Electroanalytical Studies on Some Hydroxyazopyrazolopyridine Compounds

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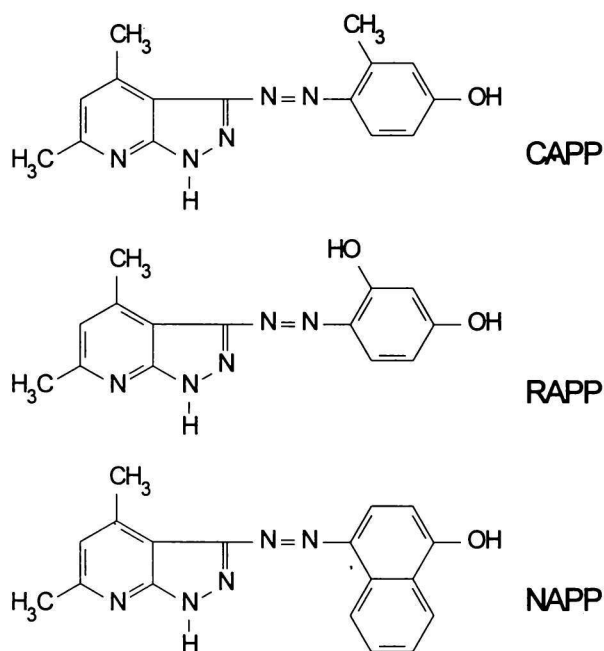*Department of Chemistry, Faculty of Science, South Valley University, Qena, Egypt*

Protonation constants of some azo compounds were determined using the pH-metric and polarographic techniques. Also the polarographic behaviour was examined to throw some light on the reduction process of the studied compounds. The reduction process occurs through an irreversible 4-electron step corresponding to the reduction of the N=N centre. The resulted reduction peaks were used to quantify the mentioned compounds using cathodic stripping voltammetric technique.

The azo compounds are a special class of organic compounds used as dyes, metallochrome indicators or histological stains [1]. Azo compounds containing the pyrazolopyridine moiety are of particular interest due to their biological and therapeutical importance [2, 3]. This is why the protonation constants of these compounds have been studied by many authors [1, 4, 5]. The present study describes the determination of the protonation constants of 3-[(4-hydroxy-2-methylphenyl)azo]-4,6-dimethylpyrazolo[3,4-b]pyridine (CAPP), 3-[(2,4-dihydroxyphenyl)azo]-4,6-dimethylpyrazolo[3,4-b]pyridine (RAPP), and 3-[(4-hydroxynaphthyl)azo]-4,6-dimethylpyrazolo[3,4-b]pyridine (NAPP) using pH-metric measurements. The polarographic method was used to study the reduction mechanism of these compounds, while the cathodic stripping voltammetric technique was used to study analytically the mentioned compounds. This technique was applied successfully in the determination of several organic compounds [6—8]. It is based on the preconcentration of the studied compounds to the electrode surface followed by scanning to negative direction.

Scheme 1

EXPERIMENTAL

An Orion research 601 A digital ionalyzer pH-meter was used for the pH-metric measurements. The sampled DC and linear sweep voltammetry were done using EG&G princeton applied research (potentiostate model 263 with Electrochemistry system 250/270 version 4.0). The equipment was connected with 303A cell. Sargent—Welch model 3001 was used to carry the effect of mercury height on the diffusion currents of the polarographic waves. Hanging mercury drop electrode was used as a working electrode for stripping and cyclic voltammetric measurements. Dropping mercury electrode was used as a working electrode for DC polarography. Pt wire and Ag/AgCl were as auxiliary and reference electrodes, respectively, for all techniques.

Hydroxyphenylazopyrazolopyridine used in this work was prepared as reported previously [9, 10]. Stock solutions ($c = 10^{-3}$ mol dm^{-3}) of the studied compounds were prepared by dissolving the appropriate amounts of the solids in the required volumes of

ethanol—water mixture to give concentration of 10^{-3} mol dm^{-3}. All other reagents were of anal. grade.

RESULTS AND DISCUSSION

The pH-metric measurements were carried out by titrating 50 cm^3 of the following solutions against 0.02 mol dm^{-3} carbonate-free sodium hydroxide.

a) 0.002 M-HNO$_3$ + 0.1 M-NaNO$_3$
b) *a* + 0.002 M ligand (CAPP, RAPP or NAPP)

The obtained data were drawn as a relation between pH and the volume of added NaOH to find the titration curves.

