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Using of complex formation of 1-hydroxy-7-diethylaminophenoxazone-(3) with some anorganic ions

USING OF COMPLEX FORMATION OF 1-HYDROXY-7-DIETHYLAMINOPHENOXAZONE-(3) WITH SOME ANORGANIC IONS

LUBOMÍR ČÁP, ANTONÍN HAVIGER, MILAN MARTINEK

The variously substituted phenoxazine dyes which have suitable position of the functional groups are able to form complex compounds with some inorganic ions. These have a different colour from the original dyes and some of them are suitable for the qualitative estimation or quantitative determination of these ions. From this point of view the gallocyanine and its derivatives appear to be the most studied oxazine dyes[1-11].

Base groups involving dyestuffs are undergoing protonisation in the acid medium and they are able to form with complex anions some compounds which may be extracted into nonpolar solvents. This was used for the determination of some metal and nonmetal elements [12-26].

1-hydroxy-7-dimethylaminophenoxazone(3) was alredy followed from analytical point of view[28, 29]. It forms in pH-medium from 3,0 to 7,0 some bluecoloured complex solutions with Hg^{2+}, Ni^{2+}, Co^{2+}, Pd^{2+}, In^{3+}, Zr^{4+}, V^{IV}, V^V, Mo^{VI} $(HgI_4)^{2-}$ as well as Cu^{2+}. Some of them, such as Cu^{2+}, Pd^{2+}, Hg^{2+} and Mo^{VI} are unstable so that decolorizing of solutions and some precipitation take place. More attention was paid to the reaction with Cu^{2+} ions running in glacial acetic acid medium in the presence of natrium acetate, where the blue colour appears to be stable and most expressive[29]. This dye was used as well for estimation of vanadium (V) and for vanadium (V, IV) determinations as well[28]. This dyestuff was further used as indicator in mercurometry[29].

In this work 1-hydroxy-7-diethylaminophenoxazone(3) was used instead of its dimethylderivate because it was expected to be more suitable for this purpose. Our interest was focused to the formation of bluecoloured complex dyestuff solutions with Co^{2+} and Ni^{2+} ions.

Apparatus and chemicals

The absorption curves were measured on the spectrophotometer „Spectromom 201". The other dependences were followed on the spectral colorimeter "Specol".

1-hydroxy-7-diethylaminophenoxazone- (3) represents the original substance which was prepared under reaction of 6,4 g p-nitrosodiethylanilinhydrochloride with 2,5 g phloroglucinol heated under reflux in 250 ml anhydrous ethylalcohol medium; when the original colour of the solution becomes blue-violett the

reaction is finished. This requires nearly two hours. After cooling the solution, a cristalline substance was precipitated, which was then purified with twofold cristallization process from ethanol. The yield was about 30 %.
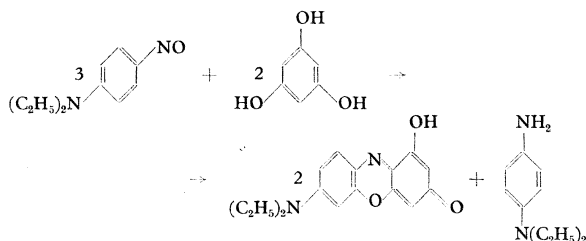
The newly synthetized dyestuff having summary formula $C_{16}H_{16}N_2O_3$ was identified by means of elementary analysis:

calc.	C — 67,67	H — 5,66	N — 9,83
found	C — 67,10	H — 5,72	N — 9,71

This dyestuff is very poorly soluble in benzene, fairly in ethanol and acetone, where its solutions are gaining some redviolett tint turning red under addition of the surplus quantity of ammonia or alkaline solutions. This dyestuff does not melt until 350 °C.

