^2=0.9860^a$ (n=3)	$CC^2=0.9983^b$ (m=1) $CC^2=0.9376^b$ (m=2) $CC^2=0.8550^b$ (m=3)
In(III)-PAR-MTT	$CC^2=0.9686^c$ (n=1) $CC^2=0.9923^c$ (n=2) $CC^2=0.9604^c$ (n=3)	$CC^2=0.9892^d$ (m=1) $CC^2=0.9534^d$ (m=2) $CC^2=0.8793^d$ (m=3)

a – PAR varies from 4.0×10^{-5} mol L^{-1} to 2.4×10^{-4} mol L^{-1}; $C_{TTC}=8.0\times10^{-4}$ mol L^{-1}
b – TTC varies from 4.0×10^{-5} mol L^{-1} to 6.0×10^{-4} mol L^{-1}; $C_{PAR}=4.0\times10^{-4}$ mol L^{-1}
c – PAR varies from 6.0×10^{-5} mol L^{-1} to 4.0×10^{-4} mol L^{-1}; $C_{MTT}=6.0\times10^{-4}$ mol L^{-1}
d – MTT varies from 4.5×10^{-5} mol L^{-1} to 4.5×10^{-4} mol L^{-1}; $C_{PAR}=6.0\times10^{-4}$ mol L^{-1}

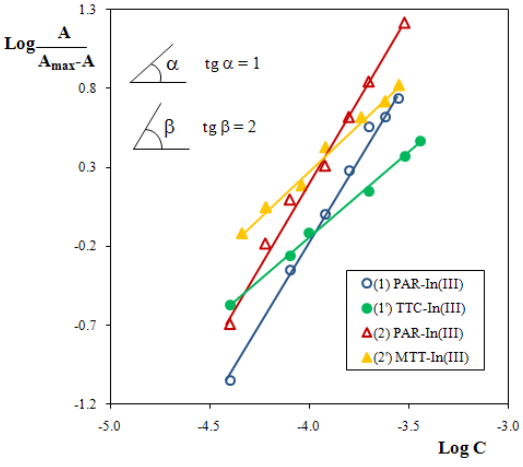


Figure 3. Determination of the PAR-to-In(III) (straight lines 1 and 2) and TZS-to-In(III) (straight lines 1' and 2') molar ratios by the Equilibrium shift method at pH=8.1, $C_{In(III)}=1\times10^{-5}$ mol L^{-1} and the following reagent concentrations: (1) $C_{TTC}=8.0\times10^{-4}$ mol L^{-1}; (1') $C_{PAR}=4.0\times10^{-4}$ mol L^{-1}; (2) $C_{MTT}=6.0\times10^{-4}$ mol L^{-1}; (2') $C_{PAR}=6.0\times10^{-4}$ mol L^{-1}

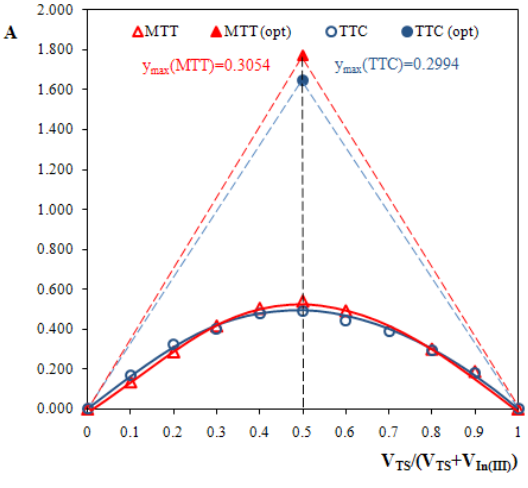


Figure 4. Determination of the constants of extraction (K_{ex}) by the Likussar-Boltz method at $k=C_{In(III)}+C_{TZS}=5\times10^{-5}$ mol L^{-1}

