



Analytical Applications of some N,NBPAD Schiff's base for Spectrophotometric Determination of Chromium(VI)

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Abstract

In this study, the synthesis of two Schiff's bases, PAD and N,NBPAD, was accomplished through the condensation of o-phenylenediamine with p-aminoacetophenone, resulting in an intermediate that subsequently reacted with benzil in ethanol to yield a macro Schiff's base. The identification of the Schiff's base was carried out utilizing infrared spectra, UV/VIS spectrophotometry, elemental analyzer, and melting point analysis. The potential applications of the Schiff's base as analytical reagents were investigated through the use of a UV/VIS spectrophotometer in conjunction with various metal ions, including Pb(II), Cr(VI), Cu(II), Cd(II), V(V), Ni(II), Hg(II), Zn(II), Co(II), Fe(II), and Fe(III). The study aimed to determine the optimal conditions for the analytical application of the Schiff's base, considering factors such as solvent effect, micelle effect, and the presence of foreign metal ions. Notably, good results were obtained for the determination of Cr(VI) using N,NBPAD, with respect to linearity, detection limit, and interference. Moreover, the potential environmental applications of the synthesized Schiff's bases were explored, particularly in the removal of heavy metal ions from aqueous solutions. The adsorption capacities of PAD and N,NBPAD were evaluated, revealing promising results for the efficient removal of Pb(II), Cu(II), and Cr(VI). These findings highlight the versatility and potential utility of Schiff's bases in both analytical and environmental contexts.

Keywords: N, NBPAD Schiff's base, Chromium Ions, Selective reagents, Spectroscopy, micelle.

1. Introduction

In environmental samples, chromium is normally discovered in oxidation states: trivalent chromium (chromium⁻³, Cr(III), Cr³⁺) and hexavalent chromium (chromium⁻⁶, Cr(VI), Cr⁶⁺) Toxicity of chromium relies upon on it specifically pharmaceutical compounds; Cr(III) compounds are plenty less toxic than Cr(VI) compounds [1]. Cr(III) occurs evidently in flora, animals, and rocks, whilst Cr(VI) is specifically synthesized and utilized in diverse business procedures [2]. Consequently, correct willpower of chromium (VI) in samples is important to reveal its concentration and save you damaging consequences. Although there are a few spectrophotometric strategies for the dedication of chromium(VI), most of them have barriers consisting of low sensitivity, absorption of different ions, or complicated strategies so easy spectrophotometric methods, are sensitivity and selectivity are had to stumble on chromium(VI) in real samples. Several methods for the size of chromium ions were said within the literature, inclusive of ultraviolet-seen (UV-Vis) spectrophotometry [3] [4], excessive-performance liquid chromatography [5], capillary electrophoresis [6], and adsorptive-. Stripping voltammetry [7], flame-oven atomic absorption



spectroscopy [8] [9], and mass spectrometry [10]. Among these, spectrophotometric techniques are preferred because of their simplicity, sensitivity, precision, and rapidity. The accessibility of the tool has made this technique crucial for current analytical chemists [11]. In this study, we aim to develop a new spectrophotometric method for the determination of chromium (VI) using N,NBPAD Schiff's base. The use of N, NBPAD Schiff's base as a selective reagent for the determination of chromium (VI) is a novel approach that could contribute to the monitoring of its levels in various samples and the prevention of its adverse effects. The development of a simple, sensitive, and selective spectrophotometric method for the determination of chromium(VI) is of great importance for the monitoring of its levels in water, soil, and industrial effluents, which can help in the prevention of its adverse effects on human health and the environment [12] [13].

