

The average value of $\log {}^pK^H$ (9.20) obtained by the pointwise calculation is in good agreement with the half-integral value (Table I).

TABLE I
Stability constants of bivalent complexes with
2-hydroxy-5-nitropropiophenoneoxime
(Temp. = $40 \pm 1^\circ \text{C}$, $\mu \simeq 0.1 \text{M NaClO}_4$)

Method	Half- integral	Least squares	
H(I)	..	-18.88	$\log {}^pK_1^H \cdot \log {}^pK_2^H$
	..	-10.02	$\log {}^pK_1^H$
	9.21	8.86	$\log {}^pK_2^H$
Ni(II)	11.74	11.74	$\log \beta_2$
	6.17	5.64	$\log K_1$
	5.57	6.10	$\log K_2$
Co(II)	13.95	14.03	$\log \beta_2$
	8.66	8.71	$\log K_1$
	5.29	5.32	$\log K_2$
Zn(II)	8.87	8.89	$\log \beta_2$
	4.72	4.17	$\log K_1$
	4.15	4.72	$\log K_2$
Mn(II)	8.98	8.99	$\log \beta_2$
	5.31	5.38	$\log K_1$
	3.67	3.61	$\log K_2$

In all the systems the highest values of \bar{n} are more than 1, indicating that 1:1 and 1:2 complexes are formed. The $\log K_1$ and $\log K_2$ values were calculated by the methods of half-integral and least squares (Table I). The results, given in Table I, show that the order of stability is $\text{Zn} < \text{Co} > \text{Ni} > \text{Mn}$. It can be seen that the order is in agreement with Irving Williams order⁵.

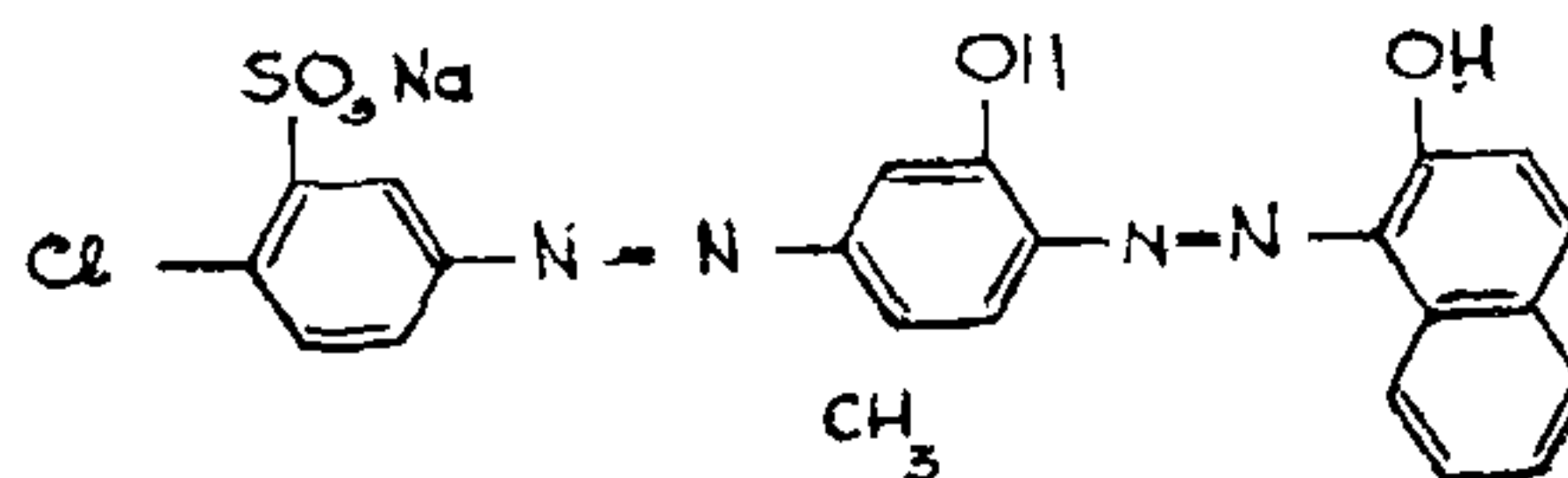
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SPECTROPHOTOMETRIC DETERMINATION OF CINCHONINE BY SOLOCHROME GREEN V 150

