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Extraction-spectrophotometric investigations on two ternary ion-association complexes of gallium(III)

Research Article

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Abstract: Complex formation and liquid-liquid extraction were studied in systems containing Ga(III), azoderivative of resorcinol {4-(2-pyridylazo) resorcinol (PAR) or 4-(2-thiazolylazo)resorcinol (TAR)}, 2,3,5-triphenyltetrazolium chloride (TTC), water and chloroform. The optimum conditions w.r.t. pH, extraction time, concentration of ADR and concentration of TTC for the extraction of Ga(III) as an ion-associate complex were found.. The composition of the extracted complexes, $(TT^+)[Ga(PAR)_2]$ (I), $(TT^+)[Ga(TAR)_2]$ (II) or $(TT^+)_2[Ga(OH)(TAR)_2]$ (III), and the constants of association (β) between 2,3,5-triphenyltetrazolium cation (TT^+) with corresponding anionic chelates were established by several methods. The constants of distribution (K_D) and extraction (K_{ex}) of the principal species I and III were determined as well. The apparent molar absorptivities of the chloroform extract at the optimum extraction-spectrophotometric conditions were $\varepsilon'_{510}=9.5\times10^4$ L mol^{-1} cm^{-1} (I) and $\varepsilon'_{530}=4.6\times10^4$ L mol^{-1} cm^{-1} (III). The validity of Beer's law was checked and analytical characteristics that were calculated are reported herein.

Keywords: *Gallium • Liquid-liquid extraction • 4-(2-Pyridylazo)resorcinol • 4-(2-Thiazolylazo)resorcinol • Tetrazolium salty*

1. Introduction

Gallium, a post-transition metal of strategic importance for various priority areas of technology and science, readily forms intensively colored chelates with azo dyes, such as 4-(2-pyridylazo)resorcinol (PAR) [1-14], 4-(2-thiazolylazo)resorcinol (TAR) [15,16], 1-(2-pyridylazo)-2-naphthol [14,17-20], 2-(2-pyridylazo)-1-naphthol-4-sulfonic acid [21], 1-(2-thiazolylazo)-2-naphtol-3,6-disulphonic acid [22], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol [12,23], sulphonaphthylazo dyes [24], hydroxy naphthoic acid azo dyes [25], 5-(2-pyridylazo)-2-monoethyl-p-cresol [26], 2-(2-pyridylazo)-5-diethyl-m-aminophenol [26], Lumogallion [27], Eriochrome Black T [28,29] and sulfarsazene [30]. In many cases the azo dyes have been used for spectrophotometric or extraction-spectrophotometric determination of gallium(III) together with an auxiliary reagents such as monocarboxylic acids [5,22,27,29], antipyrine [8], cetylpyridinium chloride [23], cetyltrimethylammonium bromide [19], sodium dodecylsulfate [1,12,18], Brij 35 [12], pyridine [7], sodium acetate [7], tetraphenylarsonium chloride [11] and tetraphenylphosphonium chloride [11] which can improve the chromogenic and/or extraction characteristics of the complex. Extraction systems containing both a gallium(III) chelate and a tetrazolium salt have not been studied so far. In the present paper, we investigated complex formation and liquid-liquid extraction in the Ga(III), azoderivative of resorcinol (ADR: PAR or TAR), 2,3,5-triphenyltetrazolium chloride (TTC), water and chloroform system. Structural formulae of the reagents are presented in Table 1.

2. Experimental procedure

2.1. Reagents and apparatus

The stock solution of gallium(III) (*ca* 1.4×10^{-2} mol L^{-1}) was prepared by heating for 20 min a known amount of Ga_2O_3 (Koch-Light Laboratories Ltd., 99,99%) in 37%

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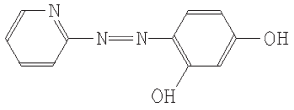
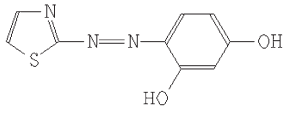
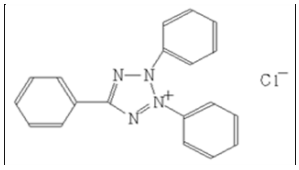
Table 1. Reagents in the present study.