2. Instrumental

1. Griffin melting point apparatus model 9100.
2. Jeneway UV/VIS spectrophotometer model 6503 and 6505.
3. Elemental analyzer model EA112.
4. Perkin Elmer I.R. spectrophotometer model 1330

3. Chemicals

All chemicals used are of analytical grade, unless otherwise stated. The water used is double distilled. The chemicals used include o-phenylenediamine, p-aminoacetophenone, benzil, ethanol, acetonitrile, dimethylformamide (DMF), glacial acetic acid

n-hexadecyltrimethylammonium bromide (N-HTAB), sodium dodecyl sulphate (SDS), ammonium iron(II) sulphate, potassium dichromate, zinc(II) acetate, copper(II) acetate, iron(III) chloride, ammonium nickel(II) sulphate, mercury(II) chloride, lead(II) acetate, cadmium(II) chloride, and cobalt(II) chloride. All chemicals were purchased from Merck (India).

4. Synthesis of reagents

4.1 Synthesis of P-aminoacetophenone o-phenylenediamine [PAD]

PAD was synthesized by addition of 3.2442g (0.03mol) of o-Phenylenediamine in 20ml of ethanol to 4.0551g (0.03 mol) of p-aminoacetophenone in 20ml of ethanol. Few drops of glacial acetic acid were added [14]. The mixture was heated under reflux for 8h and cooled to give 6g (90.2%) of yellow crystals which were recrystallized from deionized water (m.pt. 70.1°C , λ_{max} 315nm).

4.2 N N benzil p-aminoacetophenone o-phenylenediamine [N,NBPAD]

N,NBPAD was synthesized by slow addition of 1.1g (0.004 mol) of PAD in 20 ml of ethanol to 0.8402 g (0.004 mol) of benzil in 20ml of ethanol. The mixture was heated under reflux for 12h and cooled to give 1.2976g (66.81%) of yellow crystals, which were recrystallized from mixture of ethanol and deionized water (1:4) (m.pt. 81.2°C , λ_{max} 350nm).

4.3 Identification of the reagents

The Infrared Spectra

IR spectra of the macro- Schiff's bases (PAD, and N,NBPAD) were measured in IR spectrophotometer [15]. The spectra were measured at room temperature in KBr disk.

Elemental Analysis

The Elemental analysis [16], of the aforementioned compounds were recorded in elemental analyzer using packed column and the mobile phase He, at 900°C .

4.4 Preparation of Stock solutions

The preparation of stock solutions for various metal ions was carried out by dissolving specific weights of corresponding salts in 250 ml volumetric flasks. The metal ions included ammonium iron(II) sulphate, potassium



dichromate(VI), zinc(II) acetate, copper(II) acetate, iron(III) chloride, ammonium nickel(II) sulphate, ammonium monovanadate(V), mercury(II) chloride, lead(II) acetate, cadmium(II) chloride, and cobalt(II) chloride. Working solutions were prepared by serial dilutions of the stock solutions with deionized water. Additionally, 1×10^{-2} M stock solutions of micelles were prepared by dissolving specific weights of sodium dodecyl sulphate (SDS) and n-hexadecyltrimethylammonium bromide (N-HTAB) in 100 ml volumetric flasks. Working solutions were prepared by serial dilutions of the stock solutions with deionized water. Furthermore, 1×10^{-2} M stock solutions of N,NBPAD were prepared by dissolving specific weights in 60% ethanol, 40% acetonitrile, or 40% DMF in 50 ml volumetric flasks. Working solutions were prepared by serial dilutions of the stock solutions with deionized water.

5. Analytical applications of N,NBPAD with Chromium VI using ethanol as a solvent

5.1 Analytical parameters for Cr(VI)N,NBPAD complex

5.1.2 Effect of micelle N-HTAB concentrations

A series of Cr(VI) solutions were prepared using 4×10^{-5} M of the reagent, 12ppm of Cr(VI) and different micelle concentrations. The absorbance was recorded at 270 nm. The results are shown in Table 1 and Fig .1.

Micelle concentrations($\times 10^{-5}$ M)	Absorbance
0.0	0.876
2.0	1.345
3.0	1.358
4.0	1.491
5.0	1.448
6.0	1.400

5.1.2.1 Effect of N,NBPAD concentrations

A series of Cr(VI) solutions were prepared using 12ppm of Cr(VI), 4×10^{-5} M of micelle and different reagent concentrations. The absorbance was recorded at 270 nm. The results are shown in Table 2 and Fig .2.

