

EXTRACTION IN CCL₄ OF IONIC ASSOCIATES OF IODINE- IODIDE COMPLEXES WITH THE CATIONIC DYE BRILLIANT GREEN

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ABSTRACT. Investigation and efficiency increase for extraction procedure of ionic associates of iodine-iodide complexes with cationic dye brilliant green have been performed by the determination of iodide. Extraction constant of ionic associate of iodine-iodide complexes with brilliant green in CCl₄ has been estimated ($K_{extr} 115 \pm 5$).

Keywords: ionic associates, iodine-iodide complexes, extraction constant, brilliant green

INTRODUCTION

Iodide-ion is a main component among iodine-containing ions. Voltammetry and ionic chromatography with inductively coupled plasma mass spectrometry were more often used for the determination of iodine and iodine-containing ions [1-6]. These methods are highly-sensitive but they are characterized by high prices of the analyses due to usage of expensive equipment, reagents and outsourcing of qualified personnel.

Electrochemical [7, 8] and spectrophotometric methods [9-12] are more accessible. It has been reported that these methods were used jointly for the determination of iodide and bromide [13]. Therefore development of new, or updating the already existing procedures of analysis which are based on the combination of electrochemical and spectrophotometric methods for monitoring the iodine, iodide, iodate in different samples is an actual task of modern analytical chemistry.

The problem in the development of methods for determination of iodide-ions is related to the increasing of sensitivity and selectivity of determination. Spectrophotometric methods for determination of trace amounts of iodide using extraction of ionic associates of iodide-ions with

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triphenylmethane dyes have been reported [14]. Spectrophotometric method reported in the work [15] ranks below in sensitivity (by 100 times) as compared with methods based on the measurement of absorbance of iodine-iodide complexes. The determination of iodide-ions in form of ionic associates with brilliant green after electrochemical oxidation to iodate and interaction with excess of iodide has been reported in [16]. Under these conditions the sensitivity of the determination in the form of iodine-derivatives of organic dyes yields to the methods in the base of which there is a formation of ionic associates of cationic dyes with iodine-iodide complexes.

Tris-phenyl-methane dyes have an important place in analytical practice due to their high sensitivity and selectivity. Inconsistency in literature about extraction ability of these dyes and absence of uniform criteria for estimation of reagents does not allow an objective comparison and the choice of the best fitted dye. From this perspective the range of acidity of aqueous phase, concentration of dye at which absorbance of extracts is constant, extraction coefficient, molar absorptivity, time of extraction etc. are the main criteria.

The aim of this work is to establish optimal conditions of extraction in carbon tetrachloride of ionic associates of iodine-iodide complexes with cationic dye brilliant green and to estimate the extraction constant. The procedure of extraction is one of the step of methods for determination of trace amounts of iodide in form of ionic associate (IA) with brilliant green using electrochemical oxidation which has already been reported in the literature [16].

RESULTS AND DISCUSSION

Increased demands to the blank solution for which signal should be minimal and reproducible appear under the work near the limit of quantification. It was noticed that long-term storage of brilliant green solution elevates absorbance in blank solution. This effect is connected with temperature aggregation of cations of brilliant green; under the heating aggregates destruct.

Before the test, required quantity of sulfuric acid was added to the aliquot of working solution of dye and this mixture was heated to boil. This procedure results in decreased aggregation of dye and thereby, decreased absorbance value of the blank solution.

The performance of the extraction in the air results in the sufficient decreasing of absorbance value of blank solution. Because of this increasing carrying of further analysis is complicated. It is known that potassium iodide contains iodine and it is oxidized with air. During the extraction in CCl_4 the

quantity of iodine which forms ionic associates with brilliant green, increases. Consistent extractions from blank solution allow excluding contaminations but not decreasing the value of absorbance essentially. That's why necessity to carry out investigation in inert medium has appeared.

Inert medium was created in two ways:

The oxygen of air was displaced from the funnel using carbon dioxide obtained in Kipp's apparatus. Desired decreasing in values of absorbance did not occur in the medium of carbon dioxide. Dependence is given on the Figure 1:

