Scientific paper

Ion-Association Complexes of Gallium(III) – 4-(2-Pyridylazo)-resorcinol Anionic Chelates and Dicationic Tetrazolium Reagents

Kirila T. Stojnova, Kiril B. Gavazov* and Vanya D. Lekova

Department of General and Inorganic Chemistry, University of Plovdiv "Paisii Hilendatski", 24 Tsar Assen St., 4000 Plovdiv, Bulgaria

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

Received: 21-02-2013

Abstract

The formation and liquid-liquid extraction of ion-association complexes between gallium(III)–4-(2-pyridylazo)resorcinol (PAR) anionic chelates and cations of four ditetrazolium chlorides (DT^{2+}) were studied: Neotetrazolium chloride (NTC), Blue Tetrazolium chloride (BTC), Nitro Blue Tetrazolium chloride (NBT) and Tetranitro Blue Tetrazolium chloride (TNBT). The optimum extraction-spectrophotometric conditions, composition of the extracted species {1:2:1 and/or 1:2:2 (Ga:PAR:DT)}, some equilibrium constants {constants of association (β), constants of distribution (K_D) and constants of extraction (K_{ex})} and analytical characteristics {molar absorptivity (ε), Sandell's sensitivity, intervals of adherence to Beer's law, etc.} were found. Relationships involving the number of nitro groups in DT^{2+} (N_{nitro}; $DT^{2+} = BT^{2+}$, NBT^{2+} and $TNBT^{2+}$) or molecular mass of DT^{2+} (MM; $DT^{2+} = NT^{2+}$ and BT^{2+}) were discussed: Log $\beta = f(N_{nitro})$, Log $K_D = f(N_{nitro})$, Log $K_{ex} = f(N_{nitro})$, Log $\varepsilon = f(N_{nitro})$ and Log $\beta = f$(Log MM).

Keywords: Gallium-PAR chelate, bis-tetrazolium salt, nitro group, linear relationship, ion-associate, solvent extraction

1. Introduction

Ion-association reagents are usually bulky compounds capable of forming cations or anions with a charge of unity, which is distributed over the whole ion.[1] However, some organic salts can form analytically important cations with a charge of two.[2–11] Such salts, and the reactions in which they participate, are generally less studied, despite the fact that they may offer some advantages in comparison to typically used monocationic ion-association reagents.[5, 12]

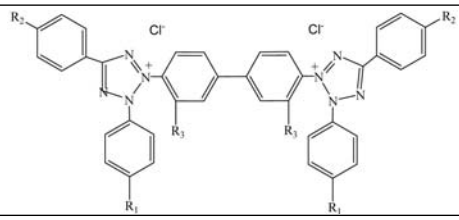
In previous papers we described the complex formation and liquid-liquid extraction from water to chloroform in systems containing gallium(III), 4-(2-pyridylazo)-resorcinol (PAR) and monotetrazolium salt {2,3,5-triphenyl-2H-tetrazolium chloride,[13] 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide,[14] 3-(2-naphtyl)-2,5-diphenyl-2H-tetrazolium chloride,[15] and 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride[15]}. Here, we focused our attention on four similar systems involving commercially available ditetrazolium chlorides (DTCs), namely: Neotetrazolium chloride (NTC), Blue Tetrazolium chloride (BTC), Nitro Blue Tetrazolium chloride (NBT) and Tetranitro Blue Tetrazolium chloride (TNBT). General formula and nomenclature names of the mentioned DTCs are shown in Table 1.

2. Experimental Procedure

2. 1. Reagents and Apparatus

A stock gallium(III) solution was prepared by dissolving 0.1312 g of Ga_2O_3 (Koch-Light Laboratories Ltd., 99,99%) in a hot concentrated HCl solution (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. Fresh working solutions (50 mL; $1.4 \cdot 10^{-4}$ mol L^{-1} Ga(III)) with pH *ca.* 1.1 were prepared every day by mixing 0.5 mL of the stock solution, 0.3 mL of 6.5 mol L^{-1} solution of HCl and distilled water. Aqueous $2 \cdot 10^{-3}$ mol L^{-1} solutions of the reagents were used: PAR, NTC, BTC and TNBT (all from Sigma-Aldrich Chemie GmbH) and NBT (from Merck KGaA). The organic solvent, chloroform, was distilled before use. 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

Table 1. Ditetrazolium chlorides (DTCs) used in the present study



Substituents			Name	Abbreviation
R_1	R_2	R_3		
H	H	H	3,3'-(4,4'-biphenylene)bis(2,5-diphenyl-2H-tetrazolium chloride) (Neotetrazolium chloride)	NTC
H	H	OCH_3	3,3'-(3,3'-dimethoxy-4,4'-biphenylene)bis(2,5-diphenyl-2H-tetrazolium chloride) (Blue Tetrazolium chloride)	BTC
NO_2	H	OCH_3	3,3'-(3,3'-dimethoxy-4,4'-biphenylene)bis[2-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride] (Nitro Blue Tetrazolium chloride)	NBT
NO_2	NO_2	OCH_3	3,3'-(3,3'-dimethoxy-4,4'-biphenylene)bis[2,5-di(4-nitrophenyl)-2H-tetrazolium chloride] (Tetranitro Blue Tetrazolium chloride)	TNBT

CH_3COOH and NH_4OH. The resulting pH was checked by HI 83140 pH meter (Italy). A Camspec M508 spectrophotometer (United Kingdom), equipped with 10 mm pathlength cells, was employed for reading the absorbance.

