# CHAPTER IV

## RESULTS AND DISCUSSION

Tartrazine , Brilliant Blue FCF and Quinoline Yellow are the food dyes studied . Even the dyes used are of food grade , their purities were examined by paper chromatographic and spectrophotometric techniques before their polarographic studies .

### 4.1 Purities of the dyes

#### 4.1.1 Paper chromatographic technique

Four solvent systems were used for testing purities of the dyes : the solvent system I ( 1-butanol , water and acetic acid ) for Tartrazine and Quinoline Yellow , the system II ( 2-methyl-1-propanol, ethanol, water and 0.88 ammonia solution ) for Tartrazine and Brilliant Blue FCF , the system III ( phenol and water ) for Brilliant Blue FCF and system IV ( 2-butanone , 2-propanone , water and 0.88 ammonia solution ) for Quinoline Yellow . The compositions of these solvent systems were described in the procedure part (3.3.1.1) in chapter 3 .

The paper chromatogram of each dye in every solvent system studied showed a well-defined spot except Quinoline Yellow by the solvent system I whose chromatogram illustrated three spots ( see Figure 4 ) . Since Quinoline Yellow dye composed of either mono and di sulfonic acid or di and tri sulfonic acid of Quinoline Yellow ,

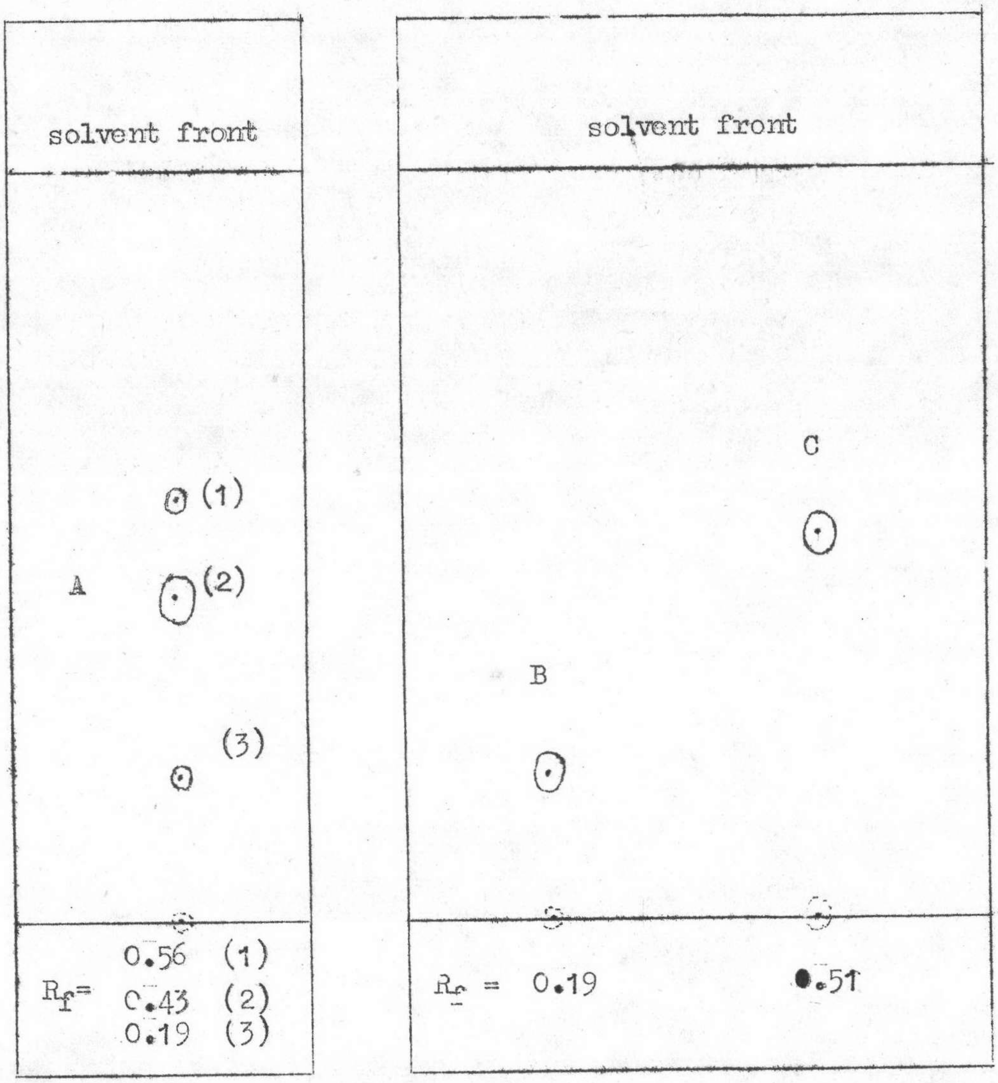


Figure 4 Paper chromatograms of the following dyes

A) Quinoline Yellow in solvent system I

B) Tartrazine in solvent system II

C) Brilliant Blue FCF in solvent system II the developing solvent system I might be very sensitive to separate the sulfonic acid functional groups , and three spots were resulted. However , by solvent system IV , Quinoline Yellow illustrated only one single spot . The $R_f$ value of each dye in the solvent system was compared to its literature value . These values were listed in Table 2 . The $R_f$ values of Tartrazine and Brilliant Blue FCF are slightly different from the literature values (32) owing to the water content in the paper used , concentration of the dye solution , the temperature and the vapor pressure of solvent in the chromatographic chamber .

### 4.1.2 Spectrophotometric techniques

#### 4.1.2.1 Visible - UV spectra

The visible , uv spectra of Tartrazine , Brilliant Blue FCF and Quinoline Yellow in 0.1 M HCl and 0.1 M NaOH solutions were performed and shown in Figure 5A -5C . The wavelengths at the maximum absorption ($\lambda$max ) of the dyes were measured and their molar absorptivities were calculated as listed in Table 3 . The molar absorptivity of each dye in the acid solution was found in the order of $10^4$ ( see Table 3 ) which indicated to a strong absorption of the dye in visible range .

#### 4.1.2.2 IR spectra

The IR spectra of Tartrazine , Brilliant Blue FCF and Quinoline Yellow in solid KBr pellets were shown in Figures 6A-6C. The spectrum of Tartrazine indicated an insignificant difference from the literature one (33), it showed the phenolic OH (3440 $cm^{-1}$), -N=N- (1640 $cm^{-1}$) , aromatic ( 1380 $cm^{-1}$ and 1490 $cm^{-1}$ -skeleton

Table 2 $R_f$ values of Quinoline Yellow , Tartrazine and Brilliant Blue FCF by solvent systems I , II , III and IV

| Dye | Solvent system I | | Solvent system II | | Solvent system III | | Solvent system IV | |
|---|---|---|---|---|---|---|---|---|
| | $R_f$ | $R_f$ (32) | $R_f$ | $R_f$ (32) | $R_f$ | $R_f$ (32) | $R_f$ | $R_f$ (32) |
| Quinoline Yellow | 0.19<br>0.43<br>0.56 | 0.50 | | | | | 0.62 | 0.60 |
| Tartrazine | 0.28 | 0.30 | 0.19 | 0.20 | | | | |
| Brilliant Blue FCF | | | 0.51 | 0.50 | 0.71 | 0.70 | | |

(32) Macek, K. Pharmaceutical Applications of Thin-layer Paper chromatography. Amsterdum : Elsevier Publishing Company, 1972. pp 622.

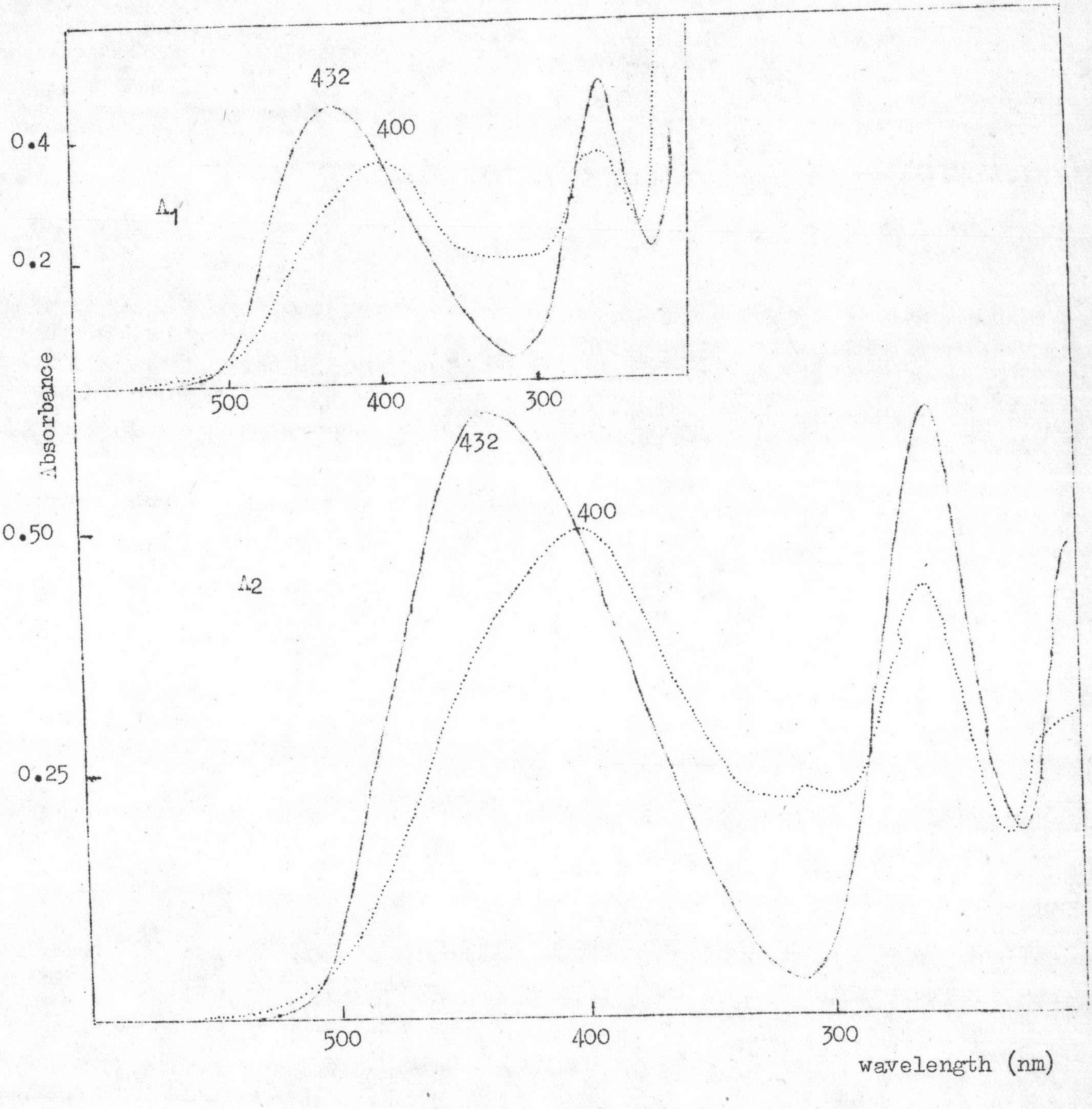


Figure 5A Comparison of UV-visible spectra of Tartrazine between A1) literature(33) and A2) experiment; ______in 0.1 M HCl ........in 0.1 M NaOH

