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# Electrochemical Behaviour of Quinazoline in Amphiprotic Media

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The electrochemical behaviour of quinazoline in aqueous methanolic solutions has been studied in detail. In acid solutions two single-electron waves of equal height are obtained whereas in neutral solutions a single two-electron wave is observed. Quinazoline gets reduced to tetrahydroquinazoline in alkaline media and very interestingly gives "reverse cathodic peaks" during cyclic voltammetric experiments. The polarographic waves are diffusion-controlled and irreversible on the basis of the usual criteria. Based on the results obtained, reduction schemes are given for quinazoline in various buffered media. A comparison of the electrochemical behaviour, between quinazoline and 4-(2′-thienyl)quinazoline (4-*TQ*) has been attempted.

*[Keywords: Electrochemical reduction; Quinazoline and 4-(2′-thienyl)quinazoline; Mechanism]*

### *Das elektrochemische Verhalten von Chinazolin in amphiprotischen Medien*

Das elektrochemische Verhalten von Chinazolin in wäßrigen methanolischen Lösungen wurde im Detail untersucht. In sauren Lösungen wurden zwei Einelektronenwellen gleicher Höhe erhalten, währenddessen in neutralen Lösungen eine einzige Zweielektronenwelle beobachtet wurde. Chinazolin wird in alkalischem Medium zu Tetrahydrochinazolin reduziert und ergibt interessanterweise „kathodische Umkehrpeaks“ während cyclischer voltammetrischer Experimente. Die polarographischen Wellen sind diffusionskontrolliert und nach den üblichen Kriterien irreversibel. Aufgrund dieser Ergebnisse werden Reduktionsschemata für Chinazolin in verschiedenen Puffermedien angegeben. Es wird ein Vergleich zwischen dem elektrochemischen Verhalten von Chinazolin und 4-(2′-Thienyl)-chinazolin (4-*TQ*) angestellt.

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## Introduction

A detailed electrochemical investigation on the reduction of quinazoline has been taken up in the present study in methanol-water mixtures at various compositions in order to understand the nature and mechanism of the electrode process. The earlier work on the reduction of this compound by *Lund*[1] was incomplete, for example with regard to the nature of the medium employed in the reduction, the effect of composition of the medium on the polarographic characteristics and quinazoline behaviour under cyclic voltammetric (CVM) conditions. Further, the present paper deals with a comparison of the electrochemical behaviour of quinazoline with 4-(2′-thienyl)quinazoline (4-*TQ*)[2]. It may be pointed out that the electrochemical behaviour of quinazoline in dipolar aprotic media has been extensively studied[3–9].

## Experimental

Quinazoline (Fluka) was used as such without further purification. Methanol (Rechem) was purified according to the standard procedure and was twice distilled before use. A *Britton-Robinson* (*BR*) buffer was used for controlling the *pH* of the experimental solutions. The polarographic measurements using a three electrode system were similar to those described previously[2]. The dropping mercury electrode (d.m.e.) in 0.1 *M* KCl supporting electrolyte at 40 cm height of the mercury column (height uncorrected for back pressure) had the following capillary characteristics under open circuit conditions: "*m*" = 0.8672 mg $s^{-1}$; "*t*" = 7.0 s. The details of the microcoulometric experiments used in the present study for determining the total number of electrons ($n_{app}$) involved in the electrode process were similar to those described earlier[2]. The cyclic voltammograms were recorded using a hanging mercury drop electrode (HMDE) of area 0.019 ± 0.002 square centimeter and an MPI integrator circuit (Model MP 1012A) in conjunction with an HP X-Y recorder.

## Results and Discussion

### *Polarography*

The polarographic data obtained for quinazoline reduction in buffered 10% (*v/v*) methanol solution (*pH* 0.19 to 12.49) are presented in Table 1. The results obtained in aqueous methanolic solutions at other compositions (20–60% *v/v*) at selected *pH* values are also included in Table 1. Fig. 1 shows typical polarograms in buffered 10% (*v/v*) methanol solution. It is seen from Fig. 1 that quinazoline in acid solutions gives two waves of almost equal height. The first wave height increases at the expense of the second wave when the *pH* is increased and a single wave is observed in the *pH* range 4.82–6.00. At *pH* > 6.00, although one more wave is observed at more negative potentials, the wave is highly distorted due to the appearance of a polarographic maximum of the first kind which is found to be suppressed by a high concentration (0.02%) of gelatin.