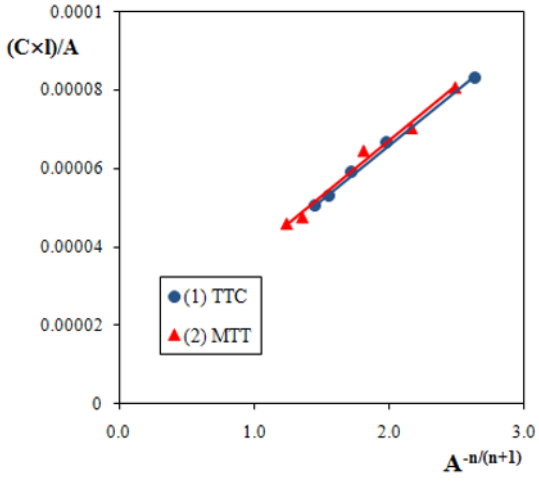


Figure 5. Determination of the constants of association (β) and true molar absorptivities (ε) by the method of Komar-Tolmachev. pH=8.1, $C_{PAR}=4\times10^{-4}$ mol L^{-1} (straight line 1) or 6×10^{-4} mol L^{-1} (straight line 2). The following stright lines (Y=aX+b) slopes (a) and Y-intercepts (b) were obtained: (1) $a=(2.77\pm0.07)\times10^{-5}$, $b=(1.08\pm0.13)\times10^{-5}$; (2) $a=(2.79\pm0.20)\times10^{-5}$, $b=(1.15\pm0.37)\times10^{-5}$. The calculated true molar absorptivities ($\varepsilon=1/b$) are $\varepsilon=(9\pm1)\times10^4$ and $=(9\pm3)\times10^4$ L mol^{-1} cm^{-1} for the complexes with TTC and MTT respectively.

(iii) Extraction of the ternary complexes from water into chloroform $[InL_2]^-_{aq} + TZ^+_{aq} \leftrightarrow \{(TZ)[InL_2]\}_{org}$ with distribution constants $K_{ex}=K_D\times\beta=[(TZ)[InL_2]]_{org} / [TZ^+]_{aq} \times [[InL_2]^-]_{aq}$.

The constants of extraction K_{ex} were determined by the method of Likussar and Bolts [50] at $k=C_{In(III)}+C_{TZS}=5\times10^{-5}$ mol L^{-1} (Fig. 4). The constants of distribution K_D were determined by comparison of the absorbance values obtained after single extraction at the optimum conditions (A_1) and triple extraction (A_3): $K_D=A_1/(A_3-A_1)$. The association constants were calculated by the method of Komar and Tolmachev [48] (Fig. 5) or by the equation $\beta = K_{ex} / K_D$ [51]. All calculations were carried out at a probability of 95%. The obtained values are presented in Table 4.

Table 4. Values of the extraction constants (K_{ex}), distribution constants (K_D), association constants (β) and recoveries (R%) for the In(III)-PAR-TZS-water-chloroform systems

Extraction system	Log K_{ex}	Log K_D	Log β	R%
In(III)-PAR-TTC-H_2O-$CHCl_3$	4.39±0.02	0.700±0.001	3.69±0.02[a], 4.1±0.6[b]	83.35±0.04[c]
In(III)-PAR-MTT H_2O-$CHCl_3$	4.40±0.06	0.580±0.001	3.82±0.06[a], 4.2±0.5[b]	79.20±0.02[c]

a – Calculated by the equation Log β=Log K_{ex}–Log K_D
b – Calculated by the method of Komar-Tolomachev
c – Calculated by the equation R%=100×K_D/(K_D+1)

Table 5. Molar absorptivities of indium(III) binary and ternary complexes with azocompounds.

