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Polarographic investigation of reduction processes of gallium(III) complexes with some o,o'-dihydroxysubstituted azo dyes

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The voltammetric behaviour of Ga(III) complexes with o,o'-dihydroxysubstituted azo dyes (eriochrome red B (ERB), eriochrome black T (EBT), calcon (Calc), and kalces (Klc)) was investigated using cyclic linear-sweep voltammetry. Two new reduction peaks caused by reduction of the Ga(III)–azo dye complex compounds were registered on the voltammograms. The effect of pH, the concentration of azo dye and Ga(III) ions, and the sweep rate on the peak current was studied. The peak current changed linearly with increasing gallium concentration. New methods were proposed for the determination of metal ions. The detection limits were 2.0×10^{-7} M for the Ga(III)–ERB complex, 1.0×10^{-6} M for the Ga(III)–EBT and Ga(III)–Calc systems, 5.3×10^{-7} M for the Ga(III)–Klc complex based on the first peak and 9.1×10^{-7} M for the same system but based on the second peak. The proposed methods were tested on the determination of gallium in intermetallic compounds of the Zn–Ga and Sm–Ga systems and in a $Gd_3Sc_2Ga_3O$ luminophore.

Gallium / Azo dye / Voltammetry / Reduction / Dropping mercury electrode

Introduction

Gallium has important physical and chemical properties, and is therefore used in different branches of industry, engineering and in medicine. The Ga^{67} isotope is used in tumor diagnosis and therapy [1,2]. Preparations based on Ga(III) ions are available for detection and treatment of infections; they are used because of the antibiotic activity of the Ga(III) ions [3,4]. Ga and its compounds are employed in industry in manufacturing low melting alloys, as a dopant to improve strength, hardness and corrosion resistance of magnesium alloys, for doping of germanium and silicon. A common use of Ga is the preparation of semiconductors [5,6]. For all these reasons there is a need in sensitive and precise methods of gallium determination in objects of different qualitative and quantitative composition.

Widely used methods for gallium determination are physical methods: atomic absorption spectrometry [7,8], inductively coupled plasma mass spectrometry [9], and neutron activation analysis [10]. These methods possess high sensitivity and precision. However, they are of limited use in many laboratories, because of the cost of the apparatus. There exist also other disadvantages: neutron activation analysis and atomic absorption spectrometry are time-consuming, which is connected with long exposure times and the time needed to select a suitable chemical modifier for the analysis of objects with difficult matrices [8]. Most spectrophotometric methods use reagents that are not selective to gallium ions and Ga determination in real objects requires previous separation steps [11]. This decreases the accuracy of the determination and can be the source of contamination. The application of relatively inexpensive, rapid and sufficiently sensitive voltammetric methods may be a valid alternative.

The reduction peak of Ga(III) ions in acidic medium is masked by the reduction peak of H^+ ions when inorganic supporting electrolytes are used. For this reason we registered only an anodic peak in the voltammogram of Ga(III) ions when scanning the potential from -0.2 to -1.7 V and utilizing an acetic buffer solution as supporting electrolyte (Fig. 1). The cathodic peak, which corresponds to the reduction of Ga(III) ions, is observed on the NH_4Cl-NH_3 background at E = -1.4 ÷ -1.8 V, but the voltammetric determination of the metal ions is not sufficiently sensitive (detection limit ~ 10^{-5} M) [11]. The sensitivity and selectivity of the analysis can be improved by introducing organic complexing reagents. Highly sensitive voltammetric methods of gallium determination based on the reduction of Ga(III) complexes with organic ligands (detection limit ~ 10^{-9} M) are known [12,13]. In this work we have elaborated a sensitive, rapid and relatively simple method of Ga(III) analysis using cyclic linear-sweep voltammetry. The determination is based on the

reduction of Ga(III) chelates with different o,o'-dihydroxysubstituted azo dyes – eriochrome red B (ERB), eriochrome black T (EBT), calcon (Calc), and kalces (Klc). The voltammetric reduction of these dyes has been investigated earlier [14-16].

Experimental

Apparatus

Voltammetric measurements were carried out on a digital device equipped with a personal computer and a temperature-controlled three-electrode cell, volume 10 ml. A dropping mercury indicator electrode, a saturated calomel reference electrode and a platinum wire auxiliary electrode were used. The dropping mercury electrode employed had the following characteristics: m=4.6×10^{-4} g/s and τ_k=10.8 s.

The pH of the solutions was measured potentiometrically with a MV 870 DIGITAL-pH-MESSGERÄT pH-meter. The required temperature of the solution was maintained using a H UTU-2/77 thermostat.

