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SPECTROPHOTOMETRIC DETERMINATION OF THE OXIDATION OF Na-l-NAPHTHYL-AMINE-4-SULPHONA TE WITH POTASSIUM DICHROMATE: A KINETIC STUDY

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ABSTRACT: Oxidation of Na-I-naphthylamine-4-sulphonate was carried out with K2Cr207 in sulphuric acid. Beer's Law holds true for the concentration range 2 x 10'3 - 5 X 10-4 ill O.027standard deviation. The most appropriate parameters for this concentration range were K2Cr207 (O.03M), H2SO4 (6M) while heated .at 85°C for 15 minutes. Kinetic study revealed

that tl;1e overall order of reaction was found to be 3rd order while it was 1st with respect to the anal~e and 2nd with respect to K2Cr207. The values of rate constant k were found to be 4.36 x 10'5 sec'l and 9.55 x 10'5 sec' L mole'(for analyte and K2Cr207 respectively.

KEY WORDS: Oxidation of Na-l-naphthyi amine-4-Sulphonate, Potassium dichromate, Spectrophotometry, Kinetics

INTRODUCTION

The compound Na-I-naphthylamine-4-sulphonate received more attention due to its applicability in many industrial as well as biological purposes. For instance Nomura *et al.* (1989) reported that this compound showed a significant role in the manufacturing of paper, either in the refining of wood pulp and chips for improving the quality of the pulp, or by increasing its yield. It also produces breaking length and tear strength with a low energy consumption. Fred (1991) showed that the leakage in the battery cells has been effectively prevented by this comp(mnd. In electroplating, Domnikov (1968) registered its use in improving the brightening effects in nickel plating. In the polymer industry report from Flanadan *et ai.* (1968) revealed that in the processing of acrylamide, this compound exhibits inhibition character for the process of polymerization.

In the biological field, Land *et ai.* (1978) reported that the salt of this compound has been used in the investigation of *in vivo* cytogenetic studies of bone marrow cells of rat. Na-l-naphthylamine-4-sulphonate, along with other dyes, has been reported to have a non-mutagenic character in the salmonella- mammalian microsome mutagenecity test as described by Thorn (1981). A report by Collins (1973) reveals its application in the study of food colouring. Studies of binding of dyes to bovin serum albumine L-tyroxin and trypan by Flanadan *et ai.* (1968) showed that these molecules are bound to bovin serum albumine at the sites where naphthylamine binding occur. In the study of the process of metabolism published by McMahon *et at.* (1972) and Norwitz *et at.* (1986) that this compound has been reported to be more actively secreted in rabbit kidneys, compared to other compounds. Regarding above characteristics, Krachmer *et al.* (1972) to determine Na-l-naphthylamine-4-sulphonate, while using various analytical methods such as spectrophoto- metric titration with BaCh while Soares *et ai.* (1968) with other reagents. In electrochemical methods, Miroslva *et ai.* (1972) used amperometry for this purpose. However, no work has been published yet concerning the oxidation of this compound with K2Cr207, in sulphuric acid.

EXPERIMENT AL

Equipment:
Spectrophotometer Shimadzu UV-160A equipped with a chart recorder was used to perform spectral studies for the oxidation reaction of analyte. GFL (W. Germany) thermostatic bath was used for temperature control.

Preparation of Stock Solutions:
The stock solution of Na-I-naphyhylamine-4sulphonate 4H2O (B.D.H.: Reagent grade) was prepared in double distilled water by weighing 0.5 g/500 mL. Stock solutions of sulphuric acid (Riedelde-Haen: synthetic grade) ranging 0.01-9 mole/dm3 were prepared in double distilled water. Stock solution of K2Cr207 (E. Merck: Extra pure) was prepared by dissolving 7.35g of the reagent in a 250mL of (0.1 M) sulphuric acid solution.