Reagent concentrations($\times 10^{-5}$ M) (($\times 10$ M)	Absorbance
0.1	1.302
0.2	1.413
0.4	1.418
0.6	1.423
0.8	1.428
2.0	1.680
4.0	1.535
6.0	1.464
8.0	1.432

5.1.2.2 Calibration Curve For Cr(VI) N,NBPAD

A series of Cr(VI) solutions were prepared using 4×10^{-5} M of micelle, 2×10^{-5} M of the reagent, and different of Cr(VI) concentrations. The absorbance was recorded at 270 nm. The results are shown in Table 3 and Fig .3.

Cr(VI) concentration (ppm)	Absorbance
8.0	0.668
5.0	0.463
2.0	0.290
0.8	0.217
0.5	0.083
0.2	0.060
0.08	0.042
0.05	0.022
0.02	0.022



5.1.2.3 Effect of foreign metal ions

In order to assess the possible analytical applications of these type complexes, the effect of some foreign metal ions was determined.

Metal ion. conc (ppm)	Absorbance					
	Hg(II)	Cu(II)	V(V)	Zn(II)	Fe(III)	Fe(II)
0.0	0.740	0.740	0.740	0.740	0.740	0.740
2.0	0.005	0.003	0.057	0.025	0.094	0.242
5.0	0.023	0.001	0.204	0.048	0.176	0.430
10.0	0.017	0.002	0.391	0.057	0.436	0.883
15.0	0.016	0.020	0.555	0.068	0.678	1.068

To study the effect of Hg(II), V(V), Cu(II), Zn(II), Fe(III), Fe(II) on the determination of Cr(VI)N,NBPAD under the optimum conditions 10ppm of Cr(VI), 2×10^{-5} M of the reagent, and 4×10^{-5} M of micelle were used while varying the concentration of foreign metal ions. The absorbance was recorded at 270 nm. The results are shown in Table 4.

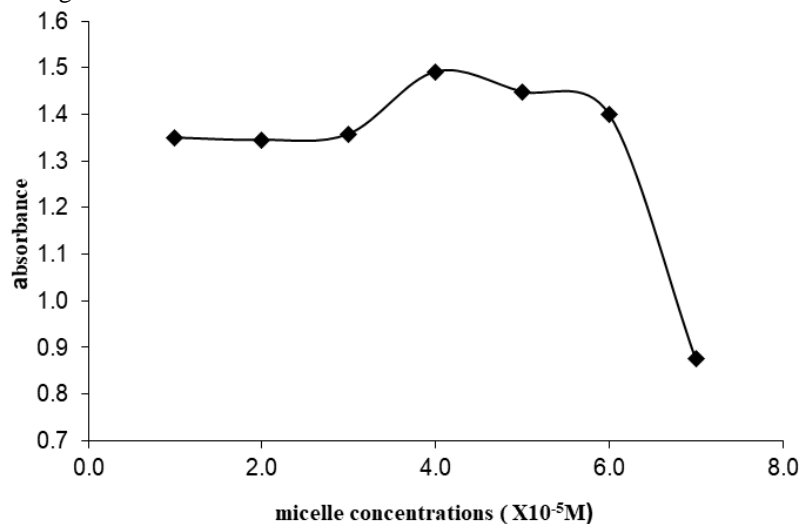


Figure 1: Effect of micelle N-HTAB concentrations on the absorbance of Cr(VI)N,NBPAD complex