2. 2. Procedure for Establishing the Optimum Operating Conditions

Aliquots of Ga(III) solution, PAR solution (up to 1 mL), DTC solution (up to 1.3 mL) and buffer solution (5 mL; pH ranging from 4 to 9.4) were introduced into separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 mL. Then 10 mL of chloroform were added and the funnels were shaken for 3–300 sec. Portions of the organic extracts were transferred through paper filters into cells. The absorbances were recorded against respective blank samples.

2. 3. Procedure for Determination of the Distribution Constants

The distribution constants K_D were found from the ratio $K_D = A_1/(A_3\text{-}A_1)$ 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.[13–16] The final volume of the measured solutions in both cases was 25 mL.

3. Results and Discussion

3. 1. Absorption Spectra

Spectra of the ternary Ga(III)-PAR-DTC complexes extracted in chloroform at the optimum conditions are shown in Fig. 1. Their chief absorption maxima are situa-

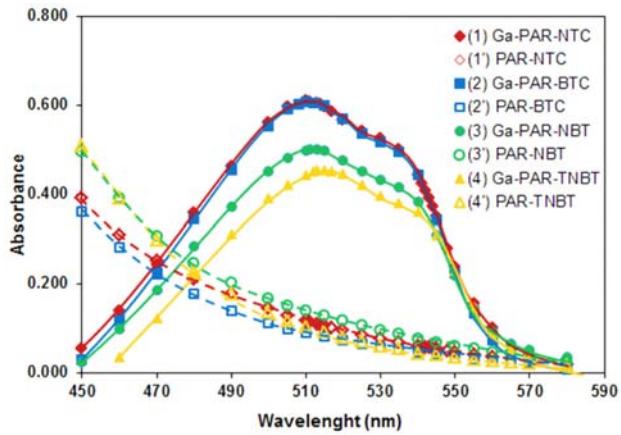


Fig. 1. Absorption spectra of the ternary complexes (curves 1-4; $C_{Ga(III)} = 7.2 \cdot 10^{-6}$ mol L^{-1}) and blank samples (curves 1'-4') in chloroform at the optimum extraction conditions. (1,1') $C_{PAR} = 1.4 \cdot 10^{-4}$ mol L^{-1}, $C_{NTC} = 1.8 \cdot 10^{-4}$, pH = 7.5; (2,2') $C_{PAR} = 1.0 \cdot 10^{-4}$ mol L^{-1}, $C_{BTC} = 1.2 \cdot 10^{-4}$, pH = 5.7; (3,3') $C_{PAR} = C_{NBT} = 1.6 \cdot 10^{-4}$ mol L^{-1}, pH = 6.0; (4,4') $C_{PAR} = 1.4 \cdot 10^{-4}$ mol L^{-1}, $C_{TNBT} = 2.0 \cdot 10^{-4}$, pH = 5.0.

Table 2. Optimum extraction-spectrophotometric conditions

Extraction systems	Extaction time, min	pH	C_{PAR}, mol L^{-1}	C_{DTC}, mol L^{-1}	λ_{max}, nm
Ga(III)-PAR-NTC	2	6.5–8.0	1.4×10^{-4}	1.8×10^{-4}	510
Ga(III)-PAR-BTC	2[a, b]	5.5–6.0[a], 7.0–8.0[b]	1.0×10^{-4} [a, b]	1.2×10^{-4} [a, b]	510 [a, b]
Ga(III)-PAR-NBT	2	5.0–7.0	1.6×10^{-4}	1.6×10^{-4}	511
Ga(III)-PAR-TNBT	2	4.9–5.1	1.4×10^{-4}	2.0×10^{-4}	513

[a] for the complex with Ga-PAR-BTC ratio of 1:2:1 [b] for the complex with Ga-PAR-BTC ratio of 1:2:2

ted in the interval 510–513 nm (see Table 2). BTC and NTC – salts which do not contain NO_2 groups – form the most intensely absorbing complexes (Fig. 1, curves 1 and 2; $\lambda_{max} = 510$ nm, $\varepsilon_{510} = 8.5 \cdot 10^4$ L mol^{-1} cm^{-1}).

