

## Effect of temperature on the polarographic behaviour of 3-methyl-(4'-substituted-benzeneazo)-2-isoxazolin-5-ones

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The polarographic behaviour of 3-methyl-4-(4'-substituted-benzeneazo)-2-isoxazolin-5-ones has been studied in 50% (v/v) dimethylformamide solution in Britton-Robinson buffer of pH 4.1 at different temperatures (303.15–333.15 K). The reduction is found to be diffusion-controlled and irreversible at different temperatures. The shift of  $E_{1/2}$  values towards more negative potentials and decrease in the values of  $\alpha n_a$  and  $k_{f,h}^0$  suggest that the electrode reaction becomes more irreversible at elevated temperatures. The thermodynamic quantities have been evaluated.

The polarographic reduction of a number of benzeneazopyrazolin-5-ones has been studied<sup>1</sup>. The studies showed that these compounds exist in the hydrazone form and undergo a four-electron irreversible reductive cleavage of  $-\text{NH}-\text{N}=\text{C}<$ . Effects of various substituents, ionic strength, surfactants, cations, anions and solvents on the electrode kinetics have been investigated in detail. Jain *et al.*<sup>2</sup> investigated the polarographic reduction of 4-aryl-hydrazono-2-isoxazolin-5-ones to identify the existing tautomeric forms. They assigned hydrazo structure for these compounds and the effect of various substituents on the reduction has been studied. However, the effect of temperature on the electrode kinetics of the irreversible reduction of benzeneazopyrazolin-5-ones and isoxazolin-5-ones has not attracted much attention. Further, the reports<sup>3,4</sup> of the effect of temperature on the electrode kinetics of the irreversible reduction of organic depolarisers are found to be conflicting.

Keeping in view of the paucity of information on the effect of temperature on benzeneazopyrazolin-5-ones, benzeneazoisoxazolin-5-ones and in view of the conflicting results reported in the literature on the effect of temperature on the organic depolarisers, we thought it worthwhile to take up a comprehensive study on the effect of temperature on the polarographic reduction of a series benzeneazopyrazolin-5-ones and benzeneazoisoxazolin-5-ones in terms of electrode kinetics and thermodynamic quantities. In our earlier studies, we reported the effect of temperature on benzeneazopyrazolin-5-ones<sup>5</sup> where a negative shift in half-wave potential has been observed with rise in temperature in Britton-Robinson buffer solution of pH 4.1. In the present paper, an attempt has been made to determine the nature of the wave, the formal heterogeneous rate constant and thermodynamic functions for the reduction of a series of substituted benzeneazoisoxazolin-5-ones in Britton-Robinson buffer solution of pH 4.1. The effect of substituents and its correlation with the Hammett substituent constant ( $\sigma$ ) have also been

investigated at all temperatures studied. Though a negative shift in half-wave potential has been observed with rise in temperature in Britton-Robinson buffer solutions of pH 1.1 to 7.1, the studies are restricted to a single pH, i.e. 4.1. In the evaluation of  $k_{f,h}^0$  values, various treatments<sup>6-8</sup> have been used in order to find the validity of the results obtained.

### Results and Discussion

Compounds 1-5 exhibit a single well-defined reduction wave in 50% (v/v) dimethylformamide solution at pH 4.1 of Britton-Robinson buffer at all the temperatures studied (303.15–333.15 K). This wave has been traced to the reduction of azo group in the hydrazone form since the unsubstituted 3-methyl-2-isoxazolin-5-one fails to exhibit the reduction wave under the experimental conditions and also due to the reports made in the literature<sup>2</sup> that the title compounds exist in the hydrazone form rather than the azo form. The diffusion-controlled nature of the reduction wave has been indicated by the linear plots of  $i_d$  vs  $h^{1/2}$  passing through the origin. The diffusion current has been found to increase with the increase in temperature. The temperature coefficients of diffusion current lie in the range 1.02–1.33 per cent/degree (Table 1). This is in agreement with the values predicted for organic molecules<sup>4</sup>. The coulometric studies indicate that each wave corresponds to a four-electron reduction process. The coulometric data of 3-methyl-4-(benzeneazo)-2-isoxazolin-5-one at a typical temperature (303.15 K) are presented in Table 2. The slope values of the plots of  $E_{de}$  vs  $\log i/(i_d-i)$  lie in the range 0.096–0.12 V, suggesting the irreversible nature of the electrode reaction<sup>4</sup>.