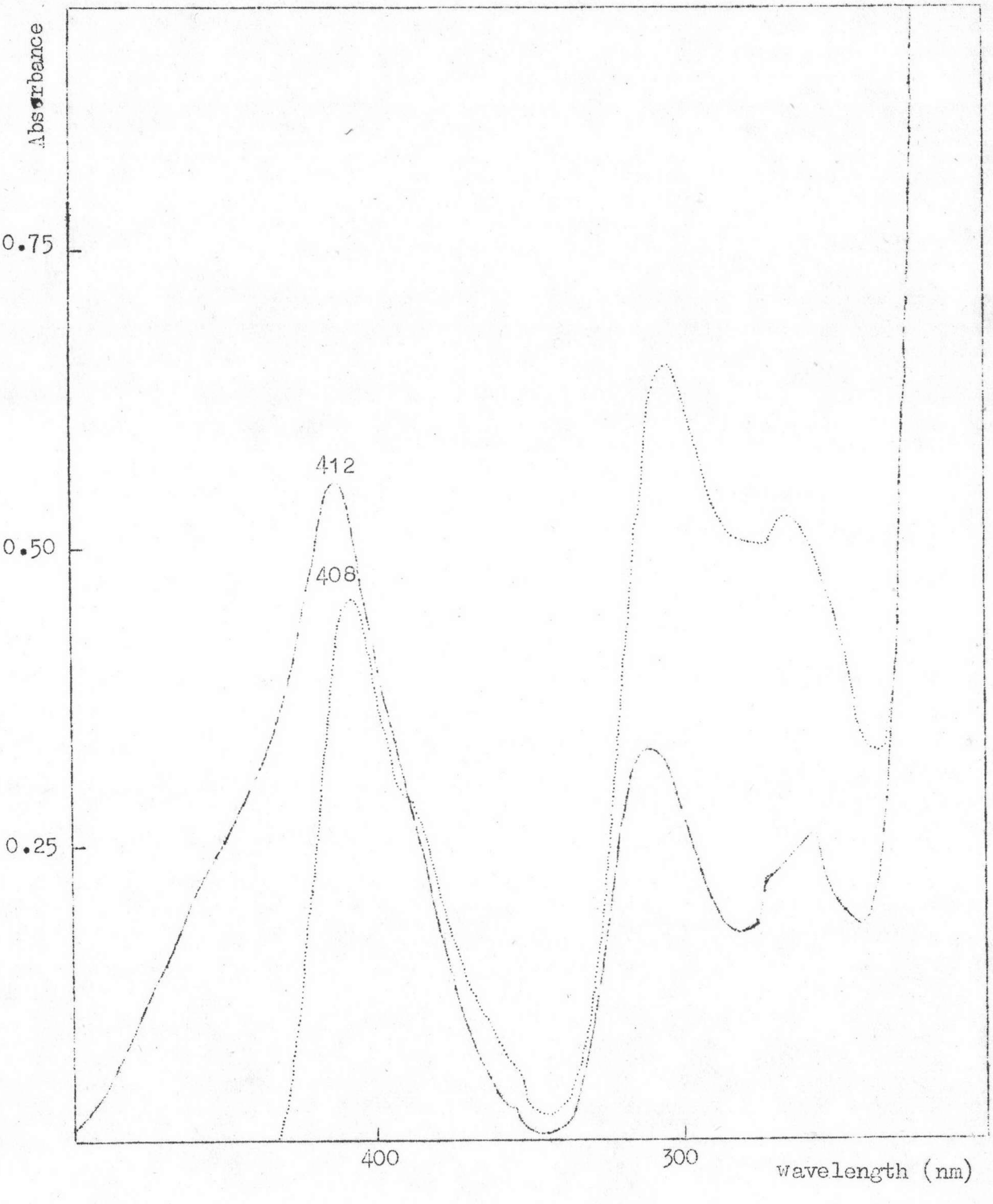


Figure 5B UV-visible spectra of Brilliant Blue FCF

______in 0.1 M HCl and ......in 0.1 M NaOH

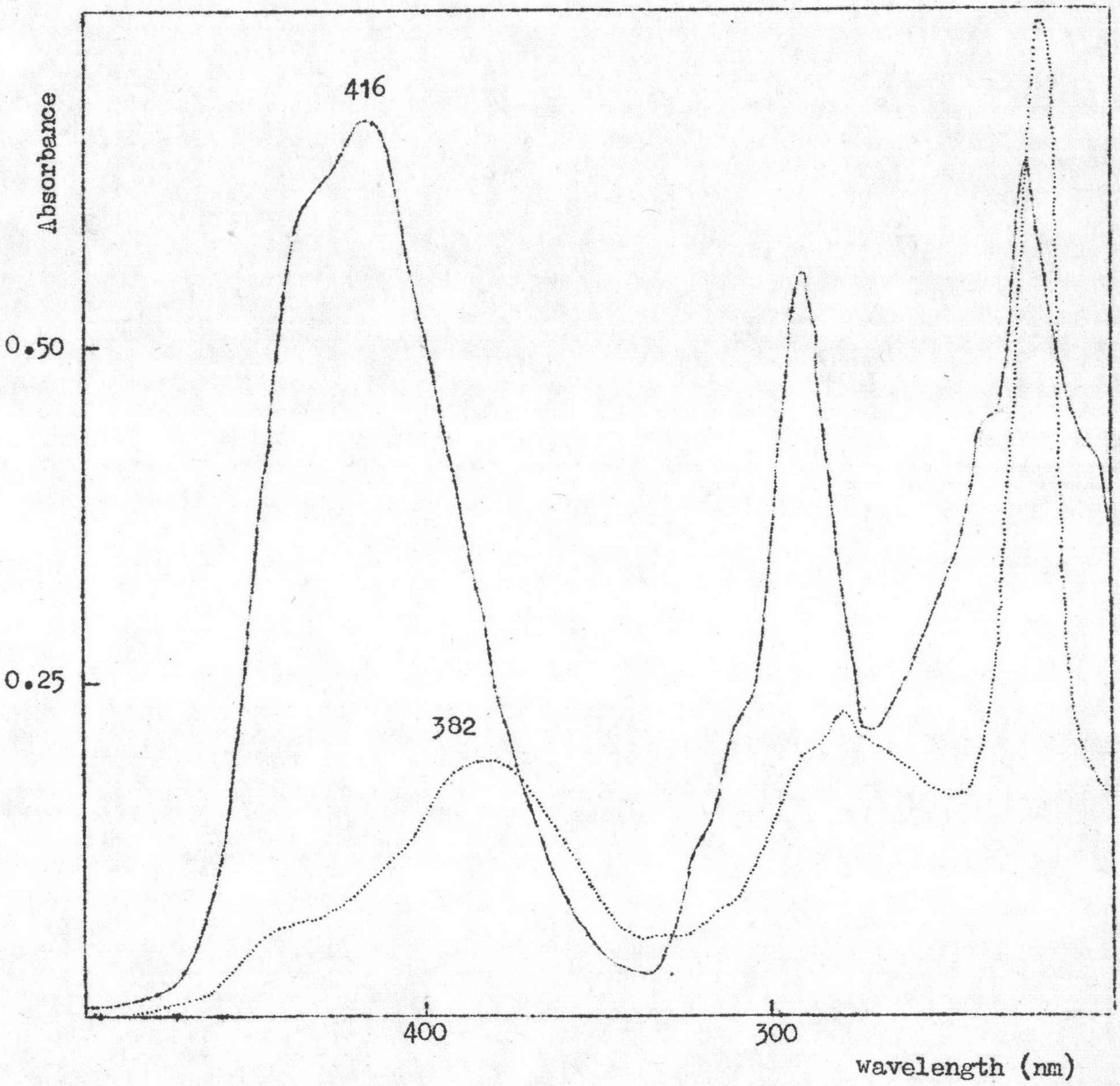


Figure 5C UV-visible spectra of Quinoline Yellow

_____in 0.1 M HCl and ......in 0.1 M NaOH

Table 3 Absorption characteristics of dyes in the visible region

| Dye | $\lambda$ max (nm) | molar absorptivity $\varepsilon$ (calculated) |
|---|---|---|
| Quinoline Yellow | 416 in acid solution | 26,600 |
| | 382 in alkali solution | 15,480 |
| Tartrazine | 432 in acid solution | 24,600 |
| | 400 in alkali solution | 19,880 |
| Brilliant Blue FCF | 412 in acid solution | 11,000 |
| | 408 in alkali solution | 9,108 |

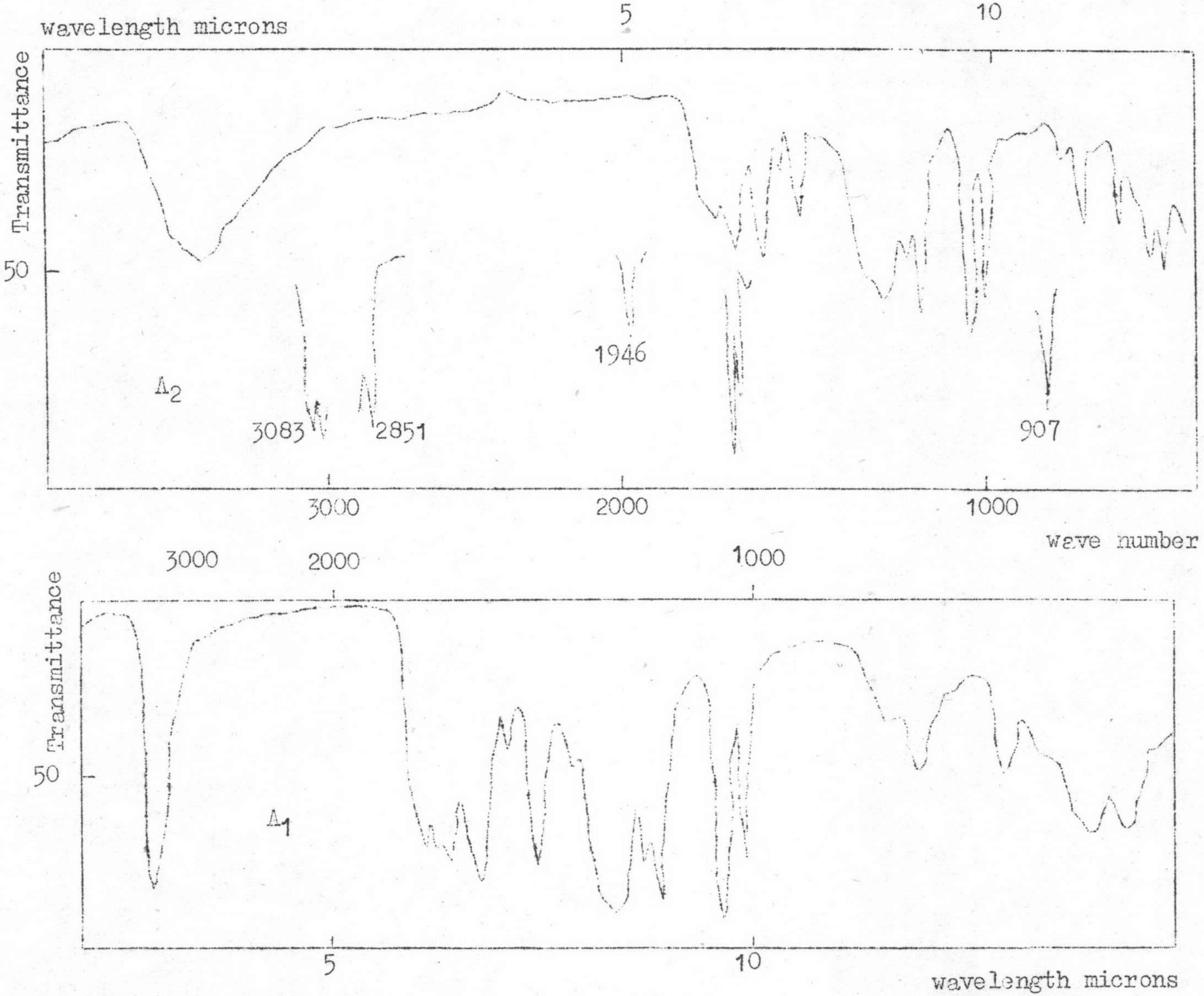


Figure 6A Comparison of IR spectra of Tartrazine in solid KBr pellet between

A1) literature(33) A2) experiment

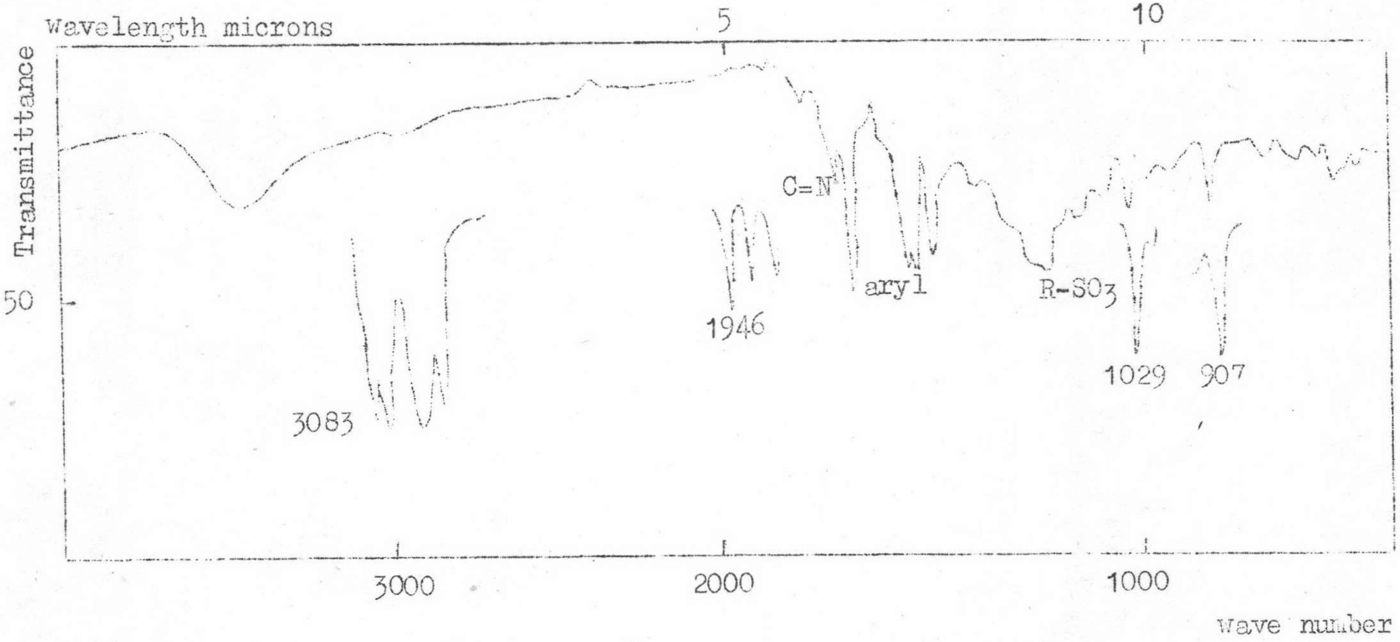


Figure 6B IR spectrum of Brilliant Blue in solid KBr pellet

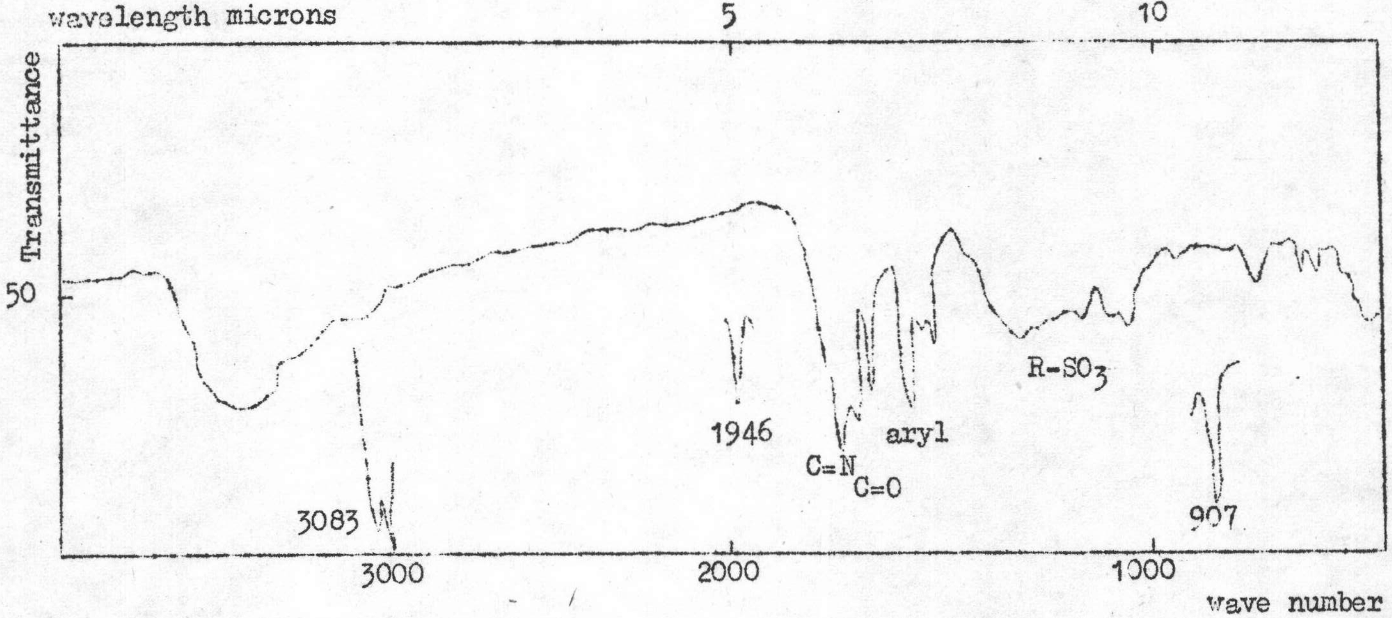


Figure 6C IR spectrum of Quinoline Yellow in solid KBr pellet carbon stretching and 700 -800 $cm^{-1}$ aromatic out of plane bending ) and ionic sulfonate ( 1120 $cm^{-1}$ and 1200 $cm^{-1}$ ) characters (see Figure 6A ) . The spectrum of Brilliant Blue FCF showed the $>C = N-$ (1640 $cm^{-1}$ ) , aromatic (1400 $cm^{-1}$ and 1550 $cm^{-1}$ - skeleton carbon stretching , and 700 -800 $cm^{-1}$ aromatic out of plane bending ) and ionic sulfonate (1030 $cm^{-1}$ and 1170 $cm^{-1}$ )characters ( see Figure 6B ). The spectrum of Quinoline Yellow showed the $>C = N-$ (1650 $cm^{-1}$ ) , $>C = O$ (1600 $cm^{-1}$ ) , aromatic ( 1440 $cm^{-1}$ and 1550 $cm^{-1}$ - skeleton carbon stretching and 750 - 800 $cm^{-1}$ aromatic out of plane bending ) and ionic sulfonate ( 1030 $cm^{-1}$ and 1200 $cm^{-1}$ ) characters see Figure 6C ).