General Procedure:
In a 25 mL volumetric flask, 4 mL (0.005 M) stock solution of K2Cr207 was taken. Various volumes of

analyte (0.1-0.5 mg/mL) were added in the volumetric flask. The reagent flask was heated in a waterbath at various temperatures ranging from 30-95°C for 15 minutes. The reacted system after cooling to the room temperature was diluted to the mark with double distilled water. A compensatory blank was prepared followed by the same procedure without adding the analyte in it. Absorbance measurements of the reacted system were recorded in the wavelength range 200-800 nm. Each set was repeated five times for the determination of standard deviation. The above procedure was repeated at different temperatures ranging 30-95°C. Various parameters such as concentration of analyte, $K_2Cr_2O_7$, and acid strength were also varied to get optimum results for the oxidation reaction. Investigations pertaining to oxidation of analyte with respect to time revealed its reaction mechanism.

RESULTS AND DISCUSSION

Spectral studies regarding the oxidation of analyte with $K_2Cr_2O_7$ in sulphuric acid, at 65°C for 15 minutes heating, resulted a coloured species having a λmax 490-513 nm, as shown in Figure-1. A broad peak appeared in this range which showed a hypsochromic shift in its λmax . Such a trend confirms the involvement of an auxochrome a functional group such as H and NH_2 etc. present in the analyte structure. The linear increasing response in absorbance, to the concentration of analyte may also be regarded as a hyperchromic shift as reported by Braun (1983). The scheme of oxidation of analyte can be described as follows:

The final product is probably analogous to the quinone formation, along with the formation of Cr (iii) product which was reported by Anwer and Awan (1990). The

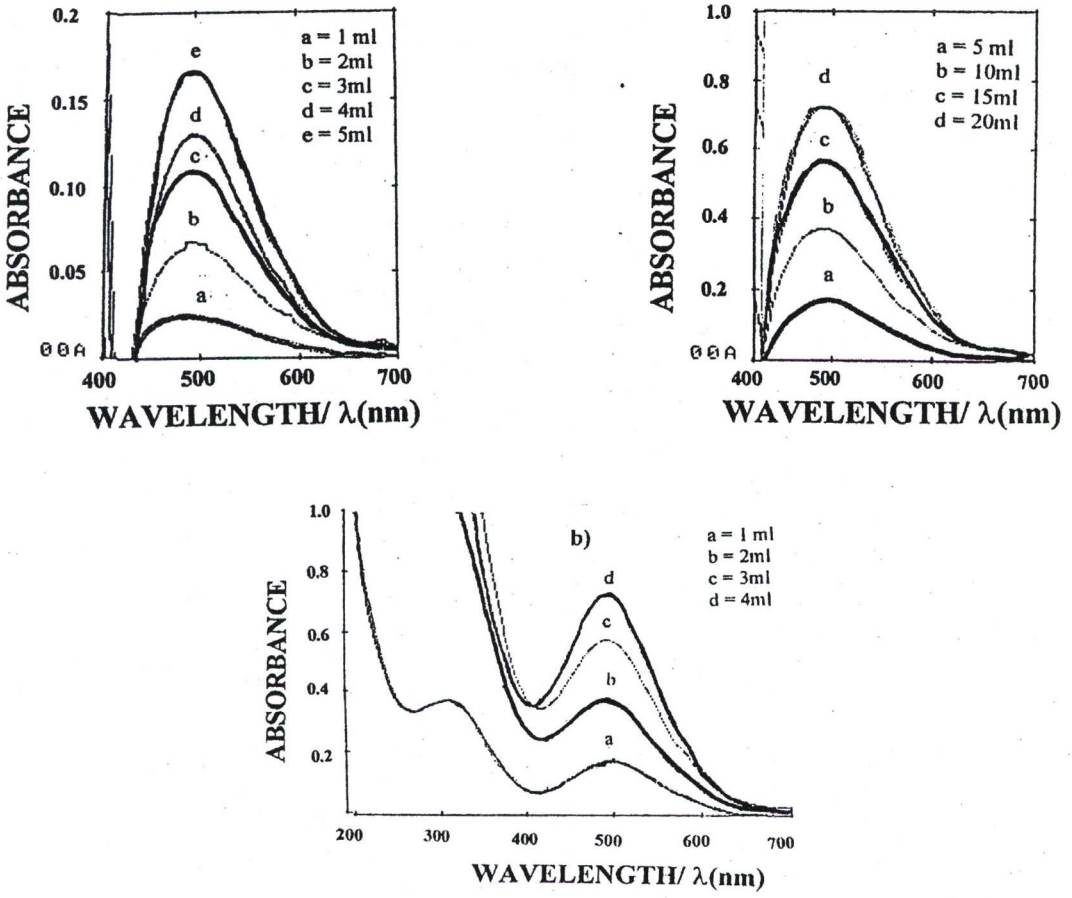

Figure 1: Overlay of various volumes of stock solution of analyte per 20mL taken vs a) compensatory blank, b) vs water.

