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Electrochemical studies of certain nitro substituted pyrazolin-5-ones

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Abstract. The polarographic behavior of 1-(Toluenyl sulfonyl)-3-amino-4-(2'-nitro aryl hydrazono)-2-pyrazolin-5-one and 1-(Toluenyl sulfonyl)-3-amino-4-(4'-nitro aryl hydrazono)-2-pyrazolin-5-one is investigated in the acidic as well as in basic media. The compounds gave two well defined, diffusion controlled, irreversible waves in Britton-Robinson buffers of pH range 1.0–7.0. In alkaline medium three well defined, diffusion controlled and irreversible waves were obtained. Effect of various solvents, cations and surfactants on the reduction is presented. The effect of substituent and its correlation with the Hammett substituent constant (δ) is detailed. Based on the results, a detailed reduction mechanism in acidic as well as basic media is proposed.

Keywords: Pyrazolin-5-ones; Polarographic behavior, Effect of various parameters, Reduction mechanism.

1. Introduction

Pyrazoles refer to the class of heterocyclic compounds containing a five membered aromatic ring composed of three carbon atoms and two nitrogen atoms in adjacent ring positions. Pyrazoles have an extensive history of application in agrochemical and pharmaceutical industry for varied purposes.

Pyrazole derivatives have been reported to demonstrate a broad spectrum biological activity including antibacterial [1], antimicrobial [2], antifungal [3], antitumor [4], analgesic [5], antiinflammatory [6], anticonvulsant [7], antipyretic [8], enzyme inhibitory activities [9].

Due to their ever growing applications, pyrazoles have received considerable interest in the field of therapeutics, therefore constitutes the important target structures in the pharmaceutical industry. Pyrazoles have immense medicinal and biological significance and hence knowledge of the effect of surfactants on their redox behavior at the solution mercury interface may prove very useful from the physiological point of view [10].

Keeping in view their wide spread applications, study of electrochemical reactions involving oxidation-reduction are the most important because they are useful for enlighting the metabolic pathway of the drug containing pyrazoles.

2. Experimental

DC recording polarograph manufactured by ELICO Private Limited, Hyderabad, India was used for polarographic studies. pH measurements were made using pH meter Model L1-10, ELICO Private Limited, Hyderabad, India.
All chemicals and solvents used were of analytical reagent grade procured from Merck, India. Double distilled water was used for the preparation of solutions.

2.1. Synthesis pyrazolin-5-ones

A mixture of appropriate diazonium cyano ester and toluene sulfonyl hydrazide in ethanol was refluxed for six hours and cooled. The crystalline solid separated was filtered, washed with water, dried and recrystalised from dimethylformamide (1:1). The physical characteristics of compounds synthesized are presented in the **Table 1**.

Table 1: Physical characteristics of compounds

S.No.	Substituent (-G)	Color	Melting point (^oC)
I	2'-NO_2	Orange	109-110
II	4'-NO_2	Orange	134-135

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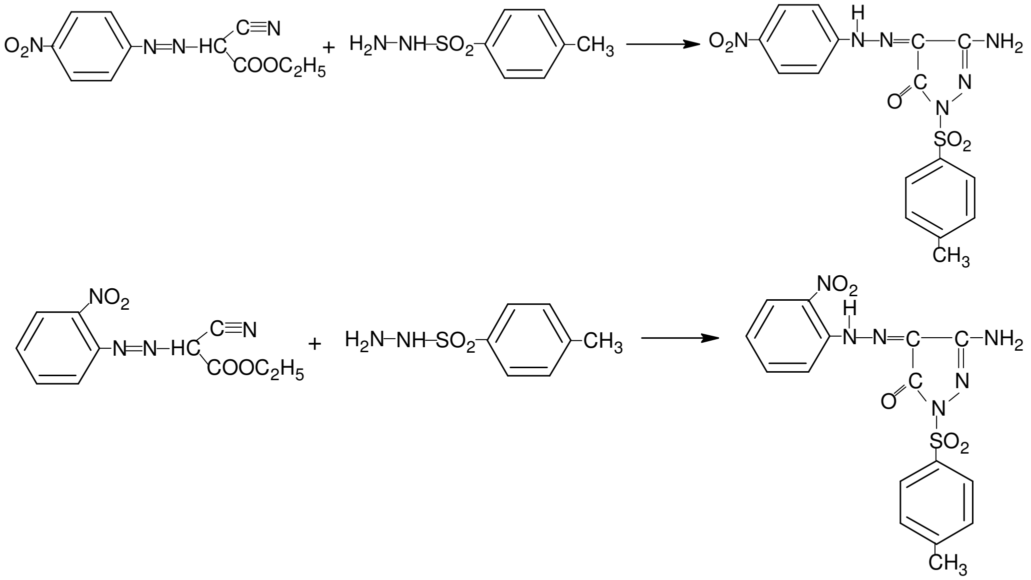


2.2. General experimental procedure

20 mL of buffer solution of required pH, 5 mL of pyrazolin-5-one (1×10^{-2} M) and 20 mL of dimethylformamide were taken into the polarographic cell. The solution was made to a total volume of 50 mL with distilled water. Polarograms were recorded after deaeration with nitrogen gas.

3. Results and Discussions

The polarographic behaviour of 1-(Toluenyl sulfonyl)-3-amino-4-(2' and 4' nitro substituted aryl hydrazono)-2-pyrazolin-5-ones (I and II) was investigated in 40% v/v dimethylformamide in Britton-Robinson buffers of pH 1.1-10.1.

3.1. Involvement of protons in the reduction process

The compounds (I and II) exhibit two well-defined waves in the pH range 1.1 - 7.1 and three waves in the pH range 8.1 - 10.1. The half-wave potential of the first and second waves observed in acidic medium increases with increase in pH where as it remains constants in alkaline medium. The $E_{1/2}$ - pH plots are shown in the **Fig. 1(A and B).**

The fact that the half-wave potential values did not vary with pH in alkaline medium, suggests that the protons were involved in the reduction process. The fractional value of P presented in the **Table 2** in different pH media suggests the heterogeneous proton transfer in the reduction process [11]. The height of the two waves observed in the acidic medium decreases with the increase in pH where as it remains constant in the alkaline medium. The decrease in wave height with increase of pH in acidic medium indicates that the reduction process was controlled by the rate of proton transfer. $-E_{1/2}$– wave height plots are shown in the **Fig. 2(A and B).**

3.2. Diffusion controlled nature of the wave

A plot drawn between wave height 'H' and square root of mercury column height '$h^{1/2}$' is shown in the **Fig. 3.** Linear dependence of H on $h^{1/2}$ indicates the diffusion controlled nature of the wave. This fact was further confirmed by the linear relationship between the wave height and the concentration of pyrazolin-5-one. The wave height - concentration plots are shown in the **Fig. 4**.