Formulae	Name	Abbreviation
	4-(2-pyridylazo)resorcinol	PAR
	4-(2-thiazolylazo)resorcinol	TAR
	2,3,5-triphenyl-2H-tetrazolium chloride	TTC

HCl (20 mL). After cooling, the clear solution obtained was collected in a 100 mL calibrated flask and diluted to the mark with 6.5 mol L^{-1} solution of HCl. Working solutions (50 mL) were prepared fresh every day by mixing 0.5 mL of the stock solution with 0.3 mL of 6.5 mol L^{-1} solution of HCl and distilled water. 2×10^{-3} mol L^{-1} or 3×10^{-3} mol L^{-1} aqueous solutions of PAR (Fluka AG), TAR (Aldrich Chem. Co) and TTC (Loba Feinchemie) reagents were used. Redistilled chloroform was used as the organic solvent. The acidity of the aqueous medium was set using the buffer solution prepared by mixing 2.0 mol L^{-1} aqueous solutions of CH_3COOH and NH_4OH. The 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.

2.2. Procedure for establishing the optimum operating conditions

Aliquots of Ga(III) solution, ADR solution (up to 2 mL), TTC solution (up to 2 mL) and buffer solution (3-6 mL; pH ranging from 4 to 9) 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 5-180 sec. 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 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 for chloroform obtained after a single extraction (at the optimum operating conditions – see Table 2) and A_3 is the absorbance for chloroform obtained after a triple extraction under the same conditions [31,32]. 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 of chloroform to the aqueous phase that 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.

3. Results and discussion

3.1. Spectral characteristics and optimum operating conditions

It has been reported that in aqueous solutions stepwise formation of two types of complexes occur with Ga-ADR ratios of 1:1 and 1:2 [4,8,16]. In the pH range of 3.5 - 8.5 and with an excess of ligand (ADR=PAR=H_2L'), the dominating species is GaL'_2^- [3,4,10,11] having λ_{max} 504-505 nm. An analogical complex (λ_{max}=525-530 nm) was supposed when ADR=TAR=H_2L'' (in 30% aqueous ethanol medium; pH~5), however, the complex formation had been complicated by hydrolysis [16]. Other species that were detected

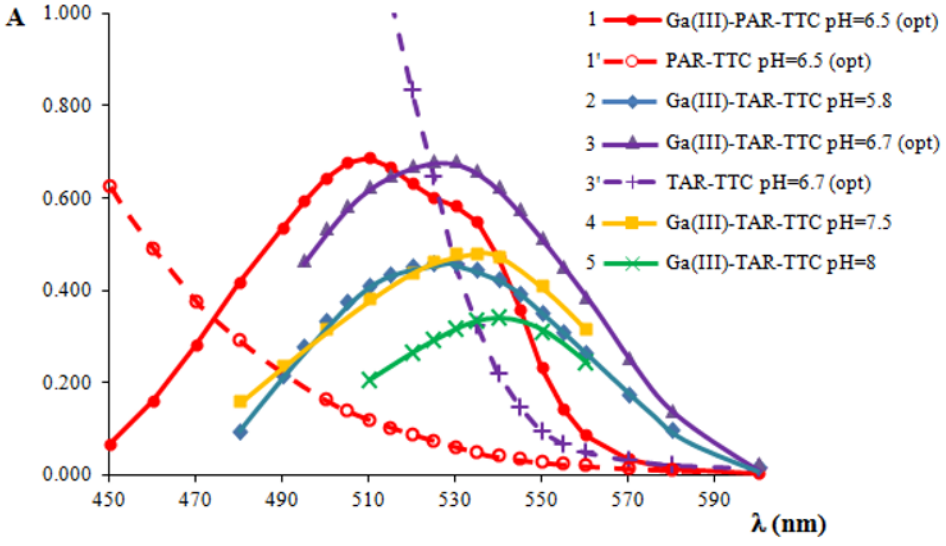


Figure 1. Absorption spectra of the ternary complexes (full lines) and blank samples (dashed lines) in chloroform.
1 – $C_{Ga(III)}$= 7.20×10^{-6} mol L^{-1}, C_{PAR}=2.0×10^{-4} mol L^{-1}, C_{TTC}=3.0×10^{-4} mol L^{-1}, pH=6.5;
1' – C_{PAR} = 2.00×10^{-4} mol L^{-1}, C_{TTC}=3.0×10^{-4} mol L^{-1}, pH=6.5;
2 – $C_{Ga(III)}$= 1.44×10^{-5} mol L^{-1}, C_{TAR}=2.2×10^{-4} mol L^{-1}, C_{TTC}=2.4×10^{-4} mol L^{-1}, pH=5.8;
3 – $C_{Ga(III)}$= 1.44×10^{-5} mol L^{-1}, C_{TAR}=2.2×10^{-4} mol L^{-1}, C_{TTC}=2.4×10^{-4} mol L^{-1}, pH=6.7;
3' – C_{TAR} = 2.20×10^{-4} mol L^{-1}, C_{TTC}=2.4×10^{-4} mol L^{-1}, pH=6.7;
4 – $C_{Ga(III)}$= 1.44×10^{-5} mol L^{-1}, C_{TAR}=1.4×10^{-4} mol L^{-1}, C_{TTC}=2.1×10^{-4} mol L^{-1}, pH=7.5;
5 – $C_{Ga(III)}$= 1.44×10^{-5} mol L^{-1}, C_{TAR}=1.4×10^{-4} mol L^{-1}, C_{TTC}=2.1×10^{-4} mol L^{-1}, pH=8.0

Table 2. Optimum operating conditions.

