

Voltammetric Investigations of 2,2'-Azobispyridine Zinc(II) and Nickel(II) Complexes

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The electrochemical behaviour of 2,2'-Azobispyridine (abpy) has been studied by using voltammetric techniques. From obtained data, electrochemical reaction mechanism of the azo compound has been suggested. At the same time, zinc(II) and nickel(II) complexes of the azo compound have been investigated in different solution media. 50% ethanol-50% KNO₃ (0.1M) medium has been chosen as optimum solution medium. The composition of the zinc(II) and nickel(II) abpy complexes has been determined to be 1:2. The optimum conditions favoring the formation of complexes were studied and their stability constants were determined by using square-wave voltammetric technique.

Keywords: 2,2'-Azobispyridine, azo dyes, voltammetry, zinc, nickel, complex, reduction.

1. INTRODUCTION

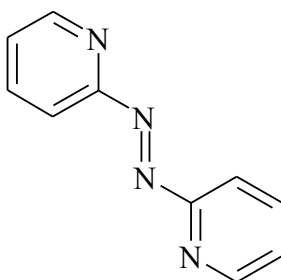
Azobenzene derivatives have been the most widely used class of dyes due to their versatile application in various fields, such as dyeing textile fiber biomedical studies, advanced application in organic synthesis and high technology areas as laser, liquid crystalline displays, electro-optical devices and ink-jet printers. At the same time azo dyes are also used in colouring agents in foods and pharmaceuticals etc [1-10].

Heterocyclic azo compounds are widely used in analytical chemistry for the spectrophotometric determination of many elements and as complexometric indicators [1,2]. Recently many researchers developed a sensitive method for the determination of metal ions with heterocyclic azo compounds as complexometric agents by polarographic and voltammetric techniques. Heterocyclic azo compound reagents have received a great deal of attention as they are sensitive and selective chromogenic

reagents. To continue improving the sensitivity, selectivity of this kind of reagents and their metal complexes, the electrochemical characteristics of the reagents and their metal complexes have been studied [3-5, 10-17].

The studies, were mainly concerned with aromatic azo compounds because of (i) the importance of this group in the dyestuff industry (ii) the interest in carcinogenic properties and (iii) the use of azo compound for indirect determination of metal ions [14,15].

The aim of this study is to elucidate the electrochemical reaction mechanism of 2,2'-azobispyridine and its transition metal (Zn(II) and Ni(II)) complex properties and to calculate the complex formation constants of these complexes. The molecular structure of the azo compound is given below (Scheme 1).



Scheme 1. Molecular structure of the 2,2'-Azobispyridine.

2. EXPERIMENTAL

Abpy dye was synthesized [18]. 1×10^{-3} M stock solution of the reagent was prepared in absolute ethanol and the stock solutions of the metals of 1×10^{-3} M were prepared by dissolving appropriate amounts of the metals in ultrapure water and were diluted as necessary. 50% ethanol-50% KNO_3 (0.1M) medium was used as supporting electrolyte and 10 mL of supporting electrolyte was established into a voltammetric cell. Then 800 μL of metal ion was added with a micropipette into a 10 mL voltammetric cell. After this, 100-3000 μL of the azo compound (1×10^{-3} M) was added into the metal solution in stepwise manner and then square-wave voltammograms, cyclic voltammograms and direct current polarograms were recorded.

Polarographic and voltammetric experiments were carried out using a computer-controlled electroanalysis system (Metrohm 757 VA Computrace Electrochemical Analyser). A three-electrode combination system was used. This consisted of a Multi Mode Electrode (DME, SMDE and HMDE), an Ag/AgCl reference electrode and a Pt wire auxiliary electrode. All measurements were carried out at room temperature. Voltammetric parameters were selected for an equilibrium time of 5 s, a purge time of 300 s, and at a potential step of 4 mV, a pulse height of 50 mV and a scan rate (ν) of 200 mVs^{-1} . The solutions were purged with purified clean dry nitrogen for five minutes prior to the experiments in order to remove dissolved oxygen from the media.

3. RESULTS AND DISCUSSION

Britton-Robinson, acetate, ammonia and KNO_3 solution media have been tested as supporting electrolyte. The best polarograms and voltammograms of abpy and its metal complexes were observed only in 50% ethanol-50% KNO_3 (0.1M) medium. Therefore, it has been selected as solution medium in all experimental studies.