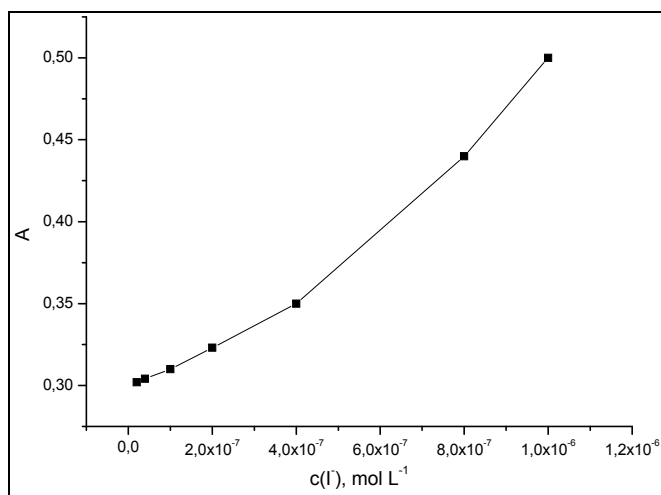


Figure 1. Dependence of absorbance of IA of iodine-iodide complexes with brilliant green on concentration of iodide-ion (in the medium of carbon dioxide).

Another way of extraction in inert medium is displacement of oxygen of air from funnel with gaseous nitrogen. Procedure of displacement of oxygen using gaseous nitrogen was used for solutions preparation, using double-distilled water saturated with gaseous nitrogen.

Saturation procedure of double-distilled water with gaseous nitrogen and passing of gaseous nitrogen through the solution in the funnel before extraction provide substantial decrease of absorbance of blank solution and allows the recording of reproducible and stable values of absorbance [17, 18].

The absorbance of extracts from the blank solution when performing the extraction without passing gaseous nitrogen through the solution in the funnel and using solution prepared with double-distilled water were recorded and they are the following (after three parallel measurements): $A_{01} = 0.250$,

$A_{02} = 0.230$, $A_{03} = 0.220$. Absorbance of extracts from the blank solution when using of double-distilled water saturated with nitrogen were determined as follows: $A_{01} = 0.068$, $A_{02} = 0.070$, $A_{03} = 0.073$. From the foregoing it is evident that gaseous nitrogen passed through the double-distilled water employed in the solution preparation decreases the value of absorbance of the blank solution.

Determination of extraction constant of ionic associates of iodine-iodide complexes with cationic dye brilliant green carbon tetrachloride

Under the extraction of ionic associates of cation (R^+) of brilliant green and anions (I_3^-) of iodine-iodide complexes the whole process can be resolved on three components:

- equilibrium of formation of complex anion, $I^- + I_2 \rightleftharpoons I_3^-$
- equilibrium of formation of ionic associates in aqueous phase, $R^+ + I_3^- \rightleftharpoons R^+ I_3^-$
- equilibrium of distribution of ionic associate between aqueous phase and organic solvent $(R^+ I_3^-)_{aq.ph.} \rightleftharpoons (R^+ I_3^-)_{org.ph.}$

Equilibrium constant of formation of complex anion ($\lg K(I^- + I_2 \rightleftharpoons I_3^-) = 2.9$) is known [19]. As to measure equilibrium constant of formation of ionic associate separately using spectrophotometric method is not possible (absorbance spectrum of cation of dye in the associate and out of it does not differ significantly), only equilibrium constant of extraction can be determined:

$$K_{extr}(R^+ + I_3^- \rightleftharpoons (R^+ I_3^-)_{org.ph.}) = \beta(R^+ + I_3^-)_{org.ph.} = \beta(R^+ + I_3^- \rightleftharpoons R^+ I_3^-) \times K_D((R^+ I_3^-)_{aq.ph.} \rightleftharpoons (R^+ I_3^-)_{org.ph.}) \quad (1)$$

Under the determination of extraction constant it is convenient to change degree of extraction of ionic associate at the change in concentration of iodide-ion in aqueous phase. In this case general reaction equation is following:

$$\begin{aligned} K(I^- + I_2 \rightleftharpoons (R^+ I_3^-)_{org.ph.}) &= K(I^- + I_2 \rightleftharpoons I_3^-)_{org.ph.} \\ &= K(I^- + I_2 \rightleftharpoons I_3^-) \times K_{extr}(R^+ + I_3^- \rightleftharpoons (R^+ I_3^-)_{org.ph.}) \end{aligned} \quad (2)$$

$$K \times K_{extr} = \frac{[R^+ I_3^-]}{[I_2] \times [I^-]}$$

$$K_{extr} = \frac{\overline{[R^+I_3^-]}}{[I_2] \times [I^-] \times K} \quad (3)$$

where, $\overline{[R^+I_3^-]}$ – equilibrium concentration of ionic associate in the phase of organic solvent;

$$\overline{[R^+I_3^-]} = A/\varepsilon l;$$

A – absorbance of ionic associate in the phase of CCl₄;

ε – molar extinction coefficient of ionic associate in CCl₄, $\varepsilon = 65000$ L mol⁻¹ cm⁻¹;

l – working size of quartz cell;

$[I_2] = c(I_2) - \overline{[R^+I_3^-]} \times V(CCl_4)/V(H_2O) - [I_3^-]$ is an equilibrium concentration of iodine in aqueous phase;

$c(I_2)$ – total concentration of iodine in aqueous phase before extraction;

$V(CCl_4), V(H_2O)$ – volumes of phases under the extraction;

$[I_3^-] = [I^-] \times [I_2] \times 10^{2.9}$ – concentration of iodide-iodide anions in aqueous phase;

$[I^-]$ – equilibrium concentration of iodide in aqueous phase.