Extraction system	Extraction time [min]	pH[a]	C_{ADR} [mol L^{-1}]	C_{TTC} [mol L^{-1}]	λ_{max} [nm]
Ga(III)-PAR-TTC-H_2O-chloroform	2	6.5	2.0×10^{-4}	3.0×10^{-4}	510
Ga(III)-TAR-TTC-H_2O-chloroform	2	6.7	2.2×10^{-4}	2.4×10^{-4}	530

[a] – *The experiments were performed in the presence of 6 mL buffer solution with concentration of 2 mol L^{-1}*

in Ga(III)-TAR aqueous system at lower pH were GaHL″$^{2+}$, GaL″$^{+}$ and GaHL″(OH)$^{+}$ [16].

The spectra of the ternary Ga-ADR-TTC complexes extracted in chloroform are shown in Fig. 1. A maximum is recorded at 510 nm (curve 1) for the complex with PAR independently from the pH in the investigated pH range (3-9). This maximum is shifted to 5-6 nm as compared to the maximum of the binary Ga(III)-PAR chelate in aqueous medium. The bathochromic effect observed is small and suggests the formation of a ion-association compound. The ion-associates of Ga(III)-PAR chelate $[GaL'_2]^-$ and tetraphenyl onium cations [11] also have maxima at 510 nm in chloroform.

Curves 2-5 in Fig. 1 represent the Ga-TAR-TTC system at different pH values. One can conclude that with increasing pH the absorption maximum is shifted to the longer wavelength. At the optimum operating conditions (Table 2 and Fig. 1, curve 2) the maximum is situated at 530 nm. The effect of pH on the extraction is shown in Fig. 2.

3.2. Composition of the complexes, reaction schemes and equilibrium constants

The molar ADR-to-Ga(III) ratio in the ternary complexes at the optimum pH were determined by the method of Asmus [33] (Fig. 3) and the mobile equilibrium method [34]. The results show that complexes with a 2:1 ADR-to-Ga(III) ratio are formed in both the cases where ADR=PAR and ADR=TAR. Such a molar ratio is in accordance with the literature describing complex formation in binary aqueous system Ga(III)-ADR [3,4,10,16] or ternary Ga(III)-ADR-TPO systems [11], where TPO is tetraphenyl'onium salt.

The molar TTC-to-Ga(III) ratios were determined by the method of Asmus, the method of continuous variations [33] (Fig. 4), and the mobile equilibrium method [34] (Fig. 5). The results show that in the presence of PAR the stoichiometry is 1:1, while in the presence of TAR the molar ratio could be 1:1 or 2:1 (TTC:Ga) depending on TTC concentration.