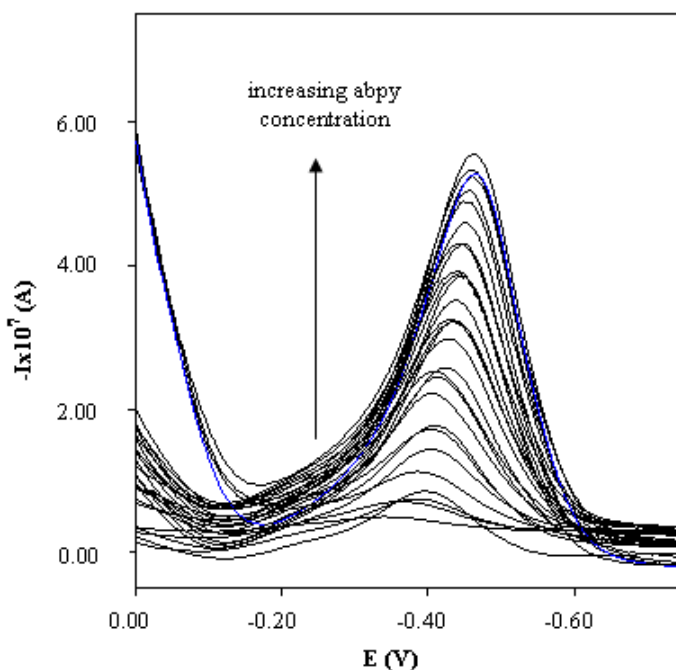


Figure 1. Square-wave voltammograms of the abpy in 50% ethanol-50% KNO_3 (0.1M) medium, $\nu = 200 \text{ mVs}^{-1}$.

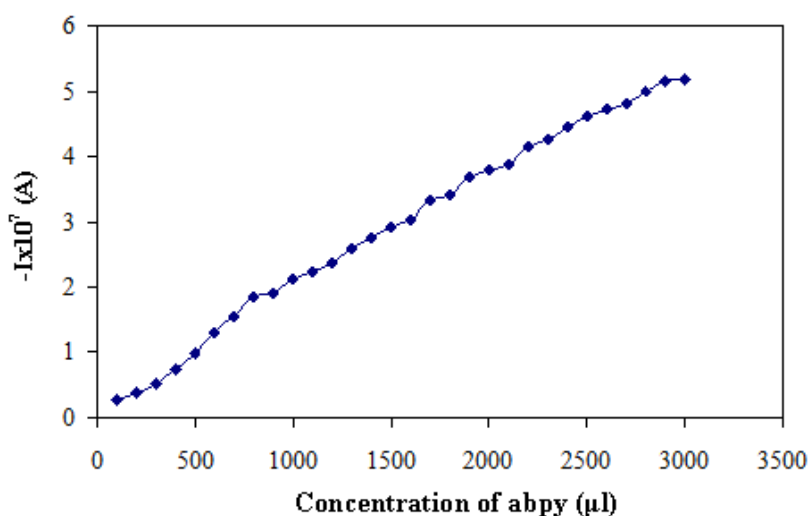


Figure 2. The change of peak currents of abpy with increasing concentration of abpy in 50% ethanol-50% KNO_3 (0.1M) medium, $\nu = 200 \text{ mVs}^{-1}$.

Square-wave voltammograms of the azo compound are given in Figure 1. One reduction peak was observed corresponding to the reduction of the azo group in 50% ethanol-50% KNO₃ (0.1M) medium. Dependence of the peak current and peak potential of the dye obtained from SWV data, on the concentration of the dye has been shown in Figure 2 and Figure 3. Peak current of the dye changes linearly ($r^2=0,992$) with increasing of dye concentration in the solution medium (Figure 2). Furthermore peak potential also changes with increasing of dye concentration (Figure 3). This situations can be explained with adsorption effect. At the same time, direct current (DC) polarogram was recorded in similar solution medium (Figure 4a). As shown in Figure 4a, peak maximum was observed in DC polarogram due to adsorption effect. These results are supported by SW voltammetric studies as shown in Figure 2 [19,20].