Reagent(s)	Molar absorptivity [L mol^{-1} cm^{-1}]	Ref.
Thorin	6.10×10^3	[37]
2-(2-Thiazolylazo)-p-cresol (TAC)	1.21×10^4	[31]
1-(2-Pyridylazo)-2-Naphthol (PAN)	$(1.87\text{-}2.00)\times10^4$	[16,20]
PAN + Cetyltrimethylammonium bromide (CTMB)	1.91×10^4	[25]
Gallion	2.20×10^4	[33]
1-(2-Pyridylazo)-2-Naphthol-Sulfonic Acid (PAN-S)	2.27×10^4	[27]
4-(2-Pyridylazo)resorcinol (PAR) + N-p-chlorophenyl-2-furohydroxamic acid	3.00×10^4	[19]
PAR	$(3.26\text{-}4.30)\times10^4$	[13,16,17]
Eriochrome Black T + Diphenylguanidine	3.60×10^4	[35]
2,2',4'-Trihydroxy-5-chloroazobenzene-3-sulfonic Acid (Lumogallion)	5.40×10^4	[34]
5-Bromo-4-(2-pyridylazo)resorcinol (BPAR)	$(5.57\text{-}5.81)\times10^4$	[20,21]
4-(2-Quinolylazo)resorcinol (QAR)	5.95×10^4	[29]
Lumogallion + Acetate	7.50×10^4	[34]
2,2';3,4-Tetrahydroxy-3',5'-disulphoazobenzene (Tetrahydroxyazon 2S)	7.70×10^4	[12]
2,4,6-Tris(2-hydroxy-4-sulfo-1-naphthylazo)-1,3,5-triazine trisodium salt (THT)	8.40×10^4	[52]

Table 6. Characteristics concerning the application of the ternary complexes for extractive-spectrophotometric determination of indium(III).

Analytical characteristics	In(III)-PAR-TTC-H_2O-$CHCl_3$	In(III)-PAR-MTT H_2O-$CHCl_3$
Apparent molar absorptivity (ε')	$(6.60\pm0.10)\times10^4$ L mol^{-1} cm^{-1}	$(7.10\pm0.10)\times10^4$ L mol^{-1} cm^{-1}
Sandell's sensitivity (SS)	1.70 ng cm^{-2}	1.60 ng cm^{-2}
Adherence to Beer's law	Up to 3.40 μg mL^{-1}	Up to 3.40 μg mL^{-1}
Coefficient of correlation (CC)	0.9998	0.9995
Limit of detection (LOD)	0.07 μg mL^{-1}	0.12 μg mL^{-1}
Limit of quantification (LOQ)	0.24 μg mL^{-1}	0.41 μg mL^{-1}

$$InCl^{2+} + H_3L^+ \leftrightarrow [In(HL)]^{2+} + Cl^- + 2H^+ \quad (1)$$

$$[In(HL)]^{2+} + HL^- \leftrightarrow [InL_2]^- + 2H^+ \quad (2)$$

$$[InL_2]^- + TZ^+ \leftrightarrow (TZ)[InL_2] \quad (3)$$

Scheme 1. Formation of ternary complexes between In(III), PAR (denoted as H_3L^+ and HL^- in acidic and neutral medium respectively) and tetrazolium cation (denoted as TZ^+).

3.4. Beer's law and analytical characteristics

The validity of Beer's law was checked at optimum conditions (Table 2). The law is valid up to 3.4 μg mL^{-1} indium(III) in both the cases (TZS = TTC or MTT). The following straight-line equations were obtained: Y=0.5752X+0.0008 (for the system containing TTC) and Y=0.6212X+0.0051 (for the system containing MTT). The corresponding molar absorptivity coefficients (6.6×10^4 L mol^{-1} cm^{-1} and 7.1×10^4 L mol^{-1} cm^{-1}) show that PAR+TZS could compete successfully with many spectrophotometric and LLE-spectrophotometric reagents for indium (Table 5). Some other analytical characteristics investigated in the present work LLE-systems are included in Table 6.

4. Conclusions

1. Indium(III) forms chloroform-extractable ternary ion-association complexes with PAR and TZS (TTC, MTT) rather well. The anionic part of the complexes ensures intensive red coloration, and the bulkiness of the cationic part, in its turn, guarantees their poor solubility in water.