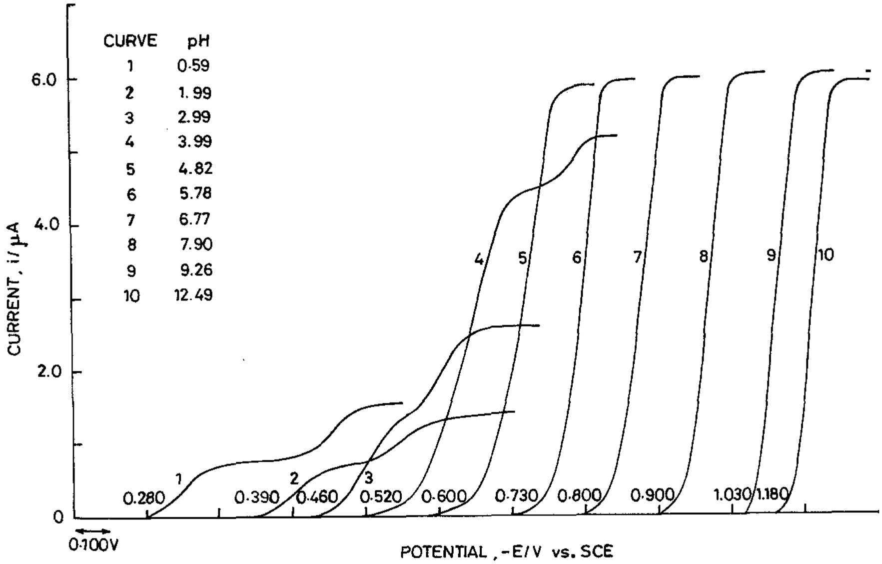

Fig. 1. Polarograms of quinazoline ($1.0 \cdot 10^{-3} M$) in buffered 10% (*v*/*v*) methanol solutions (starting voltages are indicated in the curves)

Because of this, the limiting currents as well as the potentials are affected to a considerable extent. Hence, the polarographic characteristics and the corresponding polarograms for these ill-defined waves are not included in Table 1 and Fig. 1, respectively. It is important to mention here that for quinazoline reduction in aqueous buffered solutions, the number of waves reported by *Lund*[1] in alkaline region *appears* to be three (two single-electron waves followed by a two-electron wave) whereas in the present study, two two-electron waves are observed, the second wave being ill-defined as described previously.

The total height of the wave between *pH* 1.00 and 2.00 is about twenty percent of the total height observed at $pH > 4.82$ (the wave height at $pH > 4.82$ corresponds to a two-electron transfer on the basis of the diffusion current constant, $I_d$). It is further observed that at very low *pH* values (< 1.00), the total wave height is once again increased. This observation is in accordance with the earlier work of *Lund*[1] which was attributed to the formation of an electro-inactive abnormal cation of quinazoline (called hydrated quinazolinium ion). The total wave height reported for quinazoline ($Q$) reduction[1] at *pH* 1.00 was only ten percent of the total height observed at *pH* 5.00 whereas in the present study it is twenty percent. The ten percent increase in the total height may be attributed to a shift of the equilibrium $Q + H_2O \overset{+H^+}{\rightleftharpoons} H^+Q + H_2O$,

Table 1. *Polarographic data for quinazoline ($1.0 \cdot 10^{-3} M$) reduction in buffered methanol-water mixtures*