THE trace analysis of cinchonine is of interest to toxicologists, forensic and analytical chemists. Very few spectrophotometric methods exist for the determination of cinchonine. Celap *et al*¹ described an elaborate method for its determination based on the development of molybdenum blue but the method is not sensitive and accurate. Spacu and Ianu² reported the chronic thiocyanate method, wherein the alkaloid is precipitated by potassium chromium thiocyanate and the precipitate is dissolved in acetone and analysed spectrophotometrically. The method is indirect and far less sensitive than the present method. Palumbo and Sacca³ determined cinchonine by cis-aconitic acid in acetic anhydride. For the direct spectrophotometric determination of alkaloids, the acid dye⁴⁻⁸ extraction methods are reported; these methods are relatively rapid, convenient and sensitive. A survey of the literature revealed that only one acid dye, bromothymol blue has been reported so far for the determination of cinchonine⁹. The author, in his investigations on the use of the acid dyes of Solochrome series, found Solochrome Green V 150 having the following formula,



to be extremely sensitive in the determination of alkaloids and proposed methods for strychnine¹⁰, brucine¹¹ and opium alkaloids¹². The present report gives a method for the determination of cinchonine by the extraction of the ion pair formed with Solochrome Green V 150 into chloroform and measuring the chloroform extract spectrophotometrically at 510 nm. The dye is not extracted by chloroform under the experimental conditions. The method is more sensitive than bromothymol blue method, lower limit of determination being 0.54 micrograms per ml. The interference of the commonly associated materials has been checked.

Experimental

Bausch and Lomb spectronic-20 spectrophotometer was used for the absorbance measurements. Clarke and Wallpole buffers were used. Solochrome Green V 150 (C.I. No. 26925) was supplied by Imperial Chemical Industries Limited, Calcutta, India. Standard sample of cinchonine (Koch-Light, England) was used. All other chemicals used were of analytical grade.

Results and Discussion

The aqueous solution of the dye shows a maximum at 490 nm irrespective of the pH of the solution. The dye as such is not extracted in chloroform but the ion pair of the alkaloid cinchonine with the dye is extracted as pink coloured species, showing a maximum at 510 nm. Change in pH of the solution does not affect the maximum of the organic extract. Amongst the different halogenated extractants investigated for the extraction of the ion pair, chloroform was found to be the best. The ion pair is extracted into the chloroform form pH range 1 to 7 the maximum extraction being at pH 6. The composition of the ion pair complex as found by continuous variation and molar ratio methods is 1:2 [Alkaloid (A): Dye (D)], suggesting an ion pair formation of the type $(A^{2+})(D^-)_2$.

Beer's law is obeyed in the range of 8-450 μg . The molar absorptivity of the system at 510 nm is 16,000 $\text{lit. mol}^{-1} \text{cm}^{-1}$. The sensitivity expressed by Sandell's notation is $1 \mu\text{g}/\text{cm}^2/0.004 \text{ abs. unit}$. A five fold excess of the dye is required for maximum colour development. About one minute of shaking is sufficient for complete extraction of the ion pair of the alkaloid. The following substances do not interfere even in ten fold excess: citric acid, sodium benzoate, sodium salicylate, acetyl salicylic acid (aspirin), sodium diethyl barbituric acid, sodium saccharin, saccharin, glucose and fructose.

Procedure

To a suitable aliquot of the alkaloid solution containing 0.025-0.1 mg of the alkaloid add 10 ml of buffer of pH 6 and 5 ml of 10^{-3} M aqueous solution of the dye. Shake for one minute with 15 ml of chloroform in a separatory funnel. Separate the chloroform layer and read its absorbance at 510 nm. Prepare the standards accordingly.

A set of analytical results obtained by following the above procedure are given in Table I. Each reported value is based on six determinations and the data show a precision of $\pm 1.5\%$. As is evident from the table, the method gives fairly accurate results.

TABLE I

Results of cinchonine determination by Solochrome Green V 150

Added (μg)	Found (μg) (n = 6)	Relative error (%)
50	49.6	-0.8
125	123.5	-1.2
200	200	0.0
275	278	+1.1
350	353.5	+1.0
400	406	+1.5

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PHOTOCHEMICAL AND THERMAL SYNTHESIS OF PHENANTHR [9, 10-d] IMIDAZOLES

PHOTOCHEMICAL cyclodehydrogenation reaction of stilbene and its analogues represents a prominent route for the synthesis of a number of phenanthrene derivatives¹. Recently this reaction has been used for the synthesis of phenanthro heterocyclics^{2,3}, and in some cases where some other chromophores are also present, selective cyclization of the stilbene chromophore has been found to occur^{4,5}. This paper reports on the utility of the stilbene photodehydrocyclization in the synthesis of a number of phenanthr [9, 10-d] imidazoles. Thus the direct irradiation of 4, 5-diarylimidazoles (Ia-c) in suitable solvents in the presence of iodine or oxygen has been found to result in the oxidative cyclization at the stilbene chromophore to give phenanthr [9, 10-d] imidazoles (IIa-c).

The general method for the photoconversion of I to II is as follows: a 0.005M solution of I in chloroform (150 ml) containing iodine (15-20 mgs) was irradiated in a pyrex photochemical reactor by immersing a water-cooled Philips HPK 125 W high pressure