No other functional groups even $H_2O$ molecule was found in the IR spectra of Tartrazine , Brilliant Blue FCF and Quinoline Yellow .

The evidences from paper chromatogram ,visible spectra and IR spectra of the dyes investigated indicated that Tartrazine , Brilliant Blue FCF and Quinoline Yellow had high purity .
Even the paper chromatogram of Quinoline Yellow by the solvent system I showed three spots but by the solvent system IV only one single spot was obtained and its $R_f$ value was slightly different from the literature value . In addition , its visible spectrum provided one peak and its IR spectrum showed only the functional groups of Quinoline Yellow and no other functional groups of impurity .

## 4.2 Polarographic behavior

Polarographic studies of Tartrazine , Brilliant Blue FCF and Quinoline Yellow were performed in the common supporting electrolytes such as 0.1 M KCl , 0.1 M $KNO_3$ and 0.1 M $(C_2H_5)_4NCl$ . The pH of

Tartrazine , Brilliant Blue FCF and Quinoline Yellow solutions were controlled by using McIlvaine buffer for pH 2.0 - 7.2 and Michaelis borate buffer for pH 7.6 - 12.3 . Michaelis phosphate buffer was also used for controlling pH of the Quinoline Yellow solution for pH 4.5 -8.3 .

### 4.2.1 Diffusion controlled

The polarographic reduction of Tartrazine in every electrolyte and pH studied provided one polarographic wave , as well as the reductions of Brilliant Blue FCF and Quinoline Yellow in every electrolyte and pH studied yielded two polarographic waves. These polarographic reduction processes were determined whether they were diffusion , adsorption , kinetic or catalytic controlled. Four tests were performed herein : 1) the dependence of the limiting current ( $i_1$ ) on the concentration of the dye , 2) the dependence of the $i_1$ on the mercury height ( h ) , 3 ) the dependence of the $i_1$ on $h^{\frac{1}{2}}$ and 4) the dependence of the $i_1$ on the temperature of the dye solution . The dye solutions studied were Tartrazine at pH 1.35 , Brilliant Blue FCF at pH 1.40 and Quinoline Yellow at pH 7.50. They were selected for this identification since the well separated waves were resulted .

The limiting currents obtained at various concentrations of the dyes are listed in Table 4 . A linear relationship between the limiting current and the dye concentration was obtained at the range of concentrations $1.0 \times 10^{-5} - 8.0 \times 10^{-4}$ M for Tartrazine , Brilliant Blue FCF or Quinoline Yellow (see Figure 7 for the first waves and Figure 8 for the second waves ).

Table 4 Effects of concentrations on the limiting currents of various dyes at constant mercury height[a] and temperature[b]

| Tartrazine | | Brilliant Blue FCF | | | Quinoline Yellow | | |
|---|---|---|---|---|---|---|---|
| concentration $10^5$ x conc.(M) | $i_1$ (μA) | concentration $10^5$ x conc.(M) | $i_1$ (μA) 1st wave | $i_1$ (μA) 2nd wave | concentration $10^5$ x conc.(M) | $i_1$ (μA) 1st wave | $i_1$ (μA) 2nd wave |
| 0.90 | c | 0.90 | c | c | 1.00 | c | c |
| 1.00 | c | 1.00 | 0.030 | c | 2.00 | 0.170 | c |
| 1.50 | 0.150 | 3.00 | 0.060 | c | 3.00 | 0.180 | c |
| 3.00 | 0.430 | 5.00 | 0.095 | c | 5.00 | 0.220 | c |
| 5.00 | 0.600 | 7.00 | 0.120 | 0.030 | 7.00 | 0.360 | c |
| 7.00 | 0.800 | 9.00 | 0.135 | 0.058 | 10.00 | 0.400 | c |
| 9.00 | 0.952 | 10.00 | 0.150 | 0.100 | 20.00 | 0.800 | 0.300 |
| 10.00 | 1.000 | 20.00 | 0.300 | 0.360 | 30.00 | 1.100 | 0.500 |
| 20.00 | 2.010 | 30.00 | 0.452 | 0.550 | 40.00 | 1.450 | 0.700 |
| 30.00 | 2.800 | 40.00 | 0.580 | 0.680 | 50.00 | 1.800 | 0.830 |
| 40.00 | 3.962 | 50.00 | 0.740 | 0.820 | 60.00 | 2.180 | 1.020 |
| 50.00 | 4.405 | 60.00 | 0.920 | 1.070 | 70.00 | 2.600 | 1.150 |
| 60.00 | 5.180 | 70.00 | 1.120 | 1.200 | 80.00 | 3.020 | 1.440 |
| 70.00 | 6.050 | 80.00 | 1.220 | 1.530 | | | |
| 80.00 | 7.000 | | | | | | |

[a] mercury height = 65.0 cm , [b] temperature = 30.0 °C , and [c] cannot be measured accurately

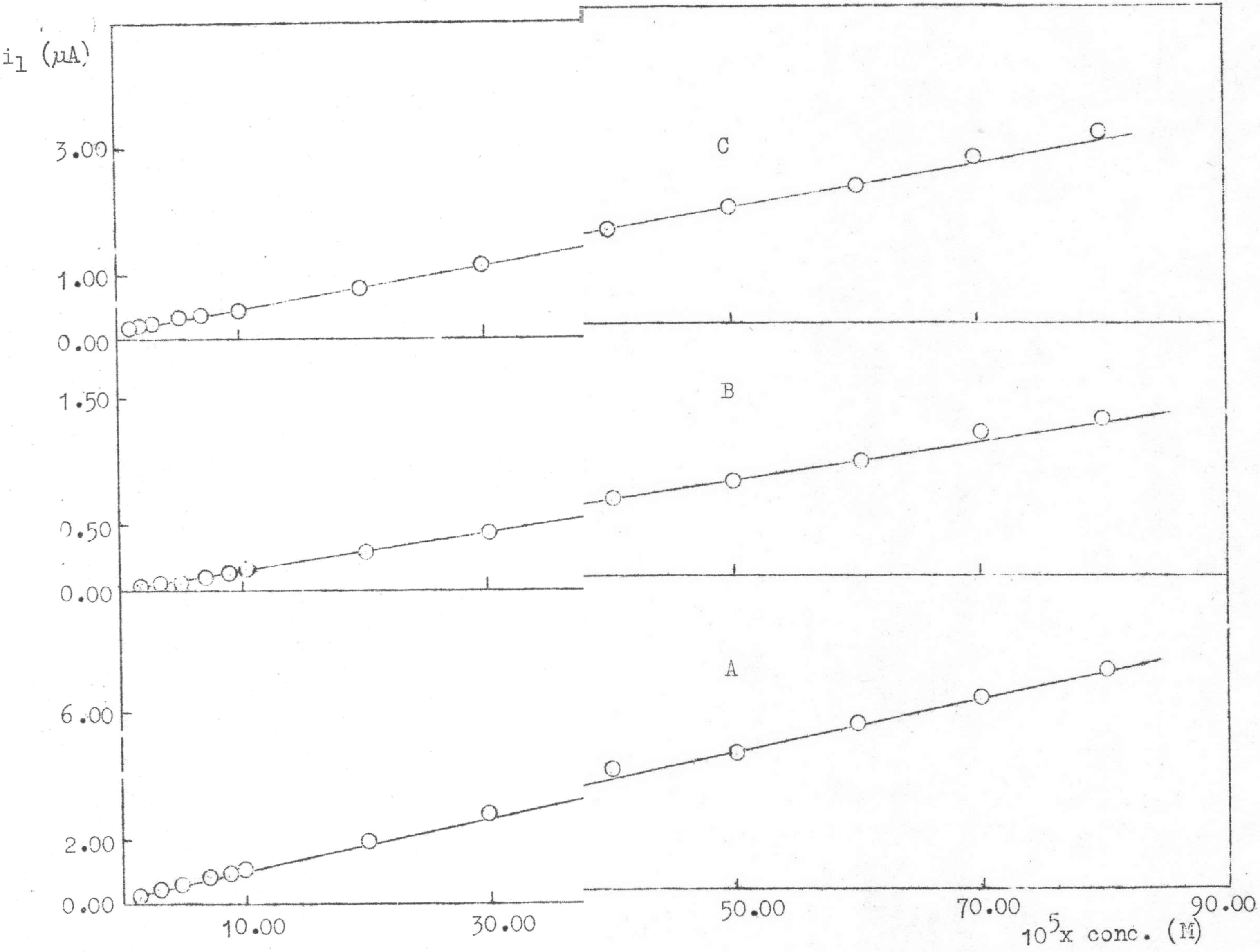


Figure 7 The dependences of concentrations on limiting currents for the first waves of various dye solutions: A) Tartrazine, B) Brilliant Blue FCF and C) Quinoline Yellow

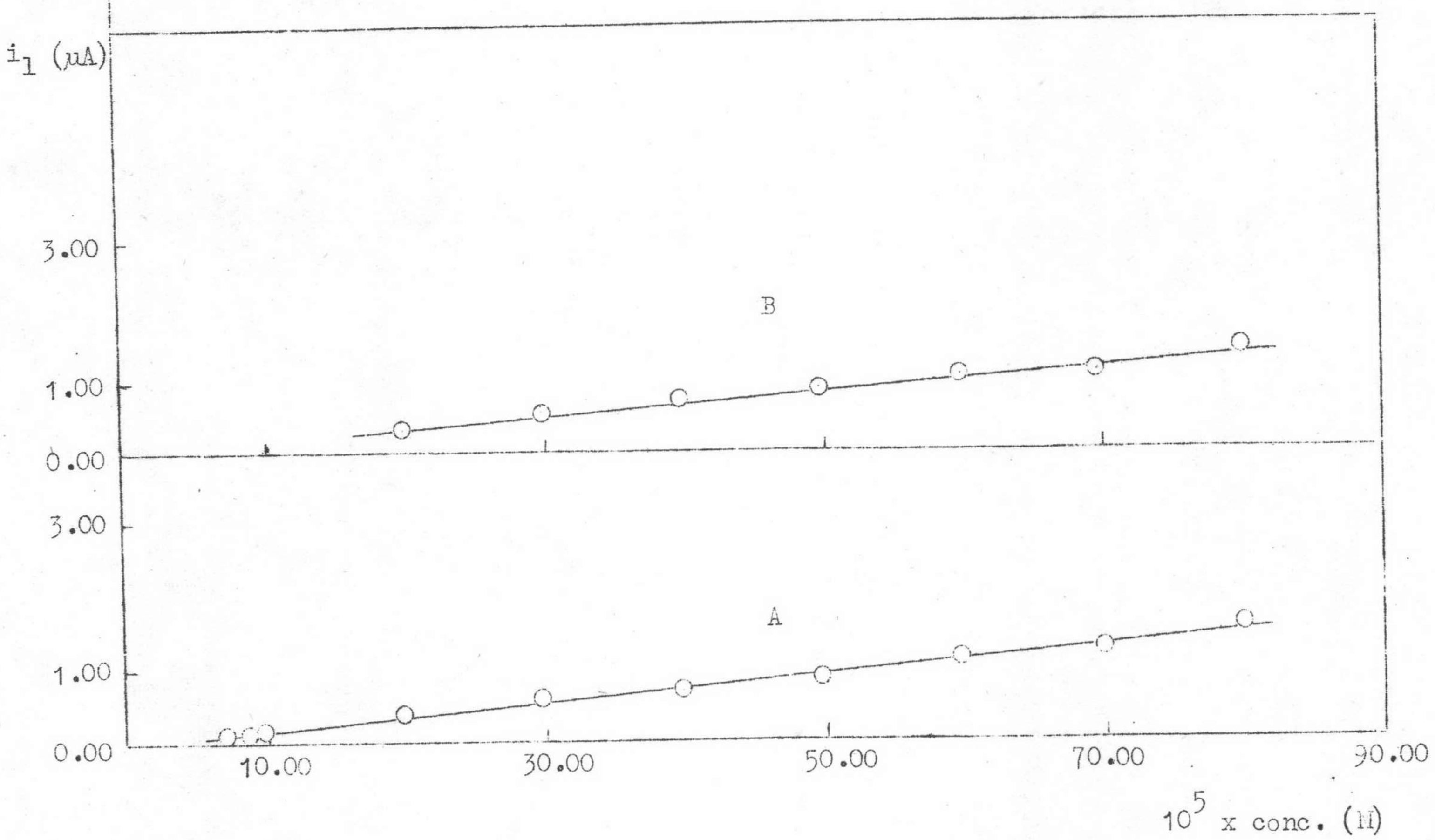


Figure 8 The dependences of concentrations on limiting currents for the second wave of various dye solutions: A) Brilliant Blue FCF, B) Quinoline Yellow

The limiting currents of $5.0 \times 10^{-4}$ M of Tartrazine , Brilliant Blue FCF and Quinoline Yellow at various mercury heights (38.0 - 63.0 cm ) are shown in Table 5 . The plots of $i_1$ against $h^{\frac{1}{2}}$ and of $i_1$ against h are shown in Figure 9 . For every dye solution studied , a linear proportion of the limiting current to the square root of mercury height and a convex curve of the limiting current against the mercury height were resulted .