| Percentage composition of methanol ($v/v$) | $pH^{a}$ | Wave | Limiting current, $i_l/\mu A^{b}$ | $-E_{1/2}/V$ vs. SCE[c] | $-(E_{3/4} - E_{1/4})/V$ | $-E_s/V$ vs. SCE[c] | $-dE/d\log[(i_l - i)/i]^{d}$ |
|---|---|---|---|---|---|---|---|
| 10[e] | 0.19[f] | I | 1.12 | 0.375 | 0.072 | — | 0.077 |
| | | II | 1.15 | 0.822 | 0.080 | — | 0.086 |
| | 0.59[g] | I | 0.76 | 0.394 | 0.066 | — | 0.078 |
| | | II | 0.78 | 0.804 | 0.082 | — | 0.086 |
| | 1.24[f] | I | 0.63 | 0.446 | 0.070 | — | 0.078 |
| | | II | 0.66 | 0.790 | 0.094 | — | 0.098 |
| | 1.99 | I | 0.68 | 0.502 | 0.078 | — | 0.078 |
| | | II | 0.74 | 0.794 | 0.114 | — | 0.114 |
| | 2.99 | I | 1.30 | 0.594 | 0.096 | 0.654 | 0.082 |
| | | II | 1.30 | 0.804 | 0.068 | — | 0.046 |
| | 3.99 | I | 4.40 | 0.760 | 0.124 | 0.814 | 0.090 |
| | | II | 0.70 | 1.050 | 0.040 | — | 0.046 |
| | 4.82 | Single wave | 5.85 | 0.826 | 0.084 | 0.893 | 0.090 |
| | 5.78 | Single wave | 5.90 | 0.894 | 0.074 | 0.945 | 0.068 |
| | 6.77 | Single wave | 5.95 | 0.952 | 0.072 | 0.982 | 0.071 |
| | 7.90 | Single wave | 6.10 | 1.034 | 0.064 | 1.084 | 0.058 |
| | 9.26 | Single wave | 6.00 | 1.122 | 0.056 | 1.145 | 0.054 |
| | 12.49[h] | Single wave | 5.95 | 1.272 | 0.040 | 1.304 | 0.043 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 20[e] | 4.00 | I | 4.65 | 0.778 | 0.132 | 0.796 | 0.129 |
| | | II | 0.25 | 1.060 | 0.044 | 1.100 | 0.055 |
| | 6.00 | Single wave | 5.65 | 0.914 | 0.076 | 0.948 | 0.071 |
| | 9.20 | Single wave | 6.00 | 1.124 | 0.063 | 1.168 | 0.058 |
| | 12.40 | Single wave | 5.70 | 1.378 | 0.050 | 1.404 | 0.051 |
| 30[e] | 4.05 | Single wave | 4.50 | 0.792 | 0.132 | 0.810 | 0.120 |
| | 7.29 | Single wave | 5.60 | 0.985 | 0.056 | 1.028 | 0.054 |
| | 9.36 | Single wave | 5.60 | 1.133 | 0.056 | 1.180 | 0.053 |
| 40[e] | 4.16 | Single wave | 4.70 | 0.805 | 0.120 | 0.835 | 0.117 |
| | 6.46 | Single wave | 5.85 | 0.952 | 0.065 | 1.000 | 0.060 |
| | 9.06 | Single wave | 5.65 | 1.102 | 0.052 | 1.146 | 0.046 |
| 50[e] | 2.41 | I | 0.74 | 0.586 | 0.064 | 0.606 | 0.063 |
| | | II | 0.65 | 0.812 | 0.076 | 0.814 | 0.075 |
| | 3.55 | I | 1.76 | 0.682 | 0.068 | 0.752 | 0.070 |
| | | II | 1.48 | 0.840 | 0.068 | — | 0.070 |
| | 6.52 | Single wave | 5.60 | 0.954 | 0.056 | 0.994 | 0.054 |
| | 10.13 | Single wave | 5.30 | 1.206 | 0.044 | 1.245 | 0.045 |
| 60[e] | 4.53 | Single wave | 5.40 | 0.816 | 0.084 | 0.848 | 0.083 |
| | 7.13 | Single wave | 5.70 | 0.986 | 0.053 | 1.030 | 0.052 |
| | 9.29 | Single wave | 5.65 | 1.140 | 0.052 | 1.180 | 0.044 |

[a] *pH* values pertain to the particular solvent composition as the standard state.
[b] Maximum current.
[c] Half-wave potential, accuracy ± 0.004 V.
[d] Values obtained from least-square fit computer programme with a correlation coefficient greater than 0.95.
[e] BR buffer.
[f] 1.0*M* aqueous HCl.
[g] 0.5*M* aqueous HCl.
[h] 0.1*M* aqueous NaOH.

towards the formation of an *anhydrous* cation of quinazoline which is electro-active in this medium. The study of the effect of height variation on the polarographic limiting currents ($i_l$) in buffered 10% (*v/v*) methanol solution indicated that at lower *pH* values (*pH* < 3.99), the limiting currents are found to be independent of the height of the mercury column showing the kinetically-controlled nature of the electrode process. On the other hand, at *pH* > 3.99 $i_l$ values are dependent on the height of the mercury column indicating a diffusion-controlled nature of the process. But, however, the slopes of ($\log i_l - \log h$) plots obtained in these media show the combined effect of kinetics and diffusion. The linearity in the [$-E$ vs. $\log (i_l - i)$] plot with a correlation coefficient greater than 0.95 clearly indicates that the reduction is predominantly diffusion-controlled.