CV voltammogram of the dye has been shown in Figure 4b. Only one cathodic and anodic peak were observed.

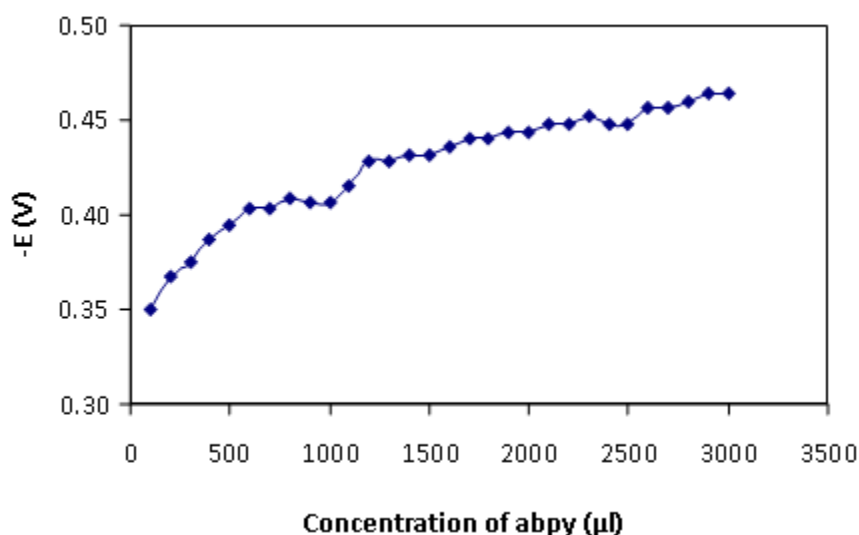
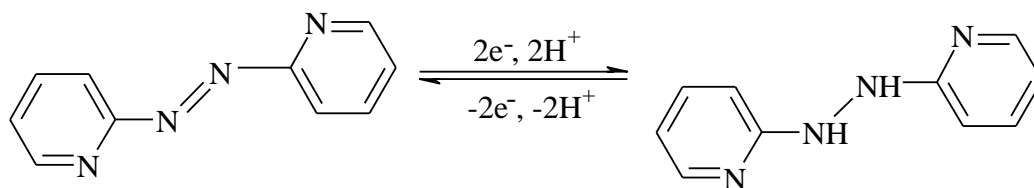


Figure 3. The change of peak potentials of abpy with increasing concentration of abpy in 50% ethanol-50% KNO₃ (0.1M) medium, $\nu = 200 \text{ mVs}^{-1}$.

Thus, the reduction mechanism of the synthesized azo dye is proposed as follows depending on literature [3-5, 19-23].



The Zn(II)-abpy and Ni(II)-abpy complexes have been studied. Firstly Zn(II)-abpy complex has been discussed. The voltammograms of the Zn(II)-abpy complex in 50% ethanol-50% KNO₃ (0.1M) medium are shown in Figure 5.

