

Liquid-liquid extraction and spectrophotometric characterization of some new ternary ion-association complexes of gallium(III) and indium(III)

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Complex formation and liquid-liquid extraction were studied in systems containing M(III) (M = gallium or indium), 4-(2-pyridylazo)resorcinol (PAR), tetrazolium salt (TZS), water and chloroform. Two different TZS were used: 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT) and 3-(2-naphthyl)-2,5-diphenyl-2H-tetrazolium chloride (Tetrazolium Violet, TV). The optimum conditions for extraction of Ga(III) and In(III) as ternary complexes with the general formula $(TZ^+)[M(PAR)_2]$ were found: pH, shaking time, concentration of PAR and concentration of TZS. Some key constants (constants of extraction – K_{ex} , constants of association – β , constants of distribution – K_D) and analytical characteristics (molar absorptivities – ϵ_{max} , Sandell's sensitivities – SS, limits of detection – LOD, limits of quantification – LOQ, etc.) were determined. The stability of the obtained ionic associates were compared with literature data for similar ternary compounds, in which TZ^+ is 2,3,5-triphenyl-2H-tetrazolium or 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium. A conclusion was made that TV forms the most stable ($\text{Log } \beta_{(Ga)} = 5.38$, $\text{Log } \beta_{(In)} = 4.58$) and intensively coloured complexes ($\epsilon_{510(Ga)} = 9.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, $\epsilon_{515(In)} = 7.9 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$). $(INT^+)[In(PAR)_2]$ is fairly unstable and this fact can be of importance for the development of an INT-based simple procedure for Ga(III)/In(III) separation.

Key words: gallium, indium, 4-(2-pyridylazo)resorcinol, tetrazolium salts, solvent extraction

INTRODUCTION

Indium and gallium (M) are the two post-transition metals of the highest industrial interest. They are attractive for use in many high technology materials and products, such as integrated circuits, optoelectronic devices, data storage devices, touchscreens, electroluminescent panels, photovoltaic devices, superconductors, cryogenic and ultra-high vacuum devices, solid-state batteries, nuclear reactor control rods, low friction surface materials, magnetic shape memory materials, low freezing point materials, dental alloys, pharmaceutical

drugs, etc. As a result, the indium and gallium usages for 2011 reached 1 500 and 310 tonnes, respectively [1] with bullish tendencies. Unfortunately, the heightened demand cannot be easily met by the known natural resources. Both elements are highly dispersed in the earth's crust and their independent minerals, such as gallite (CuGaS_2), söhngite (Ga(OH)_3), dzhalindite (In(OH)_3), indite (FeIn_2S_2) and roquesite (CuInS_2), are quite rare [2, 3]. That is why indium and gallium are commonly produced as by-products of zinc [3, 4] and aluminium [5] processing operations, respectively. Having in mind that the total known indium reserves (proven and probable, measured and indicated, and inferred) are only 49 000 tonnes [1], it is not surprising that indium is regarded as a semiprecious

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non-ferrous metal [4]; and its high and increasing price [1] is an evidence that controverts the attempts of some industrial circles to belittle the problem with indium shortage and corresponding ecological complications. In order to ensure long-term safety for supply of indium and gallium, new mining investments and appropriate recycling procedures are required [1, 6–9]. Therefore it is important to study new compounds which are prospective for the development of reliable methods of extraction, separation and sensitive determination of these strategic elements.

It is known that M(III) form intensively coloured anionic chelates with azoderivatives of resorcinol [10–18], which can readily associate with bulky cations derived from organic salts, such as 2,3,5-triphenyl-2H-tetrazolium chloride [14, 15], 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide [14, 16], tetraphenylarsonium chloride [13, 18], tetraphenylphosphonium chloride [13, 18], and tetraphenylmethylarsonium iodide [13]. The formed ion-association complexes are slightly soluble in water and easily extracted into organic solvents. In the present paper, we investigated the complex formation and liquid-liquid extraction in four systems containing M(III), 4-(2-pyridylazo)resorcinol (PAR) and tetrazolium salt (TZS). Two TZSs with high analytical potential were used: 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT) [19–22] and 3-(2-naphthyl)-2,5-diphenyl-2H-tetrazolium chloride (Tetrazolium Violet, TV) [22–24]. Their structural formulae are shown in Table 1.

