Spectrophotometric determination of the platinum metals VI.* Determination of rhodium and palladium with 4-(2-thiazolylazo)resorcinol in the presence of cation-active tensides

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The reactions of platinum metal ions with azo-dyes were studied using 4-(2-thiazolylazo)resorcinol and the effect of the presence of cation-active tensides was studied. The formation of the binary complex of Rh(III) with the dye (pH 5.0; $\lambda = 520$ nm; $\varepsilon' = 3.22 \times 10^4$ mol^{-1} l cm^{-1}) and of the ternary complexes of Rh(III) (pH 5.6; $\lambda = 545$ nm; $\varepsilon' = 3.75 \times 10^4$ mol^{-1} l cm^{-1}) and Pd(II) (pH 5.0; $\lambda = 540$ nm; $\varepsilon' = 3.02 \times 10^4$ mol^{-1} l cm^{-1}) in the presence of the micelle form of cetylpyridinium bromide formed the basis for development of a new sensitive spectrophotometric determination of the two metals (0.5—3.6 μg Rh(III) ml^{-1}; sensitivity according to Sandell $S = 3.3 \times 10^{-3}$ and 2.9×10^{-3} μg cm^{-2} for the binary and ternary complex, respectively; 0.5—3.2 μg Pd(II) ml^{-1}; $S = 3.7 \times 10^{-3}$ μg cm^{-2}).

Для изучения реакций ионов платиновых металлов с азокрасителями был использован 4-(2-тиазолилазо)резорцинол и было исследовано влияние присутствия катионных поверхностно активных веществ. Образование бинарного комплекса Rh(III) с азокрасителем (pH 5,0; $\lambda = 520$ нм; $\varepsilon' = 3,22 \cdot 10^4$ моль$^{-1}$ л см$^{-1}$) и тернарных комплексов Rh(III) (pH 5,6; $\lambda = 545$ нм; $\varepsilon' = 3,75 \cdot 10^4$ моль$^{-1}$ л см$^{-1}$) и Pd(II) (pH 5,0; $\lambda = 540$ нм; $\varepsilon' = 3,02 \cdot 10^4$ моль$^{-1}$ л см$^{-1}$), образующихся в присутствии мицеллярной формы бромида цетилпиридиния, лежит в основании новых чувствительных спектрофотометрических методов определения обоих металлов (0,5—3,6 мкг Rh(III) мл$^{-1}$; чувствительность по Сэнделлу $S = 3,3 \cdot 10^{-3}$ и $2,9 \cdot 10^{-3}$ мкг см$^{-2}$ соответственно для бинарного и тернарного комплексов; 0,5—3,2 мкг Pd(II) мл$^{-1}$; $S = 3,7 \cdot 10^{-3}$ мкг см$^{-2}$).

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* For Part V see Ref. [4].

The use of azo-dyes was studied in the framework of study of new spectrophotometric determinations of the platinum metals. In addition to 4-(2-pyridylazo)resorcinol, the heterocyclic azo-dye 4-(2-thiazolylazo)resorcinol was found suitable, especially in the presence of cation-active tensides. The presence of the micelle forms of 1-carbethoxypentadecyltrimethylammonium bromide and especially of cetylpyridinium bromide permitted the development of a new procedure for the microdetermination of Rh(III) and Pd(II). The formation of binary or ternary complexes of palladium(II) with this dye in a dimethylformamide medium and their analytical use have been described [1].

Experimental

Instruments and chemicals

The solution absorbances were measured on a recording spectrophotometer Unicam SP 800 (Pye-Unicam, Cambridge) using a cuvette with an internal dimension of 1.00 cm. The pH of the solution was measured with an N-512 pH-meter (Mera-Elmat, Wrocław) with a combined SAgP-201W electrode. Reactions at increased temperature were studied using a U 10 thermostat (VEB Prüfgeräte-Werk, Medingen, GDR).

