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Distinctive Routs:Electrochemical and Spectrophotometric Studies and Dissociation Constants Determination of Some Aminopyridine Azo-Dye Derivatives in Aqueous Media

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The electrochemical behavior of some azo compounds derived from 2-amino-3-hydroxypyridine in Britton and Robinson buffer series containing 20% (v/v) ethanol was investigated at the mercury electrode using distinctive techniques (DC, CV and DPP) to evaluate the effect of medium and substituents on the reduction process and suggestion of the electrode reaction mechanism. The obtained results indicated that these compounds were reduced undergo an irreversible 4-electron polarographic wave within the entire pH range leading to the cleavage of the N=N center. The NO_2 derivative is reduced via a single 8-electron wave and the hydroxylamine group is obtained. The CV data showed that a single cathodic peak is obtained at all pH representing the reduction of the azo center as well as the nitro group for azo compound (II). The total number of electrons involved in the reduction process was determined by controlled potential coulometry. The dissociation constants values (pk$_a$) of these compounds were determined spectrophotometrically and potentiometrically at room temperature.

Keywords: 2-amino-3-hydroxypyridine*azo dyes*, Polarography, Cyclic voltammetry, Spectrophotometry, Potentiometry, Dissociation constants.

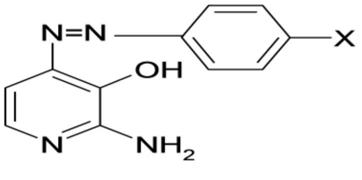
1. INTRODUCTION

Azo dyes are considered to be very important class of compounds due to the widespread applications in many areas of technology. Their applications as chromophoric and metallochromic reagents [1-3], poto-sensitizers [4, 5], non-liner optics [6-10], colorants [11-13], sensors [14-16] and analytical reagents have important attention of many chemists. Therefore, the electrochemistry of these compounds was the subject of some interesting studies [17-23]. These investigations showed that the electro-reduction of azo group (N=N) double bond undergoes [24-35]; the consumption of $2H^+ /2e^-$ to the hydrazo group (NH-NH) or the uptake of $4H^+ /4e^-$ to the amine stage ($-NH_2$) in one or two steps depending on the chemical structure of the investigated compounds, the nature of the neighboring substituents and the pH of the medium. Recently, some novel azo dyes and azo containing azomethine compounds were synthesized and studied electrochemically using cyclic voltammetry due to their widespread applications as dyes and pigments in textile, leather and plastic industries [36-40]. On the other hand, azo dyes derived from pyridine derivatives are very useful due to their important as analytical reagents their biological activity in treatment of several diseases and removal of several metal ions as well as their uses as inhibitors for metal corrosion and manufacture of some laser materials and petrochemicals. Thus, it is important to throw light on the redox potential and the reaction mechanistic pathway of these significant compounds. Although, several studies were carried out on the electro-reduction of azo compounds using different techniques [17-40] but little attention was reported for those derived from heterocyclic pyridine ring conjugated with aromatic systems [17].

The present work aims to investigate the electro-reduction of some azo compounds derived from 2-hydroxy-3-aminopyridine at the mercury electrode in aqueous solutions to follow the effect of pH of the medium on their reduction potentials ($E_{1/2}$ & E_p) and to elucidate the electrode reaction mechanism by using different electrochemical techniques (DC, DPP &CV) as well as the determination of dissociation constants of these azo compounds by means of spectrophotometric and potentiometric methods.

2. EXPERIMENTAL

All compounds used in the present investigation were of analytical grade and used without further purification. The azo compounds (I-IV) were prepared [41] by gradual addition of an aqueous cold solution of sodium nitrite (0.01 mole) to a concentrated hydrochloride acid solution of aniline, p-nitro aniline, p-amino benzoic acid, p-anisidine (0.01) mole with continuous stirring and kept for about 20 min in ice bath. The formed diazonium salt solutions were added gradually with vigorous are stirring to cold solutions of 2-amino-3-hydroxypyridine (0.01 mole) dissolved in 0.01M NaOH. After dilution, the obtained solid compounds were filtered off and washed with water. The crude materials were recrystallized from ethanol. These azo compounds were characterized by IR and ^{1}H-NMR spectra. The azo compounds obtained have the following structural formula:



X= (I) H, (II) p- NO_2, (III) p-COOH, (VI) p-OCH_3

I 2-amino-4-(phenyldiazenyl) pyridine-3-ol.

II 2-amino-4-((4-nitrophenyl) diazenyl) pyridine-3-ol.

III 4-((2-amino-3-hydroxypyridin-4-yl) diazenyl) benzoic acid.

IV 2-amino-4-((4-methoxyphenyl) diazenyl) pyridine-3-ol.

The IR spectra of the pyridine azo compounds (I-IV) showed the characteristic stretching band frequencies of OH and NH_2 groups within the range 3500-3200 cm^{-1} , N=N group within the wave number range 1535-1520 cm^{-1} . For compound II, there is band at 1530 cm^{-1} due to NO_2 group while the band appeared at .1705 cm^{-1} for compound III is due to COOH group. The band appeared at 1100 cm^{-1} for compound IV is due to OCH_3 group.

Further support for the structure of the compounds under study was performed by investigating ^{1}HNMR in DMSO-d6 as a solvent. The multiple signals appeared in compounds (I-IV) at the range of (7.2-7.5) ppm are due to aromatic protons, the singlet band appeared in the range of (8.6-9.2) ppm are due to amino protons while the singlet band appeared in the range of (5.5-5.7) ppm are due to phenolic protons. The singlet band appreaed at 12.8 ppm for the compound III is due to carboxylic proton whereas that appeared at 4.1 ppm for the compound IV is due to methoxy protons.