EXPERIMENTAL

Reagents and apparatus

- The stock indium(III) solution (100 mL) was prepared by mixing anhydrous InCl_3 from Alfa Aesar (99.99% metal

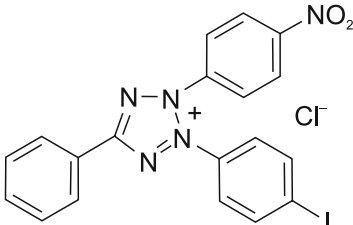
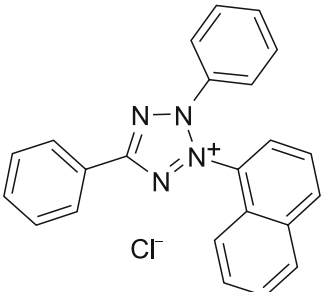
basis; ca. 0.2000 g), 5 mL 1 : 1 HCl and distilled water. Working solutions ($C_{\text{In(III)}} = 1 \times 10^{-4} \text{ mol L}^{-1}$) were prepared by diluting appropriate volumes of the stock solution [14].

- The stock gallium(III) solution was prepared by heating for 20 min a known amount (0.1346 g) of Ga_2O_3 (Koch-Light Laboratories Ltd., 99.99%) in 37% HCl (20 mL). After cooling, the obtained clear solution was collected into a 100 mL calibrated flask and diluted to the mark with 6.5 mol L^{-1} solution of HCl [15]. Fresh working solutions (50 mL) were prepared every day by mixing an aliquot of the stock solution, 0.3 mL of 6.5 mol L^{-1} solution of HCl and distilled water.
- PAR (Fluka AG, p. a.), $2 \times 10^{-3} \text{ mol L}^{-1}$ aqueous solution.
- TZSs: INT (Fluka AG, p. a.) and TV (Loba Feinchemie, p. a.), $3 \times 10^{-3} \text{ mol L}^{-1}$ aqueous solutions.
- Buffer solution, prepared by mixing 2.0 mol L^{-1} aqueous solutions of CH_3COOH and NH_4OH .
- Chloroform (redistilled).
- A Camspec M508 spectrophotometer (United Kingdom), equipped with 10 mm path-length cells.
- A HI 83140 pH meter (Italy).

Procedure for establishing the optimum operating conditions

Aliquots of M(III) solution, PAR solution (up to 2.0 mL), TZS solution (up to 2.0 mL) and buffer solution (pH ranging from 3.2 to 10) 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 (up to 8 min). A portion of the organic extract was filtered through a filter paper into a cell and the absorbance was read against a blank.

Table 1. Tetrazolium salts in the present study

Structural formula	Names and abbreviations
	2-(p-iodophenyl)-3-(p-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (Iodonitrotetrazolium chloride, INT)
	3-(1-naphthyl)-2,5-diphenyl-2H-tetrazolium chloride (Tetrazolium violet, TV)

Procedure for determination of the distribution constants

The distribution constants K_D were 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 [14, 15, 25]. 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. Absorbances A_1 and A_3 were measured against a blank.

RESULTS AND DISCUSSION**Absorption spectra**

Spectra of the extracted in chloroform ternary M(III)-PAR-TZS complexes are shown in Fig. 1. Maxima are recorded at 510 nm for the compounds of Ga(III) (curves 1 and 2) and at 515 nm for the compounds of In(III) (curves 3 and 4). These maxima are shifted to 5–6 nm as compared to the maxima of the binary M(III)-PAR chelates $[ML_2]^-$ existing in aqueous solutions with similar pH ($\lambda_{\max Ga(III)-PAR} = 504\text{--}505\text{ nm}$ [26, 27]; $\lambda_{\max In(III)-PAR} = 510\text{ nm}$ [14]). The observed bathochromic effects are small and suggest the formation of ternary compounds of the ion-association type, $Q^+[ML_2]^-$, similar to these reported for comparable extraction systems [13–16, 18] with participation of cations, Q^+ , derived from 2,3,5-triphenyl-2H-tetrazolium chloride [14, 15], 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide [14, 16], tetraphenylarsonium chloride [13, 18], tetraphenylphosphonium chloride [13, 18] and tetraphenylmethylarsonium iodide [13].