The stock 1×10^{-3} M solution of 4-(2-thiazolylazo)resorcinol (TAR) was prepared by dissolving a weighed amount of the purified dye in 30 ml of pure ethanol and diluting with distilled water to 100 ml. This solution is stable for 7 h. The commercial dye (Lachema, Brno) was purified by recrystallization from pure ethanol. The purity was then verified by thin-layer chromatography [2] on Silufol UV 254 (Kavalier, Votice) using the solvent systems benzene—acetic acid (80:20), CCl_4—acetic acid (30:8) and (30:4), and CCl_4—ethyl acetate—acetic acid (30:3:2). Only one spot was obtained for the purified dye, in contrast to the commercial dye. The composition of the purified substance (98% the active component) was verified by elemental analysis and the presence of the azo group by reductometric titration [3].

The stock 5×10^{-3} M solutions of cation-active tensides of 1-carbethoxypentadecyltrimethylammonium bromide (CPTB, Septonex) [4] and cetylpyridinium bromide (CPB) [5] were prepared in the usual manner. The purity of CPB was controlled by elemental analysis and the bromide content was found argentometrically.

The stock 5×10^{-3} M-Rh(III) solution was prepared from $RhCl_3 \cdot 4H_2O$ (Safina, Vestec) and the metal content was found gravimetrically as $[Co(NH_3)_6][Rh(NO_2)_6]$. The standard 5×10^{-4} M-Rh(III) solution was prepared from $(NH_4)_3RhCl_6 \cdot 1.5H_2O$ (Johnson, Matthey and Co., London).

The stock 1×10^{-3} M-Pd(II) solution was prepared by diluting a 10% $PdCl_2$ (anal. grade) solution containing 0.06 g Pd(II) in 1 ml (Safina, Vestec). The standard 5×10^{-4} M-Pd(II) solution was prepared by dissolving $(NH_4)_2PdCl_4$ (Johnson, Matthey and Co., London) in 12.5 ml of 0.1 M-HCl and diluting with distilled water to 500 ml.

1×10^{-3} M solutions of the other studied platinum metals, Ru(III), Os(IV), Ir(III), Ir(IV), and Pt(IV) were prepared by dissolving $(NH_4)_2Ru(H_2O)Cl_5$, $(NH_4)_2OsCl_6$,

(NH$_4$)$_3$IrCl$_6$ · H$_2$O, (NH$_4$)$_2$IrCl$_6$ and H$_2$PtCl$_6$ (all from Johnson, Matthey and Co., London) in the smallest possible volume of 0.1 M-HCl and diluting with distilled water.

All the other chemicals and solvents employed were of anal. grade. The pH values of the solution were adjusted with 0.2 M acetate buffer as described by Walpole [6] and with a mixture of HCl—KCl or HCl—NaOH; the ionic strength was not adjusted.

Determination of Rh(III)

2 ml of a freshly prepared 1×10^{-3} M-TAR solution, 10 ml of 0.2 M acetate buffer (pH 5.6), and 3 ml of 5×10^{-3} M-CPB were pipetted stepwise into a 25 ml volumetric flask. After mixing, the sample solution containing an amount of 13.0 to 90.0 µg Rh(III) is added. The solution is diluted with distilled water and heated on a boiling water bath for 15 min. After cooling and diluting to the mark with distilled water, the absorbance of the solution is measured at a wavelength of 545 nm against a blank.

Determination of Pd(II)

2 ml of a freshly prepared 1×10^{-3} M-TAR solution, 10 ml of 0.2 M acetate buffer (pH 5.0), and 3 ml of a 5×10^{-3} M-CPB solution are pipetted stepwise into a 25 ml volumetric flask. After mixing, the sample solution containing 13.0 to 80.0 µg Pd(II) is added. After diluting to the mark with distilled water, the absorbance of the solution is measured within 25 min at a wavelength of 540 nm against a blank.

Results

In a systematic study of the reactions of the platinum metals with TAR it was found that, in addition to palladium, the ions of the other platinum metals react with the agent in a 0.2 M acetate buffer medium. The results of preliminary experiments, listed in Table 1, confirm the formation of the binary complex in aqueous medium and especially the favourable effect of the presence of cation-active tenside, CPTB and CPB, where in almost every case a bathochromic shift of the absorption maximum is observed, mostly accompanied by an increase in the intensity of the colour produced, reflected in an increased absorbance value. No precipitate is formed in the presence of palladium and tenside.

The reactions of Rh(III) and Pd(II) with TAR and the effect of the tenside were studied in detail to develop a method for the spectrophotometric determination of rhodium and palladium. It was found preferable to use cation-active tenside CPB.