The half-wave potentials ($E_{1/2}$) of quinazoline are dependent on the *pH* of the medium and are found to be shifted to more negative potentials with increasing *pH* (Table 1). This is so for the case where a single wave is observed at other compositions of methanol. The *ac* summit potentials ($E_s$) are found to be more negative to *dc* $E_{1/2}$ values which indicate the irreversible nature of the process. This is further evidenced from the higher slopes of the waves and logarithmic plots (Table 1).

The $E_{1/2}$ of quinazoline in buffered and unbuffered methanol solutions does not show any regular trend with solvent composition which may be due to the following reasons: (i) in buffered solutions, the nature of the reduction process as well as the number of waves of quinazoline change and (ii) in unbuffered solutions, the composite effect due to electrical double-layer, liquid-junction potential and adsorption of the depolariser as well as the solvent on the mercury surface may affect $E_{1/2}$. The effect of change in composition of methanol from 10 to 90% (*v/v*) on the polarograms of quinazoline in unbuffered media containing 0.1*M* potassium chloride supporting electrolyte is shown in Fig. 2. It is seen from Fig. 2 that quinazoline gives two well defined waves of almost equal height in the composition range 10–40% (*v/v*). Beyond 40% (*v/v*) methanol, the second wave is ill-defined in all cases due to the shift of the decomposition potential of the supporting electrolyte to positive values with increase in methanol content. This is similar to the observation made earlier in our laboratory in the case of 4-(2′-thienyl)quinazoline reduction in unbuffered media[10]. The product of the average diffusion current constant and square root of the viscosity of the medium ($I_d \eta^{1/2}$) for the first wave of quinazoline is found to be 4.62 ± 0.34. Since for a single electron-transfer process, the $I_d$ values range from 2.40 to 3.70, it is inferred that the first wave of quinazoline corresponds to a two-electron step[11] leading to the formation of a dihydroquinazoline. In the composition range 10–40% (*v/v*) where a second wave of equal height is observed, the reduction proceeds to the tetrahydro stage.

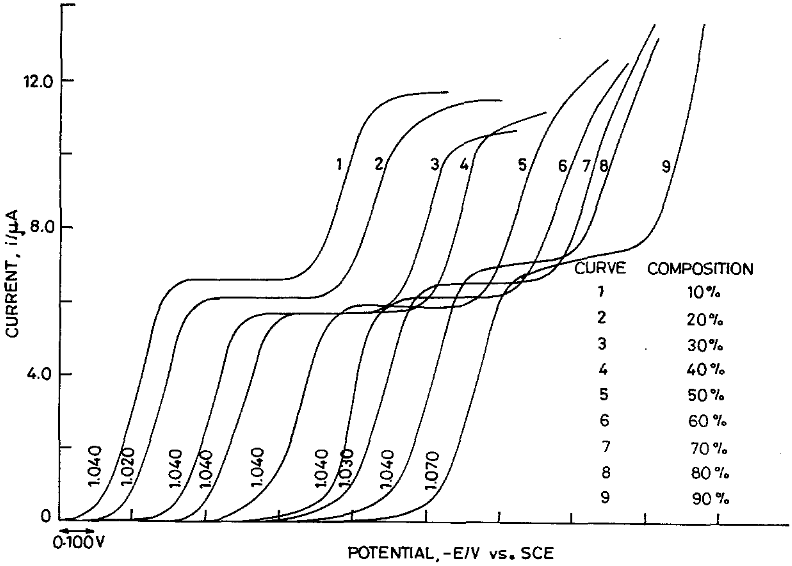

Fig. 2. Polarograms of quinazoline ($1.0 \cdot 10^{-3} M$) in unbuffered methanol solutions of varying compositions (starting potentials are indicated in the curves)

### *Controlled-Potential Electrolysis*

The $n_{\mathrm{app}}$ values obtained from microscale coulometric experiments at the limiting region of the first wave of quinazoline in buffered ($pH > 6.00$) and unbuffered 20%, 40%, and 60% (*v*/*v*) methanol solutions are, respectively, 1.95, 2.04, and 2.08 (accuracy ± 0.04). In unbuffered 20% (*v*/*v*) methanol solution, the $n_{\mathrm{app}}$ value at the limiting region of the second wave is $4.05 \pm 0.40$. The microcoulometric experiments at low *pH* values ($pH < 6.00$) could not be performed since the concentration of quinazoline responsible for the reduction is not definitely known due to the formation of hydrated cation of quinazoline in these solutions[1].