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description of the reaction mechanism may not be similar/simple, however, it may result Cr (iii) formation, as reported in the similar work. The reported green colouration justified by Anwer and Awan (1990), at λ_{max} 583.6 nm does not appear here, perhaps due to the complexation reaction between Cr and the analyte, that results in reddish brown colouration. Starting with the above experience, detailed investigations were made about the spectral studies, pertaining to the effect of concentration of analyte, oxidising agent, acid strength, reaction time, and the reaction duration to optimize the technique. The absorbance measure-ments at λ_{max} in the range 513-490 nm reveal a linear response with the concentration of the analyte as shown in Figure-2 which followed Beer's Law in the concentration range 3.2 x 10^{-4} to 2 X 10^{-3} mole/dm^{3}with the standard deviation± 0.027.

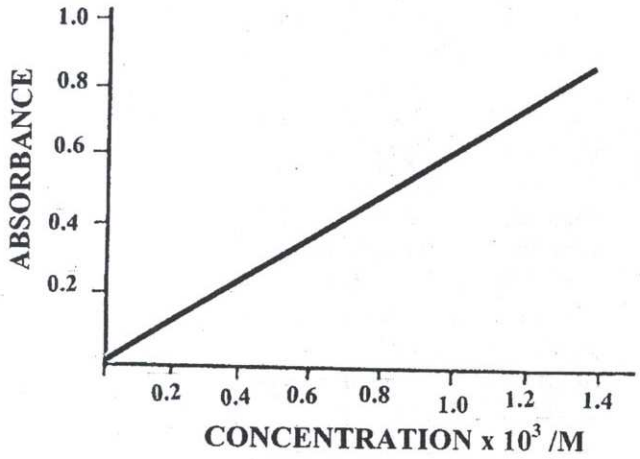

Figure 2

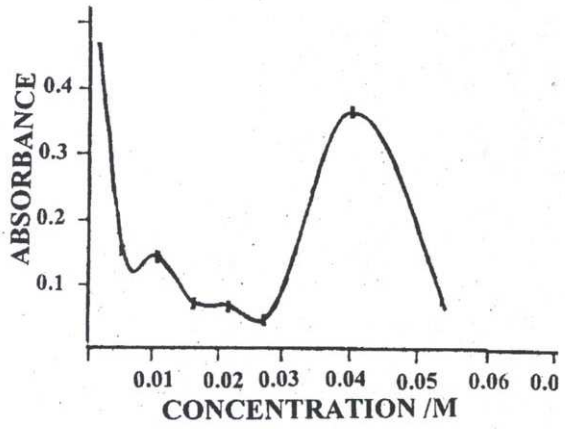

Figure 3

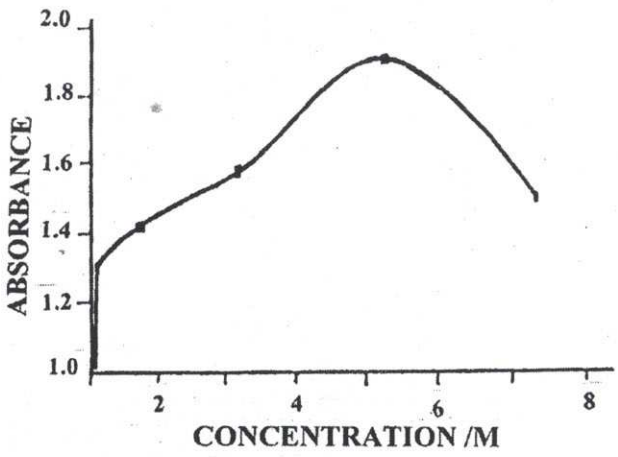

Figure 4

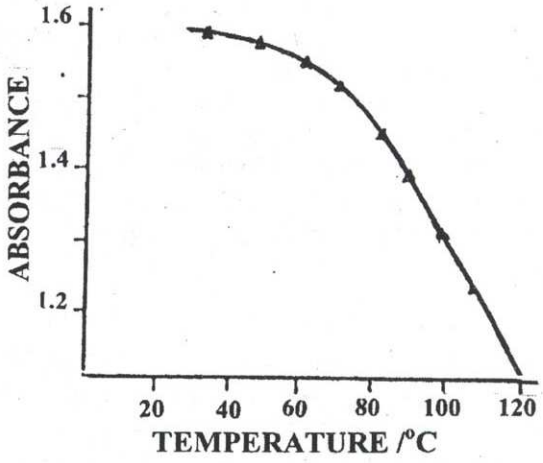

Figure 5

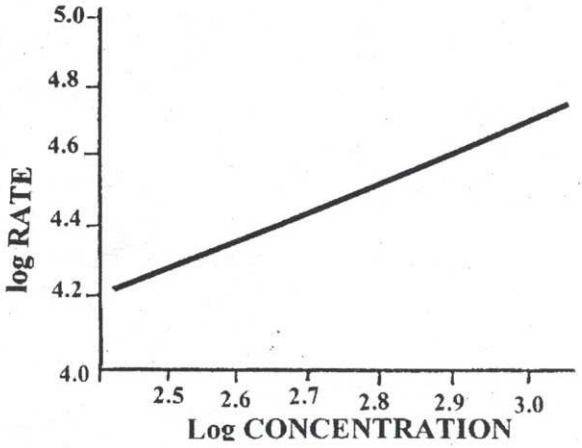

Figure 6

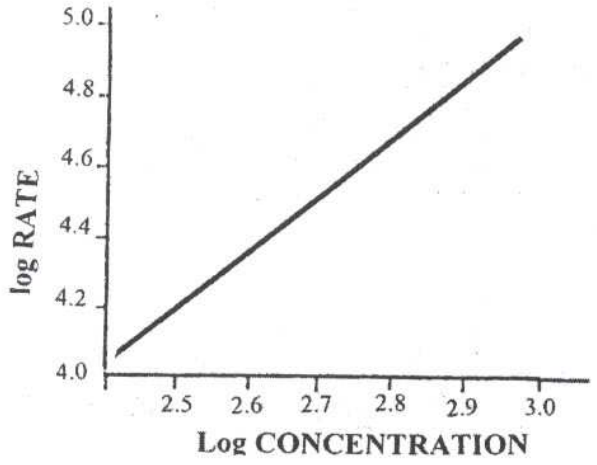

Figure 7