Chemicals

The pH values were adjusted by HCl, acetate and ammonium buffer solutions. A stock solution of 1×10^{-2} M Ga(III) was prepared by dissolving the appropriate quantity of metal (99.999 %) in a mixture of concentrated HCl and HNO_3 (cp grade). The metal solution was standardized complexometrically.

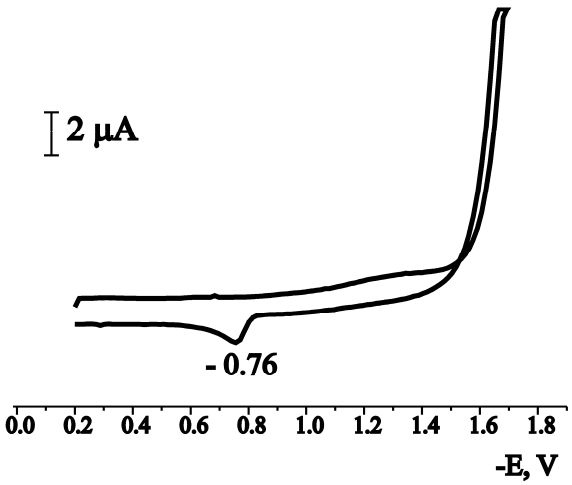

Fig. 1 Cyclic voltammogram of a 1×10^{-4} M Ga(III) solution using CH_3COOH-CH_3COONa, as supporting electrolyte, pH 4.0.

Stock standard 1×10^{-3} M solutions of azo dyes were prepared by dissolving the appropriate quantities of reagents (analytical grade) in an aqua-ethanol mixture, where the ethanol content was 40 % for ERB, 50 % for EBT, and 10 % for Calc and Klc. These solutions were standardized spectrophotometrically. Working solutions were prepared by diluting the stock solutions with doubly distilled water. Alloys prepared at the Department of Inorganic Chemistry of Ivan Franko National University of Lviv were used for the analysis.

Purified argon was used to remove dissolved oxygen.

Sample preparation

Samples of the Zn–Ga and Sm–Ga alloys and the $Gd_3Sc_2Ga_3O$ luminophore were accurately weighed and then dissolved in a mixture of concentrated HCl and HNO_3. The solutions were heated to remove nitrogen oxides. Subsequently they were diluted to 50 ml with a 1 M HCl solution.

Procedure

All solutions were prepared by mixing the constituents in the following order: buffer solutions, solutions of azo dyes and finally the Ga(III) ion solution. The working solutions were introduced into the cell and deoxygenated with argon for 10 min. The voltammograms were recorded by making a potential sweep from -0.1 to -1.2 V at a sweep rate of 0.5 V/s for the Ga(III)–ERB and Ga(III)–EBT systems and of 0.7 V/s for the Ga(III)–Calc and Ga(III)–Klc systems.

Gallium determination

The stock solutions containing the Zn–Ga and Sm–Ga alloys and the $Gd_3Sc_2Ga_3O$ luminophore were diluted 10 times. 0.3 ml and 1.0 ml of Zn–Ga with 0.1643 g and 0.0450 g sample masses respectively, 0.2 ml of Sm–Ga and 0.1 ml of $Gd_3Sc_2Ga_3O$ solutions were placed into a 25 ml flask containing the acetate buffer solution and azo dyes and were diluted with doubly distilled water to the mark. The concentration of all azo dyes was 1×10^{-4} M in the flask. The determination of the Ga(III) ions was made at pH 4.3 when using ERB and Calc and 4.6 when Klc was used. The analysis of gallium with ERB required 4 ml of ethanol, because the solutions were turbid at the concentration of 1×10^{-4} M of ERB. Ethanol was added before the azo dye. The gallium content was determined by comparison with a calibration graph obtained under the same conditions (pH, dye concentration).

Results and discussion

Voltammetric behaviour of Ga(III)–azo dye systems

Fig. 2 shows cyclic voltammograms of ERB, EBT, Calc, and Klc solutions and of 4×10^{-5} M Ga(III) ion solutions containing the above-mentioned dyes. The presence of metal ions caused the appearance of two

Table 1 Voltammetric characteristics of Ga(III)–azo dye systems.