3. 2. Effect of pH

The effect of pH on the extraction is represented in Fig. 2. The differences in the pH intervals for maximum extraction are an indication of a different ability of DTCs (NTC, BTC, NBT and TNBT) to facilitate deprotonation of 1-hydrohyl group in the complexed PAR during the formation of ternary species; another explanation can be their ability to stabilize complex anions with different composition and charge.[17]

A narrowest pH interval for maximum extraction is recorded for the system containing TNBT (curve 4). A similar behaviour of this DTC (in comparison to other DTCs) has been reported for the extaction systems containing V(V)–PAR,[17] V(IV)–4-(2-thiazolylazo)resorcinol[17] and In(III)-PAR.[16] The complicated course of curve 2 (DTC = BTC) will be discussed in Sec. 3.5.

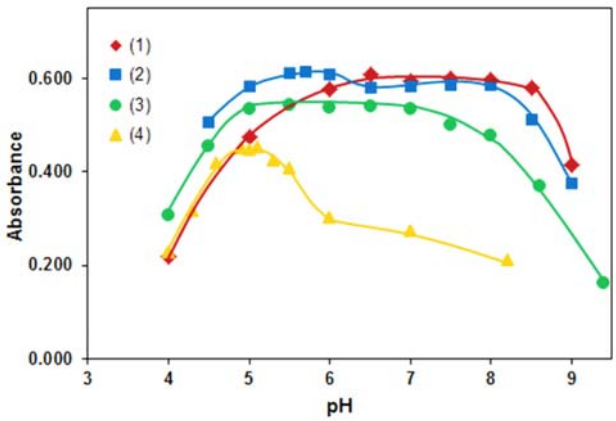


Fig. 2. Absorbance of Ga(III)-PAR-DTC complexes in chloroform *vs*. pH of the aqueous phase plots. C_{Ga}(III) = 7.2 · 10^{-6} mol L^{-1}; $C_{PAR} = C_{DTC} = 2.0 \cdot 10^{-4}$ mol L^{-1}. (1) DTC = NTC, λ = 510 nm; (2) DTC = BTC, λ = 510 nm; (3) DTC = NBT, λ = 511 nm; (4) DTC = TNBT, λ = 513 nm.

3. 3. Effect of Shaking Time

The extraction equilibrium for Ga(III)-PAR-DTC systems is reached for about 60–90 seconds (Fig. 3). In all cases, longer shaking time does not affect the absorbance. In order to avoid accidental errors, caused by a combination of short shaking times and different shaking rates, we extracted in our further experiments for 2 min.

3. 4. Effect of Reagents Concentration

The effect of PAR and DTC concentrations on the absorbance of the extracted species is shown in Fig. 4 and Fig. 5, respectively. One can conclude that the saturation with PAR and DTC is reached most easily in the system in which DTC = BTC (Fig. 4, curve 2 and Fig. 5, curve 2). The optimum reagent concentrations deduced from the mentioned figures are shown in Table 2.

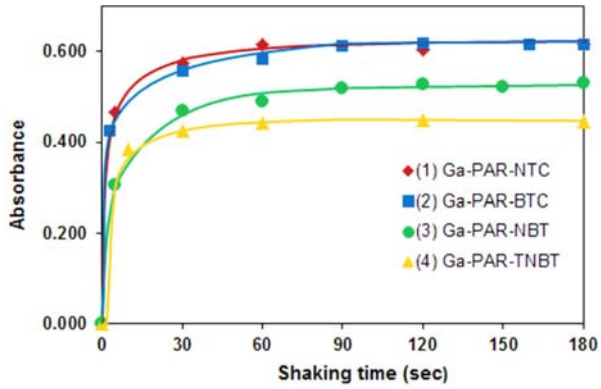


Fig. 3. Effect of shaking time on the extraction. $C_{Ga(III)} = 7.2 \cdot 10^{-6}$ mol L^{-1}; $C_{PAR} = C_{DTC} = 2.0 \cdot 10^{-4}$ mol L^{-1}.

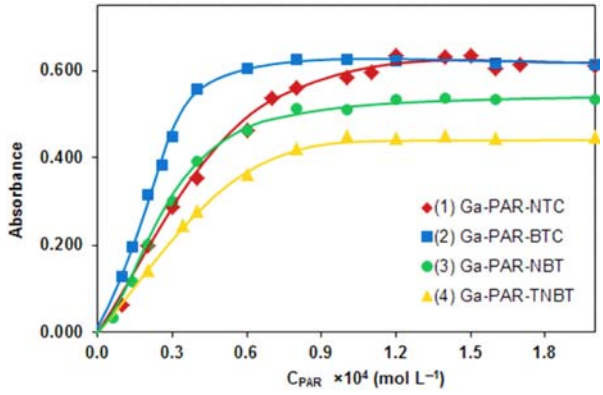


Fig. 4. Absorbance of the extracted ternary Ga(III)-PAR-DTC complexes *vs*. concentration of the PAR plots. $C_{Ga(III)} = 7.2 \cdot 10^{-6}$ mol L^{-1}, $C_{DTC} = 2.0 \cdot 10^{-4}$ mol L^{-1}. (1) pH = 7.5, λ = 510 nm; (2) pH = 5.7, λ = 510 nm; (3) pH = 6.0, λ = 511 nm; (4) pH = 5.0, λ = 513 nm.