The protonation constants of the ligands CAPP, NAPP or RAPP calculated according to *Irving* and *Rossotti* [11] were found to be 9.28, 8.45, and 7.55, respectively. These values agree very well with the reported data [1]. The $\bar{n}_A$—pH plots for the studied ligands ($\bar{n}_A$ is the average number of protons attached per ligand) are shown in Fig. 1. The values of $\bar{n}_A$ were calculated at different pH values using the following equation [11]

$$\bar{n}_A = Y - \frac{(V_2 - V_1)(c_0' + c_o)}{(V_o + V_1)c_L}$$

where Y is the number of displaceable hydrogen atoms per ligand molecules, c_o and c_L are the initial concentrations of the mineral acid and the ligand, respectively, V_1 and V_2 are the volumes required at given pH for the titration of the acid and the ligand, respectively, V_o is the original volume, and c_0' is the concentration normality of the alkali.
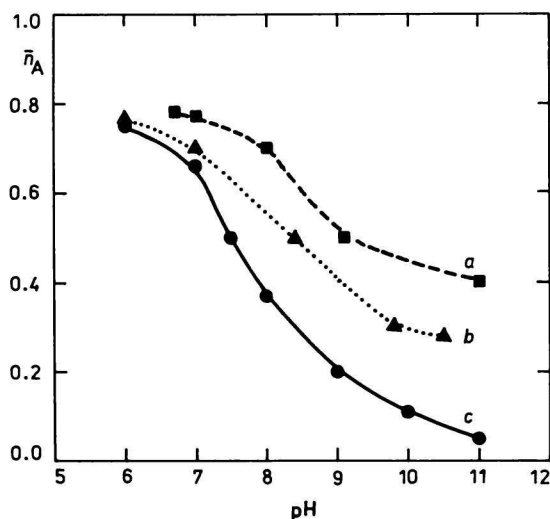

Fig. 1. Proton—ligand formation curves for: *a*) CAPP, *b*) NAPP, *c*) RAPP.

The measured pH values in the ethanol—water media were corrected according to the following equation

$$pH^* = pH(R) - \delta$$

where pH* is the corrected value and pH(R) is the pH-meter reading obtained in the water—ethanol mixture. Values of δ were determined as recommended by *Douheret* [12, 13]. The resulting pH values are plotted against $\bar{n}_A$ (Fig. 1) and the method of *Irving—Rossotti* [11] was applied to evaluate log K^H for the above-mentioned ligands. The obtained values are listed in Table 1.

Table 1. Protonation Constants of CAPP, NAPP, and RAPP

Ligand	Present paper	Reported values [1]
CAPP	9.28	9.05
NAPP	8.45	8.33
RAPP	7.55	7.50

DC Polarography

A series of solutions containing 5×10^{-5} mol dm^{-3} azo compounds in an electrolyte universal buffer was studied at different pH values using DC technique. The recorded polarograms exhibit a single wave corresponding to the reduction of the N=N centre. The reduction wave of the compound RAPP splits into two waves of unequal heights, the i_d of the second wave increases while the first wave decreases on increasing pH (from 7 to 11) of the electrolysis solution, confirming an acid-base equilibrium [14]. The $E_{1/2}$'s were shifted to more negative values on increasing pH.

Cyclic voltammetric measurements of the mentioned compounds were done. The voltammograms of all compounds exhibit one peak in the cathodic scan which represents the reduction of the N=N centre. Four electrons were consumed in the reduction process and splitting in the molecules occurred in this place. This result was confirmed by controlled potential coulometry using a mercury pool cathode.

The variation of the peak potential E_p with the scan rate (Fig. 2) reveals that the reduction process is irreversible. The nature of the reduction process is controlled mainly by diffusion, in which the plot of i_p *vs.* the square root of scan rate gave a straight line passing through the origin [15]. This result was confirmed from the effect of mercury height on the limiting current of the polarographic wave.

Analytical Applications

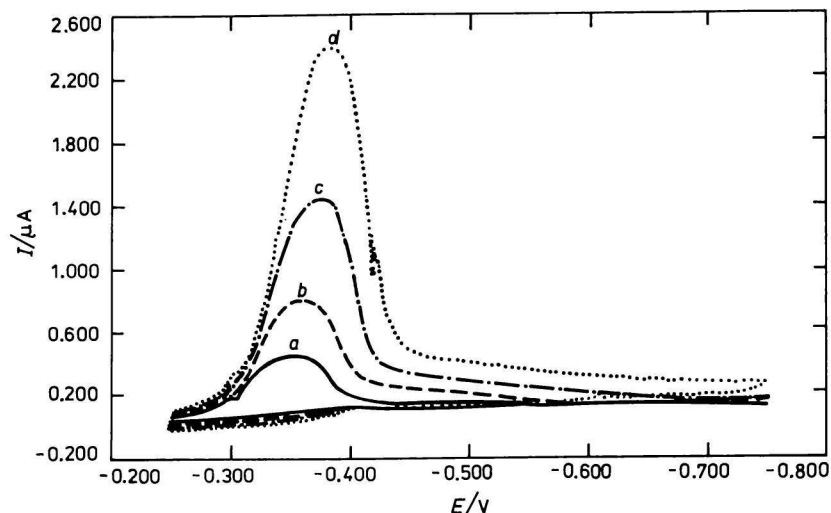The preliminary experiments showed that the peak current response increased with increasing preconcen-

Fig. 2. Cyclic voltammograms of 10^{-5} M-RAPP in NaClO$_4$ (pH 5.5). Scan rates/(mV s^{-1}): a) 20, b) 50, c) 100, d) 200.

tration time or concentration of the investigated compounds. So the reduction peaks of the compounds RAPP, CAPP, and NAPP were used to determine these compounds in a low level using cathodic stripping voltammetry. The repetitive cyclic voltammograms of the studied compounds of $c = 1 \times 10^{-5}$ mol dm^{-3} using the scan rate of 150 mV s^{-1} showed a decrease in the peak current of the second and third cycle. This may be due to the rapid desorption of the studied compounds. A linear scan voltammetric technique with a scan rate up to 250 mV s^{-1} is preferable for such compounds.