The temperature coefficients ( between 30.0 °C and 50.0 °C ) were calculated and are shown in Table 6 . They are in the range of 1.18 - 2.25 % .

From these tests , the limiting current of every dye studied is directly proportional to the dye concentration , and to the square root of mercury height . These proved that the limiting current of each dye studied is diffusion current . In addition , the temperature coefficient of the limiting current of every dye studied is also in the range of diffusion controlled process .

Therefore , the polarographic reduction processes of Tartrazine , Brilliant Blue FCF and Quinoline Yellow in 0.1 M $(C_2H_5)_4NCl$ were diffusion controlled . These dyes in 0.1 M KCl and 0.1 M $KNO_3$ also provided the same results .

### 4.2.2 Effect of pH on the polarographic wave

The polarographic waves of most organic compounds are pH dependence . Thus, a variety of pH of the dye solution was studied. The final pH of the dye solutions are reported in this polarographic section .

Table 5 Effect of mercury heights on the limiting currents of various dyes at constant temperature[a]

| Compound | pH | h (cm ) | $h^{\frac{1}{2}}$ ($cm^{\frac{1}{2}}$) | $1^{st}$ wave | $2^{nd}$ wave |
|---|---|---|---|---|---|
| | | | | $i_1$ (µA) | $i_1$ (µA) |
| Tartrazine | 1.35 | 33.0 | 5.7 | 0.269 | - |
| | | 38.0 | 6.1 | 0.286 | - |
| | | 43.0 | 6.5 | 0.300 | - |
| | | 48.0 | 6.9 | 0.313 | - |
| | | 53.0 | 7.2 | 0.330 | - |
| | | 58.0 | 7.5 | 0.345 | - |
| | | 63.0 | 7.9 | 0.362 | - |
| Brilliant Blue FCF | 1.40 | 38.0 | 6.1 | 0.330 | 0.315 |
| | | 43.0 | 6.5 | 0.340 | 0.360 |
| | | 48.0 | 6.9 | 0.360 | 0.400 |
| | | 53.0 | 7.2 | 0.370 | 0.433 |
| | | 58.0 | 7.5 | 0.380 | 0.470 |
| | | 63.0 | 7.9 | 0.393 | 0.500 |
| Quinoline Yellow | 7.50 | 33.0 | 5.7 | 0.563 | 0.390 |
| | | 38.0 | 6.1 | 0.610 | 0.420 |
| | | 43.0 | 6.5 | 0.653 | 0.443 |
| | | 48.0 | 6.9 | 0.686 | 0.470 |
| | | 53.0 | 7.2 | 0.726 | 0.490 |
| | | 58.0 | 7.5 | 0.753 | 0.510 |
| | | 63.0 | 7.9 | 0.783 | 0.533 |

[a] temperature = 30.0°C

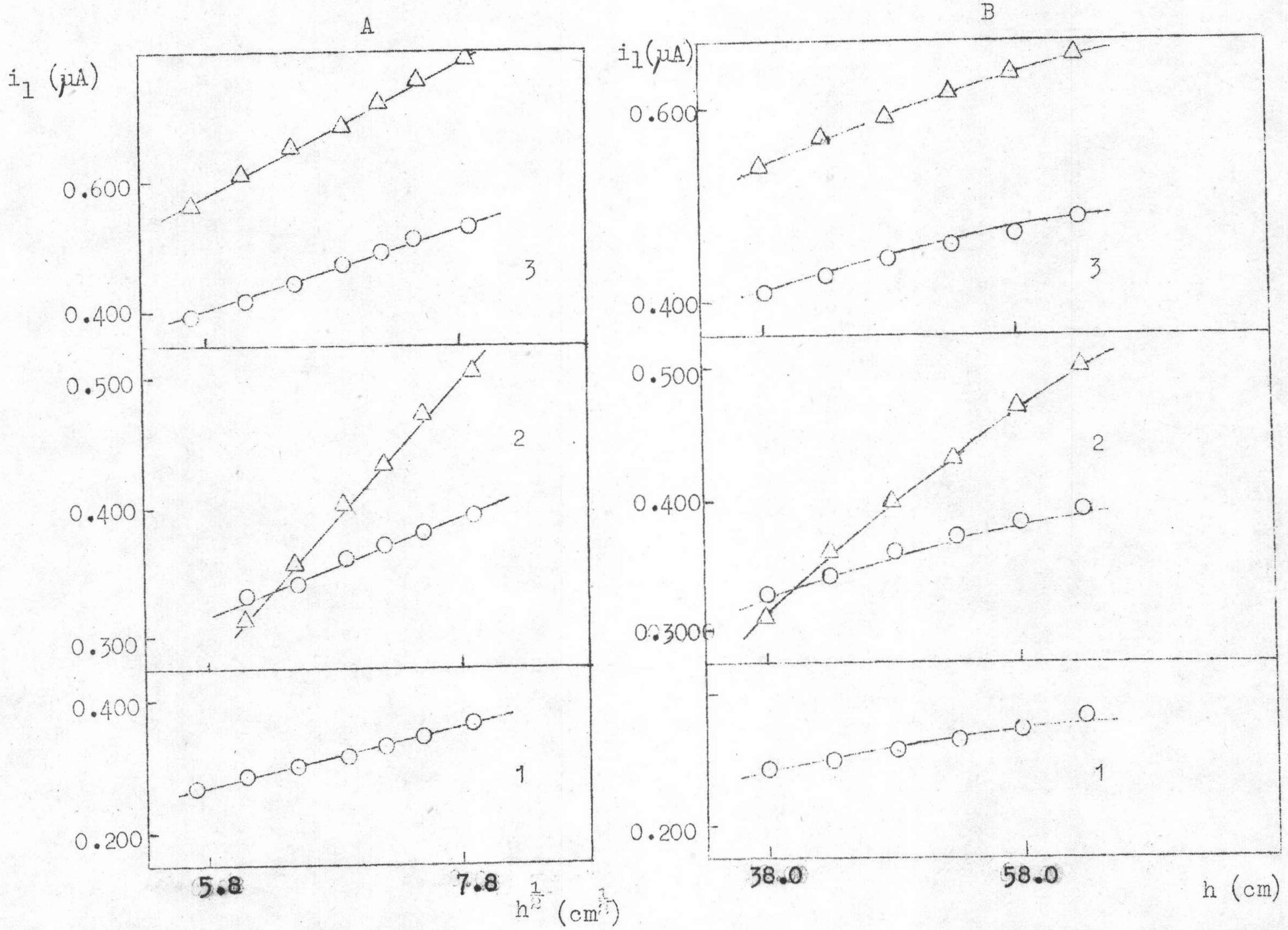


Figure 9 The dependences of limiting currents of various dye solutions: 1) Tartrazine 2) Brilliant Blue FCF, 3) Quinoline Yellow on A) square root of mercury height B) mercury height. ( The sign, ○ is for the first wave and △ is for the second wave)

Table 6 Effects of temperatures on the limiting currents of various dyes at constant mercury height[a]

| Compound | pH | $1^{st}$ wave, $i_l$, μA | | | | $2^{nd}$ wave, $i_l$, μA | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Temp., °C | | | Temp. coeff. av. % | Temp., °C | | | Temp. coeff. av. % |
| | | 30.0 | 40.0 | 50.0 | | 30.0 | 40.0 | 50.0 | |
| Tartrazine | 1.35 | 0.357 | 0.403 | 0.453 | 1.18 | - | - | - | - |
| Brilliant Blue FCF | 1.40 | 0.350 | 0.430 | 0.530 | 2.07 | 0.560 | 0.700 | 0.880 | 2.25 |
| Quinoline Yellow | 7.50 | 0.703 | 0.843 | 1.013 | 1.82 | 0.503 | 0.606 | 0.726 | 1.83 |

[a] mercury height = 65.0 cm , Temperature coefficient $= \frac{1}{i_d} \frac{d\, i_d}{d\, T}$

### 4.2.2.1 Tartrazine

The concentration of Tartrazine understudied in every electrolyte at any pH is $5.0 \times 10^{-4}$ M . The polarogram of Tartrazine in 0.1 M $(C_2H_5)_4NCl$ , 0.1 M KCl , or 0.1 M $KNO_3$ at any pH in the range of 1 - 12 showed a single reduction wave (see Figure 10-12). The wave is a well-defined wave at every pH in the electrolytes studied except at pH higher than 11.6 the wave is too small and unable to identify. The effects of pH on the polarographic waves are demonstrated in Figure 10 for Tartrazine in 0.1 M $(C_2H_5)_4NCl$ , Figure 11 for Tartrazine in 0.1 M KCl and Figure 12 for Tartrazine in 0.1 M $KNO_3$ . Data for explaining this effect are also listed in Tables 7,8 and 9 , respectively . For every electrolyte studied , as the pH of the dye solution increases , its half wave potential shifts to more negative value . The shift of the half wave potentials at pH lower than 4.5 is more than the shift of the half wave potentials at pH higher than 4.5 . The plot of the half wave potential versus pH of the dye solution showed linearities of two sections (see Figure 13). The first section at pH 1.3 - 4.5 provided a slope of -0.100 in 0.1 M $(C_2H_5)_4NCl$ or in 0.1 M KCl and a slope of -0.101 in 0.1 M $KNO_3$ . The second section at pH 4.5 - 12.0 , yielded a slope of -0.060 in every electrolyte . The intersection points of these lines were found at pH 4.40 in 0.1 M KCl and 0.1 M $KNO_3$ and at pH 4.00 in 0.1 M $(C_2H_5)_4NCl$ . These pH are the pKa of Tartrazine (16) . The diffusion current seemed to be independent on pH at the pH range 2.2 -6.2 of every electrolyte studied . However , it **started** to decrease as pH of the dye solution increased from pH higher than 6.2 (see Figure 14 ).

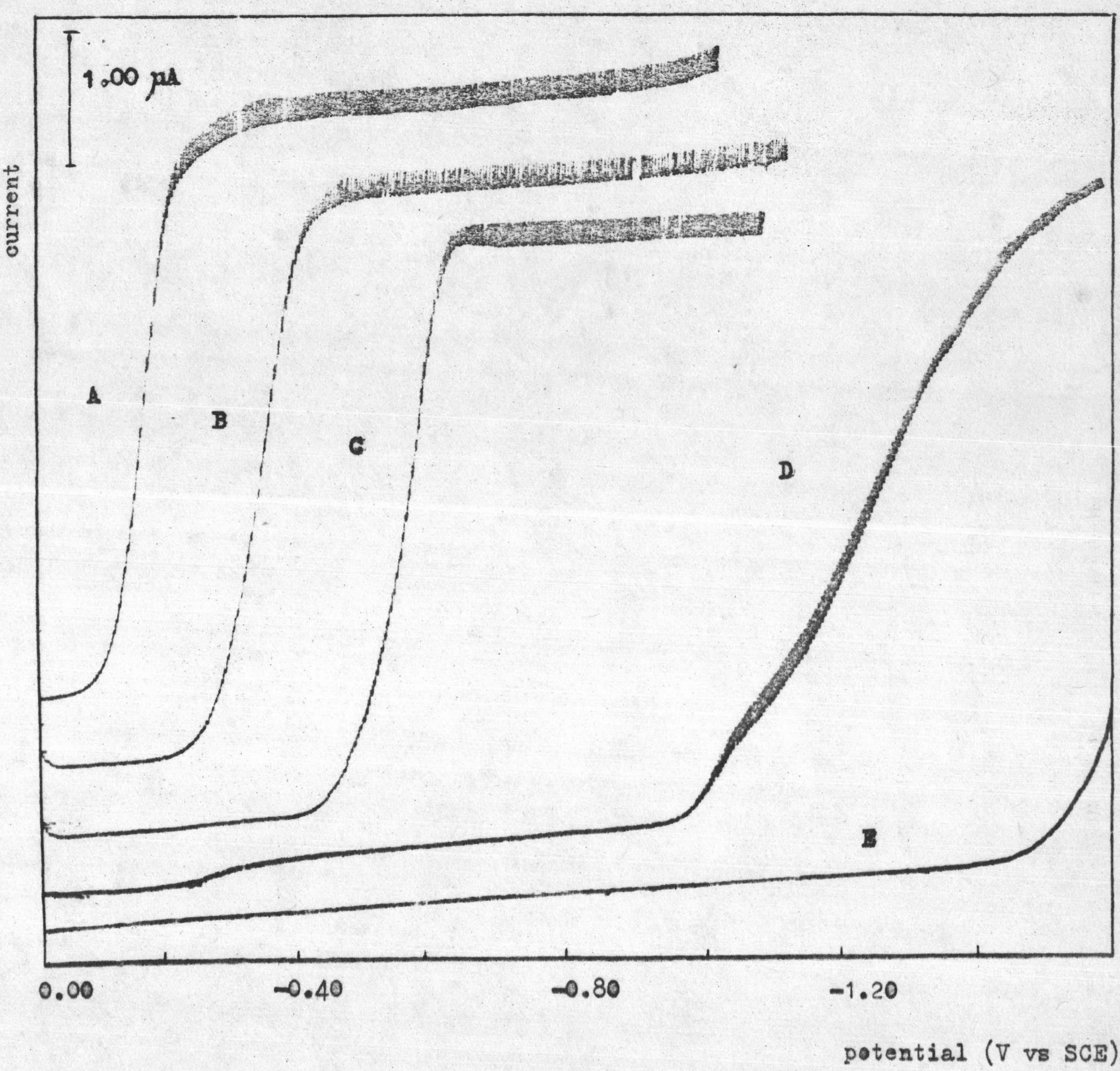


Figure 10 The polarograms of Tartrazine in 0.1 M $(C_2H_5)_4NCl$ at pH A) 1.50 B) 3.10 , C) 6.55 , D) 11.82 and the polarogram of 0.1 M $(C_2H_5)_4NCl$ (E)