Dye	pH ranges for the appearance of peaks P' and P"		Optimal pH value		$-E_P$ (V) at optimal pH	
	P'	P"	P'	P"	P'	P"
ERB	2.0-9.4	2.0-6.5	3.4-4.4 7.5-8.2	4.0-4.6	0.51-0.60 0.94	0.99
EBT	2.0-9.8	2.5-6.8	4.1-4.5 8.3-8.7	4.4	0.41-0.44 0.66-0.67	0.95
Calc	2.4-7.5	2.4-7.5	3.7-4.5	4.3-5.3	0.40-0.43	0.97-0.98
Klc	2.5-7.5	2.5-6.2	3.9-5.2	4.9-5.2	0.37-0.43	0.96

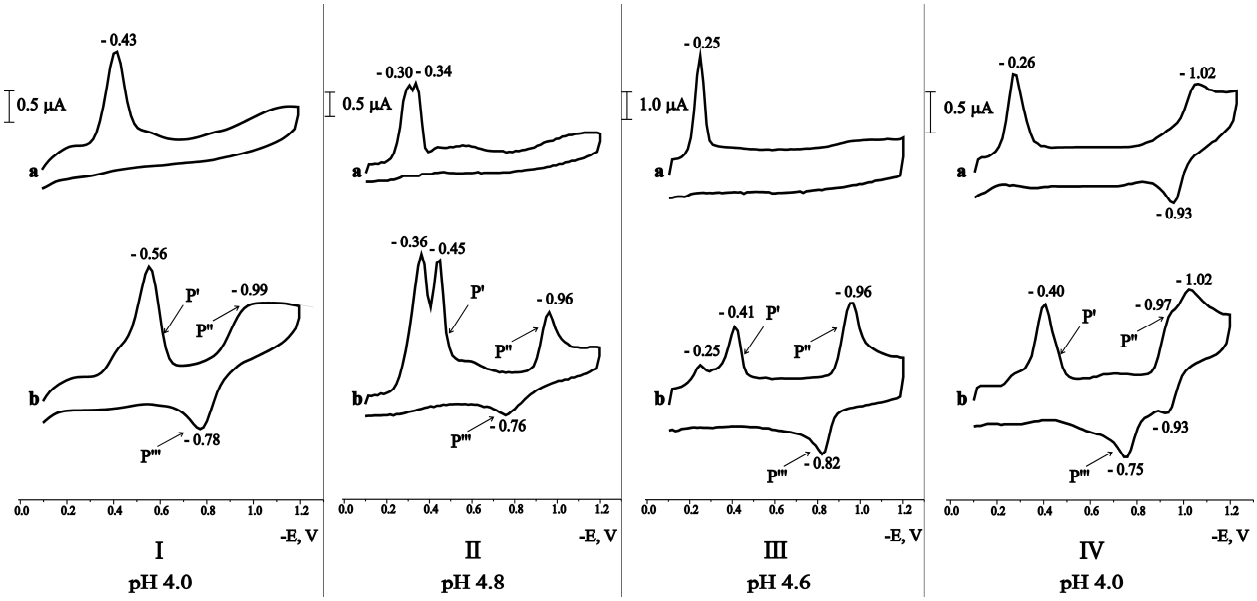

Fig. 2 Cyclic voltammograms of (Ia) ERB, (IIa) EBT, (IIIa) Klc, and (IVa) Calc, $C_{azo\ dye}=4\times10^{-5}$ M, and of (Ib) ERB–Ga(III), (IIb) EBT–Ga(III), (IIIb) Klc–Ga(III), (IVb) Calc–Ga(III) complexes, $C_{Ga(III)}=C_{azo\ dye}=4\times10^{-5}$ M.

new cathodic peaks, P' and P", which are shifted to more negative potentials than the reduction peaks of the organic reagents. A third peak, P"', was observed in the anodic branch. Since Ga(III) ions cannot be reduced in the investigated potential range, the peaks P' and P" correspond to the reduction of Ga(III)–azo dye complexes.

Influence of different parameters on the reduction of the complex

The influence of pH on the voltammetric characteristics of the Ga(III)–azo dye was investigated using acetate and ammonium buffer solutions. The pH dependence of the P' peak current is presented in Fig. 3(I) and the potential in Fig. 3(II). Table 1 gives the pH ranges for the existence of the peaks P' and P" and the optimal pH value for voltammetric determination of Ga(III) ions utilizing ERB, EBT, Calc, or Klc. The P' and P" peak currents of the Ga(III)–Calc and Ga(III)–Klc systems are maximal and constant in weakly acidic medium. In contrast to these systems, the pH dependence of the P' peak current for the Ga(III)–ERB and Ga(III)–EBT complexes shows two maxima: in weakly acidic and weakly basic media. Thus, there are two optimal pH intervals for the voltammetric Ga(III) determination using ERB and EBT. The interaction between Ga(III) ions and ERB and EBT is similar to that of REE(III)-ERB, In(III)-ERB and REE(III)-EBT complexes; the maximal value of the peak current corresponding to the reduction of these complexes was observed at pH>7.0 [14,15,17].