Table 2: Polarographic characteristics and kinetic parameters of pyrazolin-5-ones (1×10^{-3} M); Medium: Aqueous dimethylformamide (40% v/v)

-G	pH	$\Delta E_{1/2}/\Delta pH$ (mV)		αn_a		Number of protons (P)		$D \times 10^2$ $m^2\ sec^{-1}$		$I^* \times 10^3$		$K^{\circ}_{f,h}$ $m\ sec^{-1}$		ΔG^* Kj $mole^{-1}$	
		I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave
2'-NO_2	1.1	0.0926	0.0886	0.42	0.31	0.657	0.465	3.578	0.880	6.889	2.278	2.713×10^{-4}	1.013×10^{-5}	16.627	20.172
	2.1			0.42	0.31	0.657	0.465	3.295	0.796	6.611	2.167	1.149×10^{-4}	2.883×10^{-6}	17.556	21.546
	3.1			0.42	0.31	0.657	0.465	3.131	0.756	6.444	2.111	4.201×10^{-5}	1.362×10^{-6}	18.649	22.366
	4.1			0.42	0.31	0.657	0.465	2.971	0.717	6.278	2.056	1.107×10^{-5}	5.699×10^{-7}	20.093	23.308
	5.1			0.35	0.24	0.548	0.360	2.816	0.678	6.111	2.000	3.237×10^{-6}	5.439×10^{-7}	21.424	23.358
	6.1			0.35	0.24	0.548	0.360	2.664	0.641	5.944	1.944	1.058×10^{-6}	2.078×10^{-7}	22.638	24.400
	7.1			0.35	0.24	0.548	0.360	2.468	0.605	5.722	1.889	2.609×10^{-7}	7.223×10^{-8}	24.153	25.547
	8.1			0.24	0.15	0.376	0.225	1.783	0.382	4.722	1.500	3.474×10^{-7}	1.388×10^{-7}	23.844	24.840
	9.1			0.24	0.15	0.376	0.225	1.783	0.382	4.722	1.500	3.474×10^{-7}	1.388×10^{-7}	23.844	24.840
	10.1			0.24	0.15	0.376	0.225	1.783	0.382	4.722	1.500	3.474×10^{-7}	1.388×10^{-7}	23.844	24.840
4'-NO_2	1.1	0.0965	0.0916	0.42	0.31	0.685	0.480	1.344	1.362	4.222	2.833	1.412×10^{-4}	1.594×10^{-5}	17.334	19.699
	2.1			0.42	0.31	0.685	0.480	1.140	1.108	3.889	2.556	4.876×10^{-5}	4.956×10^{-6}	18.485	20.964
	3.1			0.42	0.31	0.685	0.480	0.953	0.968	3.555	2.389	1.671×10^{-5}	2.214×10^{-6}	19.645	21.838
	4.1			0.42	0.31	0.685	0.480	0.783	0.796	3.222	2.167	3.478×10^{-6}	7.645×10^{-7}	21.349	22.990
	5.1			0.34	0.24	0.555	0.372	0.582	0.570	2.778	1.833	9.007×10^{-7}	4.987×10^{-7}	22.810	23.454
	6.1			0.34	0.24	0.555	0.372	0.536	0.536	2.667	1.778	3.422×10^{-7}	1.435×10^{-7}	23.860	24.802
	7.1			0.34	0.24	0.555	0.372	0.430	0.440	2.389	1.611	8.160×10^{-8}	6.160×10^{-7}	25.413	25.719
	8.1			0.24	0.15	0.392	0.232	0.880	0.382	2.278	1.500	1.526×10^{-7}	1.560×10^{-7}	24.735	24.710
	9.1			0.24	0.15	0.392	0.232	0.880	0.382	2.278	1.500	1.526×10^{-7}	1.560×10^{-7}	24.735	24.710
	10.1			0.24	0.15	0.392	0.232	0.880	0.382	2.278	1.500	1.526×10^{-7}	1.560×10^{-7}	24.735	24.710

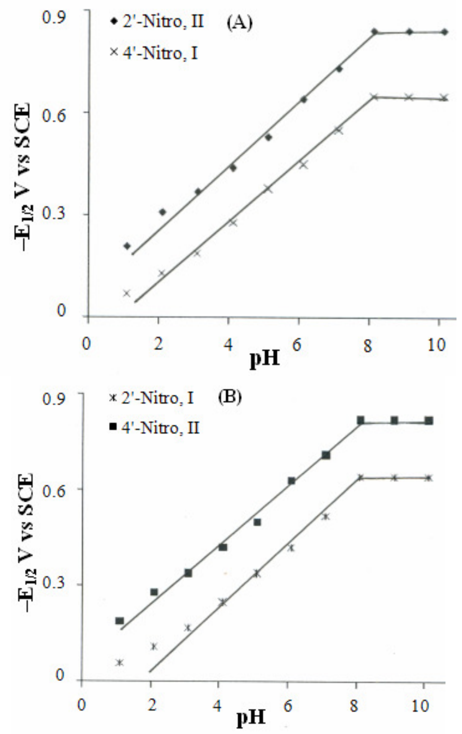


Fig. 1(A and B). Effect of pH on half wave potential. [pyrazolin-5-one] = 1×10^{-3} M; Medium: Aqueous dimethylformamide (40% v/v)

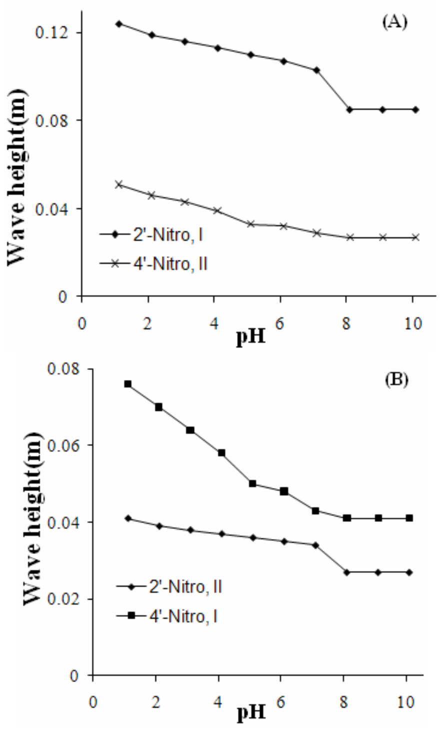


Fig. 2(A and B). Effect of pH on wave height. [pyrazolin-5-one] = 1×10^{-3} M; Medium: Aqueous dimethylformamide (40% v/v)