2.1. Voltammetric measurements:

DC- polarograms were recorded on an ink recording SARGENT WELCH Polarograph model 4001. The capillary used as a dropping mercury electrode has the following characteristics in 0.1 M KCl (open circuit): m = 1.7 mg/s, t = 3 sec., at mercury height (h) = 60 cm. The mercury used was purified according to the recommended method [42]. DP polarograms and cyclic voltammograms of the studied compounds were recorded with a Metrohm VA 797 Computrace Electrochemical Analyzer with a Multi Mode Electrode (DME and HMDE), a Ag/AgCl reference electrode and a Pt wire auxiliary electrode. A digital coulometer (Model 179) from EG&G was used for the coulometry measurements.

2.2. Coulometry measurements (Controlled potential electrolysis):

A digital coulometer (Model 179) from EG & G was used for the coulometry measurements. The cell was designed by Princton Applied Research Corporation which has a mercury working electrode with a large surface area, the reference electrode is a saturated calomel electrode and the counter electrode is a platinum gauze. The potential of the working electrode is maintained constant with respect to that of the reference electrode. The selected potential was adjusted to be equal to the polarographic half-wave potential plus 0.1 volt or at the beginning of the limiting current of the polarograpic wave. Firstly, the background current is measured for the supporting electrolyte after bubbling the solution by pure nitrogen gas for about 15 minutes. The electrolysis is continued until the background current attains a constant value which is compensated by controlling on the coulometer, then the depolarizer solution is introduced into the coulometric cell and the electrolysis is allowed to proceed until completion (the color of the azo dye disappears completely and the digital coulometer reads a constant Q value). The accumulated charge (Q in coulombs) is read directly from the digital coulometer which is plugged directly into the potentiostat.

2.2. UV and visible spectra:

Electronic absorption spectra were recorded at room temperature within the wavelength range 200- 600 nm using a Shimadzu UV- visible spectrophotometer model UV-1800.

2.3. Potentiometric measurements:

Potentiometric measurements were performed using a Digital ORION pH- meter Model 211 having combined glass and calomel electrodes, with a magnetic stirrer and a semi micro burette with divisions of 0.01 ml. The following solution mixtures (A & B) were prepared:

(A) 5 ml HCl (0.001 M) + 5 ml KCl (1M) +10 ml ethanol+ 30 ml distilled water.

(B) 5 ml HCl (0.001 M) + 5 ml KCl (1 M) + 5 ml azo compound (5×10^{3}M) + 5 ml ethanol + 25 ml distilled water. These solutions were titrated potentiometrically with 0.02 M NaOH solution. The NaOH solution was titrated against a standard solution of sodium carbonate.

3. RESULT AND DISCUSSION

3.1. Voltammetric Studies

3.1.1. DC-polarography

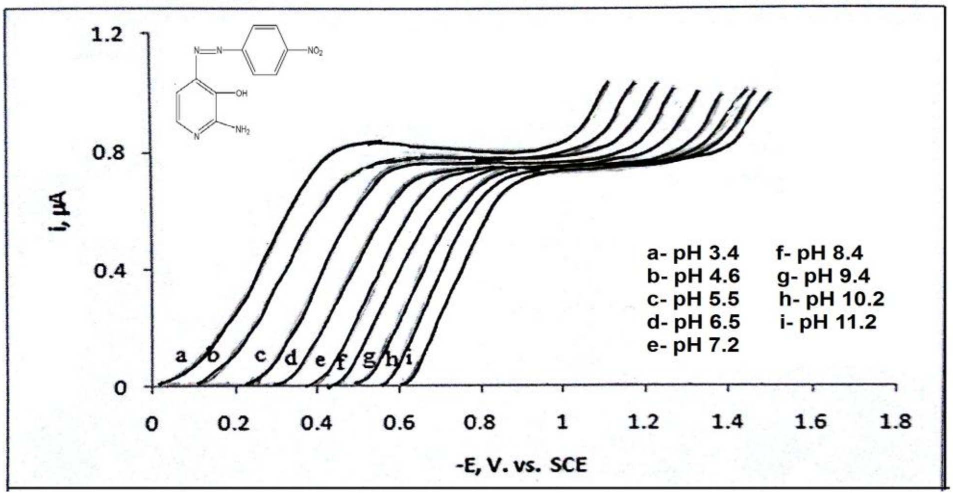


Figure 1. DC polarograms of 1x10^{4} M of pyridine azo compound (II) in solutions of different pH values containing 20% (v/v) ethanol

The DC-polarograms of 1×10^{-4} M of pyridine azo compounds (I-IV) were recorded in Briton-Robinson buffer solutions of pH 2–11 containing 20% (v/v) ethanol. The DC- polarograms of all azo compounds exhibited a single polarographic wave in all buffer solutions. The limiting current (i_l) of the polarographic wave decreases slightly on increasing the pH of the solution. Fig. 1 represents the DC-polarograms of azo compound (II) as a typical example of this series.

The half-wave potential ($E_{1/2}$) of the polarographic wave shifted to more negative values on increasing the pH of the solution, denoting the consumption of protons in the reduction process and the proton uptake precedes the electron transfer [43]. The effect of mercury height (h) on the limiting current (i_l) of the polarographic waves using the equation [44]: $i_l = k\ h^x$, revealed that the reduction process for all azo compounds is controlled mainly by diffusion with some adsorption contribution. The value of the exponent (x) amounts to (0.5-0.75) (Table 1).

Table 1. DC – Polarographic data of pyridine azo compounds (I-IV) in buffer solutions of different pH values.