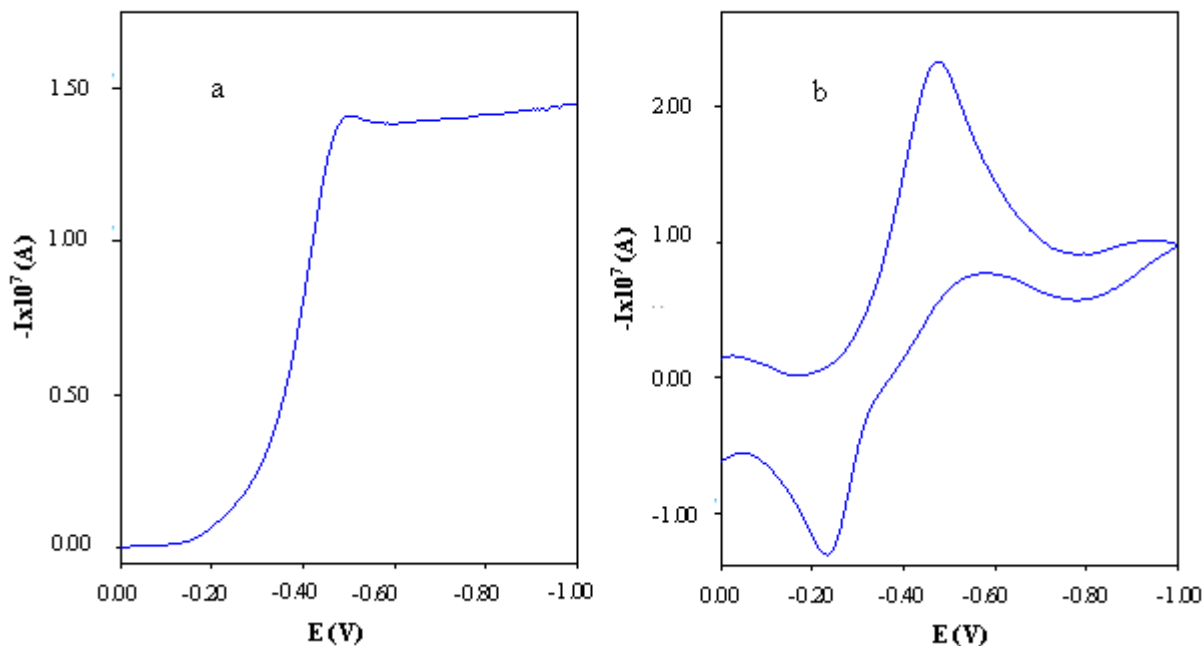


Figure 4. (a) DC polarogram (b) CV voltammogram of the abpy in 50% ethanol-50% KNO₃ (0.1M) medium, $\nu = 200 \text{ mVs}^{-1}$.

The reduction peak of the azo compound is clearly seen at -0.40 V without the complexed-metal peak. In the presence of the Zn(II) ion, metal-ligand complex reduction peak occurred at a potential of -0.19 V and the metal ion at -1.0 V as shown in Figure 5. For determining the metal:ligand ratio, peak currents and potentials of the ligand, complex and the metal ion obtained from square-wave voltammograms were plotted versus increasing concentration of the azo compound (Figures 7, 9, 11). According to Figure 7, by adding 200-900 μl of abyp in stepwise manner into the 800 μl Zn(II) solution, a decreasing was observed in the peak current of Zn(II) ion at -1.0 V. And the potentials of Zn(II) ion, Zn(II)-abpy complex and ligand, shifted to more negative values by increasing of abyp concentration (Figure 11). It is also seen that the peak current of Zn(II)-abpy complex which is observed at -0.19 V reaches a constant value after adding 1000 μl of abyp solution and there is not a significant change in the potential of the Zn(II)-abpy complex by adding of abyp solution (Figure 9). As seen in SW voltammograms, ligand peak occurred as a shoulder peak (from the point where the ratio of metal to ligand is 1:2) nearby the complex peak when adding the excess concentration of abyp into the metal solution (Figure 5).

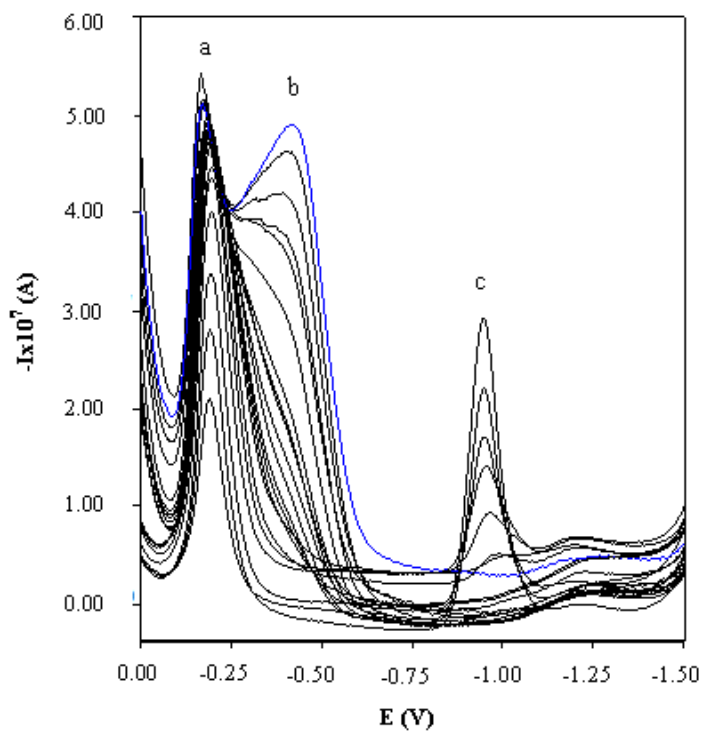


Figure 5. Square-wave voltammograms of the Zn(II)-abpy complex in 50% ethanol-50% KNO₃ (0.1M) medium, (a) Zn(II)-abpy complex peak current, (b) Abpy peak current, (c) Zn(II) ion peak current, $\nu = 200 \text{ mVs}^{-1}$.