3.3. Irreversible nature of the wave

The linear plots drawn between the -E_{dme} Vs log $\frac{\bar{i}}{\bar{i}_d - \bar{i}}$ (semi log plots) are shown in the **Fig. 5.** The non integer slope values (0.049, 0.051 and 0.048, 0.053 respectively for first and second waves) calculated from semi log plots were different from those expected for reversible reductions. This indicates the irreversible nature of the polarographic reduction. The trend of irreversibility increases with the increase in the pH of the medium.

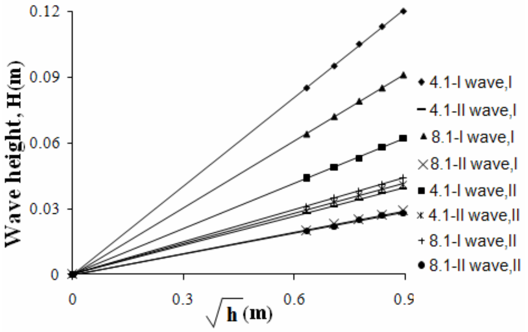


Fig. 3. Effect of mercury column height on wave height. [pyrazolin-5-one] = 1×10^{-3} M; Medium: Aqueous dimethylformamide (40% v/v)

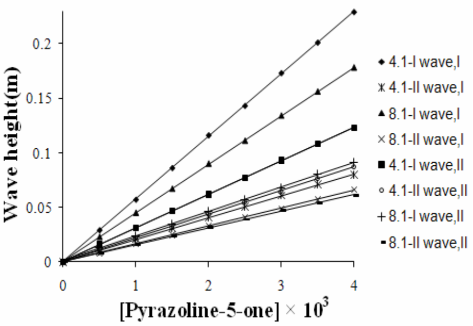


Fig. 4. Effect of concentration of pyrazolone-5-one on wave height. Medium: Aqueous dimethylformamide (40% v/v)

The effect of temperature on the polarographic reduction of compounds I and II was studied at pH 4.1. The results are presented in the **Table 3.**

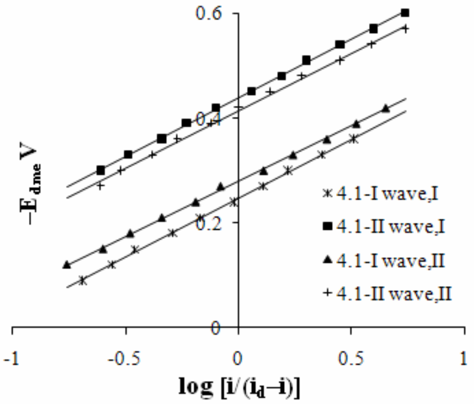


Fig. 5. Semi log plots of pyrazolone-5-one. [pyrazolin-5-one] = 1×10^{-3} M; Medium: Aqueous dimethylformamide (40% v/v)

Table 3: Effect of temperature on the polarographic characteristics of pyrazolin-5-ones (1×10^{-3} M); pH: 4.1; Medium: Aqueous dimethylformamide (40% v/v)

Temperature K	Half-wave potential, $-E_{1/2}$ V vs SCE		Wave height H (m)		Temperature Coefficient % deg^{-1}		αn_a		D x 10^2 $m^2\ sec^{-1}$	
	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave
2'-Nitro										
303	0.25	0.44	0.113	0.037	-	-	0.43	0.83	2.971	0.717
313	0.33	0.52	0.125	0.041	1.01	1.03	0.37	0.77	3.636	0.880
323	0.41	0.60	0.139	0.046	1.06	1.15	0.32	0.73	4.496	1.108
333	0.51	0.70	0.152	0.052	1.09	1.23	0.28	0.69	5.376	1.416
4'-Nitro										
303	0.28	0.42	0.058	0.039	-	-	0.42	0.81	0.783	0.796
313	0.36	0.50	0.065	0.044	1.14	1.21	0.36	0.75	0.983	1.013
323	0.44	0.58	0.073	0.05	1.16	1.28	0.31	0.71	1.240	1.309
333	0.54	0.68	0.082	0.057	1.16	1.31	0.27	0.67	1.565	1.701

Table 4: Kinetic and thermodynamic parameters of polarographic reduction of pyrazolin-5-ones (1 × 10^{-3} M); pH: 4.1; Medium : Aqueous dimethylformamide (40% v/v)

