recorded at room temperature on a Bruker 60 instrument. The PMR spectrum of $[C_6H_5OC_6H_4TeCl_3 (CH_3)_2SO]$ exhibit a three-proton singlet in the region $\delta 2.65$-2.95 assignable to —CH_3 protons. Two doublets of one proton each at δ 8.4 and $\delta 7.05$ in p-phenoxyphenyl derivatives of tellurium have been attributed to *ortho* and -*meta* protons of aromatic ring. A complex signal at $\delta 7.37$ may be assigned to phenoxyprotons (C_6H_5O-) in $[C_6H_5OC_6H_4TeCl_3$.-$(CH_3)_2SO]$.

The PMR spectrum of $CH_3OC_6H_4TeCl_3TMTS$ exhibits two three-proton singlets in the region $\delta 3.15$-3.45 and $\delta 3.7$-3.85 assignable to —CH_3 and —OCH_3 protons respectively. Two doublets at $\delta 7.02$ and 8.47 are observed due to -*meta* and -*ortho* protons of aromatic ring bonded to tellurium atom in the adduct. Thus, the probable structure for the adducts with monodentate ligands is square pyramidal with five coordinated tellurium atom, while that with bidentate ligands is octahedral.

Antimicrobial activity — A few adducts were screened for their antibacterial activities against bacteria *Streptococcus faecalis, Klebsiella pneumoniae, Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus* and five fungi *Candida albicans, Cryptococcus neoformans, Sprorotrichum schenikii, Trichophyton mentagrophytes, Aspergillus fumigatus.*

The antimicrobial activity of the adducts were evaluated with two-fold serial dilution methol[16]. The complexes show moderate activity towards bacteria used. All the adducts including starting materials are inactive at 100 ppm against all the fungi used.

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Solvent Effect on Polarographic Reduction of *m*-Nitroacetophenone oxime

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The polarographic behaviour of *m*-nitroacetophenone oxime has been studied in the pH range 3-10, in water and aqueous solution of methanol, methoxyethanol and isopropanol. A strong interaction between —NHOH (the first reduction product of nitro group) and $>C=N$ group is noticed in acid solutions.

THE polarographic reduction of an aromatic compound is influenced by a reducible substituent present in it, sometimes in a manner[1] other than the one predicted by linear free energy relations[2]. The present authors in their studies[3] on polarographic reduction of *m*-nitroacetophenone oxime observed that the azomethine group in the *meta*-position affected the reduction of nitro group in solutions of $pH < 5$ and > 8. Subrahmanaya et al.[4,5] reported that the reduction of nitrobenzene in aqueous solutions is greatly influenced by the presence of organic co-solvents. In order to verify our observation made earlier[3] and those of Subrahmanaya et al.[4,5], the polarographic reduction of *m*-nitroacetophenone oxime in aqueous methanol, methoxyethanol and isopropanol in the pH range 3 to 10 has been investigated.

Polarograms were recorded on a CL 25 ELICO DC pen recording polarograph in Briton-Robinson buffers and the data are presented in Tables 1 and 2.

Reduction at pH 3-5 — It is seen from the data in Tables 1 and 2 that one wave is observed in aqueous organic media in contrast to two waves in pure water medium. The second wave in pure aqueous solutions may be due to the non-faradaic transformation product of the species formed in the reduction of nitro group in the first wave or due to the reduction of protonated azomethine group. Based on the position of the wave on voltage axis, we believe that the second wave is not due to reduction of either the nitro group or the azomethine group, but is a result of mutual interaction of these two groups. Subrahmanaya et al.[4,5] reported that in aqueous organic media the second wave is highly ill-defined. Krishna Rao[6] observed a wave ($E_{1/2} = -1.40$ V vs SCE) at pH 5 for acetophenone oxime in 50% aqueous methanol. The absence of the second wave in aquo organic solvents, therefore, clearly suggests the presence of mutual interaction between —NHOH and $>C = N$ in aquo organic media to an extent of even eliminating the second wave. The shift in the half-wave potential of the first wave with change of organic solvent suggests that the shift is dependent on the proton donating ability of the organic co-solvent, which is expected to be in the order : methanol — methoxyethanol > isopropanol. The splitting of the first wave at pH 3.2 in 50% aquo methanol can be traced[7]

TABLE 1 — HALF-WAVE POTENTIALS OF THE REDUCTION OF *m*-NITROACETOPHENONE OXIME IN AQUEOUS AND AQUEOUS ORGANIC MEDIA AT DIFFERENT *p*H VALUES