Comp.	pH	i_l (μA)	$-E_{1/2}$ (V)	S_1 (mV)	α		S_2 (mV)	Z_H^+	δlogi/δlogh
					n_a=1	n_a=2			
I	3.1	0.48	0.15	80	0.74	0.37	90	0.64	0.47
	7.0	0.44	0.46	85	0.67	0.34		0.61	0.55
	9.5	0.4	0.68	73	0.81	0.41		0.69	0.66
II	3.4	0.84	0.2	87	0.68	0.34	70	0.40	0.70
	7.2	0.72	0.42	60	0.49	0.49		0.58	0.62
	9.4	0.72	0.64	60	0.98	0.49		0.58	0.65
III	3.0	0.51	0.1	72	0.82	0.41	79	1.09	0.57
	7.0	0.45	0.38	75	0.79	0.39		1.05	0.73
	9.0	0.45	0.58	84	0.70	0.35		0.94	0.75
IV	2.8	0.45	0.20	66	0.89	0.44	83	1.24	0.57
	7.1	0.4	0.54	76	0.77	0.38		1.08	0.57
	9.9	0.4	0.76	80	0.73	0.37		1.03	0.75

$S_1=0.0591/\ \alpha n_a$ $S_2=\delta E_{1/2}/pH$ $Z_{H+}= S_2/S_1$

Analysis of the polarographic waves using the basic equation for reversible polarographic wave [42] showed that the electrode reaction proceeds irreversibly. The value of the transfer coefficient (α) and the number of electrons participating in the rate-determining step (n_a) were determined from the reciprocal slopes (S_1) of the logarithmic analysis plots and given in Table 1. It was found that, the most probable (α) values were obtained at n_a equals to one or two depending on the pH of the medium and the type of substituent, which revealing that the rate-determining step of the reduction process may involve one or two electrons.

The $E_{1/2}$ – pH plots of all azo compounds gave straight lines of slope values (S_2) which given in Table 1. The number of protons (Z_H^+) participating in the rate-determining step was determined from the slopes values (S_2) and (S_1) using the following relation [45]

$Z_H^+ = (\delta E_{1/2} / \delta pH)/ (0.0591/ \alpha n_a) = S_2 / S_1$

The value of Z_H^+ for all compounds were calculated at different pH values and found approximately equal to unity (Table 1).

3.1.2. Cyclic voltammetry measurements

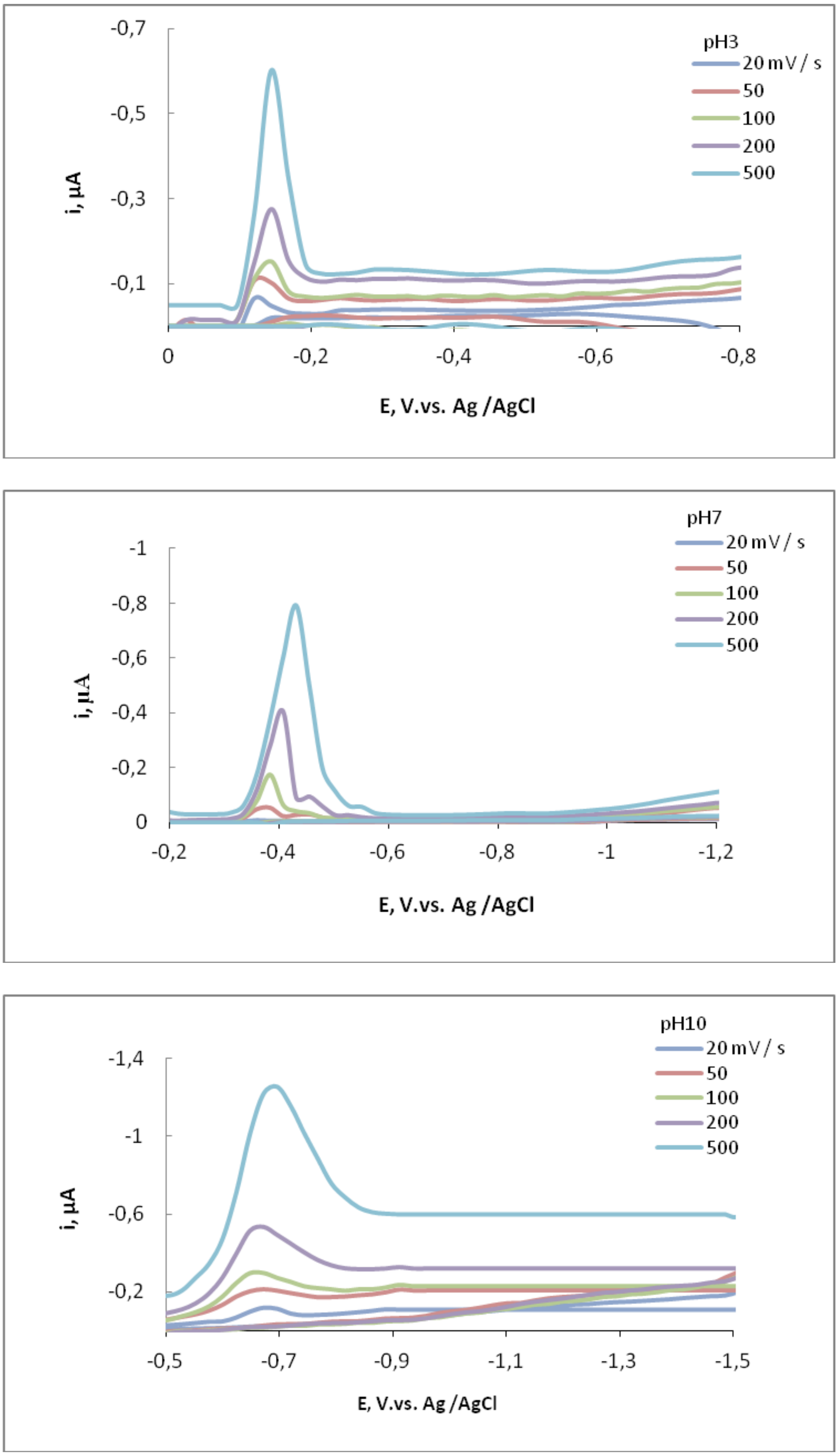


Figure 2. Cyclic voltammograms of $1\text{x}10^{4}$ M of pyridine azo compound (II) in B-R buffer solutions of different pH values containing 20% (v/v) ethanol

The cyclic voltammetry of azo compounds (I-IV) was measured in buffer solutions of different pH values containing 20% (v/v) ethanol**.** The voltammograms were recorded at different scan rates (20 –500 mV/s).