Determination of RAPP

For the compound RAPP, the reduction peak of $c = 1 \times 10^{-8}$ mol dm^{-3} was observed at -0.37 V in an electrolyte sodium perchlorate (pH 5.5) with a height of 82 nA after 240 s preconcentration time. The peak response was characterized with respect to the supporting electrolyte, pH, preconcentration potential, scan rate, deposition time, and other variables.

The effect of supporting electrolyte was examined. Acetate, borax, phosphate, and sodium perchlorate were tested. It was found that the sodium perchlorate ($c = 0.1$ mol dm^{-3}) gave the best response.

The effect of scan rate was studied over the range 20—250 mV s^{-1}. It was observed that the peak height increased with increasing the scan rate up to 200 mV s^{-1}. After a broadened peak was obtained, 200 mV s^{-1} scan rate was used for further work.

The effect of accumulation potential was studied in the range from +0.1 to -0.1 V. The best peak current was obtained on applying a potential of 0.0 V.

The optimum conditions for the analytical purpose were unbuffered NaClO$_4$ (pH 5.5), accumulation potential 0.0 V, and scan rate of 200 mV s^{-1}. Under these conditions, the calibration plot showed a linear
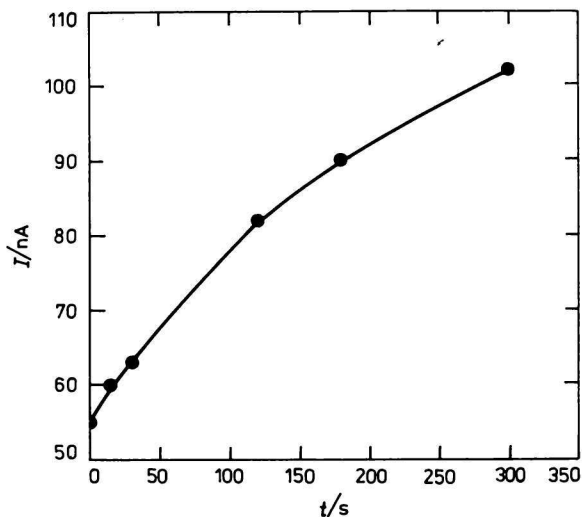

Fig. 3. Current—time graph for 10^{-8} M-CAPP in borate buffer (pH 7.3), scan rate = 100 mV s^{-1}.

behaviour over the concentration range 1×10^{-8}—6 $\times 10^{-7}$ mol dm^{-3} with variation coefficient of 0.9987.

A detection limit of 1×10^{-9} mol dm^{-3} RAPP was achieved using the described technique.

Determination of CAPP

CAPP of the concentration of 1×10^{-8} mol dm^{-3} was examined in the presence of 0.025 M buffer borate of pH 7.3 using cathodic linear sweep voltammetric technique. A well defined peak was observed at -0.35 V. The conditions which may affect the peak response were optimized. The resulting i_p was plotted vs. deposition time (Fig. 3). From the graph one can observe that the peak current increases linearly with time up to 120 s, then a deviation from the linearity was observed. The effect of CAPP concentration

on the peak current was studied over the 5×10^{-9}—5×10^{-7} mol dm^{-3} range in an electrolyte borate buffer and the other used conditions are illustrated in Fig. 3. The collected i_p at different CAPP concentrations are plotted against [CAPP]. The graph (not shown) indicates a deviation from the linearity at the concentration higher than 3×10^{-7} mol dm^{-3}.

The study indicated that CAPP of the concentration of 5×10^{-9} mol dm^{-3} can be detected using the above-mentioned conditions.

Determination of NAPP

The cathodic linear sweep voltammetric measurements showed that the peak current of NAPP increases with increasing preconcentration time and consequently, the reduction peak ($E_p = -0.42$ V) could be used to determine this compound in a low level. To optimize the analytical conditions, NAPP of the concentration of 1×10^{-8} mol dm^{-3} was studied in the presence of different supporting electrolyte and also the effect of the solution pH was investigated. The resulting peak current showed that universal buffer (pH 6.6) gave the best response. The effect of accumulation potential as an effective parameter on the accumulated quantity was studied and a potential of 0.0 V was selected for further work.

A linear dependence of i_p on [NAPP] was observed over the range 1×10^{-8}—6×10^{-7} mol dm^{-3} with correlation coefficient of 0.9987. The studied compounds could be determined up to 9×10^{-10} mol dm^{-3}.

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