Measured data of absorbance of extracts of ionic associates of brilliant green and anions of iodine-iodide complexes in CCl₄ at the different concentrations of iodide-ions in aqueous phase are given in the table 1. $c(I_2) = 5 \times 10^{-6}$ mol L⁻¹. Volumes of phases are the same: $V(CCl_4) = V(H_2O) = 50$ mL.

Table 1. Absorbances of extracts of ionic associates of brilliant green and anions of iodine-iodide complexes in CCl₄ at the different concentrations of iodide-ions in aqueous phase

$c(I^-)$, mol L ⁻¹	$A_{extr}, n = 3$		
1×10^{-2}	0.260	0.258	0.261
1×10^{-3}	0.257	0.256	0.258
1×10^{-4}	0.233	0.234	0.232
5×10^{-5}	0.210	0.208	0.212

Concentration ratio $[I_3^-]/[I_2]$ depends on the concentration of iodide in water:

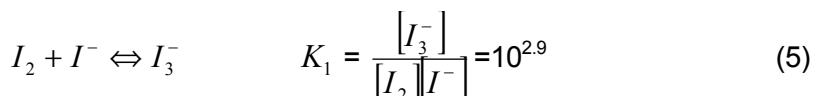
$$l[I_2] = [I^-] \times 10^{2.9} \quad (4)$$

At the $c(I^-) = 1 \times 10^{-4}, 5 \times 10^{-5}$ mol L⁻¹ anionic complexes are only $10^{-1.1} = 0.068$ and $10^{-1.4} = 0.040$.

Extraction constant value has been estimated using measurement at the $c(I^-) = 1 \times 10^{-4}, 5 \times 10^{-5}$ mol L⁻¹ by the equation (3). After the averaging out the value of extraction constant (K_{extr}) was 115 ± 5 .

Determination of iodine in form of ionic associate of iodine-iodide complexes with brilliant green

It appears that ionic associates extract only at sufficiently high concentration of iodide-ion, if to perform determination of iodine in iodide in the solution without addition of excess of iodide using spectrophotometric method with brilliant green. Equilibrium of formation of complex I_3^- from I_2 and I^- is characterized with constant $\lg K_1 = 2.9$ [19]. From the expression of law of mass action follows that yield of form of I_3^- depends from concentration of I^- :



At the equilibrium concentration of iodide ($[I^-] = 1$ mol L⁻¹), equilibrium concentration of complex ($[I_3^-]$) is $10^{2.9} [I_2]$ that is part of iodine in iodine-iodide complexes is ~ 0.999 , but when $[I^-] = 10^{-6}$ mol L⁻¹ equilibrium concentration of complex ($[I_3^-]$) is $10^{-2.9} [I_2]$, that is part of iodine in complex form is ~ 0.001 .

Dependence of extraction degree (R) of iodine in form of ionic associate on logarithm of iodide-ion concentration in the solution is given at the figure 2.

If we assume that practically complete extraction of component in organic phase is possible at the $R > 0.9$ after two consistent extraction, then total value of extraction degree exceeds the value $R_{\Sigma} \geq 0.99$. $R_{\Sigma} = R_1 + R_2 = R + R \times (1 - R) = 0.9 + 0.9 \cdot 0.1 = 0.99$.

According to the figure 2 such completeness of the extraction of iodine in carbon tetrachloride in form of ionic associates of iodine-iodide complexes with cationic dye brilliant green is possible at the $c(KI) > 10^{-4}$ mol L⁻¹.