The value of number of protons ( $P$ ) involved per molecule of the reactant in the rate-determining step is calculated from the slopes of  $E_{1/2}$  – pH and  $E_{de}$  vs  $\log i/(i_d-i)$  plots by the equation,

$$\frac{\Delta E_{1/2}}{\Delta \text{pH}} = \frac{0.05915}{\alpha n_a} P \quad (1)$$

The calculated values of  $P$  lie in the range 0.65–0.86, showing the involvement of one proton in the rate-determining step. Further, the half-wave potential of the wave observed in acidic solutions (pH 2.1–7.1) shifts towards more negative values with the increase in pH. The dependence of  $E_{1/2}$  on pH suggests that prior to the first electron uptake the proton transfer occurs.

**Table 1.** Effect of temperature on the polarographic characteristics of 3-methyl-4-(4'-substituted-benzeneazo)-2-isoxazolin-5-ones (1-5)

Concn. = 1 mM, pH = 4.1, medium : 50% (v/v) DMF

Compd. no.	Temp. K	$-E_{1/2}$ V vs SCE	$i_d$ $\mu$ A	Temp. coeff. %/K	$\alpha n_a^*$	$D \times 10^6$ cm <sup>2</sup> s <sup>-1</sup>
1	303.15	0.75	7.0	—	0.45	2.56
	313.15	0.81	7.8	1.07	0.42	3.18
	323.15	0.87	8.8	1.20	0.39	4.05
	333.15	0.93	10.0	1.27	0.37	5.24
2	303.15	0.79	8.0	—	0.49	3.35
	313.15	0.85	9.0	1.18	0.46	4.24
	323.15	0.91	10.2	1.25	0.44	5.45
	333.15	0.98	11.6	1.28	0.41	7.05
3	303.15	0.81	5.4	—	0.43	1.53
	313.15	0.87	6.0	1.05	0.40	1.88
	323.15	0.93	6.7	1.10	0.37	2.35
	333.15	1.02	7.5	1.13	0.34	2.95
4	303.15	0.82	6.5	—	0.43	2.21
	313.15	0.88	7.2	1.02	0.40	2.71
	323.15	0.94	8.0	1.05	0.38	3.35
	333.15	1.02	9.0	1.18	0.35	4.24
5	303.15	0.70	5.0	—	0.43	2.21
	313.15	0.76	5.6	1.13	0.40	1.64
	323.15	0.82	6.3	1.18	0.38	2.08
	333.15	0.90	7.2	1.33	0.35	2.71

\*Product of transfer coefficient ( $\alpha$ ) and number of electrons involved in the rate-determining step ( $n_a$ ).

**Table 2.** Coulometric data of 3-methyl-4-(benzeneazo)-2-isoxazolin-5-one (1) AT 303.15 K

pH = 4.1, concn. = 1 mM

Current $\mu$ A	Time s	$n$ -value
7.0	0	—
6.1	7200	3.8
5.8	10800	4.1

It is seen from the Table 1 that half-wave potential ( $E_{1/2}$ ) values of the depolariser shift to more negative potentials with increase in temperature. The value of  $\alpha n_a$  decreases with increase in temperature. But in the present studies the observed value of  $n_a$  is equal to 1. Since the decrease in  $\alpha n_a$  values with increase in temperature is indiscrete and at no stage the two consecutive values vary by a factor of 1, the possibility of decrease in the value of the product  $\alpha n_a$  due to a change in  $n_a$  may be ruled out.

Thus it may be concluded that the transfer of electron(s) is made increasingly difficult as the temperature is

elevated. In other words, the electrode reaction of benzeneazoisoxazolin-5-ones is rendered more irreversible. The shift in  $E_{1/2}$  values towards more negative potentials lends support to the above conclusion. The values of  $k_{f,h}^0$  have been evaluated by the following equations of Meites-Israel<sup>6</sup>, Oldham-Parry<sup>7</sup> and Gaur-Bhargava<sup>8</sup>,

Meites-Israel :

$$E_{1/2} = -0.2412 + \frac{0.05915}{\alpha n_a} \log \frac{1.349 k_{f,h}^0 t^{1/2}}{D^{1/2}} \quad (2)$$