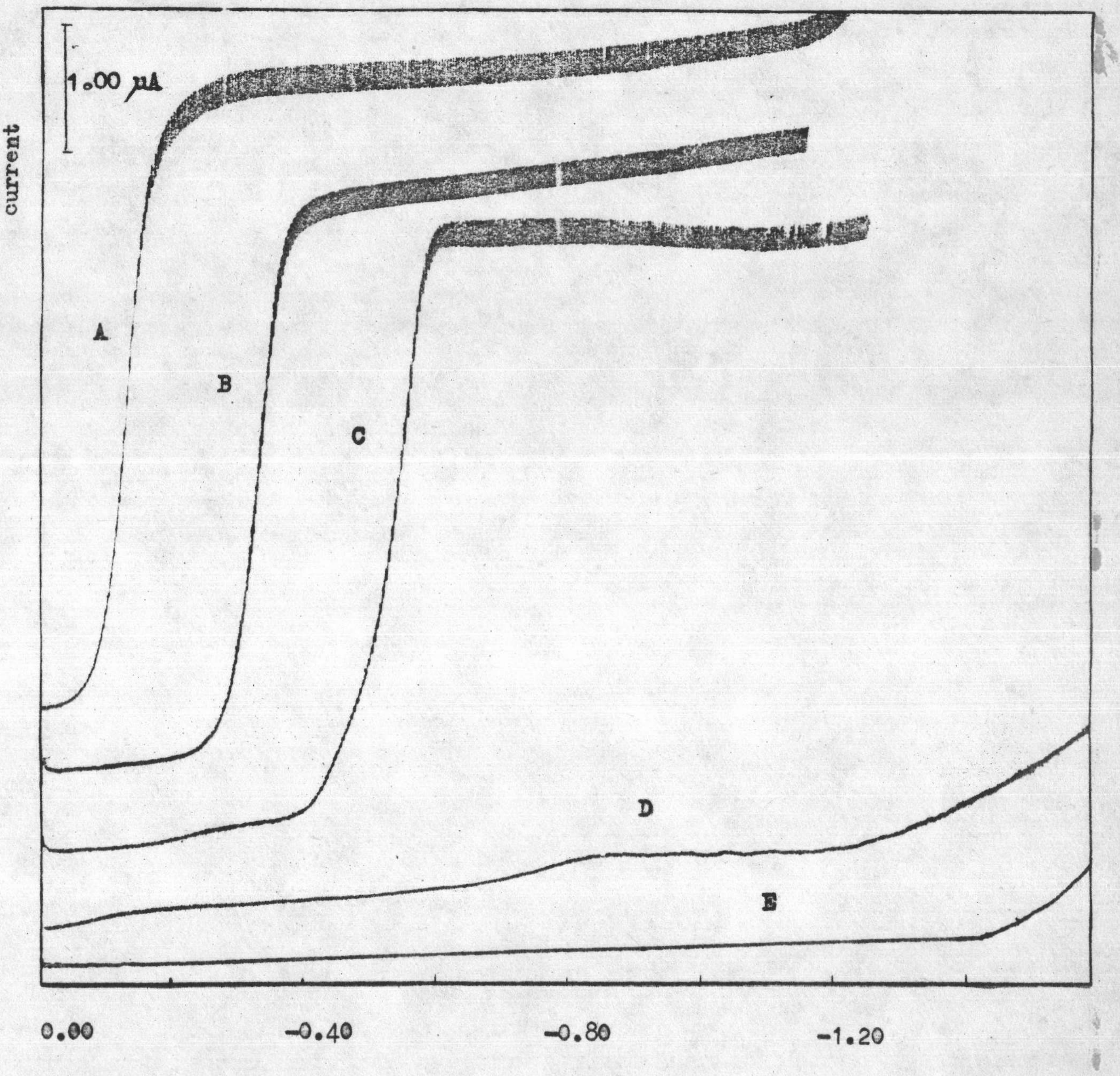


Figure 11 The polarograms of Tartrazine in 0.1 M KCl at pH A) 1.31 , B) 3.00 , C) 6.02 , D) 12.10 and the polarogram of 0.1 M KCl (E)

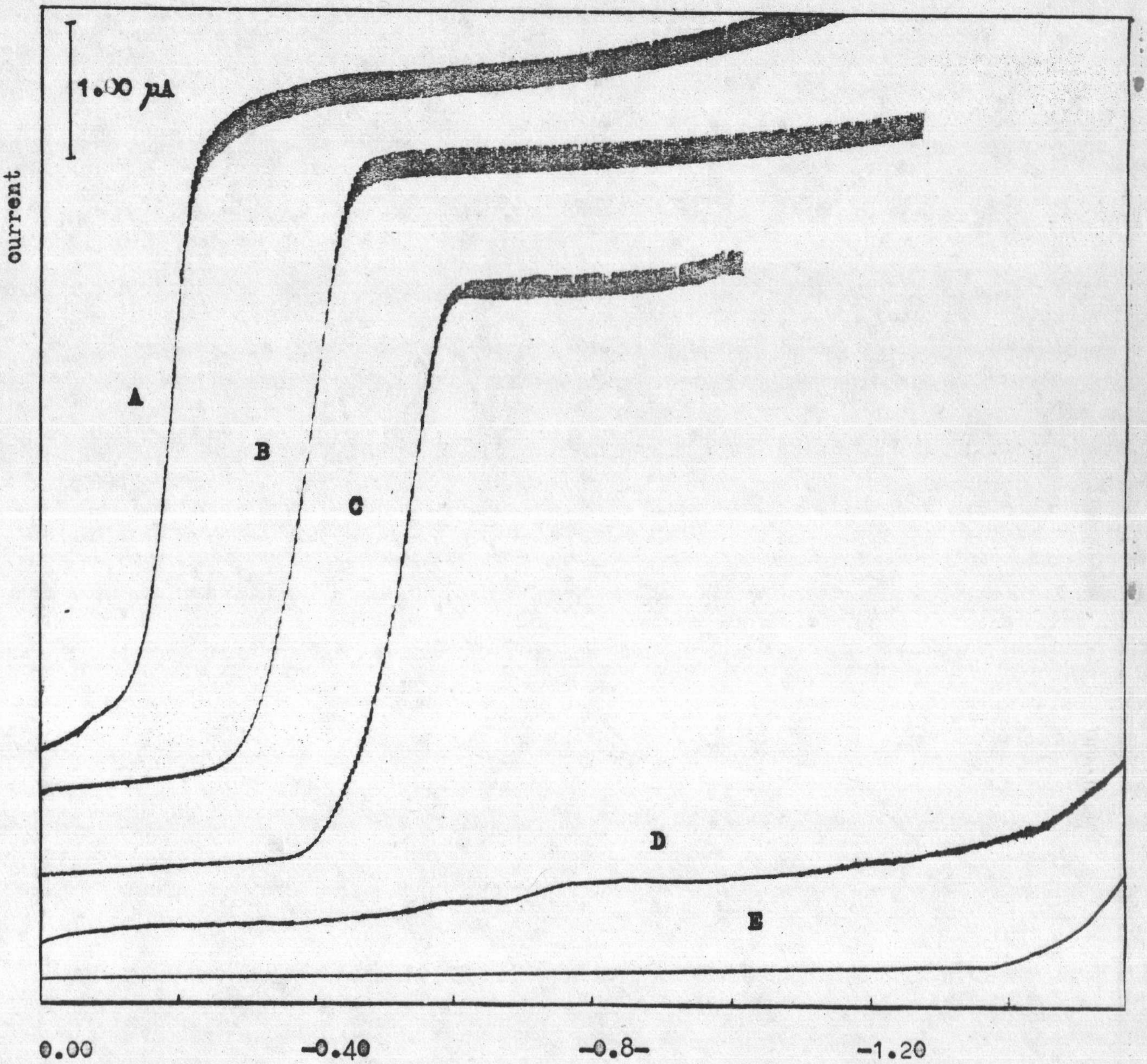


Figure 12 The polarograms of Tartrazine in 0.1 M $KNO_3$ at pH A) 1.82 , B) 3.10 , C) 6.50 , D) 11.68 and the polarogram of 0.1 M $KNO_3$ (E)

Table 7 Effect of pH on the polarographic wave of Tartrazine in 0.1 M $(C_2H_5)_4NCl$

| pH | $E_{\frac{1}{2}}$ (V) | $i_d$[a] (µA) | Remarks |
|---|---|---|---|
| 1.50 | -0.162 | 3.900 | well-defined wave |
| 2.20 | -0.235 | 4.150 | well-defined wave |
| 3.10 | -0.310 | 4.200 | well-defined wave |
| 3.85 | -0.415 | 4.220 | well-defined wave |
| 4.58 | -0.465 | 4.290 | well-defined wave |
| 5.15 | -0.500 | 4.300 | well-defined wave |
| 5.60 | -0.535 | 4.350 | well-defined wave |
| 6.18 | -0.567 | 4.250 | well-defined wave |
| 6.55 | -0.585 | 4.180 | well-defined wave |
| 6.98 | -0.600 | 3.880 | well-defined wave |
| 8.22 | -0.695 | 3.800 | well-defined wave |
| 9.00 | -0.725 | 3.600 | well-defined wave |
| 9.65 | -0.763 | 3.240 | well-defined wave |
| 10.25 | -0.805 | 2.880 | well-defined wave |
| 11.82 | -0.b | b | ill -defined wave |

[a] mercury height = 65.0 cm ; $m^{\frac{2}{3}}t^{\frac{1}{6}}$ = 0.61

[b] cannot be measured accurately

Table 8 Effect of pH on the polarographic wave of Tartrazine in 0.1 M KCl

| pH | $E_{\frac{1}{2}}$ (V) | $i_d$[a] (μA) | Remarks |
|---|---|---|---|
| 1.31 | -0.102 | 4.000 | well-defined wave |
| 2.20 | -0.180 | 4.400 | well-defined wave |
| 3.00 | -0.280 | 4.400 | well-defined wave |
| 4.02 | -0.390 | 4.300 | well-defined wave |
| 4.60 | -0.440 | 4.250 | well-defined wave |
| 5.20 | -0.480 | 4.320 | well-defined wave |
| 5.52 | -0.500 | 4.380 | well-defined wave |
| 6.02 | -0.525 | 4.300 | well-defined wave |
| 6.50 | -0.560 | 4.210 | well-defined wave |
| 7.00 | -0.580 | 3.900 | well-defined wave |
| 8.02 | -0.660 | 3.800 | well-defined wave |
| 8.98 | -0.720 | 3.500 | well-defined wave |
| 9.72 | -0.760 | 3.150 | well-defined wave |
| 10.60 | -0.820 | 2.700 | well-defined wave |
| 12.10 | b | b | ill-defined wave |

[a] mercury height = 65.0 cm ; $m^{\frac{2}{3}} t^{\frac{1}{6}} = 0.61$

[b] cannot be measured accurately

Table 9 Effect of pH on the polarographic wave of Tartrazine in 0.1 M $KNO_3$

| pH | $E_{\frac{1}{2}}$ ( V ) | $i_d$[a] ( µA ) | Remarks |
|---|---|---|---|
| 1.82 | -0.098 | 4.100 | well-defined wave |
| 2.30 | -0.200 | 4.150 | well-defined wave |
| 3.10 | -0.280 | 4.150 | well-defined wave |
| 4.10 | -0.370 | 4.300 | well-defined wave |
| 4.55 | -0.425 | 4.400 | well-defined wave |
| 5.25 | -0.445 | 4.380 | well-defined wave |
| 5.58 | -0.480 | 4.250 | well-defined wave |
| 6.15 | -0.518 | 4.150 | well-defined wave |
| 6.50 | -0.540 | 3.900 | well-defined wave |
| 6.82 | -0.560 | 3.700 | well-defined wave |
| 7.25 | -0.585 | 3.550 | well-defined wave |
| 8.20 | -0.640 | 3.500 | well-defined wave |
| 9.05 | -0.692 | 3.250 | well-defined wave |
| 9.39 | -0.712 | 3.250 | well-defined wave |
| 10.10 | -0.760 | 3.000 | well-defined wave |
| 11.68 | b | b | ill-defined wave |

[a] mercury height = 65.0 cm ; $m^{\frac{2}{3}} t^{\frac{1}{6}} = 0.61$

[b] cannot be measured accurately

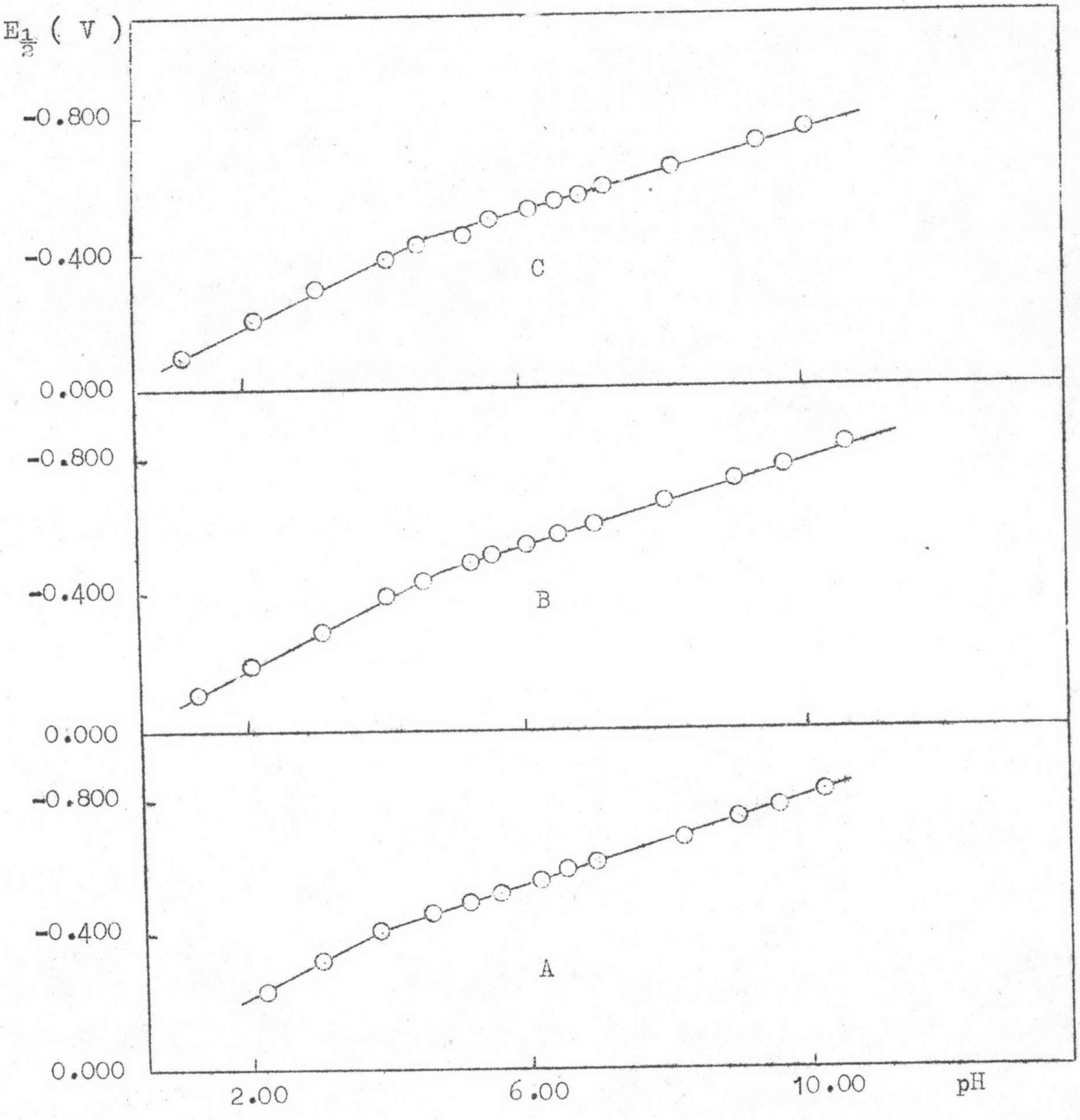


Figure 13 The effects of pH on the half wave potentials of Tartrazine in various supporting electrolytes: A) 0.1M $(C_2H_5)_4NCl$, B) 0.1M KCl and C) 0.1M $KNO_3$