As shown in Fig. 2 (as a typical example), a single cathodic peak was observed for all pyridine azo compounds. The absence of any peaks in the reverse scan (anodic direction) for all the voltammograms confirmed the irreversibility of the reduction process of these compounds. The peak potential (E_p) shifts to more negative values on increasing the pH of the solution.

On plotting the peak current (i_p) as a function of the square root of sweep rate $(v)^{1/2}$ according to the following equation [46]:

$$i_P = 2.69\times10^5 n^{3/2} A C_o v^{1/2} D_o^{1/2}$$

linear relations were obtained which deviated from the origin**,** confirming that the reduction process is mainly controlled by diffusion with some adsorption contribution. The values of the transfer coefficient (α) were determined using Galus equation [47]:

$$E_p = -1.14(RT/\alpha n_a F)\ln(k^o_{f,h}/D^{1/2}) - RT/2\alpha n_a F\ln(\alpha n_a v),$$

which relates the values of E_p and αn_a. The plots of E_p versus lnv (logarithm of sweep rate) were straight lines, from these slopes; α values were calculated and given in Table 2.

Table 2. Data of cyclic voltammetry of pyridine azo compounds (I-IV) in buffer solutions of different pH values at scan rate 100 mV/s

Comp.	pH	E_p (V)	δEp/ (lnv)	α	
				n_a= 1	n_a= 2
I	3.0	0.18	0.014	0.84	0.42
	7.0	0.46	0.01	1.18	0.59
	10.0	0.65	0.012	0.98	0.49
II	3.0	0.16	0.01	1.18	0.59
	7.0	0.42	0.015	0.79	0.40
	10	0.62	0.02	0.59	0.30
III	3.0	0.14	0.01	1.18	0.59
	7.0	0.38	0.13	0.9	0.45
	10.0	0.61	0.01	1.18	0.59
IV	3.0	0.20	0.01	1.18	0.59
	7.0	0.52	0.014	0.84	0.42
	10.0	0.70	0.012	0.98	0.49

It was found that the most probable values of (α) were obtained at n_a = 1.0 or 2.0 depending on the type of the substituent and the pH of the electrolysis solution. From the data given in Tables 1 and 2, it is important to notice that the results of DC-polarography are agreed with those of cyclic voltammetry.

3.1.3. Differential pulse polarographic measurements

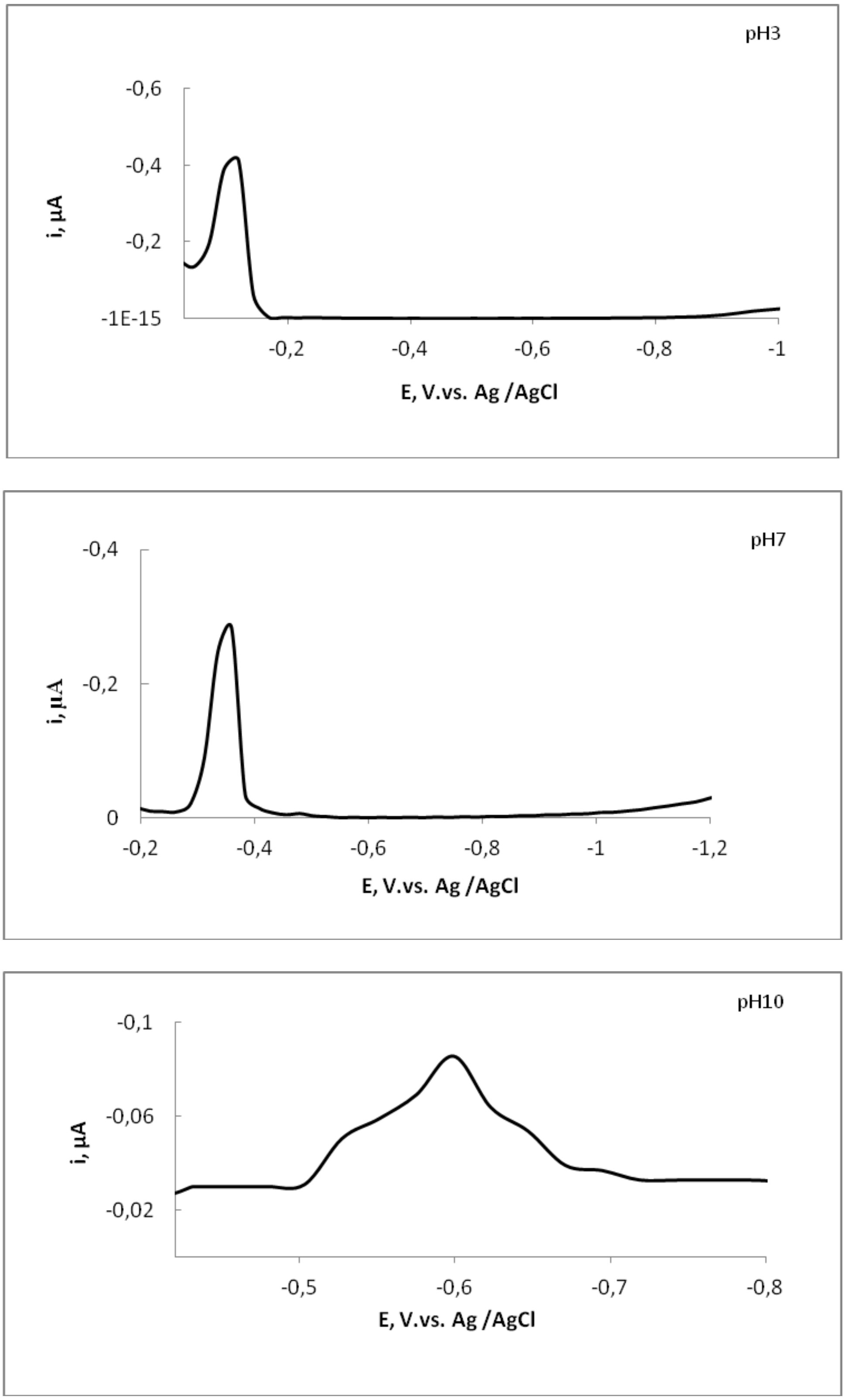


Figure 3. DP polarogram of $1x10^{4}$ M of pyridine azo compound (II) in B-R buffer solutions of different pH values containing 20% (v/v) ethanol