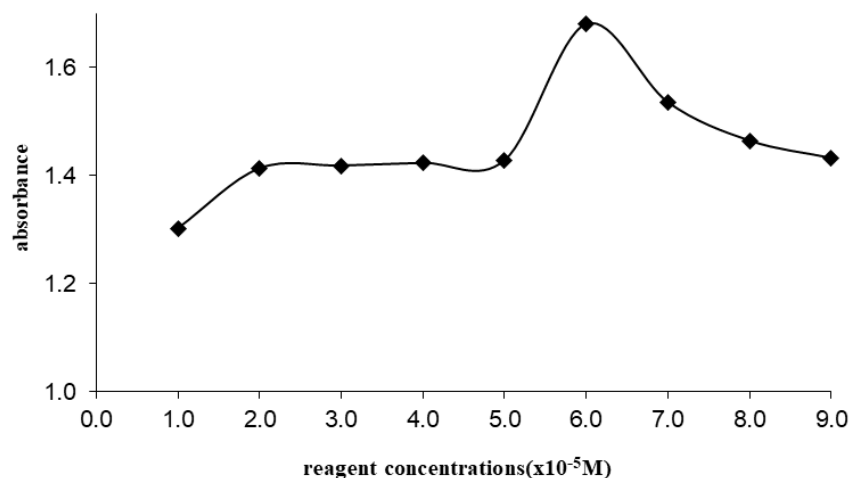


Figure 2: Effect of N,NBPAD concentrations on the absorbance of Cr(VI)N,NBPAD complex



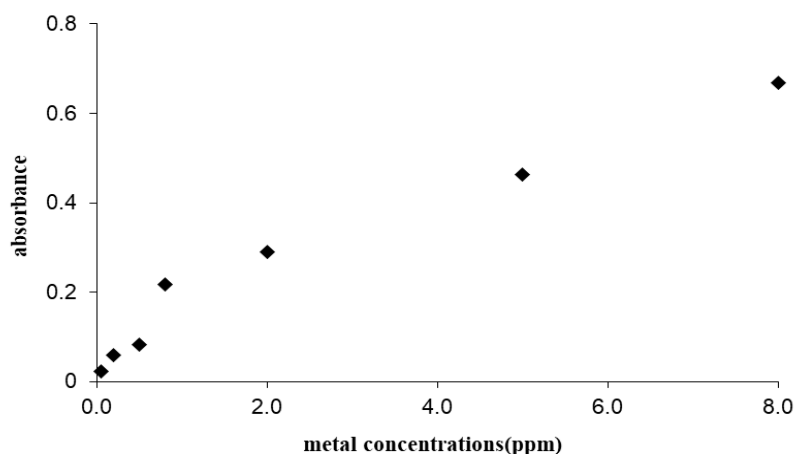


Figure.3: Calibration curve for Cr(VI)N,NBPAD complex

6. Effect of micelle SDS concentrations

A series of Cr(VI) solutions were prepared using 4 ppm of Cr(VI) 4×10^{-5} M of the reagent and different micelle concentrations. The absorbance was recorded at 220 nm. The results are shown in Table 5 and Fig. 4.

Micelle concentrations($\times 10^{-6}$ M)	Absorbance
0.0	0.362
1.0	0.646
2.0	0.665
4.0	1.043
6.0	0.551
8.0	0.480

6.1 Effect of N,N BPAD concentrations

A series of Cr(VI) solutions were prepared using 4 ppm of Cr(VI) 4×10^{-6} M of micelle, and different reagent concentrations. The absorbance was recorded at 220 nm. The results are shown in Table 6 and Fig. 5.

Reagent concentrations ($\times 10^{-5}$ M)	Absorbance
0.6	0.349
0.8	0.393
2.0	0.360
4.0	0.350
6.0	0.337
8.0	0.320