The solution of 1-hydroxy-7-diethylaminophenoxazone- (3) To enable the qualitative test saturated dyestuff solutions in ethanol (96 %) and acetone media were prepared. For the purpose of photometric measurements $5,0 . 10^{-4}$ M dyestuff solution in ethylalcohol was prepared. Precise concentration processes were potentiometrically controlled under titration of titanium chloride. The purity of the dyestuff was followed by means of thin layer chromatography. It is necessary to work always with freshly prepared dyestuff solutions.

0,10 N aqueous NiSO$_4$ solution — the precise concentration was established in the electrogravimetrical way. Solutions with lower concentration-degrees were prepared by diluting this stock-solution.

0,10 N aqueous CoSO$_4$ solution — the precise concentration was determined in the electrogravimetrical way. The solutions applied were prepared by diluting the stock solution.

0,50 M aqueous urotropine solution

Qualitative reaction

In an acid medium with pH = 1,0—3,0 there comes to the reaction of Hg^{2+} ions with the dyestuff (pD = 4,8). In this medium is the dyestuff red, in the presence of Hg^{2+} ions the dyestuff becomes blue. This reaction is time depending and that's why it cannot be used for the mercurimetric titrations. Moreover, in an acid medium Pd^{2+} ions react with the dyestuff under complex formation (pD = 5,5). The blue tint of the complex is unstable and turns grey-green in a little while. A number of ions are reacting in acetate buffer medium with pH =
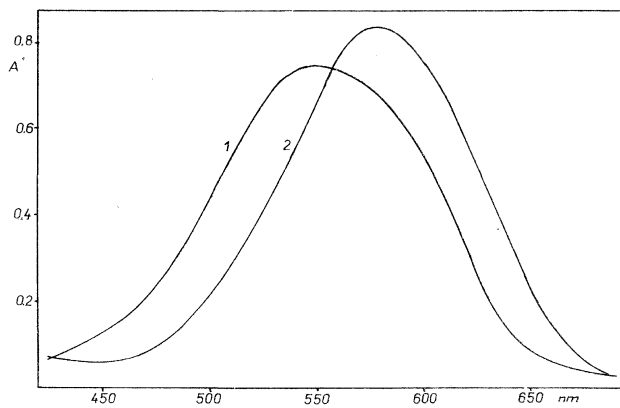
Fig. 1 Absorption curves ot dyestuff only (1) and dyestuff complex with Ni^{2+}
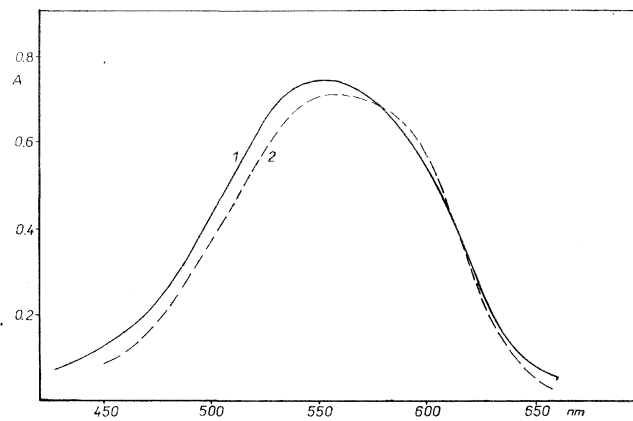(20 % ethanol, 0,1N urotropine, 2,50 . 10^{-5}M deystuff, d = 1,00 cm: (2) — 2,00 . 10^{-3}N Ni^{2+})

Fig. 2 Influence of ethylalcohol on the absorption curve of the dyestuff
(0,1N urotropine, 2,50 . 10^{-5}M dyestuff, d = 1,00 cm; (1) — 20 % ethanol, (2) — 80 % ethanol)

= 4,0—5,0. More expressive reactions are given by V^{IV} (pD = 5,1), Mo^{VI} (pD = 4,8), In^{3+} (pD = 4,5) and V^V (pD = 4,8). In an urotropine medium there comes to reactions of Hg_2^{2+} (pD = 5,8), Hg^{2+} (pD = 4,1), Cu^{2+} (pD = 5,5), Cd^{2+} (pD = 5,1), Ni^{2+} (pD = 6,1) and Co^{2+} (pD = 5,7).