The differential pulse polarographic of azo compounds (I-IV) was investigated in B.R. buffer solutions of different pH values containing 20% (v/v) ethanol. The DP-polarograms of all azo compounds (I-IV) showed a single dp- polarographic peak in all solutions. Fig. 3 represents the DP-polarograms of azo compound (II) as a typical example of this series. The results of the DPP measurements are in agreement with those obtained from DC and CV measurements.

3.1.4. Determination of the total number of electrons in the electrode reaction

The total number of electrons involved in the electrode reaction was determined using controlled potential electrolysis technique (coulometry) using a mercury pool cathode. The accumulated charge (Q) was taken from the digital coulometer at a potential corresponding to the limiting current of the polarographic wave. Applying the equation:

$Q = n\ Fw / M$

where w is the weight of the sample (in grams) and M its molecular weight, the values of (n) for the pyridine azo compounds (I-IV) was found to be 4 electrons for azo compounds I, III and IV and 8 electron for azo compound II (Table 3).

Table 3. Controlled potential electrolysis (coulometry) of pyridine azo compounds (I-IV) at different pH values.

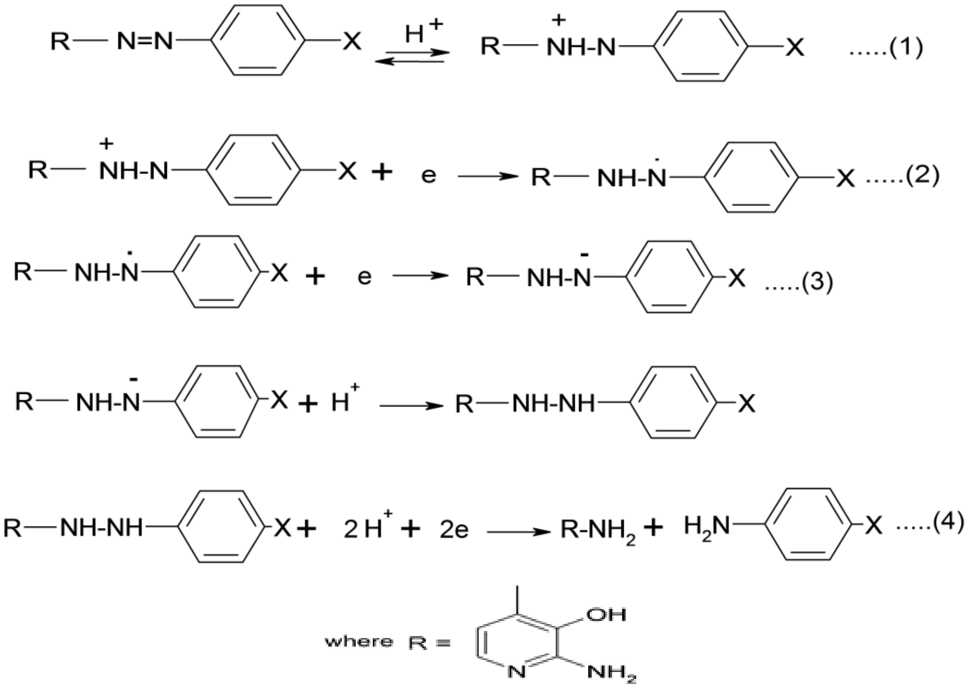
Compd.	Mol. Wt.	pH	Applied potential (v)	Weight of sample (g) $\times 10^{-4}$	Number of coulombs	Total number of electrons
I	214	3.0	-0.5	2.85	0.520	4.05 ≈ 4
		9.0	-1.0	2.85	0.500	4.01 ≈ 4
II	259	3.0	-0.5	2.59	0.757	7.85 ≈ 8
		9.0	-1.0	2.59	0.748	7.75 ≈ 8
III	258	3.0	-0.3	2.58	0.371	3.85 ≈ 4
		9.0	-0.8	2.58	0.357	3.70 ≈ 4
IV	244	3.0	-0.3	2.44	0.400	4.15 ≈ 4
		9.0	-0.8	2.44	0.381	3.95 ≈ 4

3.1.5. Mechanism of the electrode reaction

The data obtained from coulometric measurements for pyridine azo compounds (I, III & IV) revealed that the electro reduction process of these compound involved 4 electrons and 4 protons leading to the cleavage of the N=N center within the entire pH range and the corresponding amine (aniline, p-amino benzoic acid or p-anisidine) and 2-amino-3-hydroxypyridine are obtained, but for pyridine azo compound (II), 8 electrons and 8 protons are involved which represent the reduction of the nitro group via the uptake of 4 electrons and 4 protons and the corresponding hydroxylamine is obtained as well as the reduction of the azo group similar to azo compounds I II and IV. It is important to note that for pyridine azo compounds (II) the reduction of N=N center and NO_2 group occurs at the same potential, thus a single wave (8-electron step) is observed.