	Parameter	Meites – Israel Treatment				Oldham-Parry Treatment				Gaur-Bhargava Treatment			
		Temperature (K)				Temperature (K)				Temperature (K)			
		303	313	323	333	303	313	323	333	303	313	323	333
2'-nitro, First Wave	$K^{o}_{f,h} \times 10^{3}$ (m sec^{-1})	6.345	2.223	1.068	0.503	6.331	2.224	1.069	0.504	9.584	3.126	1.496	0.682
	ΔH^{*}_{p} (Kj $mole^{-1}$)	71.007	71.007	70.995	71.007	71.1787	71.179	71.179	71.179	65.528	65.528	65.528	65.528
	ΔG^{*} (Kj $mole^{-1}$)	23.433	25.392	27.062	28.804	23.4374	25.392	27.058	28.799	22.981	24.978	26.669	28.440
	ΔS^{*} (Kj $mole^{-1}$)	148.691	137.414	127.732	118.414	149.2435	137.962	128.276	118.941	132.102	121.235	111.984	103.051
4'-nitro, First Wave	$K^{o}_{f,h} \times 10^{3}$ (m sec^{-1})	1.998	0.786	0.418	0.220	1.998	0.787	0.418	0.220	2.965	1.120	0.577	0.295
	ΔH^{*}_{p} (Kj $mole^{-1}$)	53.941	53.941	53.941	53.941	54.0371	54.037	54.037	54.0371	53.501	53.510	53.510	53.510
	ΔG^{*} (Kj $mole^{-1}$)	24.697	26.569	28.155	29.796	24.7016	26.569	28.155	29.796	24.266	26.171	27.778	29.444
	ΔS^{*} (Kj $mole^{-1}$)	88.195	79.132	71.509	64.184	88.5004	79.442	71.8101	64.473	88.1945	79.023	71.342	63.945
2'-nitro, Second Wave	$K^{o}_{f,h} \times 10^{4}$ (m sec^{-1})	5.854	0.953	0.162	0.021	5.881	0.929	0.163	0.022	6.909	1.009	0.165	0.020
	ΔH^{*}_{p} (Kj $mole^{-1}$)	143.492	143.492	143.492	143.492	142.3952	142.395	142.395	142.395	149.754	149.754	149.754	149.754
	ΔG^{*} (Kj $mole^{-1}$)	31.085	34.162	37.322	40.906	31.0769	34.191	37.314	40.893	30.901	34.099	37.301	40.9893
	ΔS^{*} (Kj $mole^{-1}$)	362.663	340.979	320.376	299.747	359.0709	337.379	317.006	296.490	383.923	361.172	339.815	318.287
4'-nitro, Second Wave	$K^{o}_{f,h} \times 10^{4}$ (m sec^{-1})	13.530	2.206	0.405	0.0571	13.580	2.218	0.408	0.057	16.470	2.489	0.425	0.055
	ΔH^{*}_{p} (Kj $mole^{-1}$)	138.092	138.092	138.092	138.092	138.6654	138.665	138.665	138.665	146.364	146.364	146.364	146.364
	ΔG^{*} (Kj $mole^{-1}$)	30.169	33.211	36.251	39.738	30.1643	33.208	36.272	39.729	29.951	33.0778	36.196	39.775
	ΔS^{*} (Kj $mole^{-1}$)	347.865	326.763	306.976	287.038	349.7738	328.609	308.688	288.784	375.882	353.617	332.754	311.761

The compounds I and II exhibit two well-defined waves at all temperatures studied (303-333 K) in media of pH 4.1. The temperature coefficient values (1.01 - 1.31% deg^{-1}) were in good agreement with the values reported in the literature [12] for other similar compounds. The irreversible nature of the wave was further supported by the shift of half-wave potential towards more negative values with raise in temperature. Further the decrease in transfer coefficient value 'αn_a' (**Table 2**) with increase in temperature signifies the increasing irreversible nature with the increase in temperature.

The thermodynamic parameters, enthalpy of activation (ΔH^*), free energy of activation (ΔG^*) and entropy of activation (ΔS^*) and the heterogeneous formal rate constant ($K^{o}_{f,h}$) shown in the **Table 4** were evaluated using the procedures proposed by Meites-Israel [13], Oldham-Parry [14] and Gaur-Bhargava [15].

Following points may be inferred from the **Table 4.**

1) The decrease in $K^{\circ}_{f.h}$ with increase in temperature suggests that the electrode reaction is becoming increasingly irreversible with the raise in temperature.
2) The positive values of ΔH^* indicate that the process was endothermic.
3) The positive values of ΔG^* indicate that the process was not spontaneous.

The negative values of ΔS^* indicate that the process was entropically unfavorable. Further the negative ΔS^* values suggest that the activated state had more rigid structure than the initial state.

3.4. Millicoulometry

The number of electrons involved in the reduction of compounds I and II were found to be six and four for the first and second wave respectively in Britton-Robinson buffers of pH 4.1 containing 40% v/v dimethylformamide. Similarly three waves involving four, four and two electrons were noticed in media of pH 8.1. The millicoulometer of De Vries and Kroon [16] with the mercury pool cathode was employed to determine the value of 'n'. The results are presented in **Table 5.**

Based on the above discussions the mechanisms shown in **Schemes 1-4** were proposed for the polarographic reduction of compounds I and II.

3.5. Nature of the waves in acidic medium

The compounds I and II exhibit two waves in acidic medium. The compounds under investigation contain nitro ($-NO_2$) and hydrazono (>C=N-NH-) groups which are more susceptible for reduction at dropping mercury electrode under the given experimental conditions. Generally nitro group undergoes reduction at more negative potential than the azo group (-N=N-). However the latter in the hydrazono form (>C=N-NH-) undergoes reductive cleavage at more negative potentials than the nitro group [17]. The compounds under investigation exhibit the azo-hydrazono tautomerism [11, 18-20]. The increase in half-wave potential with increase in pH (1.1-7.1) indicates the involvement of the protons in the reduction process. A comparison of the half-wave potentials of the first wave with those of nitro benzene [21] suggests that the first wave was due to the reduction of the nitro group ($-NO_2$) to hydroxy ammonium ion ($-\overset{+}{N}H_2OH$).

The second step of the first wave corresponds to the two-electron reduction of hydroxyl ammonium ion ($-\overset{+}{N}H_2OH$) to amine ($-NH_2$). However phenyl hydroxyl amine is resistant to reduction in alkaline medium. In view of this, first wave observed in acidic medium in the present investigation is expected to have wave heights one and half times more than the first wave in alkaline medium. The results presented in the **Table 6** reveal that up to pH 5 the wave height is one and half times more than the wave height of the first wave in alkaline medium.

The first wave was a composite wave and was due to the four-electron reduction of $-NO_2$ to $-\overset{+}{N}H_2OH$ and two-electron reduction of $-\overset{+}{N}H_2OH$ to $-NH_2$. Both the steps were taking place at the same potential, hence a single wave was noticed for the six-electron reduction of $-NO_2$ to $-NH_2$. The second wave may be attributed to the four-electron reductive cleavage of >C=N-NH- group. This fact was confirmed by millicoulometric data (**Table 5**). Similar observations [22] were reported in the literature.

3.6. Nature of the waves in alkaline medium

The compounds I and II exhibit three waves in alkaline medium (8.1 - 10.1). The waves were diffusion controlled and irreversible. Half-wave potential and wave height did not change with increase in pH (8.1 - 10.1).

The first wave was due to the four-electron reduction of -NO_2 to -NHOH. The -NHOH did not undergo reduction in alkaline medium as it is stabilized in alkaline medium. The second wave was due to the four-electron reduction of azomethine anionic form $(>C=N-\bar{N}-)$. The anionic form (5 in **Scheme 2** and 11 in **Scheme 4**) was susceptible to chemical cleavage to form heterocyclic carbonyl compound. The third wave was due to the two-electron reduction of heterocyclic carbonyl compound to the corresponding alcohol.