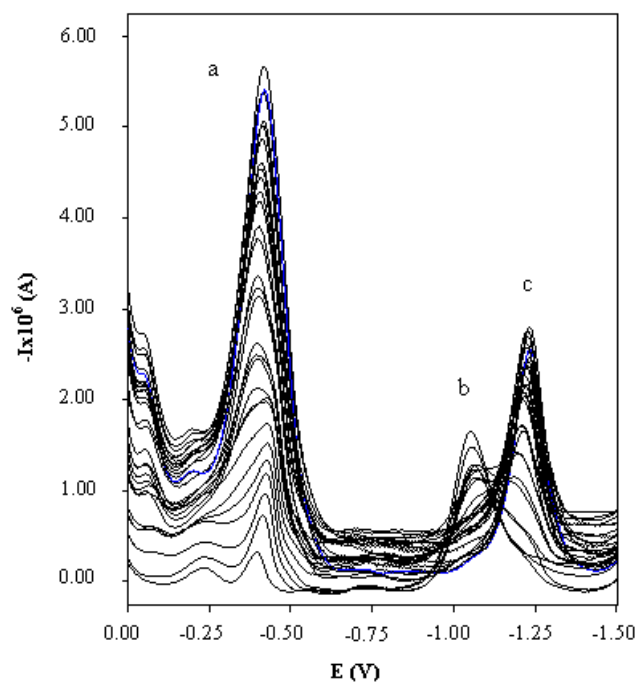


Figure 6. Square-wave voltammograms of the Ni(II)-abpy complex in 50% ethanol-50% KNO₃ (0.1M) medium, (a) Ni(II)-abpy complex peak current, (b) Ni(II) ion peak current, (c) Ni(II) ion peak current in the Ni(II)-abpy complex, $\nu = 200 \text{ mVs}^{-1}$.

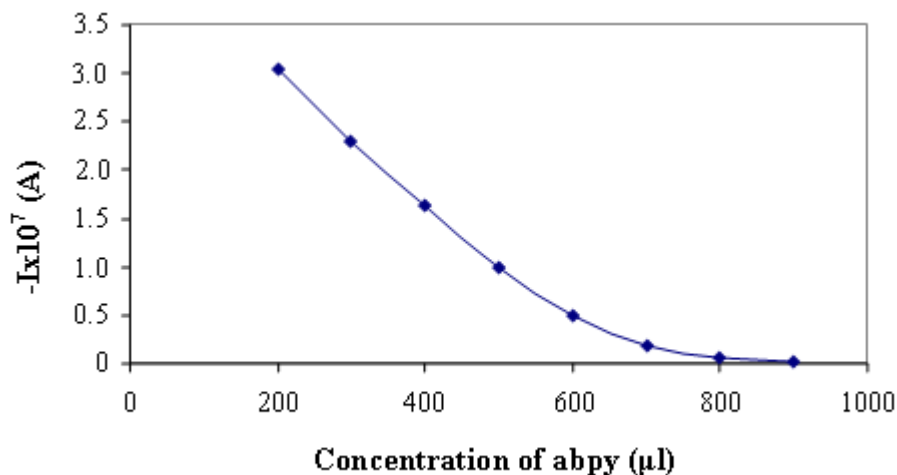


Figure 7. The change of reduction peak current of Zn(II) ion by adding 200-900 μl of abpy for Zn(II)-abpy complex, $\nu = 200 \text{ mVs}^{-1}$.