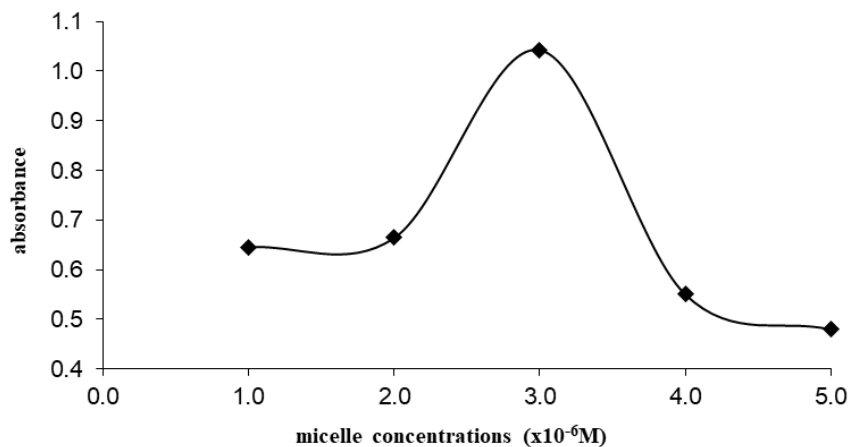


Figure 4: Effect of micelle SDS concentrations on the absorbance of Cr(VI)N,NBPAD complex



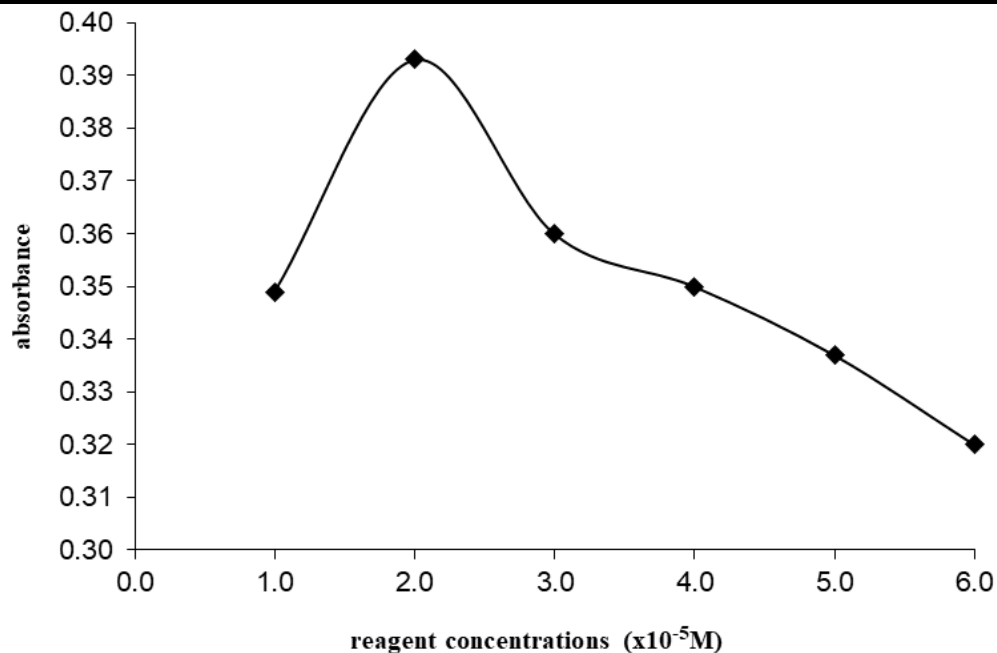


Figure 5: Effect of *N,NBPAD* concentrations on the absorbance of *Cr(VI)N,NBPAD* complex

6.1.2 Calibration curve for *Cr(VI) N,NBPAD* complex

A series of *Cr(VI)* solutions were prepared using 4×10^{-6} M of micelle, and 8×10^{-6} M of the reagent, and different metal concentrations. The absorbance was recorded at 220 nm. The results are shown in Table 7 and Fig .6.

<i>Cr(VI)</i> concentration (ppm)	Absorbance
8.0	0.635
5.0	0.420
2.0	0.206
0.8	0.096
0.5	0.074
0.2	0.050
0.08	0.030
0.05	0.011
0.02	0.007
0.008	0.007