Table 2. Optimum operating conditions

Extraction system	Extraction time, s	pH	$C_{PAR}, \text{mol L}^{-1}$	$C_{TZS}, \text{mol L}^{-1}$	$\lambda_{\max}, \text{nm}$
Ga(III)-PAR-INT-H ₂ O-chloroform	60–180	6.0–7.0	$(1.6\text{--}2.0) \times 10^{-4}$	$(1.6\text{--}2.0) \times 10^{-4}$	510
Ga(III)-PAR-TV-H ₂ O-chloroform	60–180	6.0–7.5	$(1.0\text{--}2.0) \times 10^{-4}$	$(1.0\text{--}2.5) \times 10^{-4}$	510
In(III)-PAR-INT-H ₂ O-chloroform	20	8.0–8.5	$(2.0\text{--}3.0) \times 10^{-4}$	$(3.5\text{--}4.0) \times 10^{-4}$	515
In(III)-PAR-TV-H ₂ O-chloroform	120–150	7.5–8.3	$(1.7\text{--}3.0) \times 10^{-4}$	$(3.0\text{--}3.5) \times 10^{-4}$	515

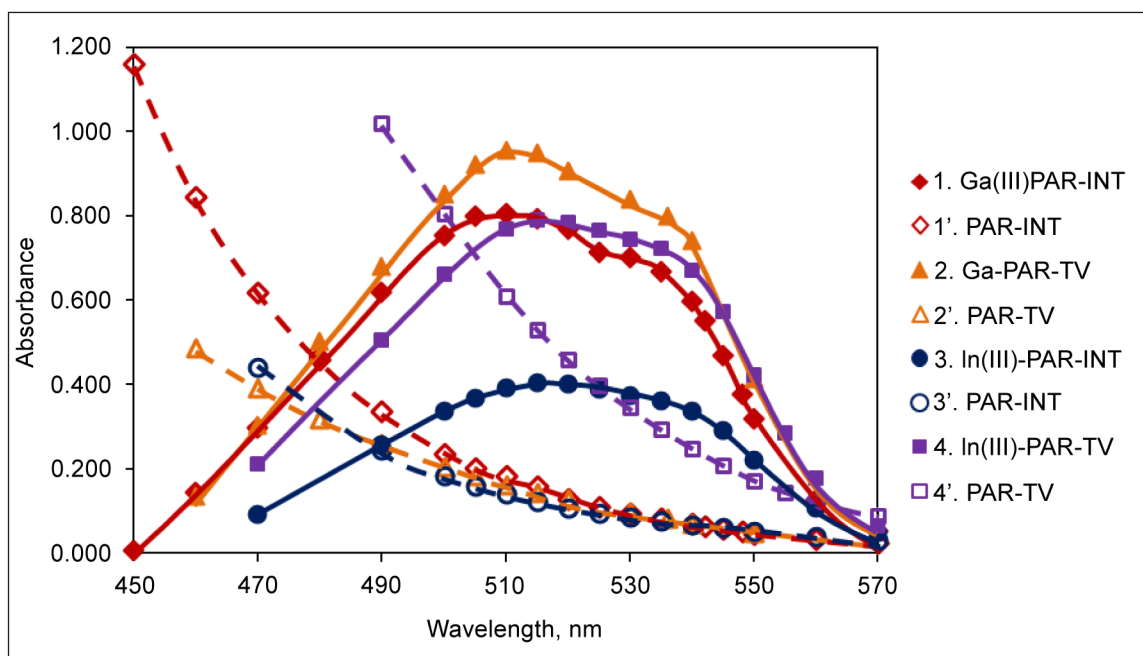


Fig. 1. Absorption spectra of the ternary complexes (curves 1–4; $C_{M(III)} = 1 \times 10^{-5} \text{ mol L}^{-1}$) and blank samples (curves 1'–4') in chloroform
 1, 1' – $C_{PAR} = C_{INT} = 2.0 \times 10^{-4} \text{ mol L}^{-1}$, pH = 6.5;
 2, 2' – $C_{PAR} = 1.2 \times 10^{-4} \text{ mol L}^{-1}$, $C_{TV} = 2.4 \times 10^{-4} \text{ mol L}^{-1}$, pH = 7;
 3, 3' – $C_{PAR} = 2.0 \times 10^{-4} \text{ mol L}^{-1}$, $C_{INT} = 4.0 \times 10^{-4} \text{ mol L}^{-1}$, pH = 8;
 4, 4' – $C_{PAR} = 4.0 \times 10^{-4} \text{ mol L}^{-1}$, $C_{TV} = 4.5 \times 10^{-4} \text{ mol L}^{-1}$, pH = 8.

The following other comments can be made regarding the spectra shown in Fig. 1:

a) The absorbances of both gallium complexes (Ga-PAR-TV and Ga-PAR-INT; curves 1 and 2) are higher than those of the indium complexes (In-PAR-TV and In-PAR-INT; curves 3 and 4).

b) The absorbances of both TV-containing complexes (Ga-PAR-TV and In-PAR-TV; curves 2 and 4) are higher than those of the corresponding INT-containing complexes (curves 1 and 3).

c) The absorbance of the indium complex with participation of INT (curve 3) is significantly lower than that of the corresponding gallium complex (curve 1).

d) Shoulders at about 530–540 nm are clearly observable in addition to the main absorption maxima discussed above.

e) The absorbance of the blank at λ_{max} can be significant (curve 4') if the experiments are performed at high pH and reagent concentrations. If necessary, it can be doubly reduced by measuring at $\lambda_{\text{shoulder}}$.