With increasing pH the P' peak potential of all the studied Ga(III) complexes with azo dyes shifted to more negative values. The shift of the potential can be related to the participation of H^+ ions in the reduction process. In basic medium the shift of the P' peak potential was negligible for the Ga(III)–ERB and Ga(III)–EBT complexes.

At room temperature and optimal pH the P' peak current of the Ga(III)–Calc system remained constant

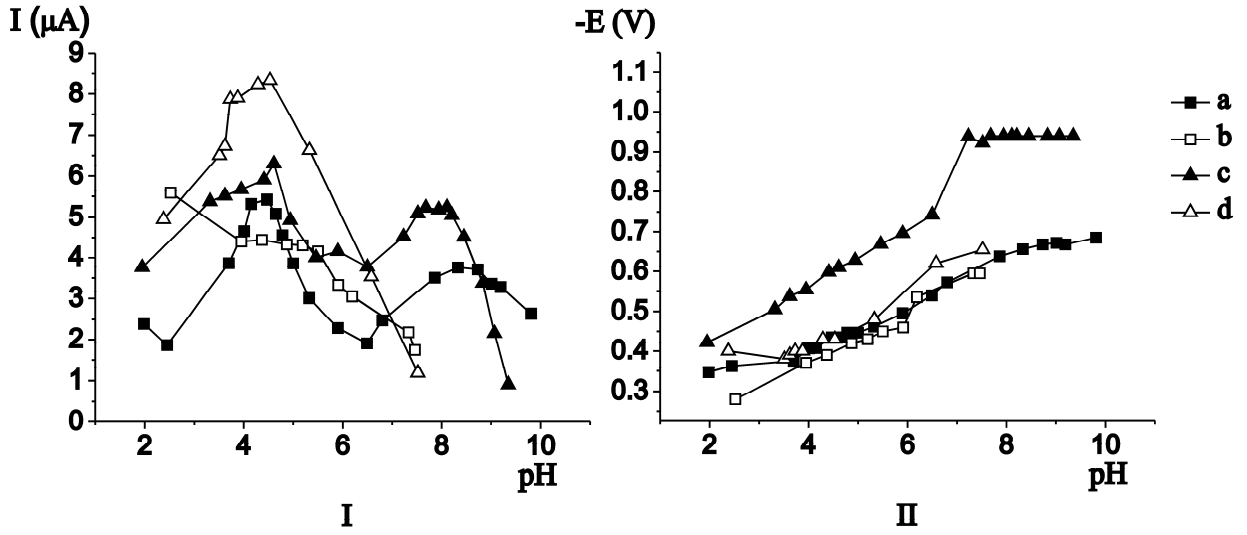

Fig. 3 Dependence of the P' peak current (I) and P' peak potential (E) on pH for (a) Ga(III)–EBT, (b) Ga(III)–Klc, (c) Ga(III)–ERB, and (d) Ga(III)–Calc complexes.