Oldham-Parry :

$$E_{1/2} = E_T + \frac{0.0592}{\alpha n_a} \log \frac{1.35 k_{f,h}^0 t^{1/2}}{D^{1/2}} \quad (3)$$

Gaur-Bhargava :

$$E_{1/2} = -0.2412 + \frac{0.0569}{\alpha n_a} \log \frac{k_{f,h}^0 t^{1/2}}{1.128 D^{1/2}} \quad (4)$$

The values of  $k_{f,h}^0$  calculated by the above methods show the same trend and agree with each other. These values are given in Table 3. The low values of  $k_{f,h}^0$  confirm the irreversible nature of the wave. Further, the values of  $k_{f,h}^0$  decrease with increase in temperature. This signifies that the electrode reactions are rendered more irreversible with increase in temperature. This observation is in harmony with the conclusion arrived at on the basis of  $\alpha n_a$  values. The values of  $k_{f,h}^0$  evaluated by Meites-Israel and Oldham-Parry methods are almost one and the same. This is because of the fact that the equations employed for the evaluation of  $k_{f,h}^0$  by these two methods are almost one and the same. Whereas the Gaur-Bhargava equation differs from the remaining two having a factor 1.128 in the denominator instead of 1.349/1.35 in numerator in the remaining equations. Because of this difference in the equation, the  $k_{f,h}^0$  values are observed to be little high in Gaur-Bhargava treatment. Even then the values show the same trend and suggest an increase in the irreversibility with rise in temperature. However, the  $k_{f,h}^0$  values do not show any consistency with Hammett substituent constant ( $\sigma_p$ ) in any of the three treatments. The values are a little high for chloro substituted compound compared to the compounds having other substituents, being very low for methyl substituted compound. The values are in the order :  $\text{CH}_3 < \text{OC}_2\text{H}_5 < \text{OCH}_3 < \text{H} < \text{Cl}$ .

**Table 3.** Kinetic parameters of polarographic reduction of 3-methyl-4-(4'-substituted-benzeneazo)-2-isoxazolin-5-ones calculated by different methods

Concn. = 1 mM, pH = 4.1, medium : 50% (v/v) DMF

Compd. no.	Temp. K	$k_{f,h}^0$ cm <sup>-1</sup>	$\Delta H_p^*$ kcal mol <sup>-1</sup>	$\Delta H_v^*$ kcal mol <sup>-1</sup>	$\Delta H_v^*$ kcal mol <sup>-1</sup>	$-\Delta S^*$ e.u
Meites-Israel :						
1	303.15	$6.65 \times 10^{-8}$	17.1	$4.33 \pm 0.29$	3.72	$44.1 \pm 0.66$
	313.15	$5.04 \times 10^{-8}$	17.9		3.70	45.3
	323.15	$4.44 \times 10^{-8}$	18.6		3.68	46.2
	333.15	$3.47 \times 10^{-8}$	19.3		3.66	46.9

Table-3 (contd.)