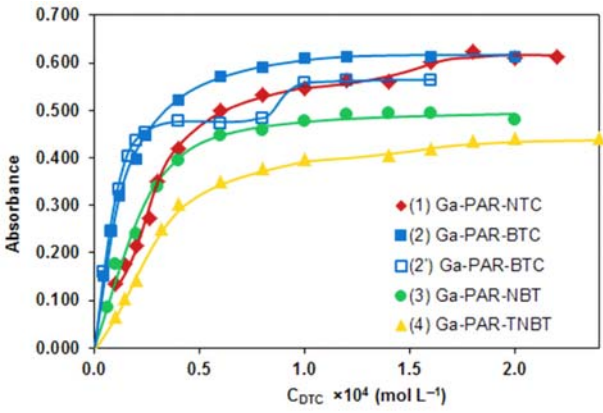


Fig. 5. Absorbance of the extracted ternary Ga(III)-PAR-DTC complexes *vs*. concentration of the DTC plots. $C_{Ga(III)} = 7.2 \cdot 10^{-6}$ mol L^{-1}. (1) $C_{PAR} = 1.4 \cdot 10^{-4}$ mol L^{-1}, pH = 7.5, λ = 510 nm; (2) $C_{PAR} = 1.0 \cdot 10^{-4}$ mol L^{-1}, pH = 5.7, λ = 510 nm; (2') $C_{PAR} = 1.0 \cdot 10^{-4}$ mol L^{-1}, pH = 7.5, λ = 510 nm; (3) $C_{PAR} = 1.6 \cdot 10^{-4}$ mol L^{-1}, pH = 6.0, λ = 511 nm; (4) $C_{PAR} = 1.4 \cdot 10^{-4}$ mol L^{-1}, pH = 5.0, λ = 513 nm.

3. 5. Composition of the Complexes, Suggested Formulae and Reaction Schemes

The saturation curves presented in Fig. 4 and Fig. 5 allowed us to determine the molar ratios PAR:Ga(III) and DTC:Ga(III) by the mobile equilibrium method[18] and straight-line method of Asmus[19] (Table 3). The results obtained by both methods show that the PAR-to-Ga(III) ratio in all cases is 2:1. However, the DTC-to-Ga(III) ratio appears to be different at the optimum extraction conditions when DTC = BTC (BTC:Ga = 1:1) or DTC ≠ BTC (DTC:Ga = 2:1). It is known that under the working pH the predominant forms of Ga(III) and PAR are $Ga(OH)_4^-$ [20] and HL^-.[21,22] Having in mind the mentioned above molar ratios, the bulkiness and envelope properties of DTCs, their ability to form DT^{2+},[7,12] and the literature describing the posible formation of ternary complexes with hydrolyzed nature[12,16,17,23] we can propose the following two different schemes for complex formation:

$$Ga(OH)_4^- + 2HL^- \rightleftharpoons [Ga(OH)L_2]^{2-} + OH^- + 2H_2O \quad (1.1)$$

$$[Ga(OH)L_2]^{2-} + BT^{2+} \rightleftharpoons (BT)[Ga(OH)L_2] \quad (1.2)$$

$$(BT)[Ga(OH)L_2]_{aq} \rightleftharpoons (BT)[Ga(OH)L_2]_{org} \quad (1.3)$$

Scheme 1. Complex formation and extraction in the system Ga(III)–PAR–BTC–water–chloroform at pH 5.7.

$$Ga(OH)_4^- + 2HL^- \rightleftharpoons [Ga(OH)_3L_2]^{4-} + H_3O^+ \quad (2.1)$$

$$[Ga(OH)_3L_2]^{4-} + 2DT^{2+} \rightleftharpoons (DT)_2[Ga(OH)_3L_2] \quad (2.2)$$

$$(DT)_2[Ga(OH)_3L_2]_{aq} \rightleftharpoons (DT)_2[Ga(OH)_3L_2]_{org} \quad (2.3)$$

Scheme 2. Complex formation and extraction in the systems Ga(III)–PAR–DTC–water–chloroform. When DTC = BTC, pH should be higher than optimum (*ca.* 7.5).

Table 3. Determination of the PAR-to-Ga(III) and DTC-to-Ga(III) molar ratios (n and m, respectively) under the optimum or non-optimum (*) extraction conditions by the method of Asmus[19] from the experimental data given in Fig. 4 and Fig. 5, respectively.