Effect of Various Parameters on Oxidation of Analyte: The optimum concentration of potassium dichromate, for the above said range, where Beers' Law holds true is 0.03M as shown in Figure-3. Here, a decrease in the absorbance was observed, other than the concentration (0.03M potassium dichromate). The effect of acid concentration and temperature are depicted in Figure-4 and 5.

Kinetic Study:
The kinetics of the oxidation of analyte with $K_2Cr_2O_7$, revealed, that the rate of reaction is linear to the concentration of analyte, as well as, $K_2Cr_2O_7$. A plot of log dC/dt vs log C, (in terms of the concentration of analyte) having a linear response is given in Figure-6 and 7. The overall order of reaction was found to be 3rd while it was 1st with respect to analyte and 2nd with respect to $K_2Cr_2O_7$ concentration. The values of rate constant, k, were found to be 4.36×10^{-5} sec^{-1} and 9.55×10^{-5} sec^{-1} L $mole^{-1}$ for analyte and $K_2Cr_2O_7$, respectively.

CONCLUSION

The present method was found to be applicable for the quantitative determination of Na-1-naphthylamine-4-sulphonate, as a result of its oxidation with potassium dichromate in acidic media. This method may be used in industrial as well as biological systems. The optimal conditions like the amount of dichromate, acid strength, reaction time, and temperature were also determined. The order of reaction both for analyte and dichromate were also determined for their kinetic study.

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