Effect of pH

Buffer solutions prepared from acetic acid and ammonium hydroxide with a concentration of 2 mol L⁻¹ were applied to control pH. The systems containing Ga(III) and In(III) were buffered with 6 mL [16] and 2 mL [14] buffer solutions, respectively. The effect of pH on the extraction of the ternary species is represented on Fig. 2. It could be seen that In(III)-PAR species are extracted in a great extent at pH values in the range 7.5–8.3 (with TV) or 8.0–8.5 (with INT). Ga(III)

complexes are extracted at lower pH: 6.0–7.5 (with TV) or 6.0–7.0 (with INT). TV appears to be a suitable reagent for simultaneous extraction of Ga(III) and In(III) (curves 2 and 4; pH = 7.5). INT, in its turn, can be used for their separation. At pH close to 5.8 Ga(III) is quantitatively extracted into the organic phase (curve 1), while In(III) remains in the aqueous phase (curve 3).

Effect of reagent concentration

The optimum concentrations of PAR and TZS are shown in Table 2. Large excesses of the reagents have no effect on the absorbance, but could make the reproducibility worse. Under the optimum conditions the colouration of the organic extracts remains constant for at least an hour at room temperature.

Effect of shaking time

The effect of shaking time on the extraction is shown in Fig. 3. The extraction equilibria for Ga-containing systems (curves 1 and 2) are reached for about a minute and longer shaking time does not affect the absorbance. However, in the case of In(III) extraction, the experimental curves have a different character showing maxima at about 20 seconds (curve 3) or 2 minutes (curve 4). The maximum for the In-PAR-INT system is fairly sharp and the absorbance of the extract drops significantly after the maximum. It should be mentioned that 8 minutes of shaking are sufficient to reduce the absorbance to nearly zero. This information could be helpful for development of a procedure for Ga(III)/In(III)

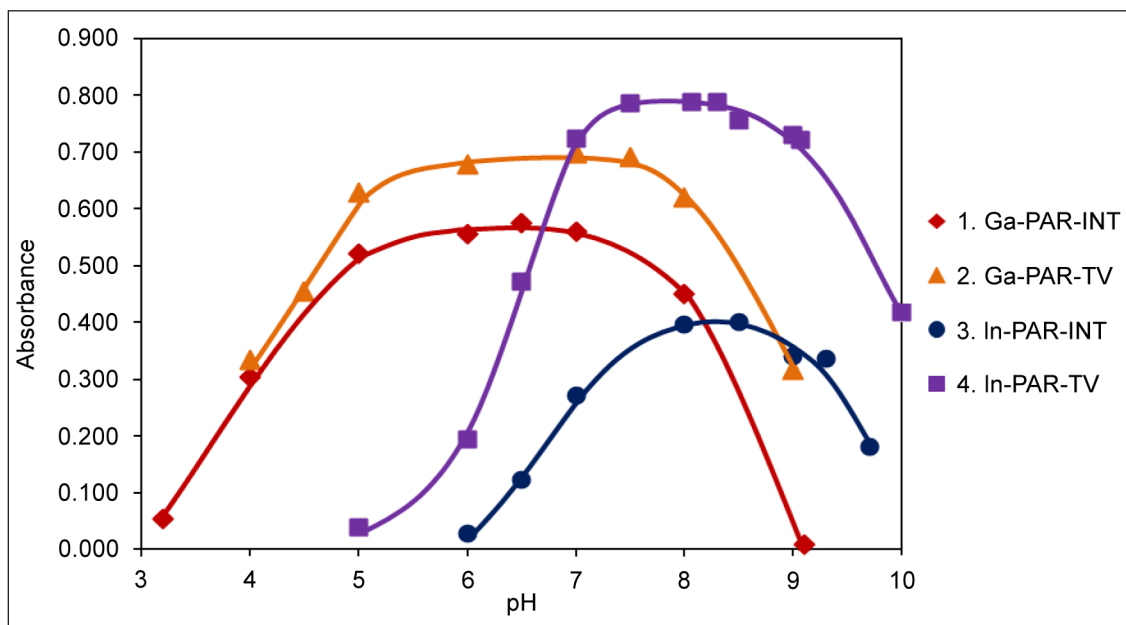


Fig. 2. Absorbance of M(III)-PAR-TZS complexes in chloroform vs. pH of the aqueous phase plots