$-E_{1/2}$ (V vs SCE)

pH	First wave				Second wave			
	I	II	III	IV	·I	II	III	IV
3.20	0.51	0.51 ⎫ 0.79 ⎬0.73 0.88 ⎭	0.82	0.92	1.44	—	—	—
4.10	0.54	0.71	0.84	0.95	1.40	—	—	—
5.10	0.58	0.81	0.94	0.96	1.52	—	—	—
6.10	0.67	0.71	0.95	0.97	1.56	1.30	1.35	—
6.98	0.91	0.94	0.96	0.98	1.44	1.23	1.30	1.37
8.10	0.71	0.81	0.92	0.94	1.89	1.23	1.29	1.30
9.10	0.74	0.81	1.22	1.24	1.89	1.10	—	—
10.10	0.72	0.83	1.21	1.26	1.89	1.10	—	—

I = Pure water medium
II = 50% aq. mathanol
III = 50% aq. methoxyethanol
IV = 50% aq. isopropanol

TABLE 2 — WAVE HEIGHTS OF THE REDUCTION WAVES OF *m*-NITROACETOPHENONEOXIME IN AQUEOUS AND AQUO ORGANIC MEDIA OF DIFFERENT *p*H VALUES

Wave heights (μA)

pH	First wave				Second wave			
	I	II	III	IV	I	II	III	IV
3.20	2.6	0.30 ⎫ 1.34 ⎬ 0.65 ⎭	2.4	3.2	5.2	—	—	—
4.10	2.5	2.5	2.6	3.1	5.0	—	—	—
5.10	2.5	2.9	2.8	2.8	5.0	—	—	—
6.10	2.4	1.9	1.7	2.4	3.3	0.97	0.80	—
6.98	2.6	1.5	1.3	1.2	1.1	1.20	0.91	2.60
8.10	2.5	1.2	0.91	0.75	4.8	1.40	1.40	2.00
9.10	2.5	0.81	2.7	3.5	4.7	1.9	—	—
10.10	2.4	0.65	2.1	4.0	3.1	2.1	—	—

I = Pure water medium
II = 50% aq. methanol
III = 50% aq. methoxyethanol
IV = 50% aq. isopropanol

to the different rates of uptake of the first, second, and the last two electrons by nitro group during its reduction to the hydroxylamine stage.

Reduction at pH 8-10 — Two waves occur in all media at *p*H 6.98 and 8.10 (Fig. 1). At *p*H 8.10 two waves are observed in pure water medium and in 50% aqueous methanol. Nitro group does not show a wave corresponding to reduction of—NHOH in alkaline medium since phenylhydroxylamine is stabilised. Hence the second wave can only be due to the reduction of the azomethine group. Krishna Rao[6] during polarographic reduction of acetophenone oxime reported a wave at—1.15 V (vs SCE) in aqueous alkaline solutions and a wave at— 1.40 V in 50% methanolic media. This therefore suggests that the second wave noticed presently is due to the reduction of the azomethine group. It is therefore inferred that addition of organic solvent completely eliminates the mutual interaction observed in pure aqueous alkaline solution. This may be perhaps due to the greater stabilization of the hydroxylamine in these media.
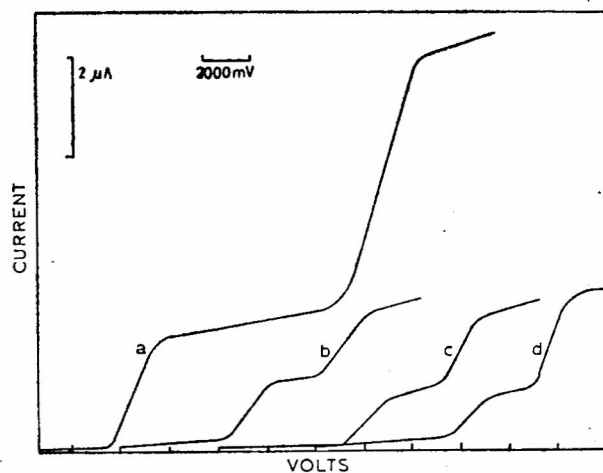

Fig. 1 — Polarograms of *m*-nitroacetophenone oxime (1 × $10^{-3}M$) at *p*H 8.1 [(a) aqueous medium; (b) 50% aq. methanol; (c) 50% aq. methoxyethanol; and (d) 50% aq. isopropanol; each curve starts at —0.3 V (vs SCE)].