2. The following formulae of the complexes are suggested: $(TT^+)[In(PAR)_2]$ and $(MTT^+)[In(PAR)_2]$.

3. The following key constants are calculated: constant of extraction (K_{ex}), constant of association (β), constant of distribution (K_D). The ion-associate involving MTT is slightly more stable and has higher apparent molar absorptivity coefficient (ε' = 7.1×10^4 L mol^{-1} cm^{-1}). Advantages of the system involving TTC are the lower absorbance of the blank and the lower limits of detection and quantification (LOD=0.07 μg mL^{-1}, LOQ=0.24 μg mL^{-1}).

4. The couple PAR-TZS could compete successfully with many reagents for the spectrophotometric and LLE-spectrophotometric determination of indium(III).

Acknowledgment

This work was supported by the Research Fund of the Plovdiv University (Grant No NI11-HF-007).

References

[1] P.I. Fedorov, R.H. Akchurin, Indij (Nauka, MAIK Nauka/Interperiodika, Moskow, 2000) (in Russian)
[2] J. Polendniok, Water, Air, Soil Pollut. 186, 343 (2007)
[3] S.A. Wood, I.M. Samson, Ore Geol. Rev. 28, 57 (2006)
[4] A.M. Alfantazi, R.R. Moskalyk, Miner. Eng. 16, 687 (2003)
[5] J. Polendniok, F. Buhl, Chem. Anal. (Warsaw) 51, 631 (2006)
[6] A. Reller, T. Bublies, T. Staudinger, I. Oswald, S. Meissner, M. Allen, GAIA 18, 127 (2009)
[7] K. Vang, F. Liu, H. Ye, X. Zhang, Iran. J. Chem. Chem. Eng. 29, 19 (2010)
[8] C. Mikolajczak, Technical papers, White papers (Indium Corporation, USA, 2011) http://www.indium.com/techlibrary/whitepapers/availability-of-indium-andgallium
[9] A.P. Paiva, Sep. Sci. Technol. 36, 1395 (2001)
[10] J.S. Liu, H. Chen, X.Y. Chen, Z.L. Guo, Y.C. Hu, C.P. Liu, Y.Z. Sun, Hydrometallurgy 82,137 (2006)
[11] J.-H. Yao, Y.-W. Li, Yejin Fenxi/Metallurgical Analysis 30, 45 (2010)
[12] A.A. Huseyinli, R. Alieva, S. Haciyeva, T. Güray, J. Hazard. Mater. 163, 1001 (2009)
[13] P.P. Kish, S.T. Orlovsky, Zh. Anal. Khim. 17, 1057 (1962) (in Russian)
[14] C.P. Vibhute, S.M. Khopkar, Analyst 111, 435 (1986)
[15] L.L. Kolomiets, I.V. Pyatnitskii, Ukr. Khim. Zh. 45, 62 (1979) (in Russian)
[16] E.A. Biryuk, R.V. Ravitskaya, Zh. Anal. Khim. 26, 735 (1971) (in Russian)
[17] Z. Marczenko, M. Balcerzak, Metod'y spektrofotometrii v UF I vidimoj oblastyakh v neorganicheskom analize (Binom. Laboratoriya znanij, Moskow, 2007) (in Russian)
[18] M. Hniličková, Collection Czech. Chem. Commun. 29, 1424 (1964)
[19] Y.K. Agrawal, V.J. Bhatt, Analyst 111, 57 (1986)
[20] A.I. Busev, V.M. Ivanov, N.S. Khlibova, Zh. Anal. Khim. 22, 547 (1967) (in Russian)
[21] S.A. Abbasi, Anal. Lett. 21, 1705 (1988)
[22] N.K. Agnihotri, S. Ratnani, V.K. Singh, H.B. Singh, Anal. Sci. 19, 1297 (2003)
[23] V.K. Singh, N.K. Agnihotri, H.B. Singh, R.L. Sharma, Talanta 55, 799 (2001)
[24] S.I. Gusev, E.M. Nikolaeva, Zh. Anal. Khim. 21, 166 (1966) (in Russian)
[25] R.L. Sharma, H.B. Singh, M. Satake, Analyst 111, 551 (1986)
[26] F.I. Lobanov, G.K. Nurtaeva, E.E. Ergozhin, Ekstraktsiya kompleksov ionov metallov s piridinovymi oksiazosoedineniyami (Nauka, Alma-Ata, 1983) (in Russian)
[27] D. Bin, W. Shuren, W. Qin, F. Jiawei, Kuangwu Yanshi/Journal of Mineralogy & Petrology 15, 97 (1995)
[28] P. Voznica, J. Havel, L. Sommer, Collection Czech. Chem. Commun. 45, 54 (1980)
[29] C. Ibraimov, S.T. Talipov, N.B. Babaev, I.M. Nurmatov, Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol. 24, 669 (1981) (in Russian)
[30] L. Sommer, M. Langová-Hniličková, Talanta 16, 681 (1969)
[31] S.L.C. Ferreira, A.C.S. Costa, H.A.S. Andrade, Microchem. J. 44, 63 (1991)
[32] A.I. Busev, T.N. Zholondkovskaya, L.S. Krysina, N.A. Golubkova, Zh. Anal. Khim. 27, 2165 (1972) (in Russian)
[33] A.P. Joshi, K.N. Munshi, Mikrochim. Acta 59, 526 (1971)
[34] I.V. Pyatnitskii, A.K. Boryak, L.L. Kolomiets, Zh. Anal. Khim. 41, 2199 (1986) (in Russian)
[35] N.N. Basargin, A.A. Kafarova, Zavod. Lab. 50, 14 (1984) (in Russian)
[36] I.V. Pyatnitskii, L.L. Kolomiets, G.M. Popovich, Zh. Anal. Khim. 38, 815 (1983) (in Russian)
[37] H.A. Mottola, Talanta 11, 715 (1964)
[38] M.S. Rizk, H.A. Mohamed, Y.M. Issa,