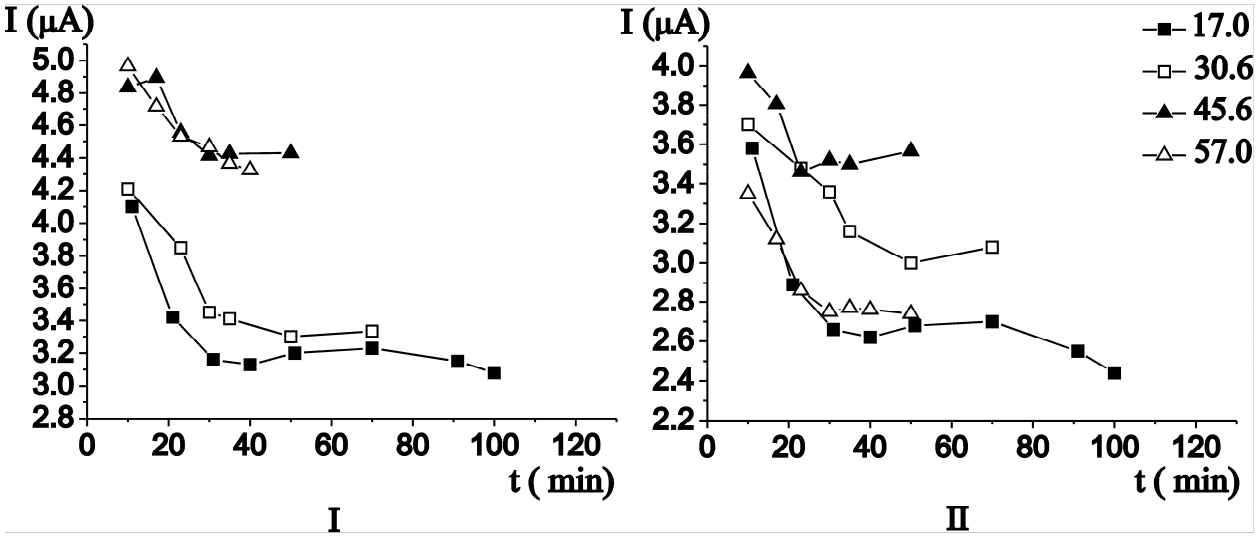

Fig. 4 Dependence of the (I) P' and (II) P" peak current on time at different temperatures (°C) for the Ga(III)–Klc complex (C_{Klc}=4×10^{-5} M, $C_{Ga(III)}$=1×10^{-5} M, pH 4.6).

during 160 min of the investigation and the P" peak current during 70 min. The P' and P" currents of the Ga(III)–ERB system at pH 4.0 and room temperature did not change for 17 h., and at pH 8.0 they remained constant during 230 min. At optimal pH the P' and P" currents of the Ga(III)–EBT system were stable during 60 min. The equilibrium in the Ga(III)–Klc system at room temperature was achieved in 30 min. A decrease of the P' and P" peak currents ($I_{P'}$ and $I_{P''}$) was observed throughout this interval of time (Fig. 4). We investigated the influence of the temperature of the solution in order to reach equilibrium faster. An increase of the temperature caused the increase of $I_{P'}$ and $I_{P''}$, but did not change the time required to reach equilibrium. The tendency of the P' and P" peak currents to decrease with time also remained (Fig. 4). Therefore, when using Klc for voltammetric determination of Ga(III), it is necessary to respect the same time interval from the moment the solutions are mixed to the moment the voltammogram is recorded.

The dependence of the P' peak current ($I_{P'}$) on the concentration of the reagent (C_R) is shown in Fig. 5. From the obtained curves it can be seen that the increase of the concentration of any of the studied azo dyes caused an increase of the value of $I_{P'}$. This indicates that the equilibrium concentration of products of the interaction was raised.

The nature of the P' and P" peak currents corresponding to the reduction of Ga(III) complexes with azo dyes was established studying

Table 2 Values of $\Delta\log i/\Delta\log v$ for peaks P' and P" observed during the reduction process of Ga(III) complexes with Calc, Klc and ERB.

Calc, $C_{Calc}=8\times10^{-5}$ M					
$C_{Ga(III)}\times10^5$ (M) at pH 3.8	$\Delta\log i/\Delta\log v$		pH at $C_{Ga(III)}=8\times10^{-5}$ M	$\Delta\log i/\Delta\log v$	
	P'	P"		P'	P"
1.0	1.04	0.69	3.8	0.86	0.52
4.0	0.91	0.63	4.7	0.99	0.43
8.0	0.86	0.52	5.9	0.99	0.47
Klc, $C_{Klc}=4\times10^{-5}$ M					
$C_{Ga(III)}\times10^5$ (M) at pH 4.5	$\Delta\log i/\Delta\log v$		pH at $C_{Ga(III)}=4\times10^{-5}$ M	$\Delta\log i/\Delta\log v$	
	P'	P"		P'	P"
0.8	1.05	0.60	3.6	1.03	0.31
2.0	1.01	0.58	4.5	0.97	0.46
4.0	0.97	0.46	5.6	1.00	0.54
ERB, $C_{ERB}=4\times10^{-5}$ M					
$C_{Ga(III)}\times10^5$ (M) at pH 4.0	$\Delta\log i/\Delta\log v$		pH at $C_{Ga(III)}=4\times10^{-5}$ M	$\Delta\log i/\Delta\log v$	
	P'	P"		P'	P"
0.8	0.95	0.50	3.6	0,95	0.32
2.0	0.90	0.56	4.6	0,89	0.54
4.0	0.90	0.55	5.4	0,99	0.55
$C_{Ga(III)}\times10^5$ (M) at pH 8.0	$\Delta\log i/\Delta\log v$		pH at $C_{Ga(III)}=4\times10^{-5}$ M	$\Delta\log i/\Delta\log v$	
	P'			P'	
0.8	0.93		7.6	0.93	
2.0	0.90		8.0	0.89	
4.0	0.89		8.4	0.89	