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Polarographic Behaviour of Nitroprusside Ion

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Polarographic behaviour of nitroprusside ion has been studied at different *p*H values. In a strongly acidic medium, only one wave is obtained; two waves appear upto *p*H 6; at *p*H > 6, all the three waves are observed. In fairly alkaline medium the first wave is completely eliminated. The analysis of the waves indicates that the first and second reduction steps are reversible and the third step is irreversible at different *p*H values. The values of rate constant and heterogeneous rate constant ($k_{f,h}^\circ$) also support the above views. The values of temperature coefficient of the half-wave potential of first and second waves are very nominal as expected for reversible reductions. The constancy in half-wave potential for the third wave with increase in temperature confirms the irreversible nature of the third step.

KOLTHOFF and Toren[1] studied the polarographic behaviour of nitroprusside ion and reported that it gives three reduction waves at the d.m.e. The first two reduction steps involved one electron each and were independent of the hydrogen ion concentration in the *p*H range 6.0-10.0. These reduction steps were found to be reversible; however, the third one corresponded to an irreversible process. The effect of the nature and concentration of the supporting electrolytes on the polarographic behaviour of nitroprusside ion and a tentative mechanism for the reduction process have already been reported in our earlier communication[2].

The present note deals with the effect of *p*H and temperature on the polarographic behaviour of nitroprusside ion, specially on the third reduction step. Kinetic and thermodynamic parameters have been calculated.

Recrystallized sodium nitroprusside dihydrate (BDH) was used for the experiments. The nitroprusside solution is light-sensitive and slowly turns green on exposure to light. Therefore, fresh solutions were prepared every alternate day and kept in dark and were exposed to diffuse light only while taking the polarograms. All other chemicals were AR reagents (BDH). The solutions were deaerated by bubbling pure nitrogen gas. The temperature was maintained at $30 \pm 0.1°C$.

Polarograms were recorded on a Toshniwal Manual polarograph in conjunction with a sensitive polyflex galvanometer.

Half-wave potentials and slope values were evaluated from $-E_{d.e.}$ vs log i/i_d-i curves. The value of transfer coefficient α has also been determined from the plot of log $(i-i_t)$ vs $-E_{d.e.}$ in the case of third reduction step.

It is interesting to note that the polarographic behaviour of nitroprusside ion varies with the *p*H. Upto *p*H 4.2, only one reduction wave is observed; at *p*H 5.8 the second wave appears; from *p*H 6.4 to 10.3 three well-defined waves are obtained. From the above observations it seems that the reduction of nitroprusside ion beyond first and second stages is not feasible in presence of high concentration of hydrogen ions and the elimination of the first reduction wave in highly alkaline medium may be due to the interaction of nitroprusside ion with hydroxyl ions which has been reported by Cambi and Szego[3] also.

In the *p*H range 6.4-10.3, the half-wave potential of the first wave is almost constant, while it varies irregularly for the second wave. The half-wave potential of the third wave shows a continuous positive shift, a characteristic of a irreversible process. The irregularity in the shift of half-wave potential of the second wave with *p*H may be due to the semi-kinetic character of the wave caused by the change in the ionic strength of the medium.

The third wave has a 2-electron height at low *p*H of about 6.4. With increasing *p*H, the sum of the heights of the three waves first increases and then decreases. However, the sum of the heights of first and second waves becomes lesser than the height of third wave with the increase in *p*H from 6.4 to 10.3. Hence, it follows that the electrode process in the third wave in the alkaline *p*H range cannot be a further reduction of the product of the electrode reaction occurring in the second wave.

The values of $k_{f,h}$ (Table 1) at different potentials have been calculated by applying Koutecky's treatment. The variation of $k_{f,h} \times D^{-1/2}$ for the third reduction step at all the *p*H values indicates that the process is completely kinetically-controlled at the foot of the wave and becomes either completely diffusion-controlled or tends towards it at the top of the wave. On the rising portion of the wave the process is partly controlled by diffusion and partly kinetically. The variation in the value of heterogeneous rate constant $k_{f,h}^\circ$ with *p*H is of interest, as it decreases first upto *p*H 8.4 and then increases for *p*H more than 8.4 (Table 1). At *p*H 8.4 the value of $k_{f,h}$ is minimum (3.98×10^{-24}) and as such the reduction process is easiest. This view is also supported by the fact that the free energy change ($\triangle G$) also increases from *p*H 6.4 to 8.4 (1.17×10^5 to 1.65×10^5) and then decreases from *p*H 9.4 to 11.3 (1.34×10^5 to 0.74×10^5). Table 1 shows that the value of $k_{f,h} \times D^{-1/2}$ at potentials 1.5 to 1.64 increases continuously upto *p*H 10.3 and then decreases. At poten-