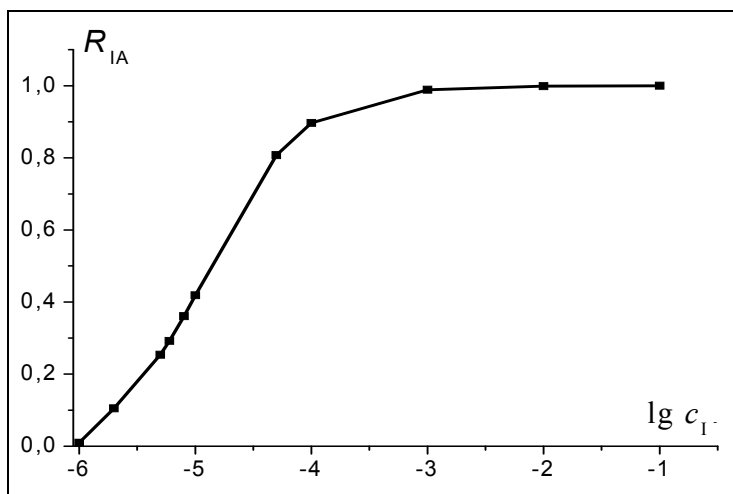


Figure 2. Dependence of extraction degree of iodine in CCl₄ in form of ionic associate of iodine-iodide complexes with cationic dye brilliant green on logarithm of iodide-ion concentration in the solution at the same volumes of phases.

Sensitivity of spectrophotometric determination of iodine in the presence of iodide by the procedure with brilliant green is much less than sensitivity of iodide determination. Iodide is determined using electrochemical oxidation [16]; under this condition sensitivity is increased 3 times.

CONCLUSIONS

1. Investigation and efficiency increase of extraction procedure of ionic associates of iodine-iodide complexes with cationic dye brilliant green have been performed at the determination of iodide:

- heating of aliquot of working solution of brilliant green in the sulfuric acid, saturation of double-distilled water with nitrogen and passing nitrogen through the funnel before extraction provide significant decreasing of absorbance of "blank test" and obtaining of reproducible and stable value of absorbance.

2. Extraction constant of ionic associate of iodine-iodide complexes with brilliant green in CCl₄ has been estimated, K_{extr} is 115 ± 5 .

3. It is necessary to create $c(KI) \geq 10^{-4}$ mol L⁻¹ for quantitative extraction of iodine-iodide anions in aqueous phase.

EXPERIMENTAL SECTION

Apparatus

Absorbance was measured using UV/Vis spectrophotometer SF – 46 (LOMO, Russia), equipped with 10 mm quartz cells.

Carbon tetrachloride (Reachim, pure for analysis) was purified by distillation with activated carbon.

Extraction was carried out using separating funnel (type VD -1 250 GOST 25336-82).

Reagents

All reagents used were of analytical and all solutions were prepared saturated with gaseous nitrogen.

Preparation of the solutions

A standard solution of potassium iodide was prepared by dissolving 0.166 g potassium iodide (Reachim, chemically pure) in double-distilled water and diluting to the mark in 100 mL volumetric flask. Solutions with less concentration are prepared with diluting of this solution.

A 1 mol L⁻¹ sulfuric acid solution was prepared by dilution of concentrated sulfuric acid (Reachim, chemically pure) with double-distilled water.

Saturated solution of brilliant green was prepared by dissolving 5 g of C₂₇H₃₃N₂C₂O₄H•H₂O (Reachim, pure for analysis) in 100 mL of double-distilled water, at which point undissolved residue was filtered out. Filtered saturated solution of brilliant green was further twice diluted with double-distilled water. Solution is kept in dark place. Solutions with less concentration are prepared with diluting of this solution.

Procedure

10 mL of brilliant green solution (5×10^{-3} mol L⁻¹) and 2 mL of H₂SO₄ (c = 1 mol L⁻¹) were mixed in beaker and warmed before extraction, then this mixture was used in extraction-photometric determination. This procedure results in decreased aggregation of dye and, thereby, decreased absorbance value of the blank solution. Warmed mixture of brilliant green and sulfuric acid, 10 mL of potassium iodide solution (c = 2×10^{-3} mol L⁻¹) and 20 mL of organic solvent were added to the separating funnel and saturated with nitrogen. Extraction was carried out for 3 min, periodically passing nitrogen through solution in funnel. Organic phase was discarded after first extraction. Extraction was repeated once more. Absorbance of second extract was

measured at absorption maximum band ($\lambda = 645$ nm) with path length of 1 cm. Absorbance value of second extract is absorbance of blank sample. After second extraction, test solution was added to separating funnel, and then extracted with 20 mL of carbon tetrachloride. Extraction was carried out for 3 min, periodically passing nitrogen through solution in funnel. Organic phase was transferred into 50-mL volumetric flask. Extraction was repeated with new portion of solvent and extracts were combined. Volume of solution was diluted to the mark with extract after third extraction. This procedure is needed to ensure recovery rate 99%. Obtained solution was mixed and absorbance of combined extract was measured at absorption maximum band ($\lambda = 645$ nm) with path length of 1 cm. To determine iodide different concentration of iodide are inserted in the funnel after the blank solution.

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