

SPECTROPHOTOMETRIC STUDY OF THE REACTIONS OF LANTHANOIDS WITH BROMOPYROGALLOL RED IN THE PRESENCE OF CATION ACTIVE TENSIDES

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Dedicated to Professor V. Suk on the occasion of his 60th birthday.

The absorption spectra of the binary complexes of lanthanoids with bromopyrogallol red were measured and the formation of ternary complexes with the cation active tenside, Septonex, was studied. Optimal conditions were found for the formation of these complexes and the possibility of their use in the photometric determination of lanthanoids was demonstrated on several examples.

In the spectrophotometric determination of lanthanoids, the most frequently used methods, in addition to measurement of characteristic absorption bands, employ the formation of coloured chelates with a number of chelating agents. This group of substances includes bromopyrogallol red, for which it has been demonstrated¹ that it forms complexes with lanthanoids with maximum absorbance at 680–720 nm in the pH range 3–9. Bromopyrogallol red has so far been used for the spectrophotometric determination of cerium², lanthanum³, neodymium⁴ and ytterbium⁵.

The use of tensides as a third component in spectrophotometric determinations frequently results in a marked improvement, primarily in an increase in the sensitivity, in the time stability of the complex, *etc.* The ternary complexes have been used for the determination of lanthanoids with bromopyrogallol red only for holmium in mixtures with ytterbium in the presence of cetylpyridinium bromide⁶.

Consequently, this work deals with the effect of the cation active tenside, carbethoxypentadecyltrimethylammonium bromide (Septonex) on the reaction of bromopyrogallol red with all the lanthanoids except Pm. A detailed study of the conditions for the formation of the binary and ternary complexes was carried out for praseodymium, dysprosium, erbium and thulium.

EXPERIMENTAL

Instruments and Reagents

The spectrophotometric measurements were carried out on a Unicam SP-800 recording spectro-

photometer (Pye-Unicam, Cambridge, England) with 1.00 cm quartz cuvettes. The pH measurements were carried out on a Mera-Elmat type N-512 instrument (Polymetron, Wrocław, Poland) with a combined SAgP-201 W electrode, calibrated with standard buffers with pH 3.52, 6.88 and 9.08 (Lachema, Brno).

The stock solution with a bromopyrogallol red (5,5'-dibromopyrogallolsulphogallein, Lachema, Czechoslovakia) concentration of $5 \cdot 10^{-4} \text{ mol l}^{-1}$ was prepared by homogenizing 0.0288 g of the purified reagent⁷ with 20 ml of pure ethanol and diluting with distilled water to 100 ml. The solution was stored in a closed flask and was used for a maximum of two days.

The Pr(III), Nd(III), Sm(III), Eu(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III) and Lu(III) solutions with concentrations of $5 \cdot 10^{-4} \text{ mol l}^{-1}$ were prepared from the corresponding oxides with a purity of 99.9%, converted to the chlorides (by evaporating with 20 ml of 1:1 HCl) and diluted with distilled water to a volume of 100 ml. The La(III) and Tb(III) solutions were prepared from 99.5% LaCl₃ and TbCl₃, respectively, the Ce(III) solution from 99% Ce₂(SO₄)₃ and the Gd(III) solution from Gd(NO₃)₃, dissolved in distilled water with addition of a small amount of HCl.

The carbethoxypentadecyltrimethylammonium bromide (Slovakofarma, Hlohovec, Czechoslovakia) solution, $c = 5 \cdot 10^{-3} \text{ mol l}^{-1}$, was prepared by dissolving 1.05642 g of the substance in 250 ml of distilled water.

The pH was adjusted using acetate and veronal buffers, prepared according to the published procedures⁸. The ionic strength of the solutions was adjusted using 1M-KCl, NaCl, KNO₃ and Na₂SO₄ solutions.

RESULTS AND DISCUSSION

Absorption Spectra

Table I lists the absorption maxima of the binary and ternary complexes of the lanthanoids (Ln) with bromopyrogallol red (DG). Figs 1 and 2 depict, as examples, the absorption spectra of the Pr(III) and Dy(III) complexes. The absorption curves were measured under optimal conditions found for formation of the particular complex.

It is apparent from Table I and Figs 1 and 2 that the properties of the complexes of the first five lanthanoids (La-Sm) with DG are somewhat different from the properties of the complexes of the heavier lanthanoids (Eu-Lu). Complexes are formed with the elements in the first group at lower pH values (4.5–6.0) and the absorption maxima of the binary complexes are not much affected by the presence of Septonex. Except for La, the maximum absorbance of the binary and ternary complexes is attained at 680–690 nm; the difference between the λ_{max} for the binary complex and that for DG ($\lambda_{\text{max}} = 560 \text{ nm}$) is thus 120–130 nm, while the difference between the λ_{max} for the ternary complex and for DG + Septonex ($\lambda = 580 \text{ nm}$) is only about 100 nm. The absorbance values for the maxima for the ternary complexes are also sometimes decreased compared to the binary complexes (Pr(III), Nd(III), Sm(III)).

