voltametric studies of some azo compounds and schiffbases and their corrosion prevention

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The present thesis includes three chapters, introduction,experimental and results and discussion.In the first chapter, a literature survey of the previous studieson the polarographic behaviour of both azo dyes and Schiff bases. Itincludes also the potentiometric studies on azo-compounds andSchiff bases and their complexes with different metal ions. Also thestudies on corrosion inhibition of carbon steel are included.The experimental part (chapter II) includes preparation of theazo-dye and Schiff bases compounds derived from 2-amino-3-hydroxy pyridine, instruments and solutions which were used for themeasurements using different techniques.Chapter (III) includes the results and discussion and itconsists of three parts:Part (A):It includes the results and data obtained from polarographicstudies of the azo dye and Schiff base compounds in aqueous buffersolutions of different pH values (2-12) containing 10% (v/v) ethanolfor azo-dyes (first series) and Schiff bases (second series).The polarographic behaviour of azo compounds of the firstseries (Ia-e) and Schiff bases of second series (IIa-e) exhibited a singlepolarographic wave within the entire pH compounds Ib and Ie. Generally, the limiting current (il) of thereduction waves of azo compounds is considered to be almost pHindependent,revealing that the total number of electrons consumedin the reduction process is the same in both acidic and alkalinesolutions. But for Schiff base, the wave height in acidic solutions isalmost twice that in alkaline ones, i.e., the reduction process ofSchiff bases involve 4 electrons in acid solutions and 2 electrons inalkaline medium.On the other hand, the half-wave potential of the waves getshifted to more negative potentials on increasing pH of theelectrolysis medium denoting that hydrogen ions are consumed inthe reduction process. The plots of the half-wave potential (E1/2) vs.pH for all the compounds give satisfactory linear correlationsconsisting of one segment except Ie consist of two segments, thebreaks occurred at pH = 5.31.The effect of mercury height on the limiting current denotedthat the reduction process of all compounds is mainly diffusioncontrolledwith some adsorption contribution, since the values of theexponent x in the relation (il = KhX) equal to 0.4-0.8 for first series(Ia-e) and 0.35-0.79 for the second series (IIa-e).Logarithmic analysis of the polarographic waves using thefundamental equation of polarography confirmed the irreversiblenature of the waves. The plots of Ed.e. vs. log [i/(id-i)] give linearcorrelations. from the slopes of these plots, values of the transfercoefficient (□) were calculated and found to be less than unity atna = 2. The number of protons (ZH+) participating in the raterange determining step was determined from slopes

of logarithmic analysisand those of E1/2-pH curves and found to be one for all depolarizersin both acidic and alkaline solutions, i.e. the rate-determining stepinvolved two electrons (na = 2.0) and one proton (ZH+ = 1.0).The kinetic parameters of the electrode reaction; the rateconstant (Kof,h) and the activation energy (□G*) were evaluated fromDC-polarographic measurements. The obtained results revealed thatthe values of Kof,h are found to be decreased and subsequently theactivation energy (□G*) increased on increasing pH of theelectrolysis medium, which denoted the more irreversible nature ofreduction process on going from acidic to alkaline part of the pHrange.Effect of substituents on E1/2 was considered, and the plots ofE1/2 as a function of Hammett substituent constant (□x) at pH values5.0 and 9.0 showed linear correlations with positive slopes.Generally, it was found that the electron withdrawing group (m-NO2) shifts the E1/2 to less negative value i.e., accelerates thereduction process, whereas electron-donating groups (p-CH3, p-OCH3, p-N(CH3)3) shift the E1/2 to more negative values, i.e. retardsthe reduction process.The diffusion coefficient values of the depolarizers of series I& II and the total number of electrons consumed in the overallreduction process were determined using Ilkovic equation. Theresults obtained revealed that the reduction process of the azocompounds (Ia-e) consumed 4 electrons / depolarizer molecule,except for