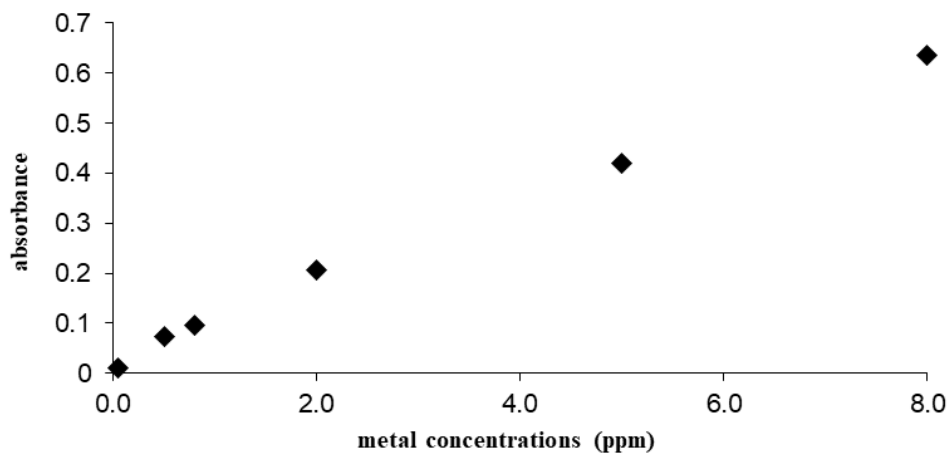


Figure.6: Calibration curve for *Cr(VI)N,NBPAD* complex

6.1.3 Effect of foreign metal ions

In order to assess the possible analytical applications of these type of complexes, the effect of some foreign metal ions was determined. To study the effect of Fe(III), Fe(II), Zn(II), V(V), Cu(II) on the determination of Cr(VI)N,NBPAD under the optimum conditions, 10ppm of Cr(VI), 8×10^{-6} M of the reagent, and 4×10^{-6} M of micelle were used while varying the concentrations of foreign metal ions. The absorbance was recorded at 220 nm. The results are shown in Table 8.

Metal ion. Conc (ppm)	Absorbance				
	Fe(III)	Fe(II)	Zn(II)	V(V)	Cu(II)
0.0	0.956	0.956	0.956	0.956	0.956
2.0	0.976	0.992	0.912	1.175	0.937
5.0	1.105	1.145	0.968	1.362	0.915
10.0	0.999	1.094	0.890	1.750	1.022
15.0	1.181	1.116	0.913	1.988	1.089

7. Result & Discussions

From this study, Cr(VI) can be determined without interference from Fe(III), Fe(II), Zn(II), and Cu(II) with N,NBPAD except from V(V), Table 8. When the micelle SDS was used, the absorbance increased by 188.12%, with Cr(VI), Table 5. On using the micelle N-HTAB the absorbance was increased by 70.2%, for Cr(VI). Table 4. Effect of micelle refers to the presence of positive charge leading to the repulsion between the micelle and some metal ions which in turn may lead to the masking effect of micelle, these results depend on the charge of micelle and metal ions. Therefore, micelle catalyzed metal complex formation. It has been generally accepted that the micellar catalysis is due to the electrostatic and the hydrophobic effect between the ligand and micelles, the present of di anionic lead to decrease in polarity of the micelle than that of the polar solvents.

There is a linear relationship between the concentration of metal ions complexes and absorbance, under optimum conditions of micelle and reagent concentrations, N,NBPAD calibration curve is linear between 0.05, 8.0 ppm for Cr(VI) complex when using ethanol as a solvent and SDS as a micelle (Fig.6).

The study also showed a good results for the determination of Hg(II) and Pb(II) if interference is removed.

There are substance present that prevent direct measurement of the amount of given ion; these are referred to as interference, and the selection of methods for separating the interference from the substance to be determined are as important as the choice of the method for determination.

8. Conclusion

In this research, a new spectrophotometric method for the determination of Cr (VI) using N,NBPAD Schiff's base as a complexing agent was developed. The method was based on measuring the intensity at $\lambda_{max} = 270$ nm under variable conditions, without stringent requirements. The results indicate that this method is reliable, simple, sensitive, and reproducible for the determination of chromium ions at low concentrations. Calibration curves were constructed under optimized conditions, demonstrating the inexpensive nature of using N,NBPAD Schiff's base. The study findings suggest potential applications in environmental and industrial analysis. Further research could explore the method's applicability in diverse sample matrices and its comparison with other analytical techniques.

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