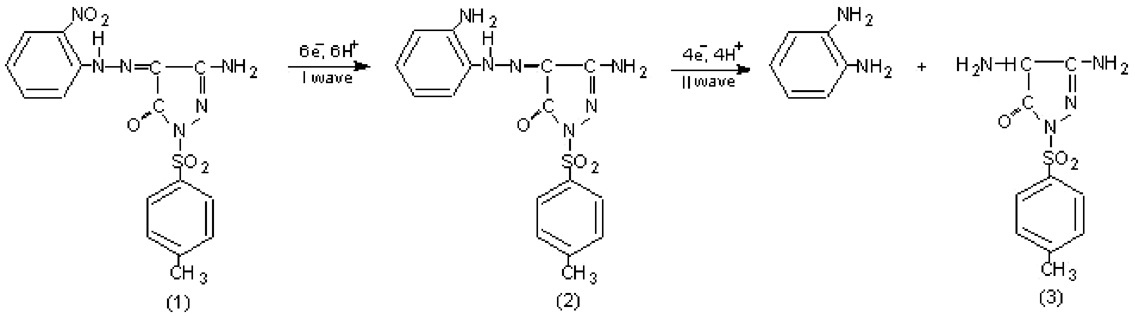
Table 5: Millicoulometric data of pyrazolin-5-ones (1×10^{-3} M); Medium: Aqueous dimethylformamide (40% v/v)

Compound		2'-nitro substituted pyrazolin-5-one						4'-nitro substituted pyrazolin-5-one					
pH	Time (sec)	I wave		II wave		III wave		I wave		II wave		III wave	
		H(m)	n	H(m)	n	H(m)	n	H(m)	n	H(m)	n	H(m)	n
4.1	0	0.113	-	0.037	-	-	-	0.058	-	0.039	-	-	-
	7200	0.098	5.9	0.034	3.6	-	-	0.054	6.1	0.036	3.6	-	-
	10800	0.091	5.8	0.033	3.7	-	-	0.052	5.9	0.035	4.0	-	-
8.1	0	0.085	-	0.027	-	0.027	-	0.041	-	0.027	-	0.03	-
	7200	0.072	3.8	0.025	3.6	0.024	1.7	0.038	4.0	0.026	4.1	0.027	2.1
	10800	0.067	4.0	0.025	3.9	0.023	1.9	0.036	3.6	0.025	3.6	0.025	1.8

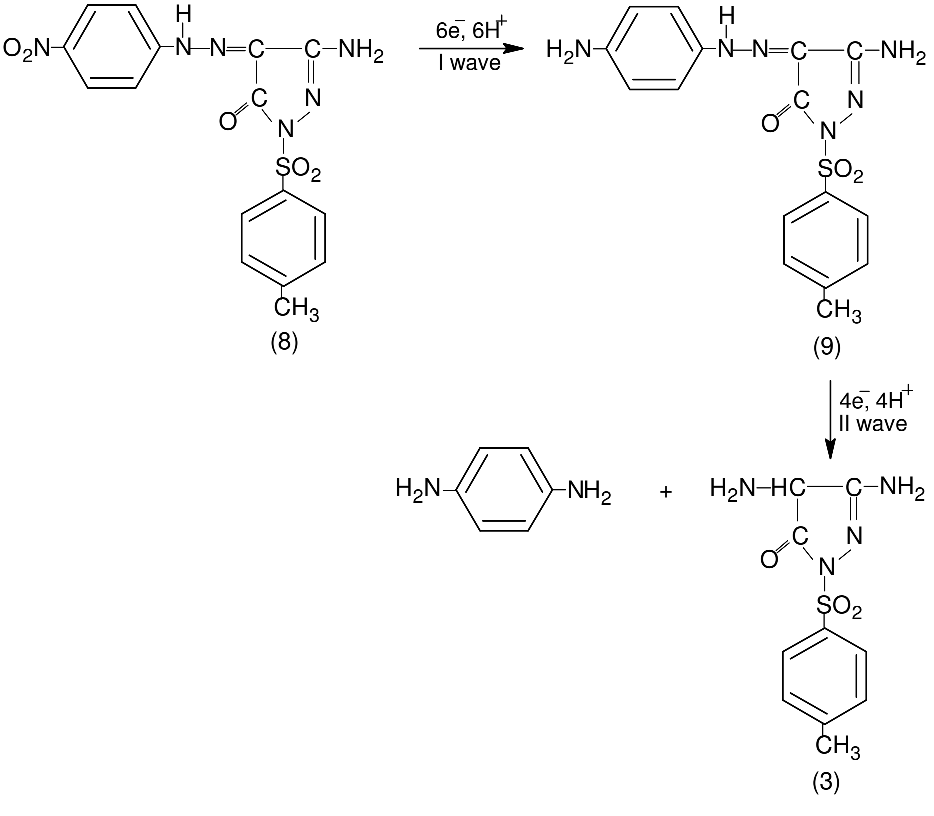
Table 6: Effect of pH on half-wave potential ($E_{1/2}$) and wave height (H) of pyrazolin-5-ones (1×10^{-3} M); Medium: Aqueous dimethylformamide (40% v/v)

Compound	2'-nitro substituted pyrazolin-5-one						4'-nitro substituted pyrazolin-5-one					
pH	Half-wave potential, -$E_{1/2}$ V vs SCE			Wave height, H (m)			Half-wave potential, -$E_{1/2}$ V vs SCE			Wave height H (m)		
	I wave	II wave	III wave	I wave	II wave	III wave	I wave	II wave	III wave	I wave	II wave	III wave
1.1	0.06	0.21	-	0.124	0.041	-	0.07	0.19	-	0.076	0.051	-
2.1	0.11	0.31	-	0.119	0.039	-	0.13	0.28	-	0.07	0.046	-
3.1	0.17	0.37	-	0.116	0.038	-	0.19	0.34	-	0.064	0.043	-
4.1	0.25	0.44	-	0.113	0.037	-	0.28	0.42	-	0.058	0.039	-
5.1	0.34	0.50	-	0.11	0.036	-	0.38	0.50	-	0.05	0.033	-
6.1	0.42	0.60	-	0.107	0.035	-	0.45	0.63	-	0.048	0.032	-
7.1	0.52	0.71	-	0.103	0.034	-	0.55	0.71	-	0.043	0.029	-
8.1	0.64	0.84	1.54	0.085	0.027	0.027	0.65	0.82	1.56	0.041	0.027	0.03
9.1	0.64	0.84	1.54	0.085	0.027	0.027	0.65	0.82	1.56	0.041	0.027	0.03
10.1	0.64	0.84	1.54	0.085	0.027	0.027	0.65	0.82	1.56	0.041	0.027	0.03