1 – $C_{\text{Ga(III)}} = 7.2 \times 10^{-6} \text{ mol L}^{-1}$, $C_{\text{PAR}} = C_{\text{INT}} = 2.0 \times 10^{-4} \text{ mol L}^{-1}$, $\lambda = 510 \text{ nm}$;

2 – $C_{\text{Ga(III)}} = 7.2 \times 10^{-6} \text{ mol L}^{-1}$, $C_{\text{PAR}} = 2.0 \times 10^{-4} \text{ mol L}^{-1}$, $C_{\text{TV}} = 3.0 \times 10^{-4} \text{ mol L}^{-1}$, $\lambda = 510 \text{ nm}$;

3 – $C_{\text{In(III)}} = 1.0 \times 10^{-5} \text{ mol L}^{-1}$, $C_{\text{PAR}} = 5.0 \times 10^{-4} \text{ mol L}^{-1}$, $C_{\text{INT}} = 4.0 \times 10^{-4} \text{ mol L}^{-1}$, $\lambda = 515 \text{ nm}$;

4 – $C_{\text{In(III)}} = 1.0 \times 10^{-5} \text{ mol L}^{-1}$, $C_{\text{PAR}} = 4.0 \times 10^{-4} \text{ mol L}^{-1}$, $C_{\text{TV}} = 3.0 \times 10^{-4} \text{ mol L}^{-1}$, $\lambda = 515 \text{ nm}$.

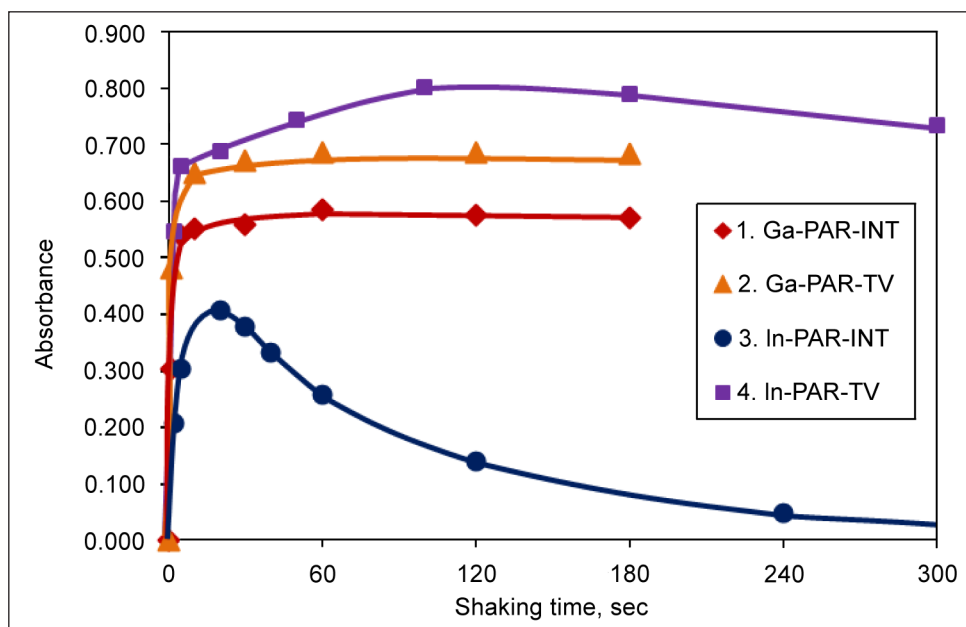


Fig. 3. Effect of shaking time on the absorbance

1 – $C_{\text{Ga(III)}} = 7.2 \times 10^{-6} \text{ mol L}^{-1}$, $C_{\text{PAR}} = C_{\text{INT}} = 2.0 \times 10^{-4} \text{ mol L}^{-1}$, $\text{pH} = 6.5$, $\lambda = 510 \text{ nm}$;

2 – $C_{\text{Ga(III)}} = 7.2 \times 10^{-6} \text{ mol L}^{-1}$, $C_{\text{PAR}} = 2.0 \times 10^{-4} \text{ mol L}^{-1}$, $C_{\text{TV}} = 3.0 \times 10^{-4} \text{ mol L}^{-1}$, $\text{pH} = 7.0$, $\lambda = 510 \text{ nm}$;

3 – $C_{\text{In(III)}} = 1.0 \times 10^{-5} \text{ mol L}^{-1}$, $C_{\text{PAR}} = C_{\text{INT}} = 4.0 \times 10^{-4} \text{ mol L}^{-1}$, $\text{pH} = 8.1$, $\lambda = 515 \text{ nm}$;

4 – $C_{\text{In(III)}} = 1.0 \times 10^{-5} \text{ mol L}^{-1}$, $C_{\text{PAR}} = C_{\text{TV}} = 3.0 \times 10^{-4} \text{ mol L}^{-1}$, $\text{pH} = 8.1$, $\lambda = 515 \text{ nm}$.

separation or elimination of In(III) interference during INT-based extraction-spectrophotometric determination of Ga(III).