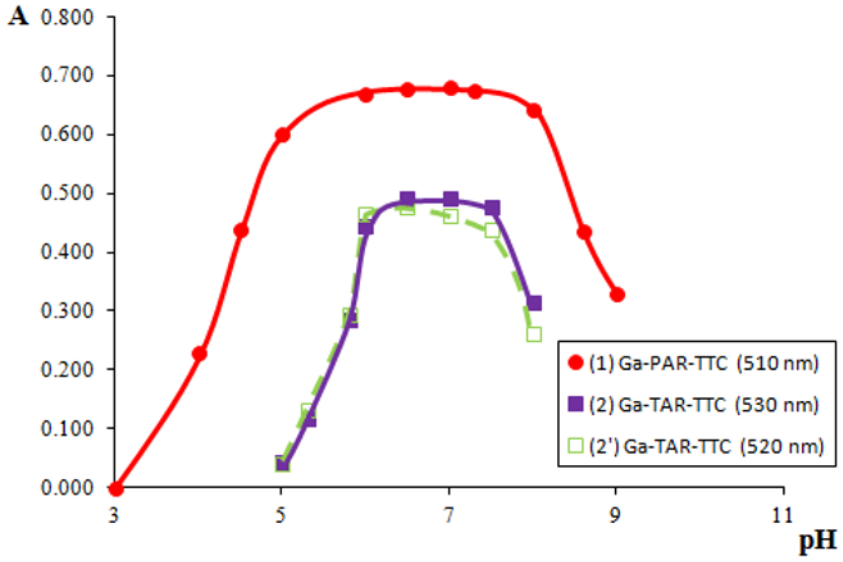


Figure 2. Absorbance of Ga(III)-ADR-TTC complexes in chloroform vs. pH of the aqueous phase plots.
1 – $C_{Ga(III)}$= 7.20×10^{-6} mol L^{-1}, C_{PAR}=2.0×10^{-4} mol L^{-1}, C_{TTC}=3.0×10^{-4} mol L^{-1}, λ=510 nm;
2 – $C_{Ga(III)}$= 1.44×10^{-5} mol L^{-1}, C_{TAR}=1.4×10^{-4} mol L^{-1}, C_{TTC}=2.1×10^{-4} mol L^{-1}, pH=6.7, λ=530 nm;
2' – $C_{Ga(III)}$= 1.44×10^{-5} mol L^{-1}, C_{TAR}=1.4×10^{-4} mol L^{-1}, C_{TTC}=2.1×10^{-4} mol L^{-1}, pH=6.7, λ=520 nm

It is known that $Ga(OH)_4^-$ are the predominant gallium species at pH >4 (at 25ºC) [35]. In the pH intervals 5.6-11.9 (PAR) and 6.23-9.44 (TAR) ADR exist as monoprotonated anions [36]. As per the molar ratios obtained for Ga(III)-PAR-TTC=1:2:1 and Ga(III)-TAR-TTC=1:2:1 or 1:2:2, one can conclude that the formation of extractable complexes at the optimum pH takes place as shown in Schemes 1 and 2.

Several equilibrium processes should be taken into account for the Ga(III), ADR, TTC, water and chloroform system, such as:

(i) Formation of ion-associate complexes in the aqueous phase according to Eqs. 2, 2a and 4;

(ii) Distribution of the complexes between the aqueous and the organic phase;

(iii) Extraction of the ternary complexes from water into chloroform.

The process (i) is described by the constant of association β; the process (ii) performed at the optimum conditions is described by the constant of distribution K_D; and the process (iii) is described by the constant of extraction $K_{ex}=K_D\times\beta$. The equilibrium processes mentioned above and values calculated for the corresponding conditional constants are represented in Tables 3 and 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) in equal volumes as described in section 2.3. The constants of association

$$Ga(OH)_4^- + 2HL'^- \leftrightarrows [GaL'_2]^- + 2OH^- + 2H_2 \quad (1)$$

$$Ga(OH)_4^- + 2HL''^- \leftrightarrows [GaL''_2]^- + 2OH^- + 2H_2 \quad (1a)$$

$$[GaL'_2]^- + TT^+ \leftrightarrows (TT)[GaL'_2 \quad (2)$$

$$[GaL''_2]^- + TT^+ \leftrightarrows (TT)[GaL''_2] \quad (2a)$$

Scheme 1. Formation of ternary complexes between Ga(III), ADR and TTC in aqueous medium at the optimum pH. PAR and TAR are denoted as HL'^- and HL''^-, respectively; 2,3,5-triphenyltetrazolium cation is denoted as TT^+. Processes 1a and 2a take place only in deficiency of TTC.

$$Ga(OH)_4^- + 2HL''^- \leftrightarrows [Ga(OH)L''_2]^{2-} + OH^- + 2H_2O \quad (3)$$

$$[Ga(OH)L''_2]^{2-} + 2TT^+ \leftrightarrows (TT)_2[Ga(OH)L''_2] \quad (4)$$

Scheme 2. Formation of ternary complexes between Ga(III), TAR (denoted as HL''^-) and 2,3,5-triphenyltetrazolium cation (denoted as TT^+) at the optimum TTC concentration.

β were calculated by the mobile equilibrium method (Fig. 5) [34], the method of Komar and Tolmachev (Fig. 6) [33], and the method of Holme-Langmihr [37]. The constants of extraction were determined by the equation Log K_{ex}= Log K_D + Log β, where Log β is the value obtained by the statistically most reliable method [37] (see the results in Tables 3 and 4). All calculations were carried out at a probability of 95%.

Table 3. Extraction equilibria and conditional equilibrium constants for the Ga(III)-PAR-TTC-water-chloroform system.