Rhodium reacts with TAR in the absence of CPB in a relatively broad pH interval from 3.6 to 5.6, with formation of a red complex with the maximum of the differential curve at 520 nm. The reaction is slow at laboratory temperature but is complete after 55 min heating on a boiling water bath. At pH above 6 a further

Table 1

Preliminary reactions of the platinum metal ions with TAR

($c_{metal} = 2 \times 10^{-5}$ M; $c_{TAR} = 8 \times 10^{-5}$ M; $c_{CPTB} = c_{CPB} = 6 \times 10^{-4}$ M; pH 4.6)

Metal ion	Tenside	$\lambda_{max}/$nm	A_{max}*	Note**
Rh(III)	—	520	0.34	b
	CPTB	545	0.32	b
	CPB	545	0.39	b
Pd(II)	—	—	—	Precipitate
	CPTB	545	0.32	a
	CPB	540	0.63	a
Ru(III)	—	530	0.12	a
	CPTB	550	0.14	a
	CPB	555	0.18	a
Os(IV)	—	520	0.09	b
	CPTB	—	—	Precipitate
	CPB	550	0.06	b
Ir(III)	—	525	0.04	b
	CPTB	540	0.05	b
	CPB	540	0.09	b
Ir(IV)	—	530	0.07	b
	CPTB	545	0.08	b
	CPB	545	0.10	b
Pt(IV)	—	505	0.05	b
	CPTB	545	0.07	b
	CPB	545	0.11	b

* The data given are for the differential curve.

** Measurement was carried out 10 min after mixing the solutions at laboratory temperature (*a*) or after heating the mixture for 15 min on a boiling water bath (*b*).

complex is probably formed, appearing in the spectra as a shift in the maximum to 540 nm.

At optimum pH, 5.0, and in the presence of at least a fivefold excess of the reagent with respect to the metal (as in the region from 7×10^{-5} M$< c_{TAR} < 1 \times 10^{-4}$ M and for $c_{Rh} = 1.7 \times 10^{-5}$ M the A_{520} value is constant), the complex with absorption maximum of the differential curve at 520 nm can be used for determining Rh(III). A complex composition of Rh:TAR = 2:3 was found by the Job method (for $\lambda = 500$, 520, and 570 nm, pH 5). The spectra of the binary Rh—TAR complex are given in Fig. 1 (curves *2* and *3*). The parameters for the spec-

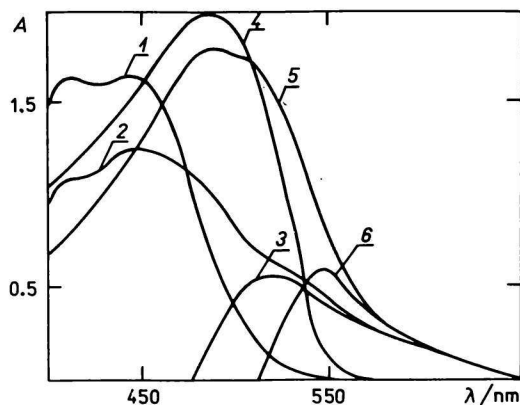Fig. 1. Absorption spectra of Rh(III)—TAR and Rh(III)—TAR—CPB complexes.
$c_{Rh} = 1.7 \times 10^{-5}$ M; $c_{TAR} = 8 \times 10^{-5}$ M; $c_{CPB} = 6 \times 10^{-4}$ M.
1. TAR; 2. Rh–TAR; 3. difference between 1 and 2; 4. TAR–CPB; 5. Rh–TAR–CPB;
6. difference between 4 and 5.
1—3: pH 5.0, measured after heating for 55 min on a boiling water bath; 4—6: pH 5.6, measured after heating for 15 min on a boiling water bath; all measured against water.

trophotometric determination are given in Table 2 (together with an estimate of the standard deviation value of the scatter around the regression straight line, $s_{x,y}$). The value of the apparent concentration stability constant of the complex, $\beta' = 1.35 \times 10^{7}$, was found from the Job curves.