Extraction system	Correlation coefficient squared values (CC^2) corresponding to molar ratios 1, 2 and 3	
	PAR:Ga(III)	DTC:Ga(III)
Ga(III)-PAR-NTC-water-chloroform	0.9461 (n = 1) 0.9986 (n = 2) 0.9849 (n = 3)	0.9410 (m = 1) 0.9904 (m = 2) 0.9646 (m = 3)
Ga(III)-PAR-BTC-water-chloroform	0.9525 (n = 1) 0.9968 (n = 2) 0.9571 (n = 3)	0.9993; 0.9148* (m = 1) 0.9215; 0.9956* (m = 2) 0.8381; 0.9731* (m = 3)
Ga(III)-PAR-NBT-water-chloroform	0.9607 (n = 1) 0.9968 (n = 2) 0.9734 (n = 3)	0.9538 (m = 1) 0.9992 (m = 2) 0.9756 (m = 3)
Ga(III)-PAR-TNBT-water-chloroform	0.9841 (n = 1) 0.9945 (n = 2) 0.9575 (n = 3)	0.9228 (m = 1) 0.9969 (m = 2) 0.9838 (m = 3)

* $C_{Ga(III)} = 7.2 \cdot 10^{-6}$ mol L^{-1}, $C_{PAR} = 1.0 \cdot 10^{-4}$ mol L^{-1}, pH = 7.5, λ = 510 nm.

The formation of a different complex with BT^{2+} (Scheme 1) could be explained in the frame of considerations given in Ref 17. However, the complicated course of the pH-curve of this reagent (Fig. 2, line 2) and the literature[12,16] gave us reason to repeat the procedure for determination of the BTC-to-Ga(III) molar ratio at higher pH (pH 7.5). The results (Table 3,*) showed that the molar BTC-to-Ga ratio grows to 2:1. Hence, the dominant processes at pH close to 7.5 are the same as in the systems with the rest of DTCs at the optimum conditions (Scheme 2).

3. 6. Equilibrium Constants

The constants of association β, characterizing Eq. 1.2 and Eq. 2.2, were calculated by the Holme-Langmyhr method,[24] Harvey-Manning method[25] and mobile equilibrium method.[18] The constants of distribution K_D, characterizing Eq. 1.3 and Eq. 2.3, were determined by comparison of the absorbance values obtained after single and triple extractions at the optimum conditions (as described in Sec. 2.3). Then, the constants of extraction (K_{ex}) and reco-

Table 4. Calculated values (P = 95%) of the extraction constants (K_{ex}), distribution constants (K_D), association constants (β) and recovery factors (R%)

Extraction system	Log β	Log K_D	Log K_{ex}	R%
Ga(III)-PAR-NTC-H_2O-chloroform	8.9 ± 0.2[a], 9.6 ± 0.6[b], 9.6 ± 1.4[c]	0.79 ± 0.01	9.7 ± 0.2[f],10.4 ± 0.6[e]	86.1 ± 0.1
Ga(III)-PAR-BTC-H_2O-chloroform	5.3 ± 0.2[a,d], 5.1 ± 0.2[b,d],5.1 ± 0.2[c,d]	0.96 ± 0.01[d]	6.3 ± 0.2[d,f], 6.1 ± 0.2[d,g]	90.0 ± 0.1[d]
	10.2 ± 0.5[a,e], 11.0 ± 0.3[b,e]	1.08 ± 0.01[e]	11.3 ± 0.5[e,f],12.1 ± 0.3[e,g]	92.4 ± 0.1[e]
Ga(III)-PAR-NBT-H_2O-chloroform	9.7 ± 0.2[a], 9.9 ± 0.3[b], 9.8 ± 0.8[c]	0.95 ± 0.01	10.7 ± 0.2[f], 10.9 ± 0.2[e]	89.9 ± 0.1
Ga(III)-PAR-TNBT-H_2O-chloroform	9.2 ± 0.2[a], 9.4 ± 0.2[b], 9.0 ± 0.8[c]	0.56 ± 0.01	9.8 ± 0.2[f], 10.0 ± 0.2[g]	78.4 ± 0.1

[a] Calculated by the Holme-Langmyhr method[24] [b] Calculated by the Harvey-Manning method[25] [c] Calculated by the Mobile equilibrium method[18] [d] at pH 5.7 [e] at pH 7.5 [f] Calculated by the equation Log K_{ex} = Log β + Log K_D, where β is the value obtained by the Holme-Langmyhr method [g] Calculated by the equation Log K_{ex} = Log β + Log K_D, where β is the value obtained by the Harvey-Manning method

very factors (*R%*) were determined by the formulae $K_{ex} = K_D \beta$ and $R\% = 100K_D / (K_D + 1)$, respectively. The results are presented in Table 4. All experiments were performed at room temperature of ~22 °C and the calculations were carried out at a probability of 95 %.

3. 7. Some Relationships Involving the Equilibrium Constants Obtained

Continuous investigations on tetrazolium ion-association complexes revealed that at least two factors noticeably influence the values of β: molecular mass of tetrazolium cation (MM) (I) and the presence of nitrophenyl substituent(s) in the tetrazolium ring (II).[7,17] The studied in the present paper DTCs are suitable for testing both (I) and (II). BT^{2+}, NBT^{2+} and $TNBT^{2+}$ differ by the number of nitro groups (N_{nitro}): 0, 2 and 4, respectively. NT^{2+} and BT^{2+} do not contain nitro groups; their MMs are 596.7 and 656.76, respectively.