Equilibrium	Equilibrium constant	Value
$Ga(PAR)_2^- + TT^+ \leftrightarrows (TT)Ga(PAR)_{2\,aq}$	$\beta=[(TT)Ga(PAR)_2] / [TT^+] \times [Ga(PAR)_2^-]$	Log β=4.79±0.04[a] Log β=4.70±0.20[b] Log β=4.40±0.80[c]
$\{(TT)Ga(PAR)_2\}_{aq} \leftrightarrows \{(TT)Ga(PAR)_2\}_{org}$	$K_D=[(TT)Ga(PAR)_2]_{org} / [(TT)Ga(PAR)_2]_{aq}$	Log K_D=0.994±0.003[d]
$Ga(PAR)_{2\,aq}^- + TT^+_{aq} \leftrightarrows \{(TT)Ga(PAR)_2\}_{org}$	$K_{ex}=[(TT)Ga(PAR)_2]_{org} / [TT^+]_{aq} \times [Ga(PAR)_2^-]_{aq}$	Log K_{ex}=5.780±0.040[e]

a – Calculated by the method of Holme-Langmihr [37]
b – Calculated by the Mobile equilibrium method [34]
c – Calculated by the method of Komar-Tolomachev [33]
d – Calculated by the equation $K_D = A_i/(A_3-A_i)$ (sec. 2.3)
e – Calculated by the equation Log K_{ex} = Log β + Log K_D, where β is calculated by the method of Holme-Langmihr [37]

Table 4. Extraction equilibria and conditional equilibrium constants for the Ga(III)-TAR-TTC-water-chloroform system.

Equilibrium	Equilibrium constant	Value
$Ga(OH)(TAR)_2^{2-} + 2TT^+ \leftrightarrows (TT)_2Ga(OH)(TAR)_{2\,aq}$	$\beta=[(TT)_2Ga(OH)(TAR)_2] / [TT^+]^2 \times [Ga(OH)(TAR)_2^{2-}]$	Log β=9.3±0.1[a] Log β=9.5±0.3[b] Log β=10±1[c]
$Ga(TAR)_2^- + TT^+ \leftrightarrows (TT)Ga(TAR)_2$	$\beta=[(TT)Ga(TAR)_2] / [TT^+] \times [Ga(TAR)_2^{2-}]$	Log β=4.5±0.3[b] Log β=4.8±0.8[c]
$\{(TT)_2Ga(OH)(TAR)_2\}_{aq} \leftrightarrows \{(TT)_2Ga(OH)(TAR)_2\}_{org}$	$K_D=[(TT)Ga(TAR)_2]_{org} / [(TT)Ga(TAR)_2]_{ag}$	Log K_D=1.078±0.004[d]
$Ga(OH)(TAR)_{2\,aq}^{2-} + 2TT^+_{aq} \leftrightarrows \{(TT)_2Ga(OH)(TAR)_2\}_{org}$	$K_{ex}=[(TT)Ga(TAR)_2]_{org} / [TT^+]_{aq} \times [Ga(TAR)_2^-]_{aq}$	Log K_{ex}=10.4±0.1[e] Log K_{ex}=10.1±0.4[f]

a – Calculated by the method of Holme-Langmihr [37]
b – Calculated by the Mobile equilibrium method [34]
c – Calculated by the method of Komar-Tolomachev [33]
d – Calculated by the equation $K_D = A_i/(A_3-A_i)$ (sec. 2.3)
e – Calculated by the equation Log K_{ex} = Log β + Log K_D, where β is calculated by the method of Holme-Langmihr [37]
f – Calculated by the method of Likussar and Boltz [38]