Heavy lanthanoids form complexes at higher pH values (6–6.5) and the presence of Septonex produces a bathochromic shift of the absorption bands of these complexes. The maximal absorbance for the binary complexes is attained in the interval 650–660 nm and for the ternary complexes at 670–680 nm. The difference between the maximum absorbance for the complexes and for DG (or DG + Septonex) is thus 90–100 nm for both the binary and ternary complexes.

Conditions for Complex Formation

It is known that the complex-forming ability increases in transition from light to heavy lanthanoids⁹. We found that the rate of the complexation reaction increases in the same direction. The complex of praseodymium with DG is formed at 20°C after standing for more than 60 min, or after heating at the temperature of a boiling water bath for 20 min. The reactions of Dy(III), Er(III) and Tm(III) with DG at 20°C take about 20 min and at 100°C 10 min.

The rate of formation and time stability of the complexes is affected greatly by the presence of Septonex. For example, the binary system of Dy(III) formed at 20°C after standing for 30 min has an absorbance maximum at 630 nm and is stable for

TABLE I

The absorption maxima of the binary and ternary complexes of the lanthanoids

Ln	λ_{\max} (Ln + DG) nm	λ_{\max} (Ln + DG + Sept.) nm	pH
La(III)	690	720	5.6
Ce(III)	690	690	5.6
Pr(III)	690	690	5.6
Nd(III)	685	680	5.6
Sm(III)	680	675	5.6
Eu(III)	660	680	6.6
Gd(III)	660	675	6.6
Tb(III)	660	675	7.3
Dy(III)	660	680	7.5
Ho(III)	650	670	7.5
Er(III)	655	680	7.5
Tm(III)	655	680	7.5
Yb(III)	655	670	7.5
Lu(III)	650	680	7.5

$$C_{\text{Ln}} = 1 \cdot 10^{-5} \text{ mol l}^{-1}, c_{\text{DG}} = 2 \cdot 10^{-5} \text{ mol l}^{-1}, c_{\text{Sept.}} = 2 \cdot 10^{-4} \text{ mol l}^{-1}.$$

120 min. After heating for 10 min at 50°C, the absorbance curve has a maximum at 650 nm and the solution is stable for 60 min; after heating for 5 min on a boiling water bath, a complex is formed with maximum absorbance at 660 nm, stable for 30 min. In the presence of Septonex, a solution with absorbance maximum at 670 nm, stable for 150 min, is obtained immediately after mixing all the components. On formation of the binary complex at the temperature of a boiling water bath following addition of Septonex, a complex is formed with $\lambda_{\max} = 680$ nm, whose absorbance does not change for 24 h. The highest λ_{\max} value is obtained using this procedure; the absorbance is, however, somewhat lower than that for the binary complexes.

Similar results were obtained for Pr, Er, and Tm, where slow colouration in a cool solution yielded a poorly stable solution with maximum absorbance at shorter wavelengths, while, after addition of Septonex to the binary complex formed at 100°C, the ternary complex was formed immediately with the λ_{\max} and ϵ values given in Table II, stable for 24 h.

The presence of Septonex also affects the pH range optimal for complex formation. The pH intervals obtained for formation of the binary and ternary complexes of Pr, Dy, Er and Tm are given in Table II. It is apparent from these values that the effect of Septonex is again different for light and heavy lanthanoids. The ternary complex of praseodymium is formed at higher pH values than the formation of the binary complex (as for neodymium), while the optimum pH for the formation of the ternary complexes of Dy(III), Er(III) and Tm(III) is shifted to lower values compared to the binary complexes.

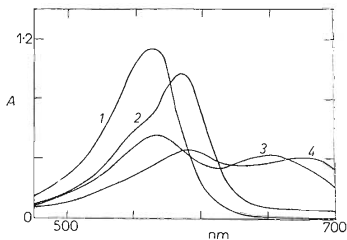


FIG. 1

Absorption curves of the praseodymium complexes. $c_{\text{Pr}} = 1 \cdot 10^{-5} \text{ mol l}^{-1}$; $c_{\text{DG}} = 2 \cdot 10^{-5} \text{ mol l}^{-1}$; $c_{\text{Sept}} = 2 \cdot 10^{-4} \text{ mol l}^{-1}$. 1 DG, 2 DG + Sept., 3 Pr + DG, 4 Pr + DG + Sept.

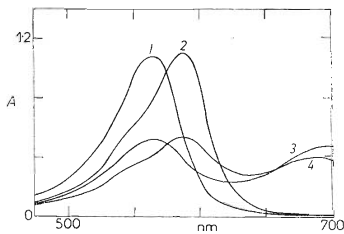


FIG. 2

Absorption curves for the dysprosium complexes. $c_{\text{Dy}} = 1 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_{\text{DG}} = 2 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_{\text{Sept}} = 2 \cdot 10^{-4} \text{ mol l}^{-1}$. 1 DG, 2 DG + Sept., 3 Dy + DG, 4 Dy + DG + Sept.