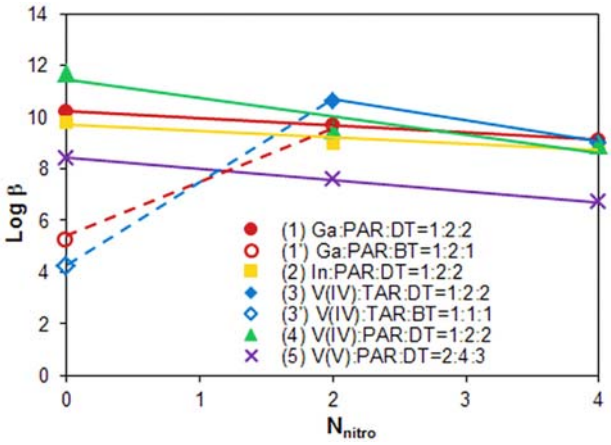


Fig. 6. Logarithm of association constants of ion-association complexes containing DT^{2+} ($TNBT^{2+}$, NBT^{2+} or BT^{2+}) *vs*. number of nitro groups in DT^{2+} plots. (1) $(DT^{2+})_2[Ga(OH)_3(PAR)_2]$; (1') $(BT^{2+})[Ga(OH)(PAR)_2]$; (2) $(DT^{2+})_2[In(OH)_3(PAR)_2]$;[16] (3) $(DT^{2+})_2[VO(OH)_2(TAR)_2]$ {TAR = 4-(2-thiazolylazo)-resorcinol); DT^{2+} is NBT^{2+} and $TNBT^{2+}$};[17] (3') $(BT^{2+})[VO(OH)_2(TAR)]$;[17] (4) $(DT^{2+})_2[VO(OH)_2(PAR)_2]$;[17] (5) $(DT^{2+})_3[VO_2(PAR)_2]_2$.[26]

Literature[2,12,16,17,23,26] and the results described in the previous section (3.6) were used in the construction of Fig. 6 and Table 5. It could be seen (Fig. 6; Table 5, row 1) that a well-defined negative linear relationship (slope of –0.275; squared correlation coefficient of 0.9973) exists between Log β and N_{nitro} for the series $(TNBT^{2+})_2[Ga(OH)_3(PAR)_2]$, $(NBT^{2+})_2[Ga(OH)_3(PAR)_2]$ and $(BT^{2+})_2[Ga(OH)_3(PAR)_2]$. Similar is the situation with the dependences Log $K_D = f(N_{nitro})$, Log $K_{ex} = f(N_{nitro})$ and Log $\varepsilon = f(N_{nitro})$ (Table 5, rows 2, 3 and 4). The slopes in row 5 (Table 5) are positive; this is a confirmation that heavier DTs^{2+} form more stable ion-associates.[7]

3. 8. Beer's Law and Analytical Characteristics

The adherence to Beer's law for each Ga(III)–PAR–DTC–water–chloroform system was examined under the optimum extraction-spectrophotometric conditions (Table 2). Calculated molar absorptivities (ε) are listed in Table 6, along with some other important analytical characteristics. One can conclude that BTC-PAR and NTC-PAR ensure highest sensitivity of determination. In this criterion, they are better than the reagents used in similar systems: Ga(III)–1-(2-pyridylazo)-2-naphthol–water–chloroform ($\varepsilon = 2.7 \cdot 10^4$ L mol^{-1} cm^{-1}),[22] Ga(III)–Eriochrom Black T–water– chloroform– n-butanol– capronic acid ($\varepsilon = 3.4 \cdot 10^4$ L mol^{-1} cm^{-1}),[27] Ga(III)–4-(2-thiazolylazo)-resorcinol–2,3,5-triphenyl-2H-tetrazolium chloride ($\varepsilon = 4.6 \cdot 10^4$ L mol^{-1} cm^{-1}),[13] Ga(III)–Pyrocatechol Violet–tridodecylethylammonium bromide–water–xylene ($\varepsilon = 8.0 \cdot 10^4$ L mol^{-1} cm^{-1}),[28] Ga(III)–PAR–tetraphenylarsonium chloride–water–1,2-dichlorobenzene ($\varepsilon = 8.2 \cdot 10^4$ L mol^{-1} cm^{-1})[29] and Ga(III)–PAR–2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride–water–chloroform ($\varepsilon = 8.2 \cdot 10^4$ L mol^{-1} cm^{-1}).[15]

Table 5. Straight-line equations ($y = ax + b$) and squared correlation coefficients (CC^2) for series of ion-associates containing DT^{2+} and PAR. DT^{2+} = BT^{2+}, NBT^{2+} and $TNBT^{2+}$ (Rows No. 1, 2, 3 and 4); DT^{2+} = NT^{2+} and BT^{2+} (Row No. 5)