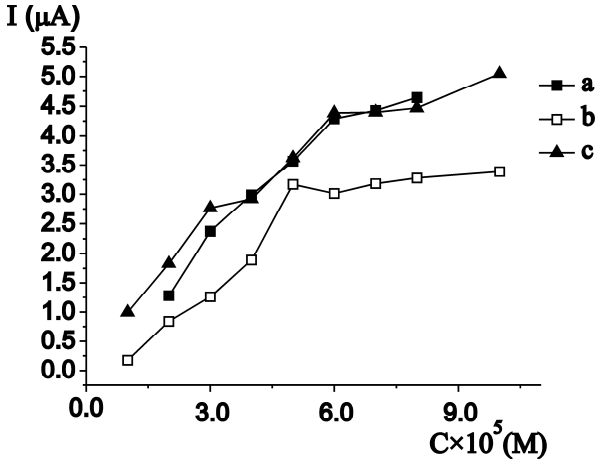

Fig. 5 P' peak current *vs.* the concentration of (a) Calc, $C_{Ga(III)}=8\times10^{-6}$ M, pH 4.0; (b) ERB, $C_{Ga(III)}=6\times10^{-6}$ M, pH 8.0; (c) Klc, $C_{Ga(III)}=8\times10^{-6}$ M, pH 4.6.

the dependence of log*i* on log*v* (where *i* is a current density and *v* is a sweep rate) [18]. The sweep rate was varied from 0.3 to 5.0 V/s. The values of the slope of the obtained log*i* *vs.* log*v* lines are shown in Table 2. For the P' peaks of the Ga(III)–ERB, Ga(III)–Calc and Ga(III)–Klc systems the values of $\Delta\log i/\Delta\log v$ are greater than 0.5, indicating adsorptive nature of the currents. The contribution of the adsorptive constituent decreased with increasing concentration of metal ions, which can be seen from the value of the Semerano criterion. The values of $\Delta\log i/\Delta\log v$ for the P" peaks of the Ga(III)–ERB and Ga(III)–Klc systems change from 0.3 to 0.5 depending on the pH, and the nature of the peak current changes from kinetic to diffusive. The P" peak current of the Ga(III)–Calc system is diffusive at all investigated pH values. At optimal pH the effect of adsorption decreases with increasing concentration of metal ions in the solution and when the Ga(III):azo dye ratio is 1:1 the P" peak current has diffusive nature for the Ga(III)–Calc and Ga(III)–Klc systems. The P" peak current of the Ga(III)–ERB complex is diffusive for all the studied Ga(III) concentrations.

Investigation of the reduction processes

The reduction of complexes formed by most of the metals and o,o'-dihydroxysubstituted azo dyes is related to the observation of a reduction peak caused by the reduction of ligands from the complexes [12,14,15,17,19]. The behavior of the Ga(III)–azo dye system differs from that of the other Me–azo dye systems and two cathodic P' and P" peaks and one anodic P"' peak were registered when the Ga(III)–azo dye system was reduced. Similar reduction processes involving gallium complexes with azo dyes and salycilic acid have been observed by other authors [11,12,19]. We have established above that the P' reduction peak current of Ga(III)–ERB, Ga(III)–Calc and Ga(III)–Klc complex compounds has adsorptive character. This is typical for reduction currents of organic reagents. That is why we suggest that the first

Table 3 Effect of pH and $C_{Ga(III)}$ on the difference of potentials $\Delta E_p = E_{p,azo\ dye} - E_{p,complex}$, $C_{azo\ dye} = 4\times10^{-5}$ M.

Ga(III)–Klc			
$C_{Ga(III)}\times10^5$ (M) at pH 4.6	ΔE_P (V)	pH at $C_{Ga(III)}=2\times10^{-5}$ M	ΔE_P (V)
0.1	0.18	2.5	0.18
0.2	0.18	3.9	0.17
0.4	0.18	4.1	0.16
0.8	0.18	4.8	0.16
1.0	0.18	5.4	0.17
2.0	0.17	5.9	0.16
4.0	0.17	6.2	0.15
8.0	0.16	7.5	0.19
Ga(III)–Calc			
$C_{Ga(III)}\times10^5$ (M) at pH 3.9	ΔE_P (V)	pH at $C_{Ga(III)}=4\times10^{-5}$ M	ΔE_P (V)
0.1	0.18	3.0	0.18
0.2	0.17	3.6	0.17
0.4	0.15	4.1	0.17
0.8	0.14	4.5	0.16
1.0	0.15	5.3	0.17
2.0	0.15	-	-
4.0	0.14	-	-
8.0	0.15	-	-
Ga(III)–EBT			
$C_{Ga(III)}\times10^5$ (M) at pH 4.7	ΔE_P (V)	pH at $C_{Ga(III)}=4\times10^{-5}$ M	ΔE_P (V)
0.1	0.12	2.0	0.11
0.2	0.10	3.6	0.08
0.4	0.09	4.4	0.08
0.6	0.09	5.0	0.08
0.8	0.09	5.6	0.09
1.0	0.10	6.2	0.11
2.0	0.09	7.1	0.11
4.0	0.08	8.7	0.11
8.0	0.07	9.8	0.08