2	303.15	$16.1 \times 10^{-9}$	18.0	$6.57 \pm 0.40$	5.96	$39.7 \pm 0.65$
	313.15	$11.7 \times 10^{-9}$	18.8		5.94	41.1
	323.15	$7.64 \times 10^{-9}$	19.7		5.92	42.6
	333.15	$6.21 \times 10^{-9}$	20.5		5.90	43.8
3	303.15	$2.80 \times 10^{-8}$	17.7	$3.02 \pm 0.45$	2.41	$50.4 \pm 0.79$
	313.15	$2.37 \times 10^{-8}$	18.4		2.39	51.1
	323.15	$2.33 \times 10^{-8}$	19.0		2.37	51.5
	333.15	$1.77 \times 10^{-8}$	19.8		2.35	52.4
4	303.15	$20.4 \times 10^{-9}$	17.9	$5.31 \pm 0.58$	4.70	$43.5 \pm 0.76$
	313.15	$17.8 \times 10^{-9}$	18.6		4.68	44.5
	323.15	$11.8 \times 10^{-9}$	19.4		4.66	45.6
	333.15	$9.1 \times 10^{-9}$	20.2		4.64	46.7
5	303.15	$16.3 \times 10^{-8}$	16.6	$6.22 \pm 0.43$	5.61	$36.3 \pm 0.80$
	313.15	$12.3 \times 10^{-8}$	17.3		5.59	37.4
	323.15	$8.5 \times 10^{-8}$	18.2		5.57	39.1
	333.15	$6.4 \times 10^{-8}$	18.9		5.55	40.1
Oldham-Parry :						
1	303.15	$6.62 \times 10^{-8}$	17.1	$4.32 \pm 0.30$	3.71	$44.2 \pm 0.79$
	313.15	$5.01 \times 10^{-8}$	17.9		3.69	45.4
	323.15	$4.42 \times 10^{-8}$	18.6		3.67	46.2
	333.15	$3.45 \times 10^{-8}$	19.3		3.65	47.0
2	303.15	$16.0 \times 10^{-9}$	18.0	$6.52 \pm 0.51$	5.91	$39.9 \pm 0.63$
	313.15	$11.6 \times 10^{-9}$	18.8		5.89	41.2
	323.15	$7.6 \times 10^{-9}$	19.7		5.87	42.8
	333.15	$6.2 \times 10^{-9}$	20.5		5.85	44.0
3	303.15	$2.78 \times 10^{-8}$	17.7	$3.00 \pm 0.30$	2.39	$50.5 \pm 0.82$
	313.15	$2.36 \times 10^{-8}$	18.4		2.37	51.2
	323.15	$2.31 \times 10^{-8}$	19.0		2.35	51.5
	333.15	$1.76 \times 10^{-8}$	19.8		2.33	52.4
4	303.15	$20.2 \times 10^{-9}$	17.9	$5.26 \pm 0.44$	4.65	$43.7 \pm 0.86$
	313.15	$17.7 \times 10^{-9}$	18.6		4.63	44.6
	323.15	$11.7 \times 10^{-9}$	19.4		4.61	45.8
	333.15	$9.0 \times 10^{-9}$	20.2		4.59	46.9
5	303.15	$16.3 \times 10^{-8}$	16.6	$6.24 \pm 0.31$	5.63	$36.2 \pm 0.78$
	313.15	$12.2 \times 10^{-8}$	17.3		5.61	37.3
	323.15	$8.5 \times 10^{-8}$	18.2		5.59	39.0
	333.15	$6.4 \times 10^{-8}$	18.9		5.57	40.0
Gaur-Bhargava :						
1	303.15	$10.2 \times 10^{-8}$	16.9	$4.27 \pm 0.33$	3.66	$43.7 \pm 0.76$
	313.15	$7.7 \times 10^{-8}$	17.6		3.64	44.6
	323.15	$6.8 \times 10^{-8}$	18.3		3.62	45.4
	333.15	$5.3 \times 10^{-8}$	19.0		3.60	46.2
2	303.15	$24.7 \times 10^{-9}$	17.7	$6.41 \pm 0.29$	5.80	$39.3 \pm 0.67$
	313.15	$18.0 \times 10^{-9}$	18.5		5.78	40.6
	323.15	$11.7 \times 10^{-9}$	19.4		5.76	42.2
	333.15	$9.5 \times 10^{-9}$	20.2		5.74	43.4
3	303.15	$4.29 \times 10^{-8}$	17.4	$3.17 \pm 0.40$	2.56	$49.0 \pm 0.78$
	313.15	$3.64 \times 10^{-8}$	18.1		2.54	49.7
	323.15	$3.57 \times 10^{-8}$	18.7		2.52	50.1
	333.15	$2.72 \times 10^{-8}$	19.5		2.50	51.0
4	303.15	$3.13 \times 10^{-8}$	17.6	$5.32 \pm 0.31$	4.71	$42.5 \pm 0.77$
	313.15	$2.74 \times 10^{-8}$	18.3		4.69	43.5
	323.15	$1.81 \times 10^{-8}$	19.2		4.67	45.0
	333.15	$1.40 \times 10^{-8}$	20.0		4.65	46.1
5	303.15	$25.0 \times 10^{-8}$	16.3	$6.23 \pm 0.24$	5.62	$35.2 \pm 0.83$
	313.15	$18.8 \times 10^{-8}$	17.1		5.60	36.7
	323.15	$13.1 \times 10^{-8}$	17.9		5.58	38.1
	333.15	$9.8 \times 10^{-8}$	18.6		5.56	39.1