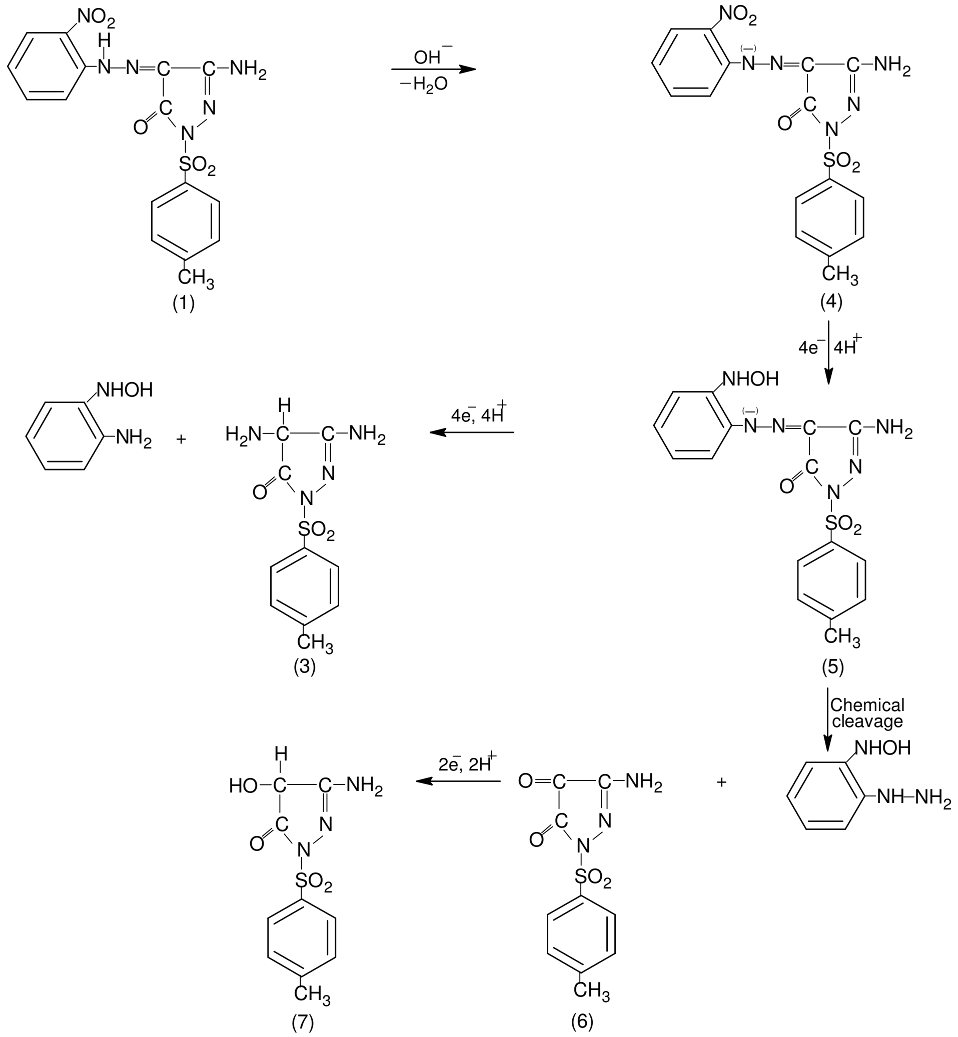
Scheme 1. Reduction mechanism in acidic medium



Scheme 3. Reduction mechanism in acidic medium



Scheme 2. Reduction mechanism in alkaline medium



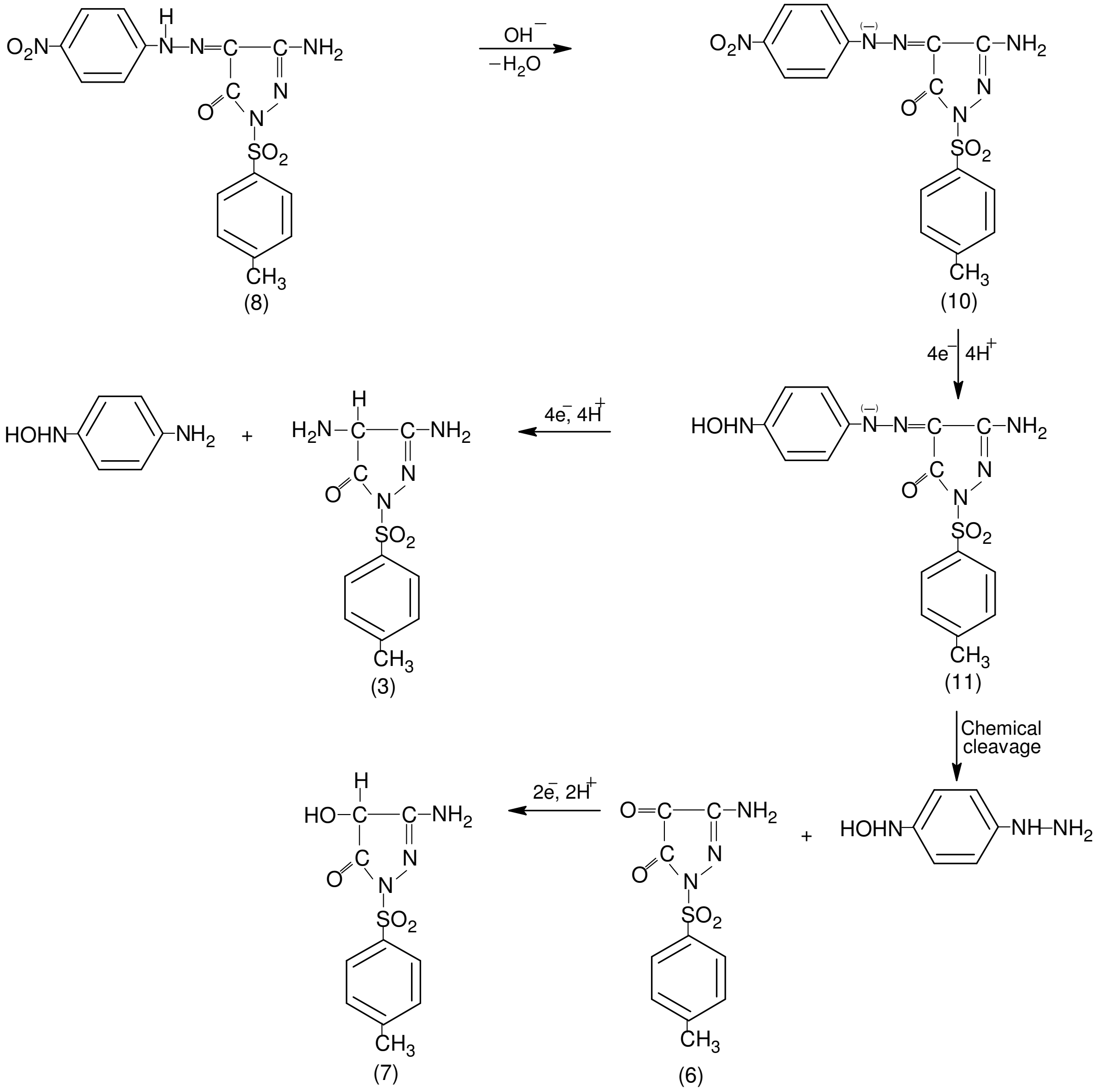
3.7. Effect of substituent on the polarographic reduction