Composition of the complexes and suggested formulae

The molar PAR-to-M(III) and TZS-to-M(III) ratios were determined by the method of Asmus [28] and the mobile equilibrium method [29]. The results clearly showed that the composition of both ternary complexes was $M : \text{PAR} : \text{TZS} = 1 : 2 : 1$. Having in mind our previous investigations on similar systems [14–16], we suggest the following general formulae of the anionic chelate and extracted species: $[\text{M}^{3+}(\text{PAR})_2]^-$ and $(\text{TZ}^+)[\text{M}^{3+}(\text{PAR})_2]^-$. In these formulae PAR is in its deprotonated form (PAR^{2-}) and TZ^+ is the tetrazolium cation (TV^+ or INT^+).

Equilibrium constants

Several processes should be taken into account for the system of $[\text{In}(\text{PAR})_2]^-$, TZ^+ , water and chloroform:

i) Association in the aqueous phase between anionic chelate, $[\text{M}(\text{PAR})_2]^-$, and the tetrazolium cation, TZ^+ , with the equilibrium constants $\beta = \frac{[(\text{TZ})[\text{M}(\text{PAR})_2]]}{[\text{TZ}^+] \times [[\text{M}(\text{PAR})_2]^-]}$.

ii) Distribution of the complexes between the aqueous and the organic phase $\{(\text{TZ})[\text{M}(\text{PAR})_2]\}_{\text{aq}} \leftrightarrow \{(\text{TZ})[\text{M}(\text{PAR})_2]\}_{\text{org}}$ with the distribution constants $K_D = \frac{[(\text{TZ})[\text{M}(\text{PAR})_2]]_{\text{org}}}{[(\text{TZ})[\text{M}(\text{PAR})_2]]_{\text{aq}}}$.

iii) Extraction of the ternary complexes from water into chloroform $[\text{M}(\text{PAR})_2]^- + \text{TZ}^+_{\text{aq}} \leftrightarrow \{(\text{TZ})[\text{M}(\text{PAR})_2]\}_{\text{org}}$ with

the extraction constants $K_{\text{ex}} = K_D \times \beta = \frac{[(\text{TZ})[\text{M}(\text{PAR})_2]]_{\text{org}}}{[\text{TZ}^+]_{\text{aq}} \times [[\text{M}(\text{PAR})_2]^-]_{\text{aq}}}$.

The constants of the association β were determined by several independent methods: Holme-Langmihir method [30], Mobile equilibrium method [29], Komar-Tolomachev method [31] and Harvey-Manning method [32].

The constants of the 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 extraction constants were calculated by the equation $K_{\text{ex}} = \beta \times K_D$ [33]. All calculations were carried out at a probability of 95%. The obtained values are presented in Table 3.

A relationship between the association constants of tetrazolium complexes and the molecular mass of tetrazolium cations

Results of several studies have shown that two factors definitely exert influence on the values of association constants β of tetrazolium complexes: the molecular mass (MM) and the presence of $-\text{NO}_2$ groups in the tetrazolium cation. According to [34], a linear relationship exists between MM and β : the higher molecular mass, the higher the association constant. However, when the tetrazolium cation contains nitro group(s), the values of β are considerably lower [22, 35–38] than those expected from the authors of [34].

Fig. 4 shows the relationship between $\text{Log } \beta$ and $\text{Log } \text{MM}_{\text{TZ}^+}$ for series of tetrazolium ion-association complexes of the type $(\text{TZ}^+)_n[\text{ML}_2]^{n-}$, where TZ^+ is 2,3,5-triphenyl-2H-tetra-

Table 3. Values of the extraction constants (K_{ex}), distribution constants (K_D), association constants (β) and recoveries (R%) for the M(III)-PAR-TZS-water-chloroform systems