The enthalpy of activation ( $\Delta H_p^\ddagger$ ) has been calculated by substituting the value of the slope of the plot ( $\log k_{f,h}^\ddagger$  vs  $1/T$ ) in the Van't Hoff's equation<sup>9</sup>,

$$\Delta H_p^\ddagger = 2.303 R \times \text{slope} \quad (5)$$

where  $R$  is the gas constant. The heat of activation at constant volume ( $\Delta H_v^\ddagger$ ) has been evaluated from the relation,

$$\Delta H_p^\ddagger = \Delta H_v^\ddagger + RT \quad (6)$$

The activation free energy change ( $\Delta G^\ddagger$ ) has been determined by the relationship,

$$k_{f,h}^\ddagger = \frac{kT}{h} r_o \exp \left( \frac{-\Delta G^\ddagger}{RT} \right) \quad (7)$$

where  $k$  is the Boltzman constant,  $h$  the Plank constant,  $r_o$  the mean distance between the depolarised ions in bulk solution,  $R$  the gas constant and  $T$  the absolute temperature. The entropy of activation ( $\Delta S^\ddagger$ ) has been calculated using the Helmholtz relation,

$$\Delta S^\ddagger = \frac{\Delta H_v^\ddagger - \Delta G^\ddagger}{T} \quad (8)$$

The plot of  $\log k_{f,h}^\ddagger$  vs  $1/T$  is presented in Fig.1. A perusal of the values of thermodynamic quantities (Table 3) shows that  $\Delta G^\ddagger$  is positive for all the systems, suggesting the non-spontaneous nature of the electrode process<sup>10</sup>. The high values of  $\Delta G^\ddagger$  also suggest that the reaction rate is slow<sup>10</sup>.

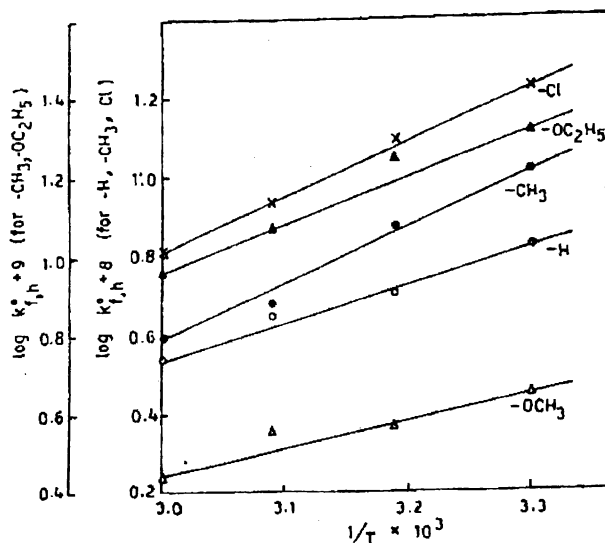


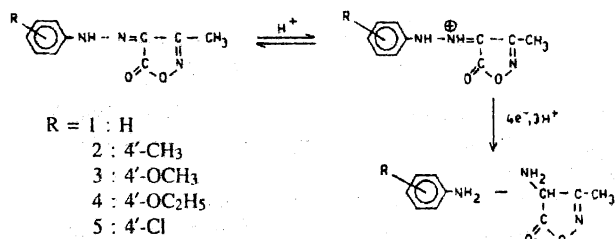
Fig. 1. Plots of  $\log k_{f,h}^\ddagger$  vs  $1/T$  for 3-methyl-4-(4'-substituted-benzeneazo)-2-isoxazolin-5-ones [Meites-Israel treatment].

The negative values of  $\Delta S^\ddagger$  indicate the formation of activated state with a decrease in entropy<sup>10</sup>. It has been observed that the compound having methoxy group in the *para*-position show entropy values which are a little negative compared to the unsubstituted compound, while compounds having ethoxy group show entropy values almost identical with unsubstituted compound, and methyl and chloro substituted compounds show little positive values of entropy. The entropy value does not show any consistency with  $\sigma_p$  value of the corresponding substituent. But with the exclusion of unsubstituted compound a regular depen-

dence of entropy values on  $\sigma_p$  values can be observed. The entropy values follow the order :  $\text{OCH}_3 > \text{OC}_2\text{H}_5 > \text{CH}_3 > \text{Cl}$ , being more negative for  $\text{OCH}_3$ .