P' peak corresponds to the reduction of ligands from the complexes, as for the reduction of azo dyes complexes with other metals ions. The diffusive or kinetic character of the P" peak current in the Ga(III)–ERB, Ga(III)–Calc and Ga(III)–Klc systems reminds the nature of the current of Ga(III) reduction to Ga^0 using KCl and NH_4Cl+NH_3 supporting electrolytes [11]. The observation of the anodic P"' peak can indicate that the P" peak corresponds to the reduction of Ga(III) ions from Ga(III)–azo dye complexes.

The ligand of the complex may be reduced in bound form (1) or the complex may first dissociate on the electrode surface and then the free ligand is reduced (2) [20]. In the first case the difference between the reduction potential of the ligand and the reduction potential of the complex ($\Delta E_p = E_{p,azo\ dye} - E_{p,complex}$) does not depend on the pH of the solution nor on the concentration of metal ions, but only on the stability constants of the oxidized and reduced forms of the complex and the dissociation constants of the oxidized and reduced forms of the azo dye. In the second case, ΔE_p depends on the stability constants of the oxidized and reduced forms of the complex and the dissociation constants of the oxidized and reduced forms of the azo dye and is also affected by the pH and the concentration of metal ions in solution.

The influence of pH and the concentration of Ga(III) ions on ΔE_p for the Ga(III)–Calc, Ga(III)–Klc and Ga(III)–EBT systems is shown in Table 3. The results of similar studies for the Ga(III)–ERB complex have been published earlier [21]. ΔE_p for the Ga(III) complexes with any of the investigated azo dyes does not depend on pH and the Ga(III) concentration. Consequently, the complexes do not dissociate on the electrode surface and the ligands are reduced in the bound state.

Calibration

An increase of the concentration of Ga(III) ions in solution causes a linear increase of the P' and P" peak current. Consequently, the linear dependence of $I_{P'}$ or $I_{P"}$ *vs.* $C_{Ga(III)}$ can be used for the voltammetric determination of Ga(III) ions utilizing ERB, EBT,

Table 4 Metrological characteristics of the voltammetric determination of Ga(III) using ERB, EBT, Calc, Klc, $C_{azo\ dye}=4\times10^{-5}$ M (R – correlation coeficient, S – standard deviation).

Reagent	pH	Peak	Calibration equation	R	S	Range of linearity (M)	Detection limit (M)
ERB	8.0	P'	$I=0.40+1.30\times10^5C_{Ga(III)}$	0.9999	0.004	1×10^{-7}-1×10^{-5}	2.0×10^{-7}
EBT	4.4	P'	$I=0.10+3.13\times10^5C_{Ga(III)}$	0.9988	0.056	1×10^{-6}-2×10^{-5}	1.0×10^{-6}
Calc	3.9	P'	$I=0.60+3.03\times10^5C_{Ga(III)}$	0.9996	0.045	1×10^{-6}-1×10^{-5}	1.0×10^{-6}
Klc	4.6	P'	$I=1.58+1.73\times10^5C_{Ga(III)}$	0.9998	0.027	1×10^{-6}-2×10^{-5}	5.0×10^{-7}
		P"	$I=1.67+1.05\times10^5C_{Ga(III)}$	0.9999	0.021	1×10^{-6}-4×10^{-5}	9.0×10^{-7}

Table 5 Results of Ga(III) ion determination in real samples (n=3, P=0.95).