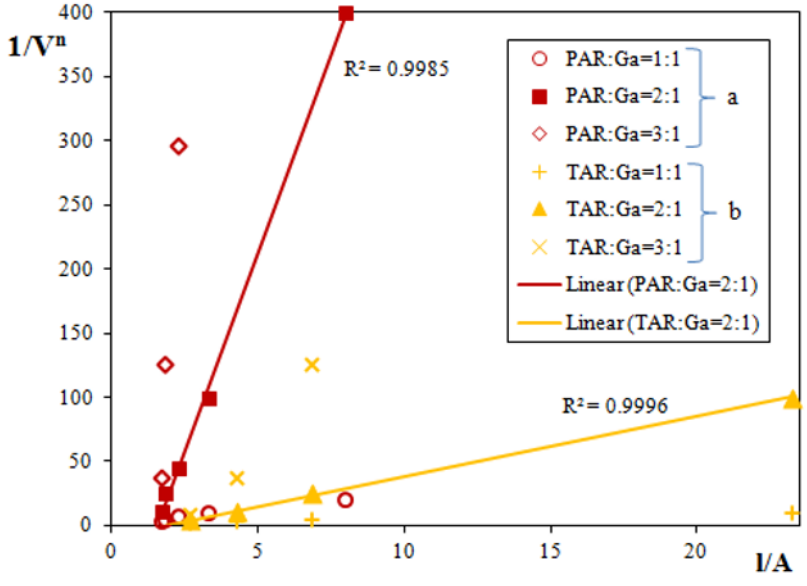


Figure 3. Determination of the ADR-to-Ga(III) molar ratios by the method of Asmus.
a) Ga(III)-PAR-TTC system at pH=6.5, $C_{Ga(III)}=7.20\times10^{-6}$ mol L^{-1} and $C_{TTC}=3.0\times10^{-4}$ mol L^{-1};
b) Ga(III)-TAR-TTC system at pH=6.7, $C_{Ga(III)}=1.44\times10^{-5}$ mol L^{-1} and $C_{TTC}=2.1\times10^{-4}$ mol L^{-1}.

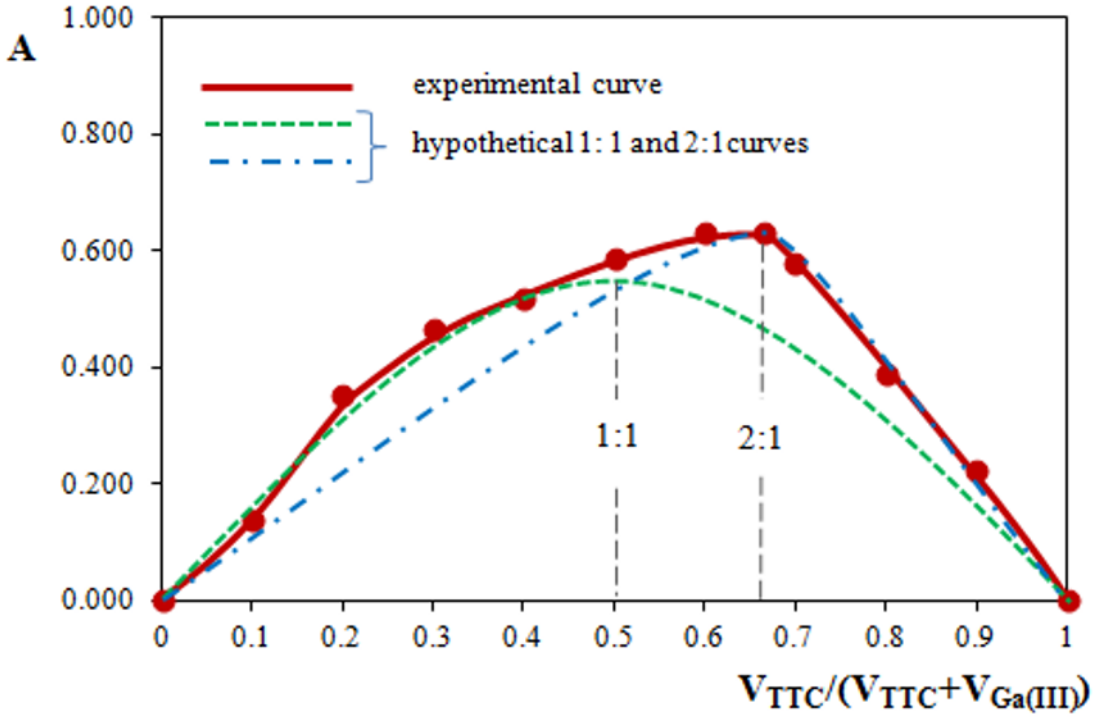


Figure 4. Determination of the TTC-to-Ga(III) molar ratio in the Ga(III)-TAR-TTC system by the method of continuous variations. pH=6.7, $C_{Ga(III)}+C_{TTC}=6\times10^{-5}$ mol L^{-1}, $C_{TAR}=2.2\times10^{-4}$ mol L^{-1}, λ=530 nm.