**Effect of substituents on reduction** : For the purpose of establishing the effect of substituents on reduction,  $E_{1/2}$  is plotted against Hammett substituent constant at all the temperatures studied. The substituent constants  $\sigma_p$  used were taken from the literature<sup>11</sup>. A linear correlation has been observed between  $E_{1/2}$  and  $\sigma_p$  at all the temperatures. Further, the correlation coefficients calculated for  $E_{1/2}$  vs  $\sigma_p$  plots ( $r = 0.985-1.0$ ) show satisfactory application of Hammett's correlation to the system under study. The values of specific reaction constant ( $\rho$ ) calculated from  $E_{1/2}$  vs  $\sigma_p$  plot are positive. The positive values of specific reaction constant suggest that electron addition step is more important. The  $\rho$  values calculated are 0.23, 0.23, 0.25 and 0.24 at 303.15, 313.15, 323.15 and 333.15 K respectively. Though a very slight increase and then a decrease has been observed in the  $\rho$  values, they may be considered identical at all the temperatures within the experimental limits. It is also observed from the plots that at all the temperatures, electron-donating substituents, viz.  $\text{CH}_3$ ,  $\text{OC}_2\text{H}_5$  and  $\text{OCH}_3$  shift the  $E_{1/2}$  towards more negative values, whereas electron-withdrawing groups shift the  $E_{1/2}$  towards more positive values, i.e. the substituents having electron-withdrawing groups are reduced more easily than those having electron-donating groups in the benzene ring. The results suggest that the presence of substituents does not hinder the mechanism of reduction of the present compounds but only makes the reduction either easy or difficult depending on the nature of the substituent.

**Mechanism of reduction** : The pH-dependence of half-wave potential indicates protonation of the depolariser prior to electron uptake. But as only a single 4-electron wave is obtained, the usual mechanistic path  $\text{H}^+$ ,  $e$ ,  $e$ ,  $\text{H}^+$  or  $\text{H}^+$ ,  $e$ ,  $\text{H}^+$ ,  $e$  is difficult to envisage. Therefore, a mechanism similar to other hydrazones<sup>11,12</sup> may be proposed for these compounds. The mechanism shown in Scheme 1 can be put forward for the pH-dependent polarographic reduction. The mechanism is consistent with the reduction of other 4-aryldiazonopyrazolin-5-ones<sup>13</sup>.



Scheme 1

## Experimental

Compounds 1-5 were prepared by the reported method<sup>14</sup>. The required primary amine was dissolved in a mixture (1 : 1, v/v) of concentrated HCl and water and

cooled to 0° in an ice-bath. Cold aqueous solution of sodium nitrite was then added to it and the diazonium salt so formed was filtered into a cooled solution of sodium acetate (5 g) and acetoacetic ester (0.01 mol) in ethanol (25 ml). The resulting solid, 2-(4'-substituted-arylhydrazono)-butyrate-1,3-dione was washed with water, dried and crystallised from ethanol. A mixture of 2-(4'-substituted-arylhydrazono)butyrate-1,3-dione (0.005 mol) in ethanol (20 ml) and hydroxylamine hydrochloride (0.005 mol) in water (5 ml) and sodium acetate (1.0 g) was refluxed for 4 h. On cooling, the resulting shining orange yellow crystals were crystallised from ethanol :  $\nu_{\text{max}}$  (KBr) 3310 (NH), 1720 (C=O cyclic), 1520 ( $-\text{NH}-\text{N}=\text{C}<$ ), 1460 and 1560  $\text{cm}^{-1}$  (five-membered heterocyclic ring);  $\delta$  (DMSO- $d_6$ ) 2.35 (3H, s,  $\text{CH}_3$ ), 7.10-7.60 (m, phenyl), 9.5 (1H, s,  $-\text{NH}-\text{N}=\text{C}<$ ).

Stock solutions of the compounds ( $1 \times 10^{-2} M$ ) were prepared in dimethylformamide (A.R.). Other chemicals used were of analytical grade. Britton-Robinson buffer<sup>15</sup> of pH 4.1 was prepared. Polarograms were recorded for deaerated solution containing stock solution (1 ml) of the compound, dimethylformamide (4 ml, the minimum volume necessary to keep the compound in solution) and buffer solution (5 ml) of pH 4.1. An Elico DC polarograph was used. The dropping mercury electrode used had the following characteristics :  $m = 1.83 \text{ mg/s}$ ;  $t = 3.00 \text{ s}$ ;  $m^{2/3} t^{1/6} = 1.80 \text{ mg}^{2/3} \text{ s}^{-1/2}$  at  $h = 80 \text{ cm}$ , in water at 0 V vs SCE. The pH was measured on an Elico LP101 pH meter. A saturated calomel electrode and a platinum foil were used as reference and counter electrodes respectively.