M.M. Abu-Agwa, Asian J. Chem. 8, 731 (1996)
[39] Y. Anjaneyulu, C.S. Kavipurapu, M.R.P. Reddy, P.C. Mouli, Analusis 15, 106 (1987)
[40] K.B. Gavazov, Z. Simeonova, A. Alexandrov, Talanta 52, 539 (2000)
[41] K. Gavazov, V. Lekova, G. Patronov, M. Turkyilmaz, Chem. Anal. (Warsaw) 51, 221 (2006)
[42] F. Genç, K.B. Gavazov, M. Türkyilmaz, Cent. Eur. J. Chem. 8, 461 (2010)
[43] K.B. Gavazov, A.N. Dimitrov, V.D. Lekova, Uspekhi Khim. 76, 187 (2007) (in Russian)
[44] K.B. Gavazov, V.D. Lekova, A.N. Dimitrov, G.I. Patronov, Cent. Eur. J. Chem. 5, 257 (2007)
[45] G.A.E. Mostafa, Talanta 71, 1449 (2007)
[46] A.G.F. Elsaid, N.M.H. Rizk, A.B.H. Matter, Asian J. Chem. 22, 1736 (2010)
[47] V. Lekova, P. Racheva, K. Stojnova, A. Dimitrov, K. Gavazov, Chemija 21, 106 (2010)
[48] M.I. Bulatov, I.P. Kalinkin, Prakticheskoe rukovodstvo po fotokolorimetricheskim i spektrofotometricheskim metodam analiza (Khimiya, Leningrad, 1986) (in Russian)
[49] T.M. Seward, C.M.B. Henderson, J.M. Charnock, Chem. Geol. 167, 117 (2000)
[50] W. Likussar, D.F. Boltz, Anal. Chem. 43, 1265 (1971)
[51] A. Alexandrov, O. Budevski, A. Dimitrov, J. Radioanal. Chem. 29, 243 (1976)
[52] H.B. Singh, P.S. Kadyan, Bull. Chem. Soc. Jpn. 61, 3689 (1988)