Reactions were carried out in a test tube containing a freshly prepared saturated ethanol dyestuff solution. It is more advantageous to use an acetonic solution being more stable in comparison with an ethanolic one. In contrast to the 1-hydroxy-7-dimethylaminophenoxazone- (3) — already studied earlier — no precipitates are formed with ions, and reactions especially that in a neutral medium are more expressive.

Tracing of dyestuff complex with Ni^{2+} and Co^{2+}

The most sensitive reactions occuring in an urotropine medium are those given by Ni^{2+} and Co^{2+} ions. That's why reaction course of these ions with the
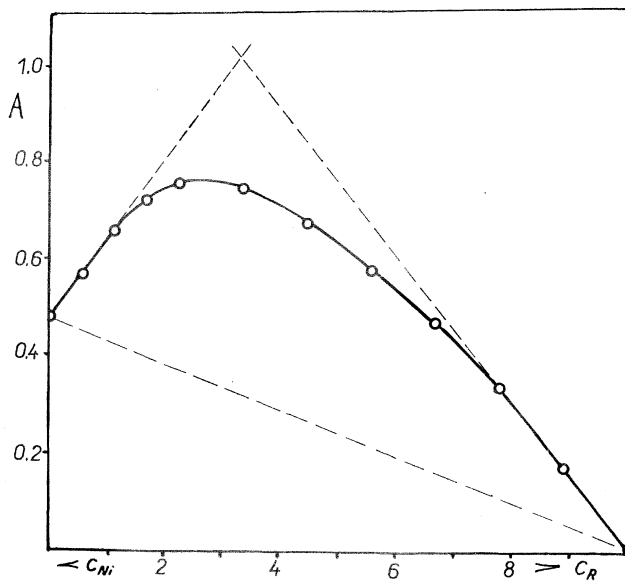

Fig. 3 Job's analysis
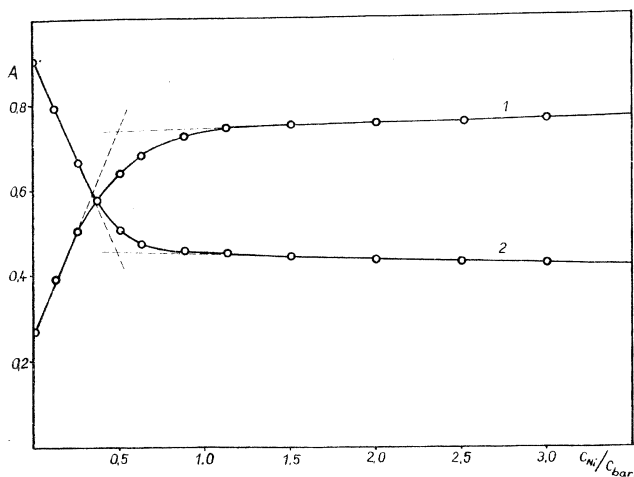(0,1N urotropine, 20 % ethanol, c = 0,0 — 11,5 . 10^{-5} d = 1,00 cm, λ = 640 nm)

Fig. 4 Photometric titration of the dyestuff with Ni^{2+} solution
(0,1N urotropine, 20 % ethanol, 6,50 . 10^{-5}M dyestuff d = 1,00 cm; (1) — λ = 640 nm,
(2) — λ = 490 nm)

dyestuff was followed in more detais. Comparing absorption spectra of the dyestuff and of the blue dyestuff complex with Ni^{2+} ions (Fig. 1), it was found that it comes to shifting of the absorption maxima of the dyestuff by about 30nm from λ = 550 nm (maximum of the dyestuff) to λ = 580 nm (maximum of the complex). With this shifting is also connected the extinction rise of the complex.