At least a two to three-fold excess of DG over the metal concentration is necessary for formation of the binary complex at laboratory temperature, and a five-fold excess is required for the ternary complex. Both the binary and ternary complexes are formed on heating on a boiling water bath with a two-fold excess of DG. A constant absorbance value is achieved for the ternary complex at a 20–200-fold excess of Septonex with respect to the metal concentration (at lower Septonex concentrations, the solution becomes turbid).

Calibration Curves

Under the optimum conditions found, given in Table II, the regions of validity of the Lambert–Beer law were found for the binary and ternary complexes of Pr(III), Dy(III), Er(III) and Tm(III). The concentration ranges and sensitivity of the individual determinations are given in Table II.

Statistical evaluation was also carried out for the results obtained for the dysprosium complexes. The parameters of the calibration curve $A = ac_{Dy} + b$ were found, and have value of $a = 0.247 \pm 0.005$, $b = -0.009 \pm 0.007$ for the binary

TABLE II

The basic characteristics of the binary and ternary complexes of the lanthanoids. $c_{DG} = 2 \cdot 10^{-5}$ mol l⁻¹, $c_{Sept.} = 2 \cdot 10^{-4}$ mol l⁻¹

Ln	pH _{opt}	λ_{max} , nm	ϵ , l mol ⁻¹ cm ⁻¹ ^a	Time stability ^b h	S, $\mu\text{g cm}^{-2c}$	$\mu\text{g ml}^{-1d}$
binary complex						
Pr(III)	4.9–6.0	690	44 000	0.5	$3.750 \cdot 10^{-3}$	0.28–2.81
Dy(III)	6.0–8.5	660	39 000	0.5	$4.769 \cdot 10^{-3}$	0.32–3.25
Er(III)	6.1–8.2	655	37 000	0.5	$5.162 \cdot 10^{-3}$	0.33–3.34
Tm(III)	6.1–8.5	655	37 000	0.3	$5.216 \cdot 10^{-3}$	0.34–3.37
ternary complex						
Pr(III)	6.3–7.6	690	39 000	24	$4.000 \cdot 10^{-3}$	0.28–2.10
Dy(III)	4.7–7.7	680	33 000	24	$5.636 \cdot 10^{-3}$	0.32–3.05
Er(III)	4.5–7.8	680	34 000	24	$5.618 \cdot 10^{-3}$	0.33–2.83
Tm(III)	5.6–7.8	680	33 000	24	$5.848 \cdot 10^{-3}$	0.34–2.64

^a Found from the maxima of the differential curve; ^b complex coloured by heating on a boiling water bath; ^c sensitivity according to Sandell; ^d region of validity of the L.B. law.

complex and $a = 0.187 \pm 0.005$ and $b = 0.005 \pm 0.007$ for the ternary complex. The evaluation was carried out for 7 points on the calibration curve and for five parallel measurements. The relative standard deviation, found from the range¹⁰ for five parallel determinations, has a value of $s_r = 2.8-10.1\%$ for the binary complex and $s_r = 2.6-4.2\%$ for the ternary complex. Consequently, the presence of Septonex has a favourable effect on the precision of the results.

It follows from these results that DG forms complexes with the lanthanoids whose absorption maxima differ from those of many other metals in that they are affected only slightly by the presence of cation active tenside (especially with the light lanthanoids), so that utilization of the ternary complexes formed for analytical purposes does not increase the sensitivity of the determination. The favourable effect of the tenside appears only in an increased rate of formation and time stability of the complexes and in improved reproducibility of the results.

The binary and ternary complexes obtained for the light and heavy lanthanoids have somewhat different absorption maxima positions, pH regions and rate of complex formation, but these differences are not so large that they could be used to determine the individual lanthanoids in the presence of one another. Thus the individual lanthanoids can be determined only after prior separation; attention is being paid to solution of this problem in our department.

REFERENCES

1. Jog M. S., Pande S. C., Shan V. L., Sangal S. P.: *J. Ind. Chem. Soc.* 51, 908 (1974).
2. Herrington J., Steed K. C.: *Anal. Chim. Acta* 22, 180 (1960).
3. Suk V.: *This Journal* 31, 367 (1965).
4. Poluektov N. S., Ovchar L. A., Ognuchenko S. F., Lauer R. S.: *Zavod. Lab.* 37, 895 (1971).
5. Srivastava K. C.: *J. Chin. Chem. Soc.* 23, 229 (1976).
6. Poluektov N. S., Lauer R. S., Ovchar L. A., Potapova S. F.: *Zh. Anal. Khim.* 30, 1106 (1975).
7. Matoušková E., Němcová I., Suk V.: *Microchem. J.* 25, 403 (1980).
8. Čihalík J., Dvořák J., Suk V.: *Příručka měření pH*, p. 215. Published by SNTL, Prague 1975.
9. Moeller T., Martin D. F., Thompson L. C., Ferrús R., Feistel G. R., Randall W. J.: *Chem. Rev.* 65, 1 (1965).
10. Eckschlager K.: *Chyby chemických rozborů*, p. 108. Published by SNTL, Prague 1971.

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