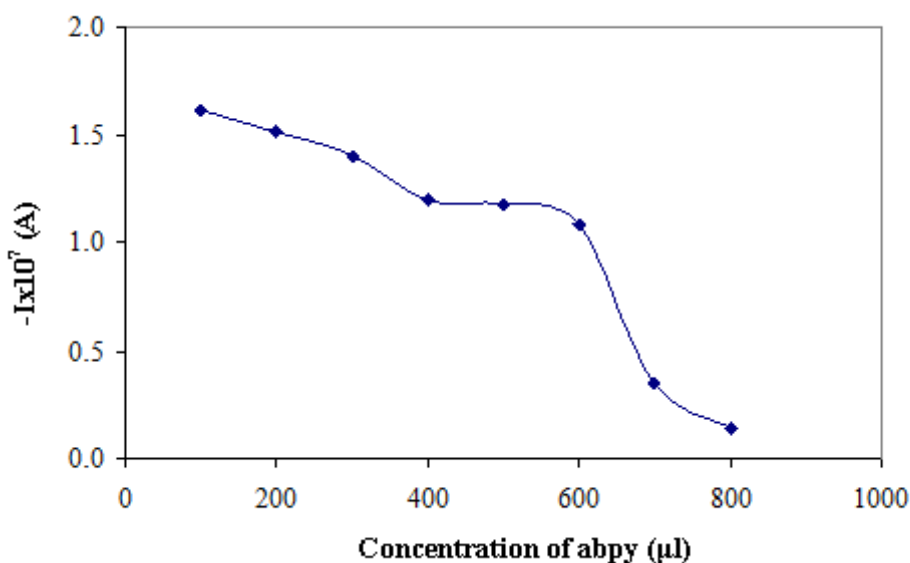


Figure 8. The change of reduction peak current of Ni(II) ion by adding 100-800 μl of abpy for Ni(II)-abpy complex, $\nu = 200 \text{ mVs}^{-1}$.

The stoichiometry of the Zn(II)-abpy complex has also been determined by following the peak current of the complex in 50% ethanol-50% KNO₃ (0.1M) medium by using as below equation. It is accepted that when all the ligand molecules complex with the metal ion, peak currents reach a constant value at the Zn(II):abpy ratio of 1:2, due to the decreasing of the concentration of the metal ion. The peak current of Zn(II) complex versus the concentration of abpy relation is given in Figure 9.

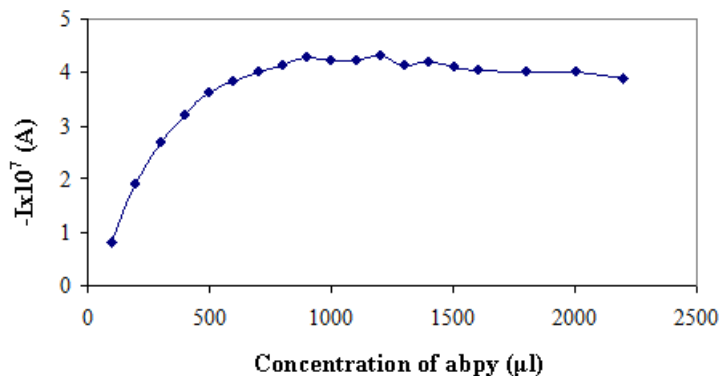


Figure 9. The change of reduction peak current of Zn(II)-abpy complex by adding 100-2200 μl of abpy, $\nu = 200 \text{ mVs}^{-1}$.

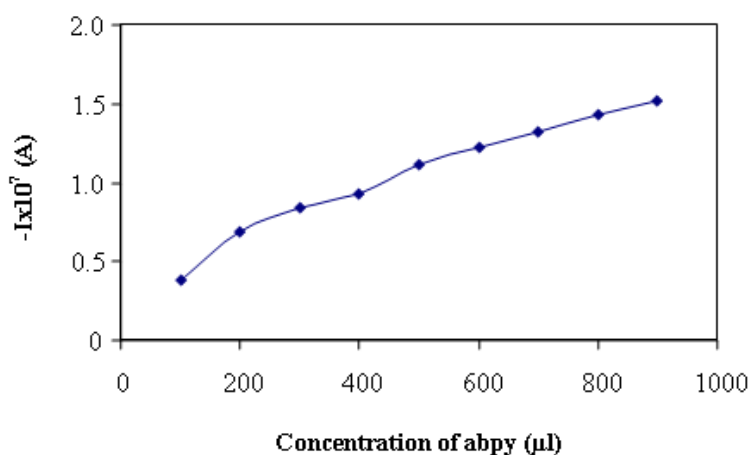


Figure 10. The change of reduction peak current of Ni(II)-abpy complex by adding 100-900 μl of abpy, $\nu = 200 \text{ mVs}^{-1}$.