The absorption curves of the dyestuff are overlapping those formed by the complex along the whole length, so that there is impossible to perform measurements with a wave length, by which merely the dyestuff or the complex would absorb. That is why it was necessary to perform one of these measurements by the wavelength, where the complex is more absorbing than the dyestuff (λ = 620 nm). Further measurement was performed by the wawelength, where ·the dyestuff is more absorbing and the complex less. (λ = 500 nm).

To prevent precipitation of the dyestuff from the aqueous solution it is necessary to work in an ethanolic medium. However, a too high concentration of ethanol leads to much greater overlapping with the curve of a complex (Fig. 2). That is why 20 % ethylalcohol medium appeared as optimum.

But even in this medium the dyestuff containing solutions does not appear to be stable. Therefore it is necessary to perform the measurements within 30 minutes after preparing the solution.

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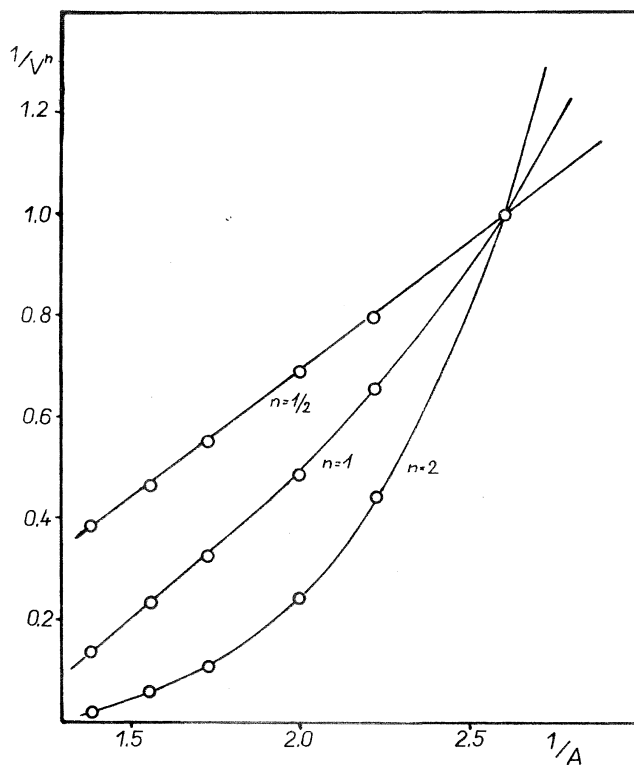
Fig. 5 Analysis of the curve (1) Fig. 4 by means of the straight line method

The result seen with the Job's method of continuous variations with the wavelengths $\lambda = 480$ and 620 nm (Fig. 3) demonstrates the complex formation with the ratio Ni^{2+} : dyestuff $= 1 : 2$. The same result was obtained in an acetate buffer medium with pH $= 5,5$.

Molar component ratio $1 : 2$ was also confirmed under photometric titration of a dyestuff with Ni^{2+} solution (Fig. 4). By extending the two branches we

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get a break having component ratio $c_{Ni}/c_{dyes.} = 0,5$, which is in good agreement with the ratio 1 : 2. The reverse titration by the solution of dyestuff is impossible because of high absorption of the dyestuff itself. Even the analysis of the gained curve accomplished by means of the straight line method provides the verification of this composition (Fig. 5)[27].

Similarly has been proceeded also in finding out the molar component ratio in the case of analogous dyestuff complex with Co^{2+} ions. The results obtained are absolutely analogous. In this case the ratio Co^{2+} : dyes. = 1 : 2 was confirmed, too. This complex seems however less stable than that with Ni^{2+} ions.

Application of dyestuff as complexometric indicator

The fact that freshly prepared ethanolic or acetonic solutions of a 1-hydroxy--7-diethylaminophenoxazonone-(3) in connection with Ni^{2+} and with Co^{2+} ions are offering some coloured complex compounds, was applied to complexometric determination of these ions. Even when the difference between absorption maxima of dyestuffs and complexes appears relatively small, the colour change in the neighbourhood of equivalence point is sufficient enough to be used for complexometric determination of both these ions.