The effect of the presence of tenside (CPB) on the formation of the complex of Rh(III) with TAR at pH 5.5 to 5.7 appears as a considerable shortening of the time required for heating the mixture on the water bath to 15 min, as a shift in the maximum absorbance of the complex to longer wavelength, 545 nm, on the differential curve and in higher sensitivity of the reaction. These spectra are given in Fig. 1 (curves 5 and 6). It was found in a study of the effect of the tenside concentration on the colour of the solution that, up to $c_{CPB} = 5 \times 10^{-4}$ M, the value of the absorbance at the maximum of the differential curve, 545 nm, increases and is constant in the optimal interval 5×10^{-4} M $< c_{CPB} < 1.4 \times 10^{-3}$ M. Study of the composition of the complex by the Job method in the presence of excess tenside ($c_{CPB} = 6 \times 10^{-4}$ M, $\lambda = 520$, 545, and 570 nm, pH 5.6) indicated the presence of one strong complex with a Rh:TAR ratio of 2:3; the shape of the Job curves does not, however, exclude the presence of other complexes which are weaker at the given pH value. The spectrophotometric parameters of the ternary complex useful for the determination of Rh(III) are given in Table 2 together with the determined optimal conditions for the method.

Table 2

Determination of Rh(III) and Pd(II) with TAR

Metal	Tenside	pH	λ_{max}/nm	$\dfrac{\varepsilon' \cdot 10^{-4}}{mol^{-1}\ l\ cm^{-1}}$	Δc/µg ml^{-1}	$\dfrac{S \cdot 10^3}{µg\ cm^{-2}}$	Note
Rh(III)	—	5.0	520	3.22	0.5—3.6	3.3	1
	CPB	5.6	545	3.75	0.5—3.6	2.9	2
Pd(II)	—	HClO₄	635	1.07	≤5.0		3
	—	5.0—5.5, DMF	555	1.80	<3.2		3
	CPB	5.0, DMF	540	3.02	0.5—3.2	3.7	4

λ_{max} — wavelength of the maximum of the differential curve.
ε' — molar absorption coefficient at the maximum of the differential curve.
S — sensitivity according to Sandell [11].
Δc — concentration range.
Note: *1.* Heated for 55 min on a boiling water bath, stable >2 h, the estimate of the standard deviation for the scatter around the regression straight line, value of $s_{x,y} = 0.0098$, intercept $a = -0.030$;
2. heated for 15 min on a boiling water bath, stable >2 h, $s_{x,y} = 0.023$, $a = -0.051$; *3.* see Ref. [2];
4. measured before 25 min standing at laboratory temperature, $s_{x,y} = 0.013$, $a = -0.026$.

Palladium reacts with the TAR reagent in aqueous medium at pH 0 to 14 to produce a brown precipitate. In the presence of 30% or 50% dimethylformamide the solution remains clear and the complex formed can be used for the determination of palladium [1].

In weakly acid medium with pH 4.8 to 5.2, addition of cation-active tenside results in the formation of a soluble red complex ($\lambda_{max} = 540$ nm for the differential curve, Fig. 2). The time stability of the coloured product formed was studied under the experimentally verified optimal conditions (pH 5.0, fourfold excess of TAR reagent with respect to the metal concentration; for $c_{Pd} = 2 \times 10^{-5}$ M and $c_{TAR} > 8 \times 10^{-5}$ M the A_{540} value remains constant) for various tenside concentrations. At lower tenside concentrations ($c_{CPB} = 6 \times 10^{-4}$ M), *i.e.* in the region given for the critical micelle concentration c_k of cetylpyridinium bromide [5, 7], the complex is formed at laboratory temperature and the value of the absorbance maximum is constant in the time interval 5 to 25 min and then decreases. After heating the solution (*e.g.* for 1 min on a boiling water bath) the same spectrum was obtained as at laboratory temperature, but after a prolonged time after cooling a brown precipitate was formed.

At tenside concentrations much higher than c_k ($c_{CPB} = 1.4 \times 10^{-3}$ M), the solution colour is completely developed after 15 min standing at laboratory temperature.