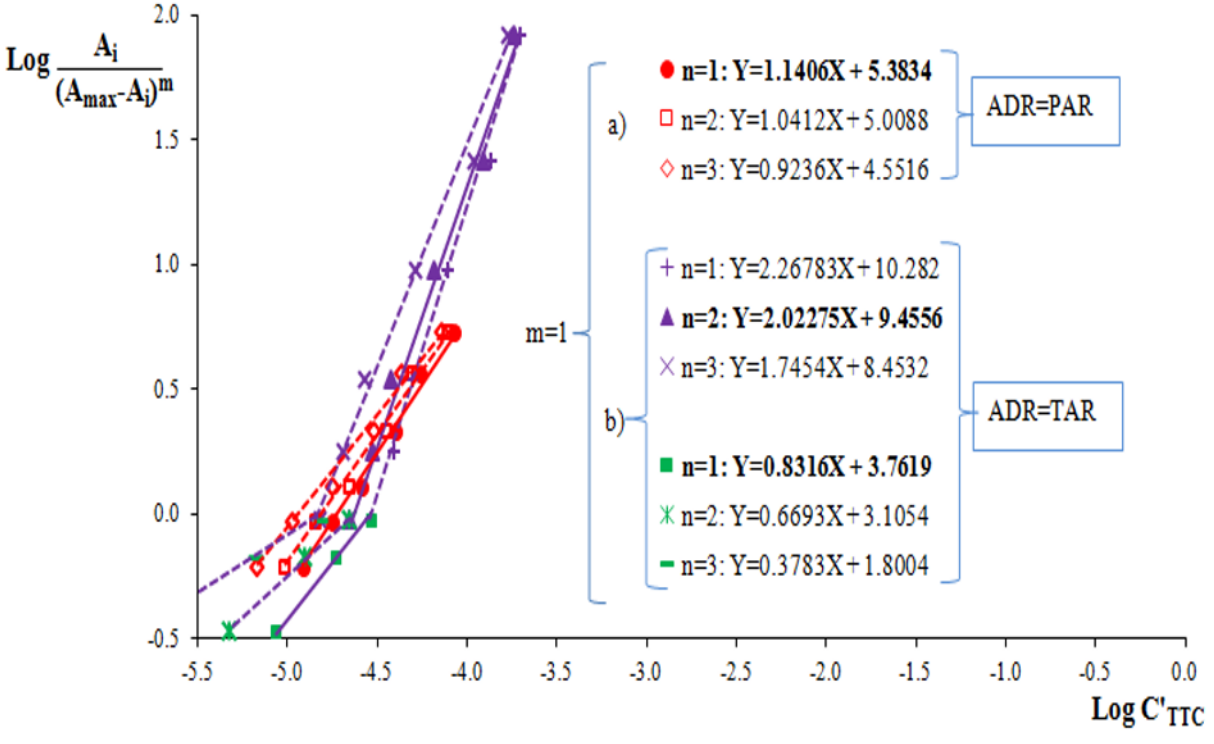


Figure 5. Determination of the constants of association (β) and the TTC-to-Ga(III) molar ratios by the mobile equilibrium method.
a) Ga(III)-PAR-TTC (red markers): pH=6.5, $C_{Ga(III)}=7.2\times10^{-6}$ mol L^{-1}, $C_{PAR}=2.0\times10^{-4}$ mol L^{-1};
b) Ga(III)-TAR-TTC (violet and green markers): pH=6.7, $C_{Ga(III)}=1.44\times10^{-5}$ mol L^{-1}, $C_{TAR}=2.2\times10^{-4}$ mol L^{-1}.

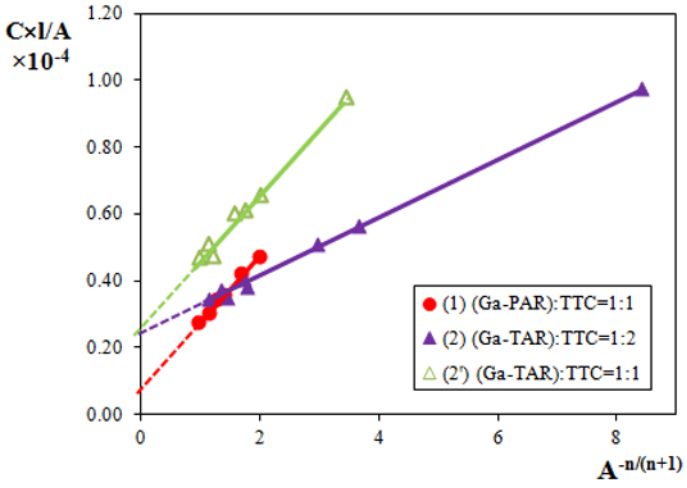


Figure 6. Determination of the constants of association (β) and true molar absorptivities (ε) by the method of Komar-Tolmachev.
pH=6.5, $C_{PAR}=2\times10^{-4}$ mol L^{-1} (straight line 1);
pH=6.7, $C_{TAR}=2.2\times10^{-4}$ mol L^{-1} (straight lines 2 and 2').
The following stright lines (Y=aX+b) slopes (a) and Y-intercepts (b) were obtained:
(1) a=(1.985±0.050)×10^{-5}, b=(8.73±0.72)×10^{-6};
(2) a=(8.722±0.014)×10^{-6}, b=(2.424±0.051)×10^{-5};
(2') a=(1.975±0.072)×10^{-5}, b=(2.67±0.15)×10^{-5}.
The calculated true molar absorptivities (ε=1/b) are ε=(1.14±0.09)×10^{5}, ε=(4.13±0.09)×10^{4} and ε=(3.7±0.2)×10^{4} L mol^{-1} cm^{-1} respectively.