### *Cyclic Voltammetry*

The CVM results obtained for quinazoline ($1.0 \cdot 10^{-3} M$) reduction in buffered methanol solutions in the composition range 20–60% (*v*/*v*) are presented in Table 2. Figure 3 shows typical cyclic voltammograms obtained in buffered 20% (*v*/*v*) methanol solutions at two sweep rates. It is seen from Fig. 3 that in acid solutions quinazoline gives two cathodic peaks (the second one being small) in the forward scan. The CVM data presented in Table 2 indicate that at lower sweep rates ($0.05 \mathrm{~V~s}^{-1}$ and less) the first cathodic peak potential value $(E_p^c)_I$ are found to be more negative

Table 2. *CVM Data for quinazoline* ($1.0 \cdot 10^{-3} M$) *reduction in buffered methanolic solutions at various compositions*

| Composition of methanol ($v/v$) | Sweep rate, $v$/V s$^{-1}$ | Cathodic peak | $i_{cp}$/µA[a] | $-E_p$/V vs. SCE[b] | Current function, $i_p v^{-1/2} C_{ox}^{-1}$ | $(E_{p/2} - E_p)$/V solutions at various compositions |
|---|---|---|---|---|---|---|
| 20% at $pH$ 4.00 | 0.05 | I | 3.30 | 0.840 | 14.76 | 0.140 |
| | | II | — | 1.060 | — | — |
| $-(E_{1/2})_{I} = 0.778$ V vs. SCE | 0.10 | I | 4.00 | 0.760 | 12.65 | 0.085 |
| | | II | — | 1.050 | — | — |
| $-(E_{1/2})_{II} = 1.060$ V vs. SCE | 0.15 | I | 4.38 | 0.760 | 11.30 | 0.080 |
| | | II | — | 1.050 | — | — |
| | 0.20 | I | 5.75 | 0.760 | 12.86 | 0.080 |
| | | II | — | 1.060 | — | — |
| | 0.25 | I | 6.13 | 0.765 | 12.25 | 0.075 |
| | | II | — | 1.070 | — | — |
| | 0.30 | I | 7.50 | 0.770 | 13.69 | 0.085 |
| | | II | — | 1.070 | Average: 12.92 ± 1.09 | — |
| 20% at $pH$ 6.00 $-(E_{1/2})_{I} = 0.914$ V vs. SCE | 0.05 | Single peak | 8.50 | 0.935 | 38.01 | 0.065 |
| | 0.10 | Single peak | 11.25 | 0.935 | 35.58 | 0.060 |
| | 0.15 | Single peak | 14.00 | 0.940 | 36.15 | 0.065 |
| | 0.20 | Single peak | 17.00 | 0.945 | 38.01 | 0.060 |
| | 0.25 | Single peak | 21.00 | 0.945 | 41.00 | 0.065 |
| | 0.30 | Single peak | 22.50 | 0.950 | 41.08 | 0.065 |
| | | | | | Average: 38.81 ± 1.75 | |
| 20% at $pH$ 9.20 $-(E_{1/2})_{I} = 1.124$ V vs. SCE | 0.05 | I | 10.00 | 1.140 | 44.72 | 0.050 |
| | | Reverse | — | 1.555 | — | — |
| | 0.10 | I | 14.00 | 1.140 | 44.27 | 0.050 |
| | | Reverse | — | 1.535 | — | — |
| | 0.15 | I | 17.50 | 1.140 | 45.18 | 0.050 |
| | | Reverse | — | 1.510 | — | — |
| | 0.20 | I | 19.50 | 1.145 | 43.60 | 0.055 |
| | | Reverse | — | 1.480 | — | — |