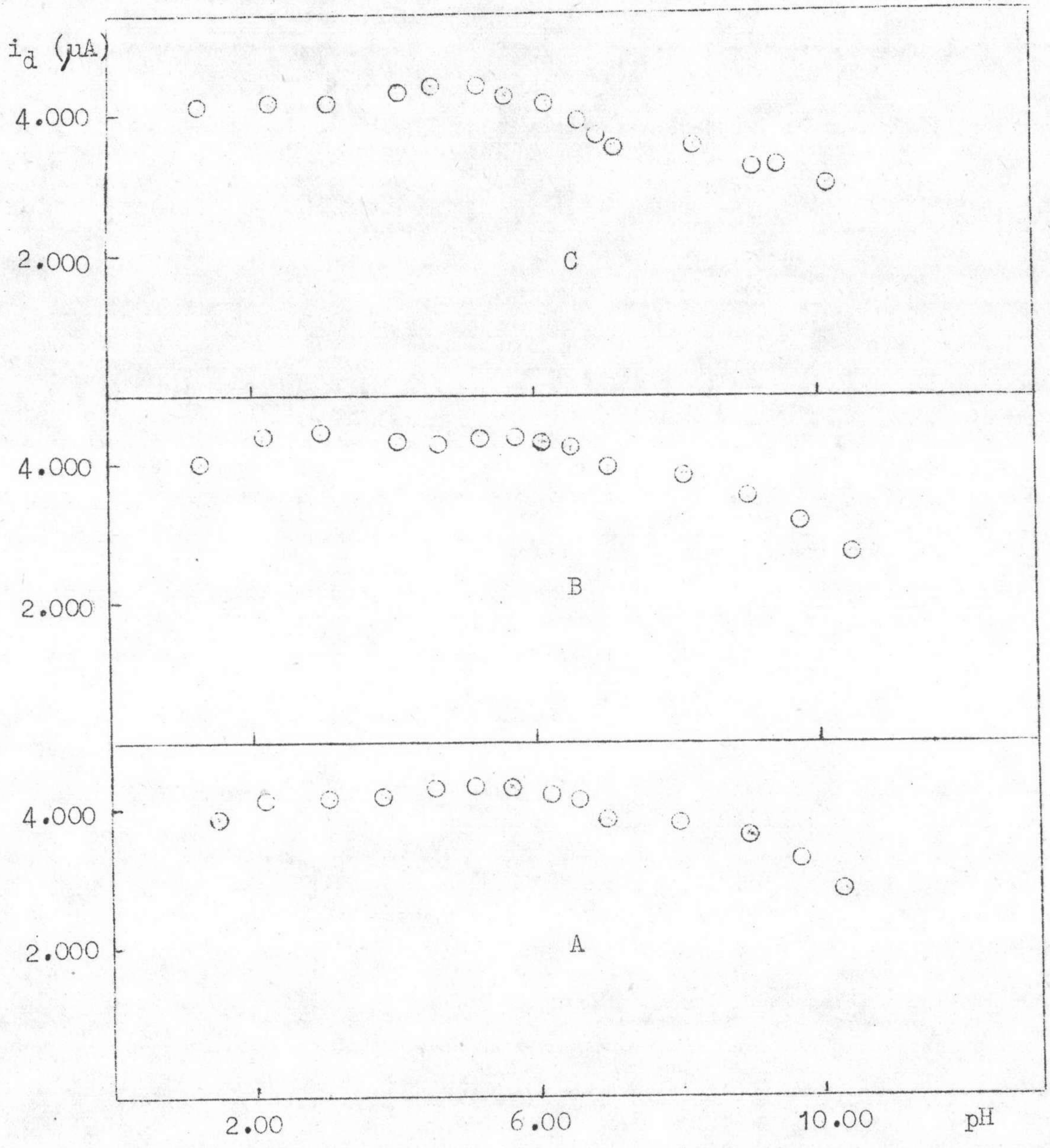


Figure 14 The effects of pH on the diffusion currents of Tartrazine in various supporting electrolytes: A) 0.1M $(C_2H_5)_4NCl$, B) 0.1M KCl and C) 0.1M $KNO_3$

### 4.2.2.2 Brilliant Blue FCF

The concentration of Brilliant Blue FCF understudied in this section is $5.0 \times 10^{-4}$ M. The polarogram of Brilliant Blue FCF in 0.1 M ( $(C_2H_5)_4NCl$, in 0.1 M KCl or in 0.1 M $KNO_3$ at any pH in the range 1-12 showed two polarographic waves. The two reduction waves were well-defined in every electrolyte for each pH studied except in 0.1M KCl and 0.1M $KNO_3$. In 0.1M KCl and 0.1M $KNO_3$, the two reduction waves became to overlap at pH between 2.7 and 4.3. The effects of pH on the polarographic waves are demonstrated in Figure 15 for Brilliant Blue FCF in 0.1M $(C_2H_5)_4NCl$ , Figure 16 for Brilliant Blue FCF in 0.1M KCl and Figure 17 for Brilliant Blue FCF in 0.1M $KNO_3$. Data for describing these effects are also listed in Tables 10, 11, 12, respectively. As the pH of the dye solution increases the half wave potentials of the first and the second wave shift to more negative values. The plot of the half wave potential of either the first wave or the second wave versus pH of the solution showed two linear sections. For the first wave, the slopes of -0.102 in 0.1M $(C_2H_5)_4NCl$, -0.100 in 0.1M KCl and -0.101 in 0.1M $KNO_3$ were obtained at pH 1.50-4.30 and at pH 4.50-11.80 the slope of -0.013 was resulted in every electrolyte. For the second wave, the slope of -0.100 was resulted in every electrolyte studied at pH 1.50-6.50 and at pH 7.00-11.80 the slopes of -0.017 in 0.1 M $(C_2H_5)_4NCl$, -0.023 in 0.1M KCl and -0.019 in 0.1M $KNO_3$ were provided ( see Figure 18).

The dependence of diffusion currents on pH of the dye solution are illustrated in Figures 19 and 20. For the first wave, the diffusion currents depend on pH and the maximum diffusion currents of Brilliant Blue FCF were obtained at pH 4.58 in 0.1M $(C_2H_5)_4NCl$, at pH 4.30 in

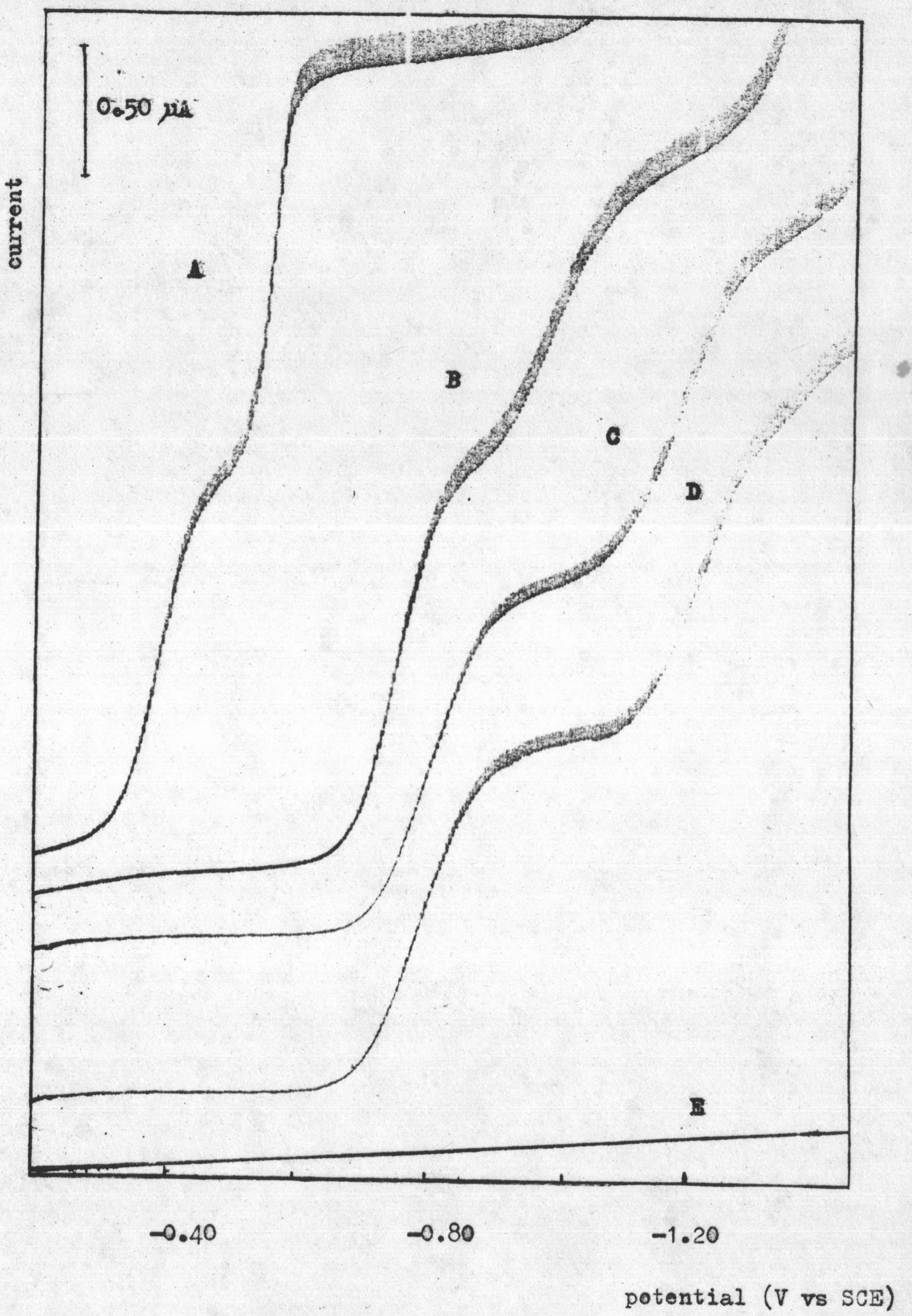


Figure 15 The polarograms of Brilliant Blue FCF in 0.1 M $(C_2H_5)_4NCl$ at pH A) 1.50 , B) 5.19 , C) 8.20 , D) 11.80 and the polarogram of 0.1M $(C_2H_5)_4NCl$ (E)

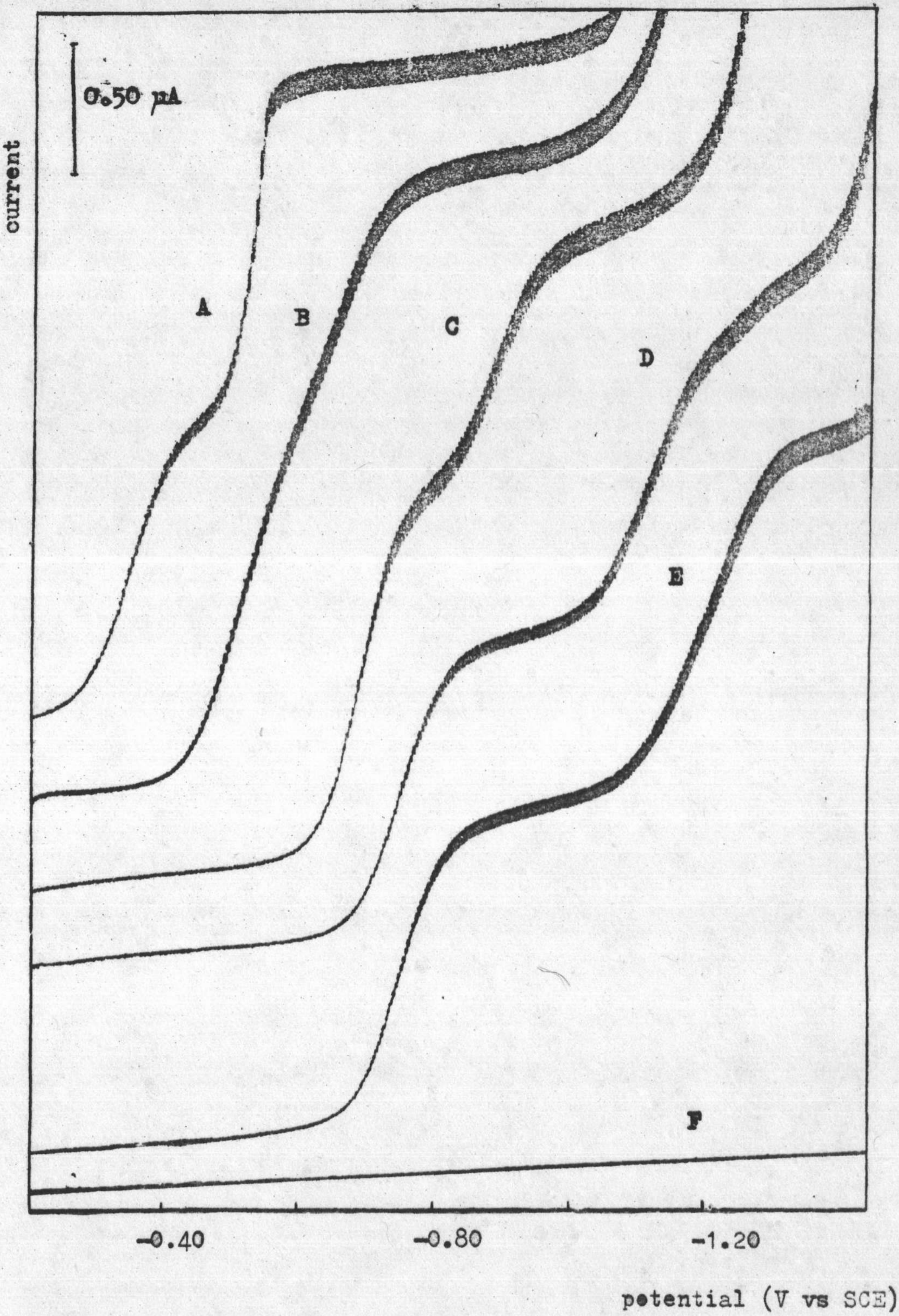


Figure 16 The polarograms of Brilliant Blue FCF in 0.1 M KCl at pH A) 1.30 , B) 3.95 , C) 4.90 , D) 8.17 . E) 11.30 and the polarogram of 0.1 M KCl (F)