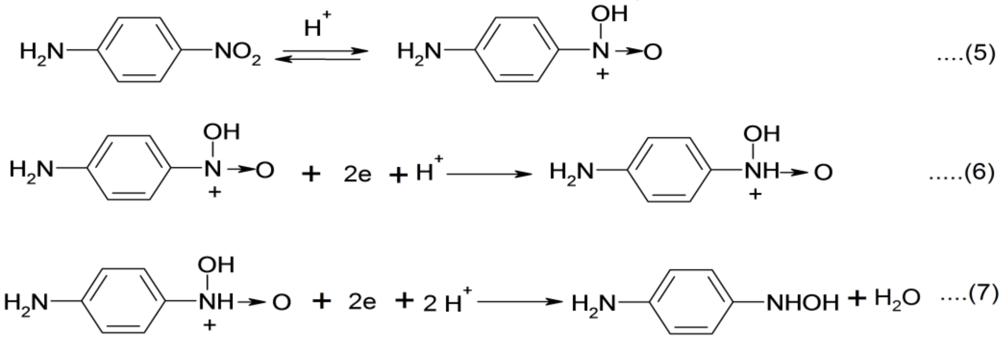
Based on the data of DC, CV and coulometry, the mechanism of the electrode reaction can be represented as follows:

a- Reduction of azo group



X = H (I), p-NO (II), p-COOH (III), p-OCH_3 (VI)

b- Reduction of nitro group:



3.1.6. Substituents effect:

The effect of substituents on the $E_{1/2}$ values of the polarographic waves of pyridine azo compounds (I-IV) was investigated in solutions of pH 4.0 and pH 9.0. The plots of $E_{1/2}$ as a function of Hammett substituent constant (σ_x) according to the following relationship [48]:

$E_{1/2\ (x)} - E_{1/2\ (H)} = p_\pi\ \sigma_x$, which gives linear correlations with slopes equal to p_π as shown in Fig. 4.

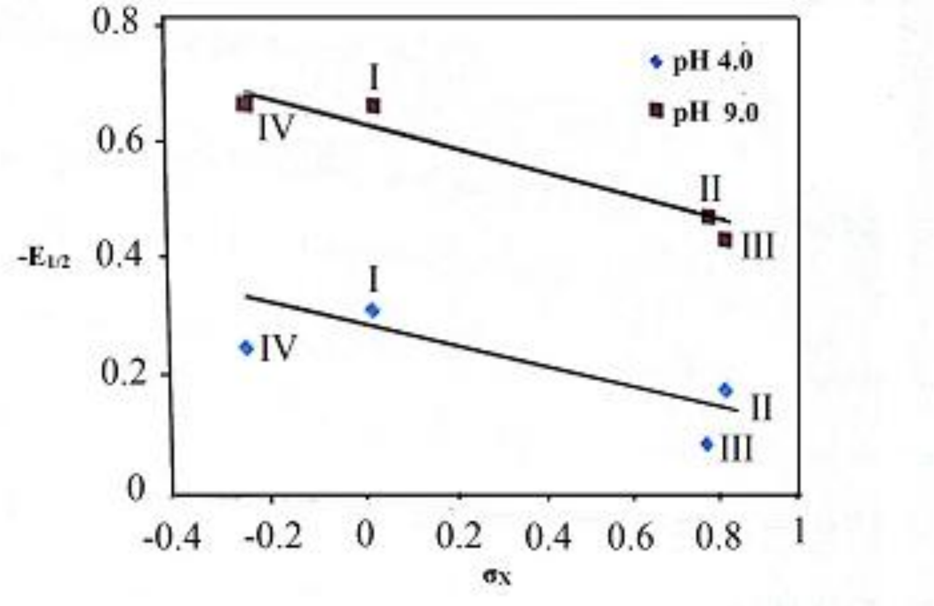


Figure 4. -$E_{1/2}$- σ_x plots of pyridine azo compounds(I-IV) at different pH values**.**

The values of σ_x are taken from the tabulation by Richie and Sagary [49]. The previous relation is valid only for both of p- and m-substituted benzonoid system.

The positive value of the slopes ($\rho_{\pi,R}$) amounting to 0.11 and 0.12 for azo compounds (I-IV) indicated that the reduction process of these azo compounds is corresponded to nucleophilic attack in the potential-determining step which supported the suggested mechanism represented in Scheme 1. The general trend of this study revealed that the compounds have withdrawing group (NO_2, COOH) are reduced at less negative potential compared to those containing electron-donating groups (OCH_3). This behavior may be explained by the fact that, electron-donating group increases electron cloud on the N=N center leading to retardation of the reduction process, whereas electron withdrawing groups (NO_2, COOH) delocalized the electron density on the N=N center, thus facilitate the reduction process.

3.2. Spectrophotometric studies

3.2.1. Electronic absorption spectra of the pyridine azo compounds

The absorption spectra of 1 x 10^{-4} M of azo compounds (I-IV) investigated in buffer solutions of varying pH (2-11) were recorded within the range 200-700 nm. Fig 5, represented the spectra of azo compound (II) as a typical example of this series. All the investigated compounds exhibited three bands; the first band (not shown) appeared at 230-250 nm is due to the local excitation of the transition of the aromatic moiety, while the second and third bands appeared within the range 275-490 nm are attributed to the charge transfer (C.T) interaction within the whole molecule. Also, a clear one or two isobestic points were observed indicating more than one species are present in equilibrium.