Heyrovsky [23, 24] was the first man to correlate the polarographic behavior of a representative number of compounds with their structure. He inferred that conjugate double bonds, triple bonds and aromatic rings play a significant role in determining the reducibility of a given compound. A perusal of the literature survey reveals that a little work was done on the effect of substituents on the polarographic behavior of substituted aryl hydrazono-2-pyrazolin-5-ones.

For the compounds in aromatic series, structural correlations are usually done with σ_P values. $-E_{1/2}$ - σ_P plots are presented in **Fig. 6(A and B)**.

The effect of substituent is discussed in terms of Hammett equation. The values of the Hammett substituent constant were taken from the literature [25]. The values of specific reaction constant (ρ) calculated are given in the **Table 7**. The low positive [26] values of ρ indicate the nucleophilic addition of electron to the substrate. This fact confirms that the electron uptake process was the potential rate determining step in all the reduction processes studied.

Scheme 4. Reduction mechanism in alkaline medium



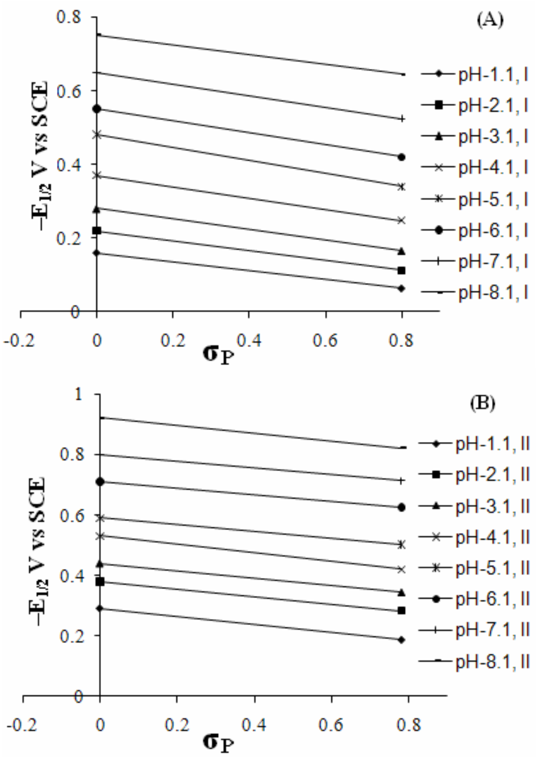


Fig. 6(A and B). $E_{1/2}$ - σ_P plots of pyrazolone-5-one. [pyrazolin-5-one] = 1×10^{-3} M; Medium: Aqueous dimethylformamide (40% v/v)

3.8. Effect of cation on the polarographic reduction

Not much work was reported [27] on the effect of cation on ρ values of the polarographic reduction. Only few reports were available on the reduction of benzylidine acetone [28] and nitrobenzene [29]. The ρ values are presented in the **Table 8**. The increase in ρ values indicates the decrease in the susceptibility for nucleophilic addition with increase in the size of the cation. Similar trend was reported for benzylidine acetones [28] and N'-Benzyl sulfonyl arylazo pyrazoles [30].

3.9. Effect of organic co-solvent on the polarographic behaviour

The presence of an organic solvent [31-44] in aqueous solutions effect the polarographic behavior. The solvent can effect both the wave height and half-wave potential.

Table 7: Effect of pH on the reaction constant for the reduction of pyrazolin-5-ones (1×10^{-3} M)

Compound	2'-nitro substituted pyrazolin-5-one		4'-nitro substituted pyrazolin-5-one	
pH	I wave	II wave	I wave	II wave
1.1	0.12	0.097	0.116	0.134
2.1	0.13	0.093	0.113	0.113
3.1	0.13	0.099	0.111	0.113
4.1	0.15	0.095	0.105	0.112
5.1	0.16	0.125	0.131	0.106
6.1	0.14	0.127	0.113	0.105
7.1	0.13	0.097	0.099	0.103
8.1	0.13	0.077	0.099	0.103
9.1	0.13	0.077	0.099	0.103
10.1	0.13	0.077	0.099	0.103

Table 8: Effect of cations on the reaction constant for the reduction of 1-(Toluenyl sulfonyl)-3-amino-4-(nitro aryl hydrazono)-2-pyrazolin-5-ones (First wave)**;** pH : 4.1; Medium :Aqueous dimethylformamide(40% v/v)

Compound	2'-nitro substituted pyrazolin-5-one		4'-nitro substituted pyrazolin-5-one	
Cation (0.1M)	I wave	II wave	I wave	II wave
LiCl	0.284	0.281	0.212	0.231
NaCl	0.358	0.309	0.250	0.280
KCl	0.436	0.354	0.316	0.331
$\overset{+}{N}(CH_3)_4Br^-$	0.535	0.444	0.403	0.387

In view of this, the polarograms of the 1-(Toluenyl sulfonyl)-3-amino-4-(nitro substituted aryl hydrazono)-2-pyrazolin-5- ones were recorded at pH 4.1 in 50% v/v and 75% v/v aqueous solutions of organic solvent. The results are presented in **Table 9.**