| | | | | | | |
|---|---|---|---|---|---|---|
| | 0.25 | I | 25.75 | 1.150 | 51.50 | 0.050 |
| | | Reverse | — | 1.430 | — | — |
| | 0.30 | I | 28.00 | 1.160 | 51.12 | 0.055 |
| | | Reverse | — | 1.400 | Average: 46.73 ± 3.27 | — |
| 40% at *pH* 4.16<br>$-(E_{1/2})_I = 0.805$ V<br>vs. SCE | 0.05 | I | 3.915 | 0.840 | 17.51 | 0.110 |
| | | II | — | 1.070 | — | — |
| | 0.10 | I | 5.125 | 0.810 | 16.20 | 0.090 |
| | | II | — | 1.075 | — | — |
| | 0.15 | I | 5.625 | 0.805 | 14.52 | 0.080 |
| | | II | — | 1.075 | — | — |
| | 0.20 | I | 6.50 | 0.810 | 14.53 | 0.080 |
| | | II | — | 1.080 | — | — |
| | 0.25 | I | 7.00 | 0.805 | 14.00 | 0.075 |
| | | II | — | 1.080 | — | — |
| | 0.30 | I | 8.375 | 0.805 | 15.29 | 0.080 |
| | | II | — | 1.080 | — | — |
| | | | | | Average: 15.34 ± 1.20 | |
| 40% at *pH* 6.40<br>$-(E_{1/2})_I = 0.952$ V<br>vs. SCE | 0.05 | Single peak | 9.50 | 0.980 | 42.48 | 0.055 |
| | 0.10 | Single peak | 12.75 | 0.980 | 40.32 | 0.055 |
| | 0.15 | Single peak | 15.00 | 0.980 | 38.73 | 0.055 |
| | 0.20 | Single peak | 17.25 | 0.985 | 38.57 | 0.055 |
| | 0.25 | Single peak | 18.50 | 0.990 | 37.00 | 0.055 |
| | 0.30 | Single peak | 21.00 | 0.990 | 38.34 | 0.060 |
| | | | | | Average: 39.24 ± 1.74 | |
| 40% at *pH* 9.06<br>$-(E_{1/2})_I = 1.102$ V<br>vs. SCE | 0.05 | I | 6.25 | 1.135 | 27.95 | 0.040 |
| | | Reverse | — | 1.540 | — | — |
| | 0.10 | I | 8.00 | 1.350 | 25.30 | 0.040 |
| | | Reverse | — | 1.520 | — | — |
| | 0.15 | I | 10.50 | 1.140 | 27.11 | 0.040 |
| | | Reverse | — | 1.500 | — | — |
| | 0.20 | I | 12.00 | 1.145 | 26.83 | 0.040 |
| | | Reverse | — | 1.470 | — | — |
| | 0.25 | I | 13.80 | 1.150 | 27.60 | 0.045 |
| | | Reverse | — | 1.440 | — | — |
| | 0.30 | I | 15.50 | 1.155 | 28.30 | 0.045 |
| | | | | | Average: 27.18 ± 0.97 | |

*Table 2 (continued)*

| Composition of methanol ($v/v$) | Sweep rate, $v$/V s$^{-1}$ | Cathodic peak | $i_p^c$/μA[a] | $-E_p^c$/V vs. SCE[b] | Current function, $i_p^c v^{-1/2} C_{ox}^{-1}$ | $(E_{p/2} - E_p)$/V solutions at various compositions |
|---|---|---|---|---|---|---|
| 60% at $pH$ 4.53 $-(E_{1/2})_I = 0.816$ V vs. SCE | 0.05 | I | 3.38 | 0.840 | 15.09 | 0.075 |
| | | II | — | 1.080 | — | — |
| | 0.15 | I | 5.38 | 0.845 | 13.88 | 0.075 |
| | | II | — | 1.095 | — | — |
| | 0.20 | I | 6.19 | 0.855 | 13.84 | 0.075 |
| | | II | — | 1.100 | — | — |
| | 0.25 | I | 7.13 | 0.860 | 14.25 | 0.075 |
| | | II | — | 1.105 | — | — |
| | 0.30 | I | 7.88 | 0.865 | 14.38 | 0.075 |
| | | II | — | 1.105 | — | — |
| | | | | | Average: 14.28 ± 0.41 | |
| 60% at $pH$ 7.13 $-(E_{1/2})_I = 0.986$ V vs. SCE | 0.05 | Single peak | 7.25 | 1.025 | 32.42 | 0.045 |
| | 0.15 | Single peak | 12.40 | 1.025 | 32.00 | 0.048 |
| | 0.20 | Single peak | 14.00 | 1.025 | 31.30 | 0.048 |
| | 0.25 | Single peak | 15.50 | 1.030 | 31.00 | 0.048 |
| | 0.30 | Single peak | 17.00 | 1.030 | 31.04 | 0.048 |
| | | | | | Average: 31.30 ± 0.76 | |
| 60% at $pH$ 9.29 $-(E_{1/2})_I = 1.140$ V vs. SCE | 0.05 | Single peak | 7.75 | 1.175 | 34.66 | 0.045 |
| | 0.10 | Single peak | 10.40 | 1.180 | 32.89 | 0.045 |
| | 0.15 | Single peak | 12.25 | 1.185 | 31.63 | 0.045 |
| | 0.20 | Single peak | 14.30 | 1.185 | 31.98 | 0.045 |
| | 0.25 | Single peak | 16.00 | 1.190 | 32.00 | 0.045 |
| | 0.30 | Single peak | 19.25 | 1.195 | 35.15 | 0.045 |
| | | | | | Average: 33.05 ± 1.37 | |

[a] Cathodic peak current.
[b] Cathodic peak potential, accuracy ± 0.005 V.