For such a determination 0,2 M urotropine medium appears as optimum. In a more acid medium the tint difference of dyestuff and of complexes appears smaller so that the change is worse observable, at higher pH-values there comes to hydrolysis of ions.

The determination was performed by using 0,02 M complexon III in 0,2 M urotropine medium. Acetonic saturated dyestuff solution which is stable served as an indicator. The results of these determinations are presented in Tabl. 1.

The determinations are interferred with Hg_2^{2+}, Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, Fe^{2+}, in higher concentrations also Ba^{2+}, Ca^{2+}, Sr^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+} and Pt^{IV}.

From mathematic-statistical evaluations follows that this determination is burdened with random errors only.

Table No 1: Complexometric determination of Ni^{2+} and Co^{2+}ions

To be determined	Number of determinations	given mg	mean value of determinations mg ($\bar{x}$)	estimation of the standard deviation mg (s)
Ni	6	11,742	11,708	0,0692
	6	5,871	5,862	0,0462
	6	1,174	1,169	0,0092
Co	6	11,787	11,761	0,0924
	6	5,893	5,881	0,0465
	6	1,179	1,171	0,0094

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SHRNUTÍ

VYUŽITÍ TVORBY KOMPLEXU 1-HYDROXY-7-DIETHYL-AMINOFENOXAZONU — (3) S NĚKTERÝMI ANORGANICKÝMI IONTY

LUBOMÍR ČÁP, ANTONÍN HAVIGER, MILAN MARTINEK

Byly sledovány reakce 1-hydroxy-7-dietylaminofenoxazonu — (3) s anorganickými ionty. Podrobněji byly sledovány reakce barviva s Ni^{2+} a Co^{2+} ionty. V obou případech vznikají v neutrálním prostředí urotropinu modře zbarvené komplexy s molárním poměrem složek Me^{2+} : barv. $= 1 : 2$. Acetonického roztoku barviva bylo použito jako komplexometrického indikátoru pro stanovení Co^{2+} a Ni^{2+} iontů.

SUMMARY

USING OF COMPLEX FORMATION OF 1-HYDROXY-7-
-DIETHYLAMINOPHENOXAZONE — (3) WITH SOME
ANORGANIC IONS

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The reactions of 1-hydroxy-7-diethylaminophenoxazon — (3) with the anorganic ions were followed. Dye reactions with Ni^{2+} as so as Co^{2+} ions were examined more closely, too. In both ions blue coloured complexes of urotropine are originating having molar ratio of components Me^{2+} : dyes. $= 1 : 2$. The acetonic solution of the dye was used as a complexometric indicator for determination of Co^{2+} and Ni^{2+} ions.

ZUSAMMENFASSUNG

ÜBER DIE AUSNUTZUNG VON KOMPLEXBILDUNG DES
1-HYDROXY-7-DIÄTHYLAMINOPHENOXAZON — (3) MIT
EINIGEN ANORGANISCHEN IONEN

LUBOMÍR ČÁP, ANTONÍN HAVIGER, MILAN MARTINEK

Es wurden Reaktionen von 1-Hydroxy-7-diäthylaminophenoxazon — (3) mit anorganischen Ionen beobachtet. Näher wurden auch Reaktionen des Farbstoffes mit Ni^{2+} sowie Co^{2+} Ionen untersucht. Bei den beiden Ionen kommt as im neutralen Urotropinmedium zur Bildung blaugefärbter Komplexe mit dem molaren Komponentenverhältnis Me^{2+} : Farb. $= 1 : 2$. Die Azetonlösung dieses Farbstoffs wurde als komplexometrischer Indikator zur Bestimmung von Co^{2+} und Ni^{2+} Ionen benutzt.