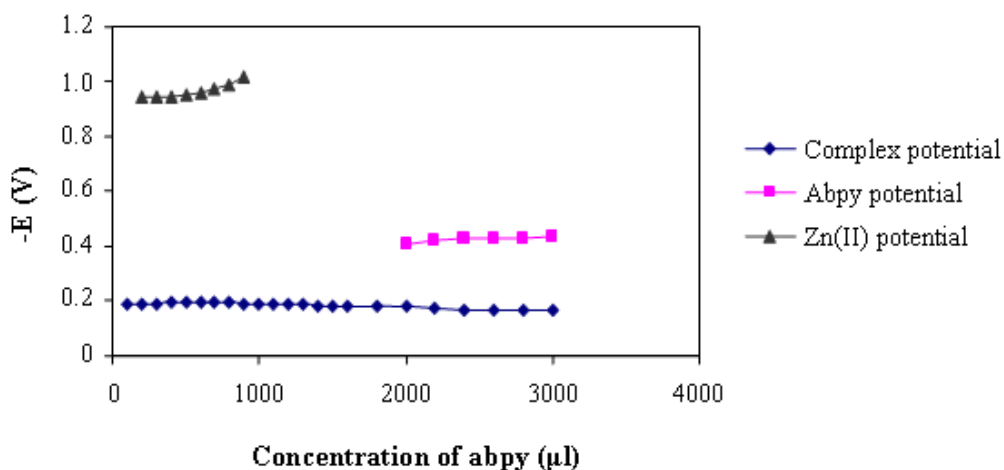


Figure 11. The change of reduction peak potentials of Zn(II)-abpy complex, abpy and Zn(II) ion by adding 3000 μl of abpy, $\nu = 200 \text{ mVs}^{-1}$.

Similar results have been carried out with Ni(II)-abpy complex in 50% ethanol-50% KNO₃ (0.1M) medium. In Figure 8, a decreasing was observed at the Ni(II) ion peak current which was occurred at -1.06 V by increasing of abpy concentration and it was observed that peak current intensity of Ni(II) ion approached zero after adding 1000 μl of abpy.

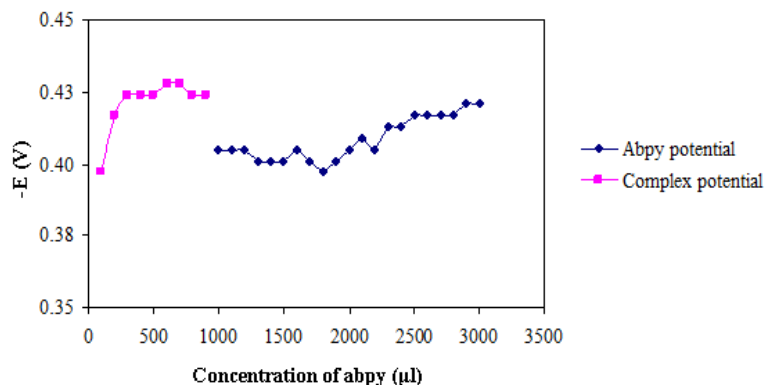


Figure 12. The change of reduction peak potentials of abpy and Ni(II)-abpy complex by adding 3000 μl of abpy, $\nu = 200 \text{ mVs}^{-1}$.

Disappearance of Ni(II) ion peak current showed that there was no Ni(II) ion in a solution medium, in other words it means that Ni(II) ion was used in complex formation. As can be seen from SW voltammograms, Ni(II)-abpy complex peak current occurred at approximately -0.4 V and Ni(II)-abpy complex peak current intensity remained constant after adding 1000 μl of abpy, because of reduction peak current of abpy was observed at the same potential (-0.4 V) with the Ni(II)-abpy complex. The complex peak of the Ni(II)-abpy has been masked at the excess of the abpy concentrations. Thus, single peak was observed at approximately -0.4 V (Figure 6). As can be seen from Figure 10, the variation of Ni(II)-abpy complex peak current versus the concentration of abpy showed that the peak currents of the complex increased linearly in relation to abpy concentration and peak potentials of the complex shifted to more negative potentials with addition of abpy solution (Figure 12).