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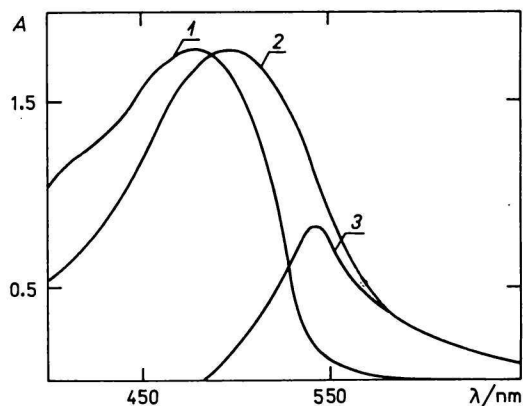Fig. 2. Absorption spectra of Pd(II)—TAR—CPB complex.
$c_{Pd} = 2 \times 10^{-5}$ M; $c_{TAR} = 8 \times 10^{-5}$ M; $c_{CPB} = 6 \times 10^{-4}$ M; pH 5.0.
1. TAR—CPB; 2. Pd—TAR—CPB; 3. difference between 1 and 2.
Measured before standing 25 min at laboratory temperature against water.

The character of the spectra of the complex formed is the same as at lower tenside concentration, its maximum absorbance is constant in the time interval from 15 to 120 min but the value is about 25% lower than at $c_{CPB} = 6 \times 10^{-4}$ M. Heating the mixture hastens the reaction but after cooling to laboratory temperature the complex formed is stable only for about 10 min and a precipitate is again formed. The use of $c_{CPB} = 6 \times 10^{-4}$ M was found satisfactory in further experiments and measurements were reproducible up to 25 min after mixing the reagents.

Under these conditions, the Pd—TAR—CPB complex is stable in the pH interval 4.8 to 5.3 for a fourfold amount of TAR reagent. Study of the dependence of the maximum of the differential curve at 540 nm on the concentration of CPB confirmed that, at low CPB concentrations ($c_{CPB} < 2 \times 10^{-4}$ M), a turbidity is formed; at concentrations of $c_{CPB} > 8 \times 10^{-4}$ M the colouration is sufficiently stable but the absorbance value decreases. A CPB concentration of 6×10^{-4} to 7×10^{-4} M was found to be optimal. It was found from study of the spectra that, with increasing CPB concentration from 2×10^{-4} to 5×10^{-4} M, the maximum of the differential curve of the complex shifts to shorter wavelengths, roughly from 550 to 540 nm. At higher CPB concentrations it no longer changes.

Cation-active tenside CPTB, which was also studied in detail in the reaction of palladium with TAR, behaves similarly.

The composition of the Pd—TAR—CPB complex was studied under optimal conditions for its formation both by the Job method in the presence of excess CPB (pH 5.0, $c_{CPB} = 6 \times 10^{-4}$ M; $\lambda = 530$, 542, and 550 nm) and also by the *Babko*

method using the isochrom of the ternary system [8]. Using the latter method, the ratio of the components of the ternary system was found to be Pd : TAR : CPB = 2 : 2 : 1. The former method was found not to be useful for determination of the composition of this complex as at higher Pd : TAR ratios a turbidity appeared.

As it followed from preliminary experiments on the reaction of the platinum metal ions with TAR reagent in the presence of CPB (as well as in its absence) that all the platinum metals react analogously, the effect of these ions on the determination of rhodium and palladium under optimal conditions was studied. It was found that the ions of the platinum metals may be present only in very low concentrations (platinum metal : determined metal < 1 : 4). The presence of chlorides also interferes (at values higher than 0.2 M) by decreasing the absorbance; nitrates do not interfere up to a concentration of 0.5 mol l^{-1}.

Discussion

The results of this work have shown that the micelle forms of cation-active tensides present under otherwise optimal conditions [9] are useful in the spectrophotometric determination of the platinum metals with azo-dyes. The determination of palladium with TAR in aqueous medium is directly dependent on micelle solubilization: the binary complexes of Pd(II) with TAR are not stable in aqueous medium and a precipitate is formed in the solution. The coloured systems formed in the presence of CPB have suitable spectral characteristics.

The spectrophotometric determination of rhodium as the binary Rh(III)—TAR complex is four times more sensitive than the described determination, e.g. with 4-(2-pyridylazo)resorcinol: ε equals 7×10^3 mol^{-1} l cm^{-1} for the determination of Rh(III) with PAR [10]. Our method employing TAR is faster (the complex with PAR is formed only after 90 min heating). The favourable effect of the CPB tenside was also confirmed here, not only in the bathochromic and hyperchromic shifts in the absorbance maxima, but also in increasing the rate of the complexing reaction.

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