Table 5. Molar absorptivities of some binary and ternary gallium(III) complexes.

Reagent(s)	Organic solvent(s)	Molar absorptivity ×10^{-4} [L mol^{-1} cm^{-1}]	Ref.
1-(2-Thiazolylazo)-2-naphtol-3,6-disulphonic Acid	–	ε_{570}=2.33	[22]
1-(2-Pyridylazo)-2-Naphthol (PAN)	chloroform	ε_{550}=2.70	[14,20]
Rutin + hexadecylpyridinum bromide	–	ε_{430}=3.10	[39]
Eriochrom black T	chloroform + n-butanol + capronic acid	ε_{620}=3.40	[29]
Semimethylthymol Blue	–	ε_{580}=4.25	[40]
Bipyridyl glyoxal bis(4-phenyl-3-thiosemicarbazone)	–	ε_{430}=4.60	[41]
Pyrocatechol Violet + tridodecylethylammonium bromide	xylene	ε_{585}=8.00	[42]
PAR + tetraphenylarsonium chloride	1,2-dichlorobenzene	ε_{510}=8.20	[6]
PAR + pyridine + sodium acetate	isopropyl ether + butyl acetate	ε_{510}=10.00	[7]
Chrome Azurol S + benzyldimethyllaurylammonium bromide	–	ε_{620}=11.00	[43,44]
Eriochrome Cyanine R + cetyltrimethylammonium bromide	–	ε_{588}=11.00	[45]
2-(5-Bromo-2-Pyridylazo)-5- diethylaminophenol + sodium dodecylsulfate + BRIJ 35	–	ε_{575}=12.00	[12]
TAR + TTC	chloroform	ε_{530}=4.60	This work
PAR + TTC	chloroform	ε_{510}=9.50	This work

3.3. 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 1.1 μg mL^{-1} or 1.2 μg mL^{-1} gallium(III) for the systems with PAR and TAR, respectively. The following straight-line equations were obtained: y=1.3255x + 0.0126 (for the system containing PAR) and y=0.6596x+0.0047 (for the system containing TAR). The corresponding squared correlation coefficients R^2 were 0.9993 and 0.9943. The apparent molar absorptivity coefficient of the PAR complex (ε'=9.5×10^4 L mol^{-1} cm^{-1}) was twice as high as that for the TAR complex. From Table 5 one can conclude that PAR & TTC could compete successfully with many spectrophotometric and extraction reagents for sensitivity in terms of gallium determination. Some important analytical characteristics of the extraction systems investigated in the present work are listed in Table 6.

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

Analytical characteristics	Ga(III)-PAR-TTC-H_2O-$CHCl_3$	Ga(III)-TAR-TTC-H_2O-$CHCl_3$
Apparent molar absorptivity (ε')	9.5×10^4 L mol^{-1} cm^{-1}	4.6×10^4 L mol^{-1} cm^{-1}
Sandell's sensitivity (SS)	0.73 ng cm^{-2}	1.5 ng cm^{-2}
Adherence to Beer's law	Up to 1.1 μg mL^{-1}	Up to 1.2 μg mL^{-1}
Limit of detection (LOD)	0.035 μg mL^{-1}	0.10 μg mL^{-1}
Limit of quantification (LOQ)	0.12 μg mL^{-1}	0.33 μg mL^{-1}

4. Conclusions

1. Gallium(III) forms chloroform extractable ternary ion-association complexes with PAR and TTC. The anionic part of the complexes ensures intense red coloration, and the bulkiness of the cationic part, in its turn, guarantees poor solubility in water.

2. The following formulae of the complexes in solution are suggested at the optimum extraction conditions: $(TT^+)[Ga(PAR)_2]$ and $(TT^+)_2[Ga(OH)(TAR)_2]$.

3. The following conditional constants are calculated: constant of extraction (K_{ex}), constant of association (β), constant of distribution (K_D). The values obtained by different methods are statistically indistinguishable and; this is an indication of the correctness of the experiments and suggested reaction schemes.

4. The apparent molar absorptivity coefficient of the Ga-PAR-TTC complex (ε'=9.5×10^4 L mol^{-1} cm^{-1}) is twice as high as that obtained for the complex of TAR. Other advantages of the system involving PAR are the lower absorbance of the blank, higher reproducibility of the results and lower limits of detection and quantification.

5. The PAR & TTC could compete successfully with many reagents for the spectrophotometric and liquid-liquid extraction for spectrophotometric determination of gallium(III).

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