Extraction system	Log β	Log K_D	Log K_{ex}^e	R%
Ga(III)-PAR-INT-H ₂ O-chloroform	4.82 ± 0.09 ^a	0.91 ± 0.03	5.73 ± 0.12	89.02 ± 0.07
	4.8 ± 0.6 ^b			
	4.5 ± 0.7 ^c			
Ga(III)-PAR-TV-H ₂ O-chloroform	5.38 ± 0.06 ^a	1.29 ± 0.01	6.67 ± 0.07	95.00 ± 0.06
	5.3 ± 0.1 ^b			
	5.0 ± 0.8 ^c			
In(III)-PAR-INT-H ₂ O-chloroform	4.02 ± 0.08 ^a	0.83 ± 0.01	4.85 ± 0.09	86.93 ± 0.07
	3.9 ± 0.1 ^b			
	3.6 ± 0.4 ^c			
	3.9 ± 0.2 ^d			
In(III)-PAR-TV-H ₂ O-chloroform	4.58 ± 0.09 ^a	0.77 ± 0.01	5.35 ± 0.10	85.03 ± 0.08
	4.5 ± 0.3 ^b			
	4.4 ± 0.6 ^c			
	4.4 ± 0.1 ^d			

a – Calculated by the Holme-Langmihir method [30].

b – Calculated by the Mobile equilibrium method [29].

c – Calculated by the Komar-Tolomachev method [31].

d – Calculated by the Harvey-Manning method [32].

e – Calculated by the equation $\text{Log } K_{ex} = \text{Log } \beta + \text{Log } K_D$, where β is the value obtained by the method of Holme-Langmihir [30].

zolum (TT^+), 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium (MTT^+), TV^+ and INT^+ ; M is dioxovanadium(V) (lines 1, 2), oxovanadium(IV) (line 3), Ga(III) (line 4) or In(III) (line 5); and L is deprotonated 4-(2-thiazolylazo)resorcinol (TAR) (line 1) or PAR (lines 2–5). Lines 1–3 have been reported previously [22, 35–37], while lines 4 and 5 are based on the present investigations and the results given in [14–16].

The following comments can be made regarding Fig. 4:

a) Lines 4 and 5 resemble very much the rest lines in Fig. 4.

- A well defined linearity can be seen for the complexes with TT^+ , MTT^+ and TV^+ (full lines);

- The values of the association constants for the complexes of NO_2 -containing TZ^+ (INT^+) are lower than these of TV^+ in spite of the fact that they have higher MM.

b) Complexes of In(III) are more unstable than the corresponding Ga(III) complexes. Especially unstable is $(INT)[In(PAR)_2]$ and this fact could be used in practice (e. g. for Ga(III)/In(III) separation).

Beer's law and analytical characteristics

The validity of the Beer's law was checked at optimum conditions (Table 2). The equations of the obtained straight lines and some important characteristics concerning the

Fig. 4. Logarithm of the association constant (β) of tetrazolium ion-associated complexes vs. the logarithm of the molecular mass of tetrazolium cation (MM_{TZ^+}) plots for the ion associates with $[VO_2(TAR)_2]^{3-}$ (line 1), $[VO_2(PAR)_2]^{3-}$ (line 2), $[VO(PAR)_2]^{2-}$ (line 3), $[Ga(PAR)_2]^-$ (line 4) and $[In(PAR)_2]^-$ (line 5). Lines 1 and 2 are taken from the literature [22, 36]. Line 3 is drawn according to [39]. Lines 4 and 5 are based on the present investigations and the results given in [14–16]. Abbreviations: TAR – 4-(2-thiazolylazo)resorcinol; TT^+ – 2,3,5-triphenyl-2H-tetrazolium; MTT^+ – 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium