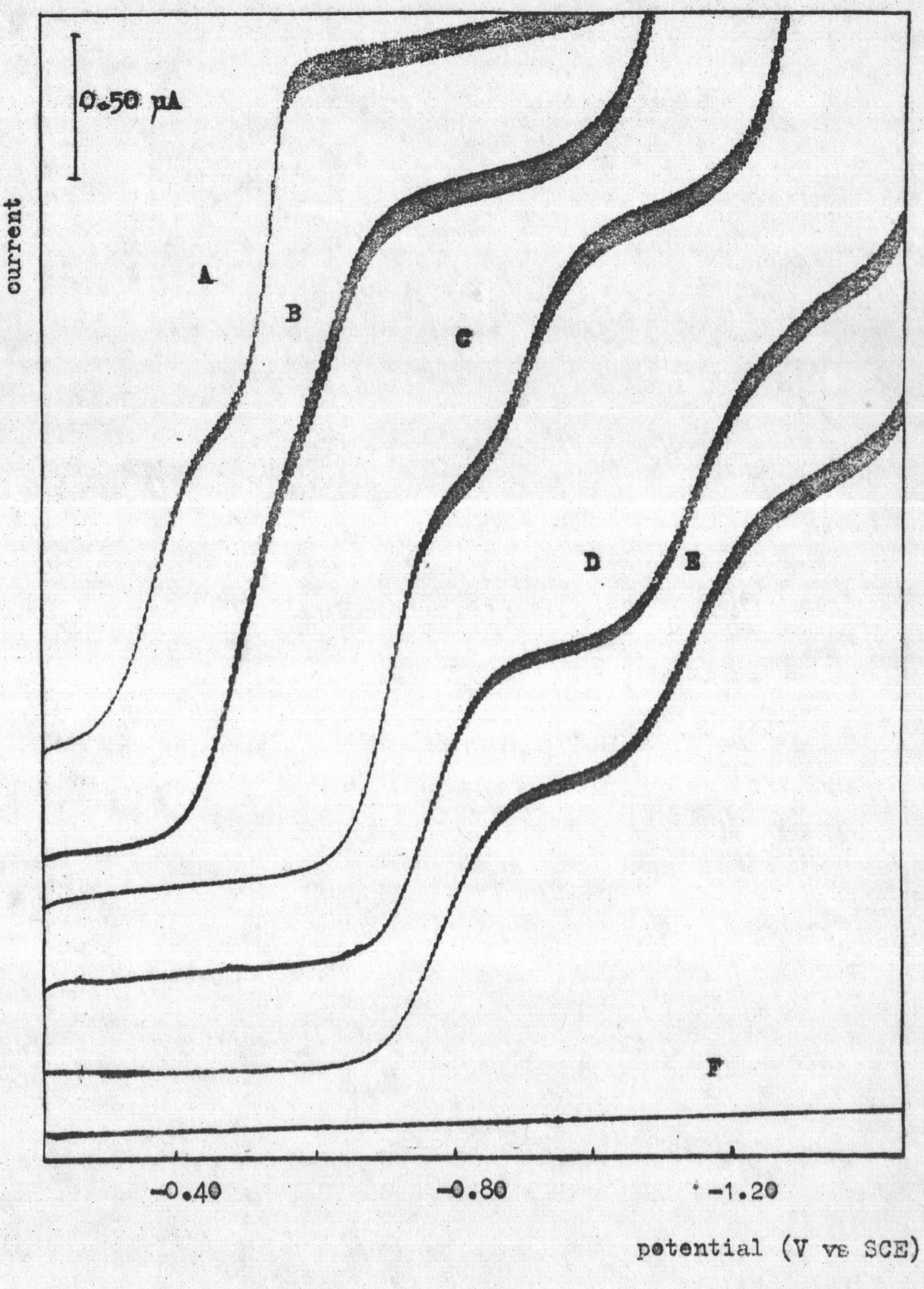


Figure 17 The polarograms of Brilliant Blue FCF in 0.1 M $KNO_3$ at pH A) 1.22 , B) 3.97 , C) 4.90 , D) 8.20 , E) 11.32 and the polarogram of 0.1 M $KNO_3$ (F)

Table 10 Effects of pH on the polarographic waves of Brilliant Blue FCF in 0.1 M $(C_2H_5)_4NCl$

| pH | First wave | | Second wave | | Remarks |
|---|---|---|---|---|---|
| | $E_{\frac{1}{2}}$ (V) | $i_d^a$ (μA) | $E_{\frac{1}{2}}$ (V) | $i_d^a$ (μA) | |
| 1.50 | -0.395 | 0.870 | -0.575 | 1.280 | well-defined waves |
| 2.20 | -0.495 | 0.810 | -0.683 | 1.130 | well-defined waves |
| 3.02 | -0.592 | 1.120 | -0.760 | 1.050 | well-defined waves |
| 4.15 | -0.699 | 1.190 | -0.870 | 0.570 | well-defined waves |
| 4.58 | -0.720 | 1.280 | -0.918 | 0.580 | well-defined waves |
| 5.19 | -0.738 | 1.160 | -0.978 | 0.580 | well-defined waves |
| 5.60 | -0.740 | 0.910 | -1.032 | 0.540 | well-defined waves |
| 6.12 | -0.755 | 1.150 | -1.090 | 0.900 | well-defined waves |
| 6.80 | -0.760 | 1.040 | -1.122 | 0.850 | well-defined waves |
| 7.20 | -0.761 | 1.150 | -1.125 | 0.900 | well-defined waves |
| 8.20 | -0.765 | 1.140 | -1.132 | 1.200 | well-defined waves |
| 8.98 | -0.800 | 1.170 | -1.140 | 1.200 | well-defined waves |
| 9.70 | -0.800 | 1.200 | -1.160 | 1.270 | well-defined waves |
| 10.30 | -0.800 | 1.050 | -1.180 | 1.150 | well-defined waves |
| 11.80 | -0.800 | 1.130 | -1.195 | 1.240 | well-defined waves |

[a] mercury height = 65.0 cm ; $m^{\frac{2}{3}} t^{\frac{1}{6}} = 0.73$

Table 11 Effects of pH on the polarographic waves of Brilliant Blue FCF in 0.1 M KCl

| pH | First wave | | Second wave | | Remarks |
|---|---|---|---|---|---|
| | $E_{\frac{1}{2}}$ (V) | $i_d$[a] (uA) | $E_{\frac{1}{2}}$ (V) | $i_d$[a] (uA) | |
| 1.30 | -0.368 | 0.770 | -0.510 | 1.120 | well-defined waves |
| 2.17 | -0.452 | 0.700 | -0.600 | 1.030 | well-defined waves |
| 2.70 | b | b | b | b | two waves overlapped |
| 3.95 | b | b | b | b | two waves overlapped |
| 4.30 | b | b | b | b | two waves overlapped |
| 4.90 | -0.718 | 1.160 | -0.890 | 0.600 | well-defined waves |
| 5.60 | -0.720 | 0.700 | -0.960 | 0.550 | well-defined waves |
| 6.00 | -0.725 | 0.950 | -1.000 | 0.750 | well-defined waves |
| 6.50 | -0.730 | 0.850 | -1.040 | 0.700 | well-defined waves |
| 7.00 | -0.730 | 0.940 | -1.105 | 0.770 | well-defined waves |
| 8.17 | -0.745 | 0.980 | -1.122 | 1.040 | well-defined waves |
| 8.85 | -0.748 | 0.980 | -1.130 | 1.070 | well-defined waves |
| 9.20 | -0.752 | 0.980 | -1.138 | 1.050 | well-defined waves |
| 9.70 | -0.755 | 0.950 | -1.140 | 1.030 | well-defined waves |
| 11.30 | -0.775 | 0.910 | -1.170 | 1.000 | well-defined waves |

[a] mercury height = 65.0 cm ; $m^{\frac{2}{3}} t^{\frac{1}{6}} = 0.61$

[b] cannot be measured

Table 12 Effects of pH on the polarographic waves of Brilliant Blue FCF in 0.1 M $KNO_3$

| pH | First wave | | Second wave | | Remarks |
|---|---|---|---|---|---|
| | $E_{\frac{1}{2}}$ (V) | $i_d^a$ (μA) | $E_{\frac{1}{2}}$ (V) | $i_d^a$ (μA) | |
| 1.22 | -0.358 | 0.750 | -0.535 | 1.110 | well-defined waves |
| 2.18 | -0.425 | 0.530 | -0.580 | 0.980 | well-defined waves |
| 2.71 | b | b | b | b | two waves overlapped |
| 3.97 | b | b | b | b | two waves overlapped |
| 4.31 | b | b | b | b | two waves overlapped |
| 4.90 | -0.702 | 1.170 | -0.912 | 0.560 | well-defined waves |
| 5.62 | -0.715 | 0.680 | -0.980 | 0.540 | well-defined waves |
| 6.02 | -0.718 | 0.950 | -1.035 | 0.730 | well-defined waves |
| 6.53 | -0.742 | 0.830 | -1.078 | 0.660 | well-defined waves |
| 7.03 | -0.745 | 0.950 | -1.112 | 0.750 | well-defined waves |
| 8.20 | -0.765 | 0.970 | -1.132 | 1.020 | well-defined waves |
| 8.87 | -0.768 | 1.000 | -1.135 | 1.100 | well-defined waves |
| 9.22 | -0.775 | 0.970 | -1.158 | 1.040 | well-defined waves |
| 9.73 | -0.795 | 0.970 | -1.160 | 1.040 | well-defined waves |
| 11.32 | -0.802 | 0.900 | -1.170 | 1.010 | well-defined waves |

[a] mercury height = 65.0 cm ; $m^{\frac{2}{3}} t^{\frac{1}{6}} = 0.61$

[b] cannot be measured

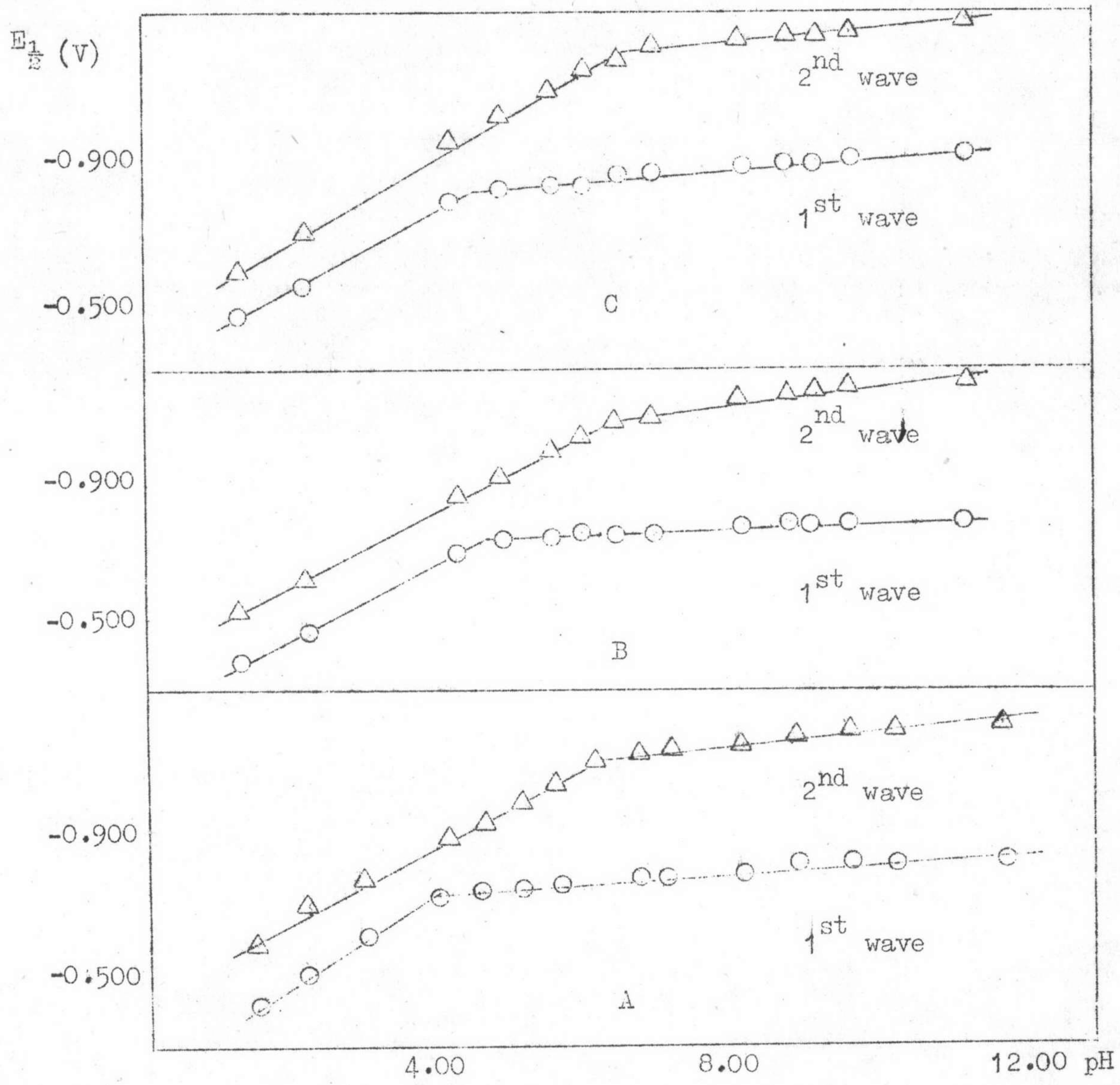


Figure 18 The effects of pH on the half wave potentials of Brilliant Blue FCF in various supporting electrolytes: A) 0.1M $(C_2H_5)_4NCl$, B) 0.1M KCl and C) 0.1M $KNO_3$