Table 9: Effect of organic co-solvent on half-wave potential of 1-(Toluenyl sulfonyl)-3-amino-4-(nitro aryl hydrazono)-2-pyrazolin-5-ones (1 × 10^{-3} M) at pH 4.1

-G	Half-wave potential, $-E_{1/2}$ V vs SCE											
	DMSO(50%)		DMF(50%)		CH_3CN(50%)		DMSO(75%)		DMF (75%)		CH_3CN(75%)	
	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave
-H	0.42	0.53	0.48	0.59	0.54	0.65	0.62	0.73	0.68	0.79	0.75	0.86
2'-NO_2	0.28	0.44	0.34	0.50	0.43	0.59	0.46	0.63	0.56	0.72	0.66	0.84
4'-NO_2	0.21	0.36	0.27	0.41	0.33	0.47	0.40	0.54	0.45	0.59	0.54	0.66

It is evident from the results that the change in composition of the solvent does not bring any change in the number of waves and the shape of the polarogram. However, there was a change in the position of the wave on the potential axis. The presence of organic solvent caused a marked decrease in the diffusion current. The decrease in the diffusion current may be attributed to the decrease in the effective diffusion coefficient value. This may be due to the increase in the viscosity of the solution or the change in the size of the solvated species [45]. The half-wave potential values were shifted to more negative values in the presence of organic solvents and the magnitude of the shift depends on the nature of the solvent. The magnitude of shift was of the order DMSO < DMF < CH_3CN < CH_3OH. The trend parallels to that of the dielectric constant of solvents. This suggests that in aqueous solutions of aprotic solvents (50% and 75% v/v) the mechanism involves the addition of electron to the unprotonated substrate followed by the protonation of the anion. The diffusion controlled nature of the polarographic wave in the presence of organic solvent was evident from the linear plot of H versus $h^{1/2}$ passing through the origin. The semi log plots were linear and their slopes were more than the theoretically expected values of reversible waves. This indicates the irreversible nature of the electrode reaction in the presence of organic solvent. This infers that the mechanism of the electrochemical reaction was similar even in the presence of organic solvents although a marked shift in the diffusion current and the half-wave potentials were observed.

3.10. Effect of surfactants on the polarographic behavior

Adsorption of the electroactive substance at dropping mercury electrode is one of the major factors that effect the reversibility [46-48] or even the mechanism of the electrode reaction. Holleck and co-workers [49-51] reported that the surfactants adsorb strongly at the dropping mercury solution interface. Therefore the added surfactants usually inhibit the electrode reaction. In view of the fact that pyrazoles have extensive medicinal and biological applications, knowledge of the effect of surfactants on their redox behavior at the solution mercury interface is useful from physiological point of view [52]. The effect of surfactants on redox behaviour of these compounds is of immense importance since the surfactants are used in drugs as emulsifiers. Malik and Rajeev Jain [53] reported that the addition of surfactants beyond the concentration just sufficient to eliminate the maximum affected the reversibility of the electrode process. In view of this, effect of different surfactants on the polarographic reduction of 1-(Toluenyl sulfonyl)-3-amino-4-(nitro substituted aryl hydrazono)-2-pyrazolin-5-ones has been investigated in solutions of pH 4.1 and the results are presented in **Table 10**. It may be noticed from the table that the reduction becomes more difficult and the wave height decreases with increase in the concentration of the surfactants. The shift of half wave potentials to more negative values may be due to the preferential adsorption of the surfactant at dropping mercury electrode.

This result in the partial desorption of the depolarizer from the electrode surface and thus lowering the surface concentration of the depolarizer. Similar results were reported in the literature [54].

Table 10: Effect of surfactants on half wave potential of pyrazolin-5-ones (1×10^{-3} M); pH 4.1; Medium: Aqueous dimethylformamide (40% v/v)

Surfactant	Half wave potential (- $E_{1/2}$ V vs SCE)						Wave height (m)					
	-H		2'nitro		4'nitro		-H		2'nitro		4'nitro	
Non Ionic	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave
Gelatin (4.0×10^{-5}%)	0.48	0.59	0.25	0.44	0.28	0.42	0.034	0.036	0.038	0.037	0.058	0.039
Triton X-100 (2.0×10^{-5}%)	0.54	0.65	0.31	0.50	0.36	0.50	0.024	0.026	0.028	0.027	0.048	0.029
2-Ethoxy ethanol (2.0×10^{-5}%)	0.54	0.65	0. 31	0.50	0.36	0.50	0.039	0.041	0.043	0.042	0.064	0.045
Ethyldigol (2.0×10^{-5}%)	0.54	0.65	0.31	0.50	0.36	0.50	0.027	0.029	0.031	0.03	0.052	0.033
Cationic												
Lauryl pyridinum chloride (3.0×10^{-10} %)	0.54	0.65	0.31	0.50	0.36	0.50	0.025	0.027	0.029	0.028	0.05	0.031
Cetyl pyridinum chloride (2.5×10^{-10} %)	0.57	0.68	0.34	0.53	0.40	0.54	0.027	0.029	0.031	0.03	0.054	0.035
Cetyl dimethyl benzene ammonium chloride (1.5×10^{-10} %)	0.51	0.62	0.28	0.47	0.32	0.46	0.037	0.039	0.041	0.04	0.064	0.045
Anionic												
Sodium lauryl sulphate (3.0×10^{-10} %)	0.57	0.68	0.34	0.53	0.40	0.54	0.032	0.034	0.036	0.035	0.054	0.035
Dodecyl benzene sulphonate (1.5×10^{-10} %)	0.55	0.66	0.32	0.51	0.37	0.51	0.029	0.031	0.033	0.032	0.05	0.031
Dioctyl sodium sulpho succinate (2.0×10^{-10} %)	0.57	0.68	0.34	0.53	0.40	0.54	0.03	0.032	0.034	0.033	0.052	0.033

4. Conclusion

Nitro substituted pyrazolin-5-ones (I and II) undergo irreversible, diffusion controlled, substituent's position dependent polarographic reduction at the dropping mercury electrode.

The effect of pH, concentration of the depolarizer, mercury column height, temperature, cation, solvent and surfactant on the polarographic behavior was presented. Based on the investigations carried out, a detailed mechanism was proposed in the acidic as well as in basic media.

The number of electrons involved in each step of the reduction mechanism was evaluated and presented.

5. References

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