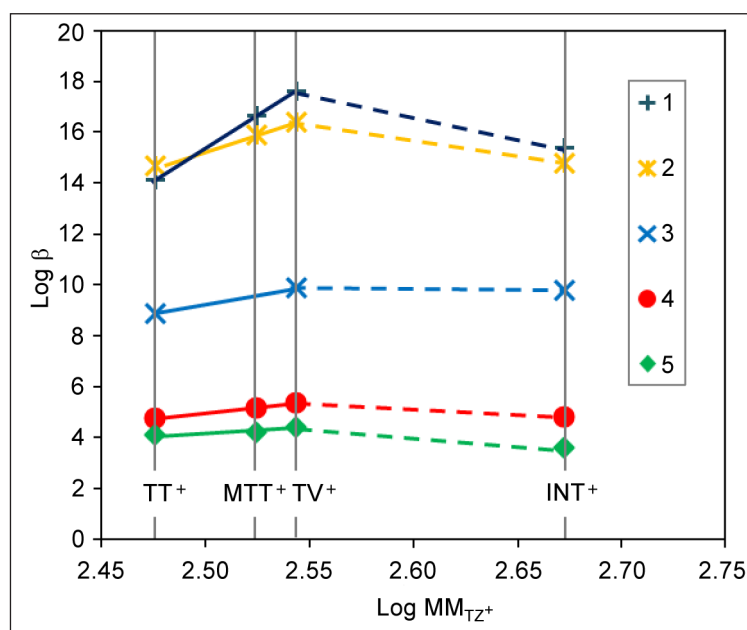


Table 4. Analytical characteristics

Characteristic	Extraction system			
	Ga-PAR-INT	Ga-PAR-TV	In-PAR-INT	In-PAR-TV
Apparent molar absorptivity (ϵ), $\text{L mol}^{-1} \text{cm}^{-1}$	8.2×10^4	9.6×10^4	4.0×10^4	7.9×10^4
Adherence to Beer's law, $\mu\text{g mL}^{-1}$	Up to 1.6	Up to 1.2	Up to 2.0	Up to 1.9
Equation of the straight line	$y = 1.2017x - 0.011$	$y = 1.3674x - 0.0005$	$y = 0.3779x - 0.020$	$y = 0.7459x - 0.021$
Coefficient of correlation	0.9992	0.9995	0.9904	0.9992
Sandell's sensitivity, ng cm^{-2}	0.85	0.73	2.9	1.4
Limit of detection (LOD), $\mu\text{g mL}^{-1}$	0.07	0.04	0.30	0.08
Limit of quantification (LOQ), $\mu\text{g mL}^{-1}$	0.23	0.13	1.0	0.27

application of the ternary complexes for extractive-spectrophotometric determination of Ga(III) and In(III) are listed in Table 4. It should be mentioned that the apparent molar absorptivity of the complexes involving TV are higher than those reported for similar systems [14–16, 18]. This fact could be attributed to higher stability of the ion-associates of this reagent.

CONCLUSIONS

1. Gallium(III) and indium(III) form well chloroform extractable ternary ion-association complexes with PAR and TZS. The anionic part of these complexes, $[\text{M}^{3+}(\text{PAR})_2]^-$, ensures intense red colouration ($\lambda_{\text{max}} = 515 \text{ nm}$ when $\text{M} = \text{In(III)}$ and $\lambda_{\text{max}} = 510 \text{ nm}$ when $\text{M} = \text{Ga(III)}$), and the bulkiness of the cationic part (TZ^+ : INT^+ or TV^+), in its turn, guarantees poor solubility in water.

2. The following equilibrium constants and analytical parameters are calculated: constants of extraction (K_{ex}), constants of association (β), constants of distribution (K_{D}), recovery factors (R%), molar absorptivities (ϵ), Sandell's sensitivities (SS), limits of detection (LOD) and limits of quantification (LOQ). The obtained by independent methods similar values of some of the mentioned above characteristics are the evidence for the correctness of the performed experiments.

3. The ion-associates $(\text{TZ}^+)[\text{M}(\text{PAR})_2]^-$ in which $\text{TZ}^+ = \text{TV}^+$ are more stable than the corresponding associates of other TZ^+ (INT^+ , TT^+ or MTT^+) and have higher molar absorptivities ($\epsilon_{(\text{Ga})} = 9.6 \times 10^4 \text{ L mol}^{-1} \text{cm}^{-1}$, $\epsilon_{(\text{In})} = 7.9 \times 10^4 \text{ L mol}^{-1} \text{cm}^{-1}$). In fact, the couple PAR-TV could compete successfully with many reagents [14, 15] for spectrophotometric and extraction-spectrophotometric determination of Ga(III) and In(III) in terms of sensitivity.

4. The In(III)-containing ion-associates are more unstable than the corresponding Ga(III) associates. Especially unstable is $(\text{INT}^+)[\text{In}(\text{PAR})_2]^-$. This peculiarity could be used for separation of Ga(III) and In(III) by two different approaches.

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NAUJŲ GALIO (III) IR INDŽIO (III) JONINIŲ KOMPLEKSŲ SKYSTINĖ EKSTRAKCIJA IR SPEKTROFOTOMETRINIS APIBŪDINIMAS

S a n t r a u k a

Buvo tiriamas kompleksų susidarymas ir skystinė ekstrakcija sistemoje, turinčiose galio(III) ar indžio(III) jonų, 4-(2-piridilazo)rezorcinolio, tetrazolio druskų, vandens ir chloroformo. Rastos optimalios sąlygos Ga(III) ir In(III) kompleksų ekstrakcijai bei nustatytos kai kurios konstantos – ekstrakcijos, asociacijos ir pasiskirstymo konstantos, o taip pat analitinės charakteristikos – moliarinis šviesos sugerties koeficientas, jautrumas, aptikimo ribos ir kt.