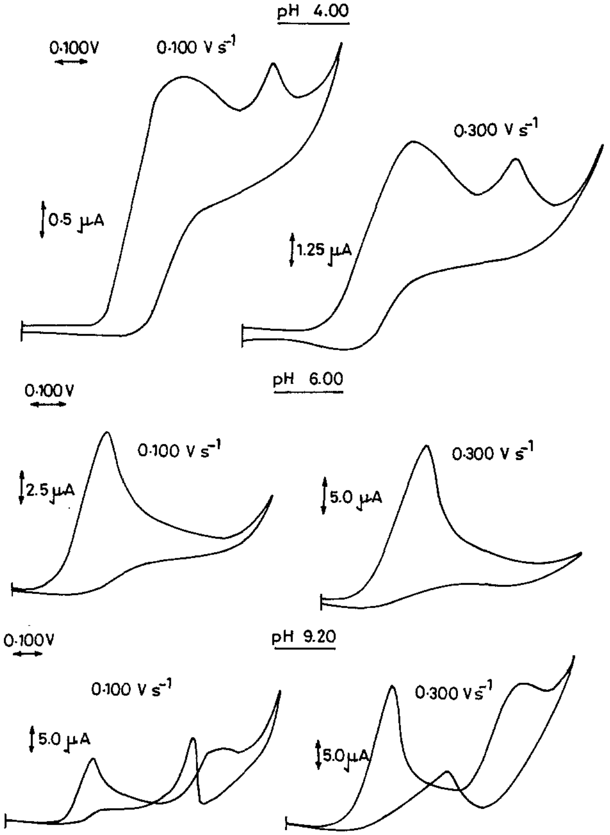

Fig. 3. Cyclic voltammograms for quinazoline ($1.0 \cdot 10^{3} M$) reduction in buffered 20% (*v*/*v*) methanol solutions (starting voltage is zero)

to the *dc* $E_{1/2}$ value corresponding to the first step in the case of 20% and 40% (*v*/*v*) methanol solutions. At higher sweep rates $(E_p^c)_I$ values either coincide or are little more positive to the *dc* $E_{1/2}$ value. This may be due to the effect of adsorption of quinazoline at mercury-solution interface[10] or due to the follow up chemical reaction. The independent nature of the first cathodic current function values with sweep rates (Table 2) indicates the diffusion-controlled nature of the electrode process. The absence of anodic peaks during the reverse scan shows the irreversible behaviour of the overall process. The cyclic voltammograms in buffered 20–60% (*v*/*v*) methanol solutions in the neutral region show a single cathodic peak (Fig. 3), corresponding to the polarographic wave observed in these media. Interestingly, the cyclic voltammograms of quinazoline in buffered (*pH* 9.20) 20% (*v*/*v*) methanol solution show "reverse cathodic peaks" during the anodic sweep (Fig. 3). The "reverse cathodic peak" potential are shifted to more positive values with increase in sweep rate (Table 2). The cause for observing the "reverse cathodic peak" may be due to the accumulation of the reduction product, namely, dihydroquinazoline on the mercury surface, which is not getting reduced during the forward scan because of the masking of the electrode surface by the tetrahydroquinazoline. It may be mentioned that a similar reduction peak in the reverse oxidation sweep has been observed in the cyclic voltammograms of α,β-unsaturated ketones by *Margaretha* and *Tissot*[12].

The peak currents and current function values observed in the acid region are about one third compared to those values in neutral and alkaline regions. This is quite understandable if we assume that a single electron is involved in the reduction in the acid region and two in the neutral and alkaline regions, since in CVM experiments the $i_p$ values under identical conditions (such as same concentration of the depolariser and constant surface area of HMDE) are proportional to $n_{\mathrm{app}}^{3/2}$, where $n_{\mathrm{app}}$ is the total number of electrons transferred in the electrode process.