No.	System Relationship	In(III)-PAR-DTC-H_2O-$CHCl_3$ [Ref. 16, 23]	V(V)-PAR-DTC-H_2O-$CHCl_3$ [Ref. 2, 26]	V(IV)-PAR-DTC-H_2O-$CHCl_3$ [Ref. 12, 17]	Ga(III)-PAR-DTC H_2O-$CHCl_3$ [This work]
1	Log $\beta = f(N_{nitro})$	y = –0.25x + 9.70 CC^2 = 0.8929	y = –0.425x + 8.42 CC^2 = 0.9988	y = –0.700x + 11.43 CC^2 = 0.9017	y = –0.275x + 10.22 CC^2 = 0.9973
2	Log $K_D = f(N_{nitro})$	y = –0.40x + 1.24 CC^2 = 0.8928	y = –0.05x + 1.37 CC^2 = 0.9932	–	y = –0.13x + 1.12 CC^2 = 0.9231
3	Log $K_{ex} = f(N_{nitro})$	y = –0.65x + 10.93 CC^2 = 0.9980	y = –0.50x + 9.80 CC^2 = 1.000	–	y = –0.40x + 11.37 CC^2 = 0.9796
4	Log $\varepsilon = f(N_{nitro})$	y = –0.152x + 4.94 CC^2 = 0.8362	y = –0.08x + 4.63 CC^2 = 0.9498	y = –0.039x + 4.557 CC^2 = 0.5773	y = –0.033x + 4.93 CC^2 = 0.9866
5	Log $\beta = f$(Log MM)	y = 24.0x – 57.9 –	y = 28.8x – 72.8 –	y = 58.6x – 153.3 –	y = 31.2x – 77.7 –

Table 6. Characteristics concerning the application of the ion-association complexes for extractive-spectrophotometric determination of gallium

Extraction system **Analytical characteristics**	**Ga(III)-PAR-NTC-H_2O-$CHCl_3$**	**Ga(III)-PAR-BTC-H_2O-$CHCl_3$**	**Ga(III)-PAR-NBT-H_2O-$CHCl_3$**	**Ga(III)-PAR-TNBT-H_2O-$CHCl_3$**
Apparent Molar absorptivity (ε), L mol^{-1} cm^{-1}	$8.5 \cdot 10^4$	$8.5 \cdot 10^4$	$7.1 \cdot 10^4$	$6.2 \cdot 10^4$
Sandell's sensitivity (SS), ng cm^{-2}	0.82	0.82	0.99	1.13
Adherence to Beer's law, μg mL^{-1}	up to 1.4	up to 0.9	up to 1.4	up to 1.4
Squared correlation coefficient (CC^2)	0.9990	0.9997	0.9957	0.9999
Limit of detection (LOD), μg mL^{-1}	0.047	0.02	0.10	0.016
Limit of quantification (LOQ), μg mL^{-1}	0.16	0.07	0.33	0.052
Absorbance of the blank at λ_{max} (in parenthesis)	0.112 ± 0.005 (510 nm)	0.089 ± 0.002 (510 nm)	0.132 ± 0.003 (511 nm)	0.93 ± 0.003 (5131 nm)

4. Conclusions

1. Ga(III) readily forms chloroform-extractable species with PAR and DTCs.

2. All investigated DTCs can form complexes with a composition of 1:2:2 (Ga:PAR:DTC) and a suggested general formula $(DT^{2+})_2[Ga(OH)_3(PAR)_2]$. Under the optimum extraction conditions BTC forms a simpler complex with a composition of 1:2:1 {suggested formula $(BT^{2+})[Ga(OH)(PAR)_2]$}.

3. With increase of the number of nitro groups (N_{nitro}) in the series BT^{2+}, NBT^{2+} and $TNBT^{2+}$ the stability, extractability and molar absorptivity of the ionic associates $(DT^{2+})_2[Ga(OH)_3(PAR)_2]$ decrease. Well-defined negative linear relationships exists between N_{nitro} and Log β (CC = –0.9986), N_{nitro} and Log K_D (CC = –0.9608), N_{nitro} and Log K_{ex} (CC = –0.9897), and N_{nitro} and Log ε (CC = –0.9933).

4. BTC appears to be the best DTC for liquid-liquid extraction and spectrophotometric determination of Ga(III).

5. Acknowledgments

The authors would like to thank the Research Fund of the Plovdiv University for its long-time support.