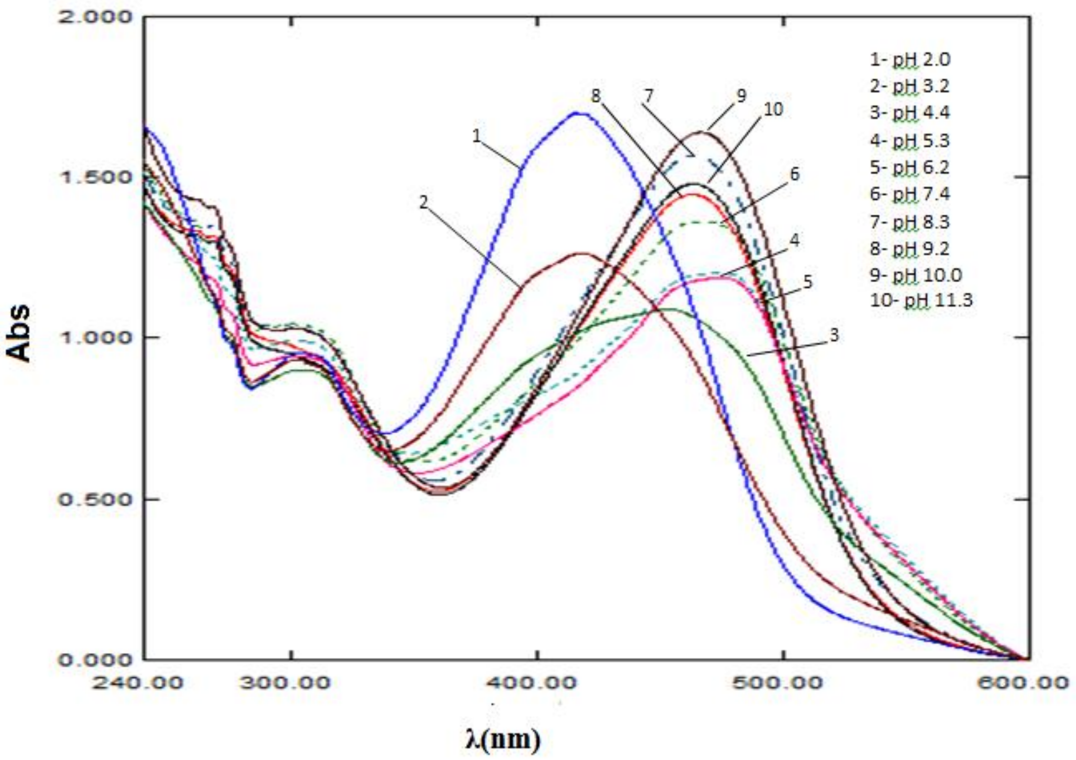


Figure 5. Absorption spectra of $1x10^4$ of pryridine azo compound (II) in B-R buffer solutions of different pH values containing 20% (v/v) ethanol

3.2.2. Determination of the dissociation constant values

To determine the dissociation constants of the azo compounds (I-IV) the following methods were used; the limiting absorbance method (LAM) [50], and the modified limiting absorbance method (MLAM) [51]. The measurements were applied at two different wavelengths for each compound.

In the (LAM), the dissociation constant values (pk$_{a)}$ were calculated using the relation [50]:

$pH = pk_a + \log (A / (A_{max} - A)$

The plots of pH vs log (A / A_{max} - A) gives linear correlations, from which the pk$_a$ values were obtained. The pk$_a$ values equal to the pH at which log (A /A_{max} - A$_{)}$ amounts to zero.

In the (MLAM), the pk$_a$ values in very dilute solutions were calculated using the relation [51]:

$pH = pk_a + \log (A- A_{min}) / (\log A_{max} - A)$

The plots of log (A- $A_{min)}$ / (A_{max} - A) vs. the pH gave linear correlations. At log (A- $A_{min)}$ / (log A_{max} - A) equal to zero the pk$_a$ values equal to the pH. The pk$_a$ values of azo compounds (I-IV) obtained from the two previous methods are given in Table (4).

The results indicated that two pk$_a$ values for each azo compounds (I, II & IV) were obtained; the first is due to the protonation of N-pyridine whereas the second is attributed to the dissociation of the hydroxyl group in the pyridine ring.

Table 4. Dissociation constants of pyridine azo compounds (I-IV) determined using spectrophotometric measurements.

Compound	λ(nm)	pk_a		
		LAM	MLAM	Mean value
I	290	3.7	3.5	3.6^{a}
		9.9	9.5	9.7^{b}
	400	3.1	3.5	3.3^{a}
		9.2	9.8	9.5^{b}
II	275	3.8	3.2	3.5^{a}
		10.6	8.6	9.6^{b}
	357	4.6	4.2	4.4^{a}
		9.4	10.0	9.7^{b}
III	273	3.8	3.2	3.5^{a}
		6.5	5.4	6.0^{c}
		10.6	10.0	10.3^{b}
	497	3.4	3.0	3.2^{a}
		6.3	5.6	6.0^{c}
		9.6	9.0	9.3^{b}
IV	302	3.0	4.0	3.5^{a}
		10.0	9.8	9.9^{b}
	463	3.0	4.3	3.7^{a}
		9.4	8.4	8.9^{b}

$^{c}pk_a{}^{3}$ $^{b}pk_a{}^{2}$ $^{a}pk_a{}^{1}$

However, for azo compound (III), three pk_a values were obtained; the third one represents the dissociation of the carboxylic group in solutions of moderate pH. The dissociation constant values of pyridine azo compounds (I-IV) are represented in Table (4).