On the contrary to the Zn(II)-abpy complex, the reduction peak current of free Ni(II) ion at -1.06 V has been disappeared and its potential shifted to -1.25 V with increasing of abpy concentration due to formation of the Ni(II)-abpy complex (Figure 6).

Considering the results that are obtained from the complex peak that is based on the reduction of abpy and the reduction of the Ni(II), the ratio of the Ni(II)-abpy complex has been determined as 1:2.

Metal to ligand ratios of heteroazo and azo dye complexes are dependent on the solution media. Many azo dyes zinc(II) and nickel(II) complex ratios have been found as 1:2 in previous studies [19,20]. These results are convenient with the above results.

3.1. Complex formation constants

Complex formation constants are determined by using square-wave voltammetric technique which is one of the important class of electrochemical methods. Different analytical methods have been improved to determine the complex formation constants due to the differences of peak currents and potentials of the complexes depending on the metal and the ligand. This methods may not give appropriate values for every system and mixture. For this purpose, optimum conditions should be investigated principally. To determine the properties of complexes Britton-Robinson, acetate and ammonia buffers which are the most common buffer solution media were tested. 50% ethanol-50% KNO₃ medium was preferred as supporting electrolyte due to providing the optimum conditions for the voltammetric measurements and improper results of other solution media. For determining the complex formation constants of the Zn(II)-abpy and Ni(II)-abpy complexes following equation was used [24,25].

$$\log(b/(b_{\max.}-b)) = \alpha \log(L) + \log\beta'$$

In this equation, b is the peak height (peak current value), b_{\max} is the maximum peak height (maximum peak current value in the studied range), L is the ligand concentration and the β' is the complex formation constant of the complex and α is the molar ratio of ligand to metal. By plotting $\log(b/(b_{\max.}-b))$ versus $\log(L)$, ligand:metal ratios and complex formation constants of abpy complexes have been determined by using slopes and intercepts of the graphs. Abpy/Zn(II) and abpy/ Ni(II) ratios were determined as 2.1292 and 2.0478 respectively from the slopes of the graphs and $\log\beta'$ values were determined as 10.015 and 9.4328 respectively from the intercepts of the graphs. Complex formation constants (β') of Ni(II) and Zn(II) complexes of abpy were calculated as 0.27×10^{10} and 1.03×10^{10} respectively. These results are summarized in Table 1.

When reduction potentials of the abpy metal complexes are compared each other, it can be observed that the peak potentials of the Zn(II) and Ni(II) complexes are -0.19 V, and -0.41 V respectively. This situation showed that the reduction of Zn(II)-abpy complex is easier than Ni(II)-abpy complex.

Table 1. Formation constants of the Ni(II) and Zn(II) abpy complexes.

Metal	Linear Equation	$\alpha = \text{abpy/metal}$	$\log\beta'$	β'
Ni(II)	$\log(b/(b_{\max.}-b)) = \alpha 2.0478 + 9.4328$	2.0478	9.4328	0.27×10^{10}
Zn(II)	$\log(b/(b_{\max.}-b)) = \alpha 2.1292 + 10.015$	2.1292	10.015	1.03×10^{10}

4. CONCLUSION

In this investigation, the voltammetric and polarographic behaviour of 2,2'-Azobispyridine (abpy) zinc(II) and nickel(II) complexes have been studied by several techniques including square-

wave voltammetry (SWV), direct current polarography (DCP), and cyclic voltammetry (CV). The electrochemical response of the complex was determined by experimental conditions such as different supporting electrolyte solutions. From the polarographic and voltammetric data, optimum conditions were found. 50% ethanol-50% KNO₃ (0.1M) medium has been chosen as optimum solution medium. Abpy/Zn(II) and abpy/ Ni(II) ratios were determined as 2. Complex formation constants (β') of Ni(II) and Zn(II) complexes of abpy were calculated as 0.27×10^{10} and 1.03×10^{10} respectively.

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