6. References

1. K. Toei, *Anal. Sci.* **1987**, *3*, 479–488.
2. K. Gavazov, Z. Simeonova, A. Alexandrov, *Anal. Lab.* **1998**, *7*, 127–133.
3. M. Kamburova, A. Alexandrov, *Chem. Anal. (Warsaw)* **1999**, *44*, 745–752.
4. P. K. Martinelango, J. L. Anderson, P. K. Dasgupta, D. W. Armstrong, R. S. Al-Horr, R. W. Slingsby, *Anal. Chem.* **2005**, *77*, 4829–4835.
5. J. L. Anderson, D. W. Armstrong, G.-T. Wei, *Anal. Chem.* **2006**, *78*, 2892–2902.
6. A. Dimitrov, V. Lekova, K. Gavazov, B. Boyanov, *J. Anal. Chem.* **2007**, *62*, 122–125.
7. K. B. Gavazov, A. N. Dimitrov, V. D. Lekova, *Uspekhi Khim.* **2007**, *76*, 187–198.
8. P. K. Martinelango, P. K. Dasgupta, *Anal. Chem.* **2007**, *79*, 7198–7200.
9. J. W. Remsburg, R. J. Soukup-Hein, J. A. Crank, Z. S. Breitbach, T. Payagala, D. W. Armstrong, *J. Am. Soc. Mass Spectrom.* **2008**, *19*, 261–269.
10. X. Lin, A. R. Gerardi, Z. S. Breitbach, D. W. Armstrong, C. L. Colyer, *Electrophoresis* **2009**, *30*, 3918–3925.
11. D. V. Kostova, M. A. Kamburova, *J. Int. Sci. Publ. Ecol. Saf.* **2010**, *4*, 162–169.
12. F. Genç, K. B. Gavazov, M. Türkyilmaz, *Cent. Eur. J. Chem.* **2010**, *8*, 461–467.
13. K. Stojnova, K. B. Gavazov, G. K. Toncheva, V. D. Lekova, A. N. Dimitrov, *Cent. Eur. J. Chem.* **2012**, *10*, 1262–1270.
14. K. Stojnova, K. Gavazov, *J. Mater. Sci. Eng. Sec. A.* **2012**, *2*, 423–429.
15. K. B. Gavazov, K. T. Stojnova, T. S. Stefanova, G. K. Toncheva, V. D. Lekova, A. N. Dimitrov, *Chemija* **2012**, *23*, 278–285.
16. T. S. Stefanova, K. B. Gavazov, *Cent. Eur. J. Chem.* **2013**, *11*, 278–289.
17. K. B. Gavazov, P. V. Racheva, V. D. Lekova, A. N. Dimitrov, M. Turkyilmaz, F. Genc, *Croat. Chem. Acta* **2012**, *85*, 53–58.
18. Z. Zhiming, M. Dongsten, Y. Cunxiao, *J. Rare Earths* **1997**, *15*, 216–219.
19. E. Asmus, *Fresenius' J. Anal. Chem.* **1960**, *178*, 104–116.
20. S. A. Wood, I. M. Samson, *Ore Geol. Rev.* **2006**, *28*, 57–102.
21. L. Marić, M. Široki, *Anal. Chim. Acta* **1996**, *318*, 345–355.
22. F. I. Lobanov, G. K. Nurtaeva, E. E. Ergozhin, Ekstraktsiya kompleksov ionov metallov s piridinovymi oksiazosoedineniyami, Nauka, Alma-Ata, **1983**.
23. T. S. Stefanova, G. K. Toncheva, K. B. Gavazov, *Chem. J.* **2012**, *2*, 146–152.
24. A. Holme, F. J. Langmyhr, *Anal. Chim. Acta* **1966**, *36*, 383–391.
25. A. E. Harvey, D. L. Manning, *J. Am. Chem. Soc.* **1950**, *72*, 4488–4493.
26. K. B. Gavazov, M. Türkyilmaz, Ö. Altun, *Bulg. Chem. Commun.* **2008**, *40*, 65–69.
27. I. V. Pyatnitskii, L. L. Kolomiets, N. D. Sulima, *Zh. Anal. Khim.* **1985**, *40*, 115–119.
28. Y. Shijo, T. Shimizu, K. Sakai, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 105–107.
29. M. Široki, M. J. Herak, *Anal. Chim. Acta* **1976**, *87*, 193–199.

Povzetek

Proučevana je bila tvorba in ekstrakcija ionskih asociatov med kompleksim Ga(III)–4-(2-pyridylazo)resorcinol (PAR) anionskim kelatom in kationi štirih ditetrazolijevih kloridov (DT^{2+}) (neotetrazolijev klorid (NTC), modri tetrazolijev klorid (BTC), nitri modri tetrazolijev klorid (NBT) in tetranitro modri tetrazolijev klorid (TNBT)). Izvedena je bila optimizacija ekstrakcijsko-spektrofotometričnih pogojev, sestava ekstrahiranih zvrsti {1:2:1 in/ali 1:2:2 (Ga:PAR:DT)} ter določene nekatere ravnotežne konstante {konstante asociacije (β), konstante distribucije (K_D) in konstante ekstrakcije (K_{ex})} in analizne karakteristike {molska absorptivnost (ε), Sandellova občutljivost, interval veljavnosti Beerovega zakona, in druge}. Obravnavan je tudi vpliv števila nitro v DT^{2+} (N_{nitro}; $DT^{2+} = BT^{2+}$, NBT^{2+} in $TNBT^{2+}$) ter molske mase DT^{2+} (MM; $DT^{2+} = NT^{2+}$ in BT^{2+}): Log $\beta = f(N_{nitro})$, Log $K_D = f(N_{nitro})$, Log $K_{ex} = f(N_{nitro})$, Log $\varepsilon = f(N_{nitro})$ in Log $\beta = f$(Log MM).