The number of electrons ( $n$ ) involved in the reduction process was determined by coulometry. Knowing the value of  $n$ , the diffusion coefficient ( $D$ ), that is necessary for the calculation of heterogeneous rate constant ( $k_{f,h}^0$ ) values for the depolarisers at different temperatures, was calculated using Ilkovic equation. The values of  $k_{f,h}^0$  were evaluated using the equation proposed by Meites-Israel<sup>6</sup>, Oldham-Parry<sup>7</sup> and Gaur-Bhargava<sup>8</sup>.

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## References

1. H. M. Fahmy, M. H. Elnagdi and L. I. Ibrahim, *Indian J. Chem., Sect. B*, 1980, **9**, 644; W. U. Malik, R. N. Goyal and R. Jain, *J. Electroanal. Chem.*, 1979, **105**, 349; R. Jain and D. D. Agarwal, *Indian J. Chem., Sect. A*, 1982, **21**, 796; R. Jain, *J. Indian Chem. Soc.*, 1983, **60**, 936; L. K. Ravindranath, S. R. Ramadas and S. B. Rao, *Electrochim. Acta*, 1983, **28**, 601; P. Venkata Ramana, B. S. Suryanarayana, L. K. Ravindranath, V. Sheshagiri, S. R. Ramadas and S. B. Rao, *Indian J. Chem., Sect. A*, 1990, **29**, 53, 864, 895; *J. Indian Chem. Soc.*, 1990, **67**, 730.
2. B. Jain, S. N. Tandon and R. N. Goyal, *Electrochim. Acta*, 1979, **24**, 477.
3. P. Y. Swamy, G. Veerabhadram and K. S. Sastry, *J. Electrochem. Soc.*, 1987, **36**, 75; R. Ratan and M. Singh, *Indian J. Chem., Sect. A*, 1979, **18**, 69; R. Rani, N. Singh and M. Singh, *Indian J. Chem., Sect. A*, 1989, **28**, 1046; S. L. Gupta and N. Kishore, *J. Inst. Chem. India*, 1968, **44**, 210.

Venkata Ramana *et al.* : Effect of temperature on the polarographic behaviour of 3-methyl-(4'-substituted-benzeneazo) *etc.*

4. L. Meites, "Polarographic Techniques", Interscience, New York, 1965, p. 324.
5. P. Venkata Ramana, B. S. Suryanarayana and L. K. Ravindranath, *Bull. Electrochem.*, 1993, **9**, 18; *Trans. SAEST*, 1993, **28**, 37.
6. L. Meites and Y. Israel, *J. Am. Chem. Soc.*, 1961, **83**, 4903.
7. K. B. Oldham and E. P. Parry, *Anal. Chem.*, 1968, **40**, 65.
8. J. N. Gaur and S. K. Bhargava, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 3314.
9. S. H. Maron and C. F. Prutton, "Principles of Physical Chemistry", Amerind, New Delhi, 1976.
10. S. Glasstone and D. Lewis, "Elements of Physical Chemistry", 2nd. ed., Macmillan India, New Delhi, 1982.
11. P. Zuman, "Substituent Effects in Organic Polarography", Plenum, New York, 1967.
12. B. Fleet and P. Zuman, *Collect. Czech. Chem. Commun.*, 1966, **32**, 2066; H. Lund, *Acta Chem. Scand.*, 1939, **13**, 240; J. W. Haas, J. D. Storey and C. C. Lynch, *Anal. Chem.*, 1962, **34**, 145.
13. W. U. Malik, R. N. Goyal and R. Jain, *J. Electroanal. Chem.*, 1979, **105**, 349.
14. H. G. Garg and P. P. Singh, *J. Med. Chem.*, 1970, **13**, 1250.
15. H. T. S. Britton, "Hydrogen Ions I", Van Nostrand, New York, 1965.