3.3. Potentiometric studies (Proton-ligand dissociation constants)

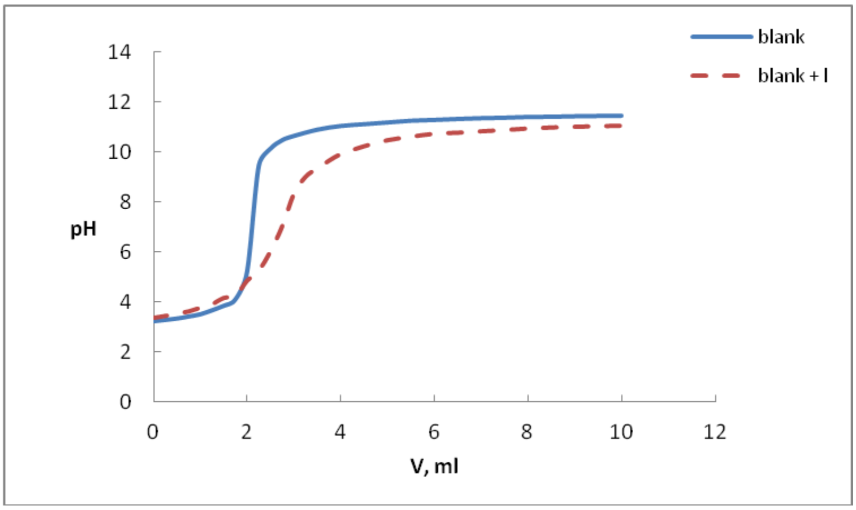


Figure 6. Potentiometric titration curves of pyridine azo compound (II) at 298 k and ionic strength 0.1M KCl

The acid dissociation constants of the pyridine azo compounds (I-IV) were calculated from the titration curves of the mineral acid of hydrochloric acid with sodium hydroxide solution in absence as well as in presence of azo substances (ligands). However, potentiometric titration of the ligands with sodium hydroxide in the presence of (10^{-3} M) hydrochloric acid was carried out at ionic strength (μ=0.1 M) adjusted by the addition of potassium chloride. Potentiometric titration curves of azo compounds (II) as a typical example are shown in Fig 6. Proton-ligand dissociation constants of these azo compounds were determined potentiometrically using the method of Irving and Rossitti [52, 53] as adapted by Fronaeus [54]. The average number of protons associated with the reagent molecules, $\bar{n}_A$ is determined at different pH values applying the Fronaeus equation [54]. Plotting $\bar{n}_A$ vs. pH gives the proton-ligand formation curves. Fig. 7 represents $\bar{n}_A$ –pH formation curve of azo compound (II) as a typical example of this series. The values of proton-ligand dissociation constants of the investigated compounds were calculated by interpolation at half $\bar{n}_A$ values, at $\bar{n}_A$ = 0.5, 1.5 and 2.5 and given in Table (5).

Table 5. Dissociation constants of pyridine azo compounds (I-IV) determined using potentiometric method

Compound	pk_a^1	pk_a^2
I	3.5	10.1
II	3.0	11.5
III	3.7	10.4
	6.6*	
IV	3.3	10.8

pk_a^3

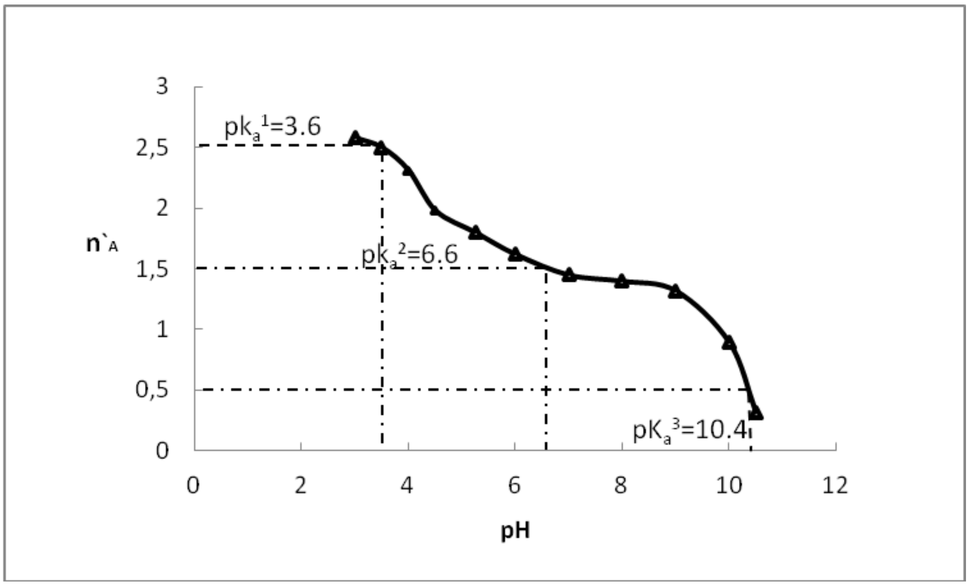


Figure 7. Formation curve of proton-ligand system at 298K and ionic strength 0.1M KCl for the stage the deprotonation stage of pyridine azo compound (II).

These values indicated that pyridine azo compounds (I, II & IV) have two dissociable protons (two pk$_a$ values). The second is due to dissociation of proton of phenolic OH group in the pyridine ring whereas the first is attributed to protonation of N-pyridine. However, for azo compound (III), three pk$_a$ values were observed, the first and second ones were explained as seen in the other azo compounds, whereas the third pk$_a$ value may be attributed to the dissociation of carboxylic group in the phenyl ring. It is important to noted that, the data obtained from potentometric measurements are satisfactory agreed with those obtained from spectrophotometric ones.

4. CONCLUSION

The presents study includes the electro-reduction of four azo compounds derived from 2-amino-3-hydroxypyridine derivative using different electrochemical techniques (DC, DPP & CV). The electro-reduction process of all azo compounds involves a single irreversible step representing the cleavage of the N=N center through the uptake of four electrons and the corresponding amine is obtained. For nitro derivative eight electrons are involved due the reduction of nitro group to the hydroxyl amine stage. The electrode reaction mechanism follows the sequence H^+, e, e, H^+. The total number of electrons involved in the reduction process was determined using controlled potential coulometry. The effect of substituents on the reduction process revealed that compounds have electron-withdrawing groups (NO_2, COOH) are reduced at less negative potentials while that has electron donating one (OCH_3) is reduced at more negative potential. The dissociation constants value (pk$_a$) of these compounds were determined spectrophotometrically and potentiometrically at room temperature. The results obtained from the two methods show satisfactory agreement.

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