### *Mechanism of Quinazoline Reduction in Amphiprotic Media*

From the polarographic and controlled-potential electrolysis results obtained for the quinazoline ($Q$) reduction, the following mechanisms are operative in various media:

*a. Mechanism (CEE-type) in Buffered Acid Media (pH < 4.82)*

$Q + \mathrm{H}^+ + \mathrm{H_2O} \rightarrow [Q\mathrm{H_3O}]^+$
(electro-inactive abnormal cation)

$[Q\mathrm{H_3O}]^+ \rightleftharpoons Q\mathrm{H}^+ + \mathrm{H_2O}$
(electro-active)

$Q\mathrm{H}^+ + \mathrm{e} + \mathrm{H}^+ \rightarrow [Q\mathrm{H_2}]^{\dot{+}}$
(first electron-transfer)

$[Q\mathrm{H_2}]^{\dot{+}} + \mathrm{e} + \mathrm{H}^+ \rightarrow [Q\mathrm{H_3}]^+$
(second electron-transfer)

Since the total wave at $pH$ 4.82 corresponds to a two-electron addition (on the basis of $I_d$ and $n_{\mathrm{app}}$ values), the number of electrons transferred below the $pH$ 4.82 is assumed to be the same. An almost equal height of the waves of quinazoline below $pH$ 2.99 indicates the participation of the same number of electrons and hence each step is considered to be a single-electron step.

*b. Mechanism in Buffered Media in the pH Range 4.82–6.00*

$Q + 2e + 2H^+ \rightarrow QH_2$
(single two-electron transfer)

*c. Mechanism (ECEC-Type) in Buffered Alkaline Media in the pH Range 6.77–12.49*

$Q + 2e + 2H^+ \rightarrow QH_2$
(first two-electron transfer)

$QH_2 + 2e + 2H^+ \rightarrow QH_4$
(second two-electron transfer, distorted wave)

The same mechanism as suggested above is operating in the case of unbuffered methanol solutions in the composition range 10–40% (*v/v*) where the reduction of quinazoline proceeds in two two-electron steps to give the tetrahydro product. In the composition range 50–90% (*v/v*) methanol where a single two-electron wave is observed, the reduction proceeds only up to the dihydro stage.

### *Comparison of the Electrochemical Behaviour of Quinazoline with 4-(2′-Thienyl)quinazoline (4-TQ)*

The following comparison between quinazoline and 4-*TQ* can be made from the results obtained on their reductions in buffered and unbuffered amphiprotic media:

a. The polarographic results and CPE experiments on the 4-*TQ* reduction[2] in buffered methanol solutions at various compositions indicate that the reduction proceeds through successive single electron-transfer steps to give the dihydro-4-*TQ* as the final product. In the case of quinazoline, except in strong acid solutions, the reduction takes place in a single two-electron step to give dihydroquinazoline. In strong acid solutions ($pH < 2.99$) protonated dihydroquinazoline is formed from the anhydrous quinazolinium ion (whose concentration is dependent on the kinetics of the dehydration of the hydrated cation of quinazoline) and hence lower limiting currents are observed in the reduction. This lowering in the limiting currents is not observed in the case of 4-*TQ* reduction, which indicates that 4-*TQ* is *not* hydrated.

b. Even though two waves are observed in the quinazoline reduction at low *pH* values, a comparison of the $E_{1/2}$ potentials of 4-*TQ* and quinazoline (under identical experimental conditions) shows (Table 3) that 4-*TQ* gets reduced more easily than quinazoline.

The ease of 4-*TQ* reduction is attributed to the electron withdrawing nature of the (2′-thienyl) group[13] at C-4 position (thus lowering the $\pi$-electron density) and making the polarographic reduction easier.

Table 3. *Comparison of half-wave potentials of 4-TQ and quinazoline in buffered 10% (v/v) methanol solution*

| | $-E_{1/2}$/V versus SCE | | | |
|---|---|---|---|---|
| *pH* | 4-*TQ* | | Quinazoline | |
| | Wave I | Wave II | Wave I | Wave II |
| 0.19 | 0.229 | 0.761 | 0.375 | 0.822 |
| 4.04 | 0.568 | 0.824 | 0.765 | 1.055 |

c. The droptime-potential measurements indicate that both quinazoline[10] and 4-*TQ*[14] get adsorbed on the mercury surface. The extent of adsorption is more in the case of 4-*TQ* (more lowering in droptime under identical conditions) when compared to quinazoline. This is to be expected because the larger the size of nitrogen heterocycle, the more easily adsorption on the electrode surface takes place. The electrocapillary curves ("non-equilibrium" type) of quinazoline[10] and 4-*TQ*[14] in methanolic solutions show a similar trend.

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