Sample	Approximate Ga(III) content (%)	Sample mass (g)	Found Ga content (%)				Comparison of means								
			Spectrophotometry	Voltammetry			t for Calc			t for Klc			t for ERB		
				Calc	Klc	ERB	Sph*	Klc	ERB	Pht	Calc	ERB	Pht	Calc	Klc
SmGa	32	0.1835	32.7±1.5	30.9±2.0	30.4±3.5	30.6±1.6	3.1	0.5	0.6	2.5	0.5	0.2	4.2	0.6	0.2
			23.6±1.8	24.8±1.7	23.1±1.7	23.8±0.2	2.1	0.7	0.5	0.7	0.7	1.6	2.6	0.5	1.6
$Zn_{60}Ga_{40}$	41	0.0450													
		0.1643	26.5±0.8	-	25.3±1.6	24.7±1.6	-	-	-	2.9	-	1.1	4.3	-	1.1
$Gd_3Sc_2Ga_3O$	26	0.3615	24.6±0.9	24.0±1.0	23.2±2.2	23.7±1.9	2.1	1.5	0.5	3.3	1.5	0.8	1.9	0.5	0.8

* spectrophotometry

Calc or Klc as reagent. Table 4 gives the metrological characteristics of such determinations in model solutions.

Since the values of the P" peak potential of the Ga(III) complex with Calc and the second peak potential of the dye (Fig. 2) are close and the P" peak can only be registered at relatively high metal ion concentrations (>1×10^{-5} M), Ga(III) determination with Calc based on the P" peak is not perspective and has no advantages over known methods of analysis.

Selectivity

We studied the interference of some ions in order to apply the method to the analysis of real objects. The selection of elements was based on the qualitative compositions of the investigated objects.

The wide pH ranges within which the reduction peaks of the Ga(III)–azo dye complexes are registered make it possible to investigate the selectivity of metal ion determination at different pH. It was observed that the determination of 8×10^{-6} M Ga(III) using **ERB** was not affected by the presence of In(III) in the ratio 1:10 at pH 7.5, Mg(II) 1:200, Ca(II) 1:100, Cu(II) 1:1, Zn(II) 1:100, Al(III) 1:40, Sc(III) 1:50, Gd(III) and Sm(III) 1:100, Cr(III) 1:1, Ti(IV) 1:1, F^- 1:1, I^- 1:5, $C_2O_4^{2-}$ 1:1, SCN^- 1:1 at pH 3.8–4.3. The determination of 8×10^{-6} M Ga(III) with **Klc** was not altered by the presence of In(III) in the ratio 1:40, Sc(III) 1:10, Gd(III) and Sm(III) 1:70 and Zn(II) 1:100 at pH 4.6. The presence of Mg(II) in the ratio 1:250, In(III) 1:10, Al(III) and Sc(III) 1:20, Gd(III) 1:70, Sm(III) 1:80, Cr(III) 1:10, Ti(IV) 1:0.5, Zn(II) 1:10 at pH 4.0-4.3 and Zn(II) 1:30 at pH 5.1 did not interfere in the determination of 8×10^{-6} M Ga(III) utilizing **Calc**.

Analysis of real objects

The proposed method was applied to the determination of Ga(III) in intermetallic compounds of the Zn–Ga and Sm–Ga systems and in a $Gd_3Sc_2Ga_3O$ luminophore. The results of the analyses are given in Table 5. The objects were also analyzed by spectrophotometry using glycincresol red [11].

The Student's test was utilized to compare the two means obtained by the proposed voltammetric methods using Calc, Klc and ERB and by the spectrophotometric method. The results are in good agreement and the difference between the means is not significant when t[1] < t (P; $f = n_1 + n_2 - 2$) [22]. The calculated values of t (Table 5) are less than the Student's test t (0.99; $f = 3 + 3 - 2) = 4.6$, indicating agreement between the results obtained by voltammetry and spectrophotometry.

[1] $t=\frac{|\bar{x}_1-\bar{x}_2|}{s}\sqrt{\frac{n_1n_2}{n_1+n_2}}$; $s=\sqrt{\frac{s_1^2(n_1-1)+s_2^2(n_2-1)}{n_1+n_2-2}}$

Conclusions

A new voltammetric method for the determination of Ga(III) ions using azo dyes – ERB, EBT, Calc and Klc – is proposed. The developed methods are relatively sensitive, the detection limits being in the range of 10^{-6}-10^{-7} M. The lowest value of 2×10^{-7} M was obtained using ERB. The high sensitivity makes it possible to determine trace amounts of gallium. The value of the detection limit is similar to and in some case lower than that of conventional voltammetric methods or atomic and molecular spectroscopy.

The Ga(III) complex compounds formed with azo dyes tend to adsorb on the dropping mercury electrode. That is why the detection limits can be decreased by several orders of magnitude if working electrodes with previous accumulation on them are used.

The developed method was successfully applied to the analysis of real objects. The determination is highly accurate, rapid and simple to perform.

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