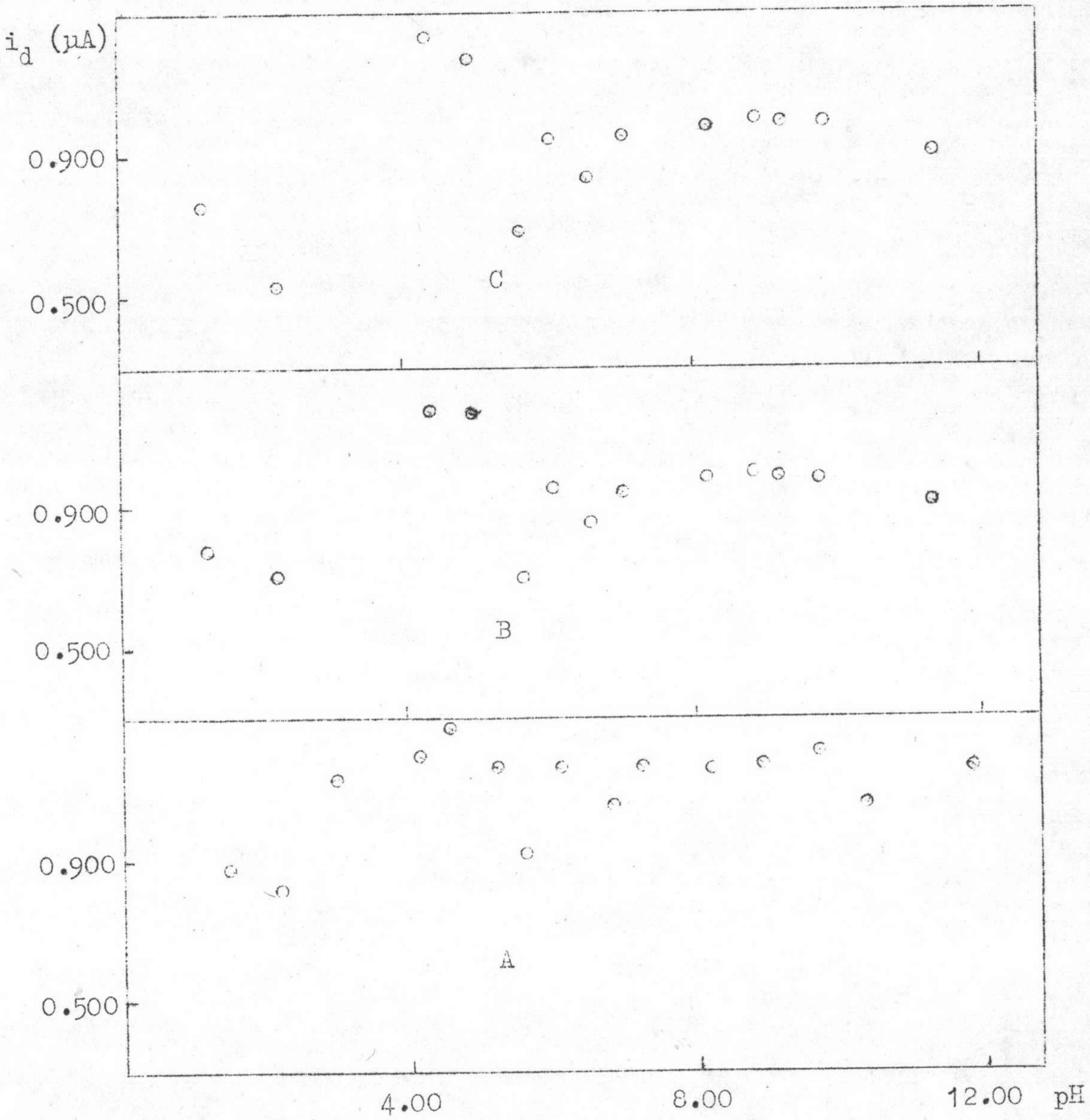


Figure 19 The effects of pH on the diffusion currents for the first wave of Brilliant Blue FCF in various supporting electrolytes: A) 0.1M $(C_2H_5)_4NCl$, B) 0.1M KCl and C) 0.1M $KNO_3$

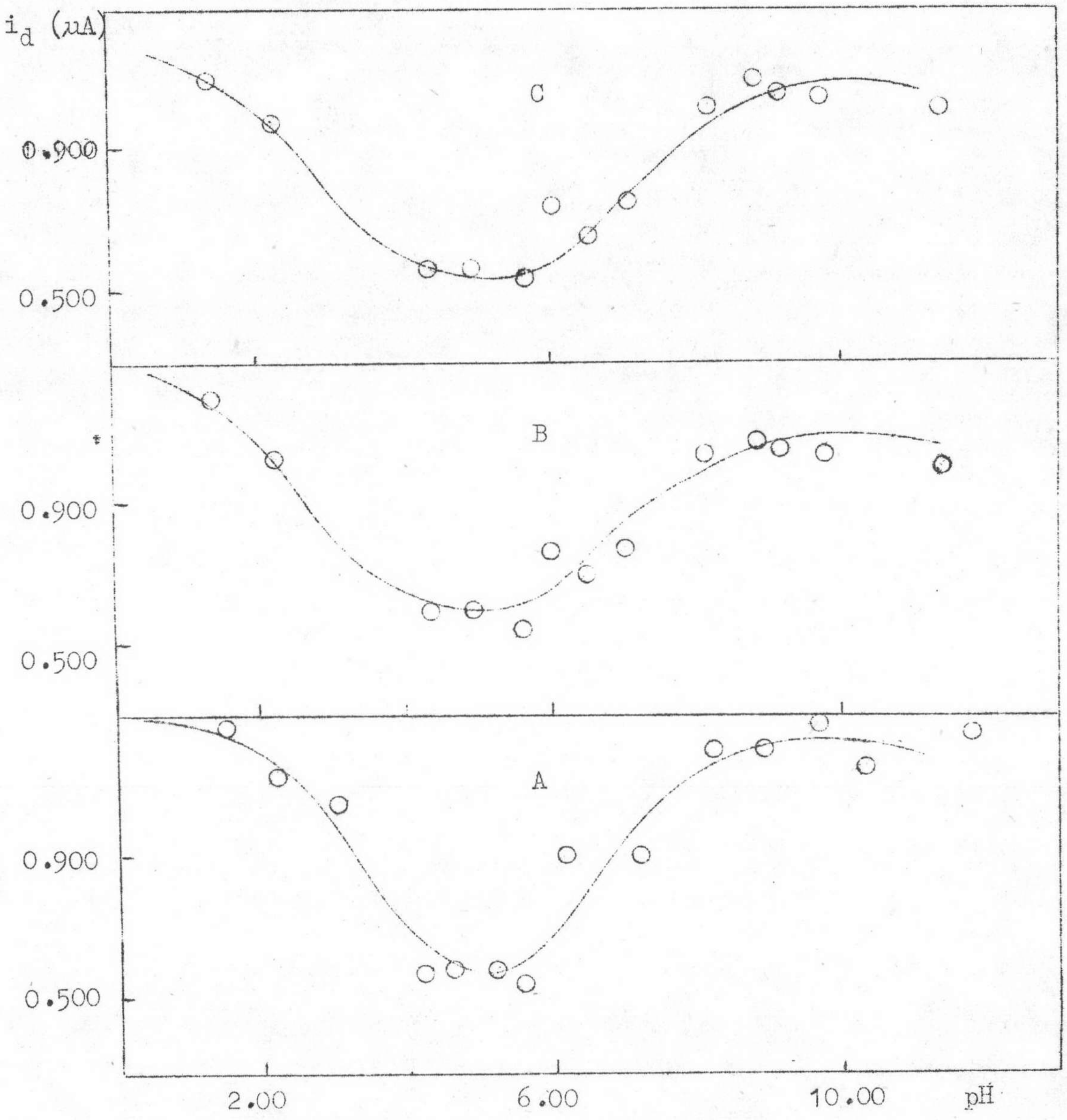


Figure 20 The effects of pH on the diffusion currents for the second wave of Brilliant Blue FCF in various supporting electrolytes: A) 0.1M $(C_2H_5)_4NCl$, B) 0.1M KCl and C) 0.1M $KNO_3$

0.1M KCl and 0.1M $KNO_3$ ( see Figure 19 ). For the second wave, a S-shaped relationship between the diffusion current and pH was resulted in every electrolyte studied and a minimum diffusion current was obtained at pH 5.60 ( see Figure 20 ).

### 4.2.2.3 Quinoline Yellow

The concentration of Quinoline Yellow understudied in every electrolyte at any pH is $5.0 \times 10^{-4}$ M.

#### 4.2.2.3.1 Borate buffer

The polarograms of Quinoline Yellow in 0.1 M $(C_2H_5)_4NCl$ , 0.1 M KCl or 0.1 M $KNO_3$ at any pH in the range 1.38 - 11.85 showed one reduction wave (see Figures 21,22 and 23 ). The well-defined wave was obtained in two pH ranges, pH 1.38 -2.15 and 8.13-11.85 . At pH 2.82 - 4.80 the wave disappears . The wave occurs again at pH of the dye solution higher than 4.80 and the wave is ill-defined until pH 8.13 . Data for describing these effects are also listed in Table 13 for Quinoline Yellow in $(C_2H_5)_4NCl$ , Table 14 for Quinoline Yellow in 0.1 M KCl and Table 15 for Quinoline Yellow in 0.1 M $KNO_3$ . As the pH of the dye solution increases the half wave potential shifts to more negative value (see Figure 24 ) . In addition, the diffusion current of Quinoline Yellow in borate buffer seemed to be independent on pH except at pH 11.80 the diffusion current dropped rapidly in every electrolyte studied (see Figure 25 ).

#### 4.2.2.3.2 Phosphate buffer

Since the polarographic waves of Quinoline Yellow disappeared in the pH range 2.82 - 4.80 of borate buffer , the polarographic reduction of Quinoline Yellow was tried again

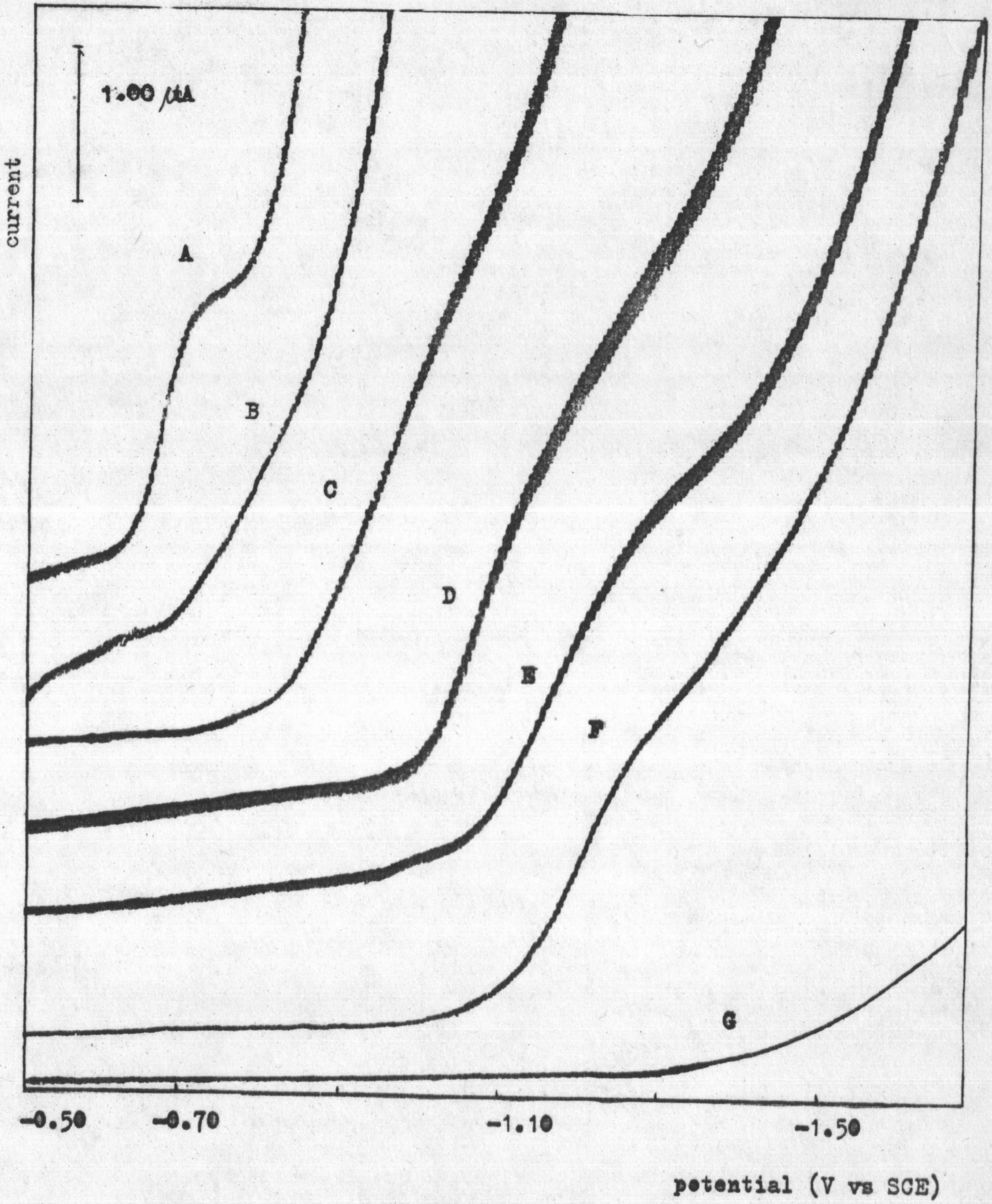


Figure 21 The polarograms of Quinoline Yellow in borate buffer and 0.1 M $(C_2H_5)_4NCl$ at pH A) 2.13 , B) 2.80 , C) 4.80 , D) 7.22 , E) 8.10 F) 11.83 and the polarogram of 0.1 M $(C_2H_5)_4NCl$ (G)

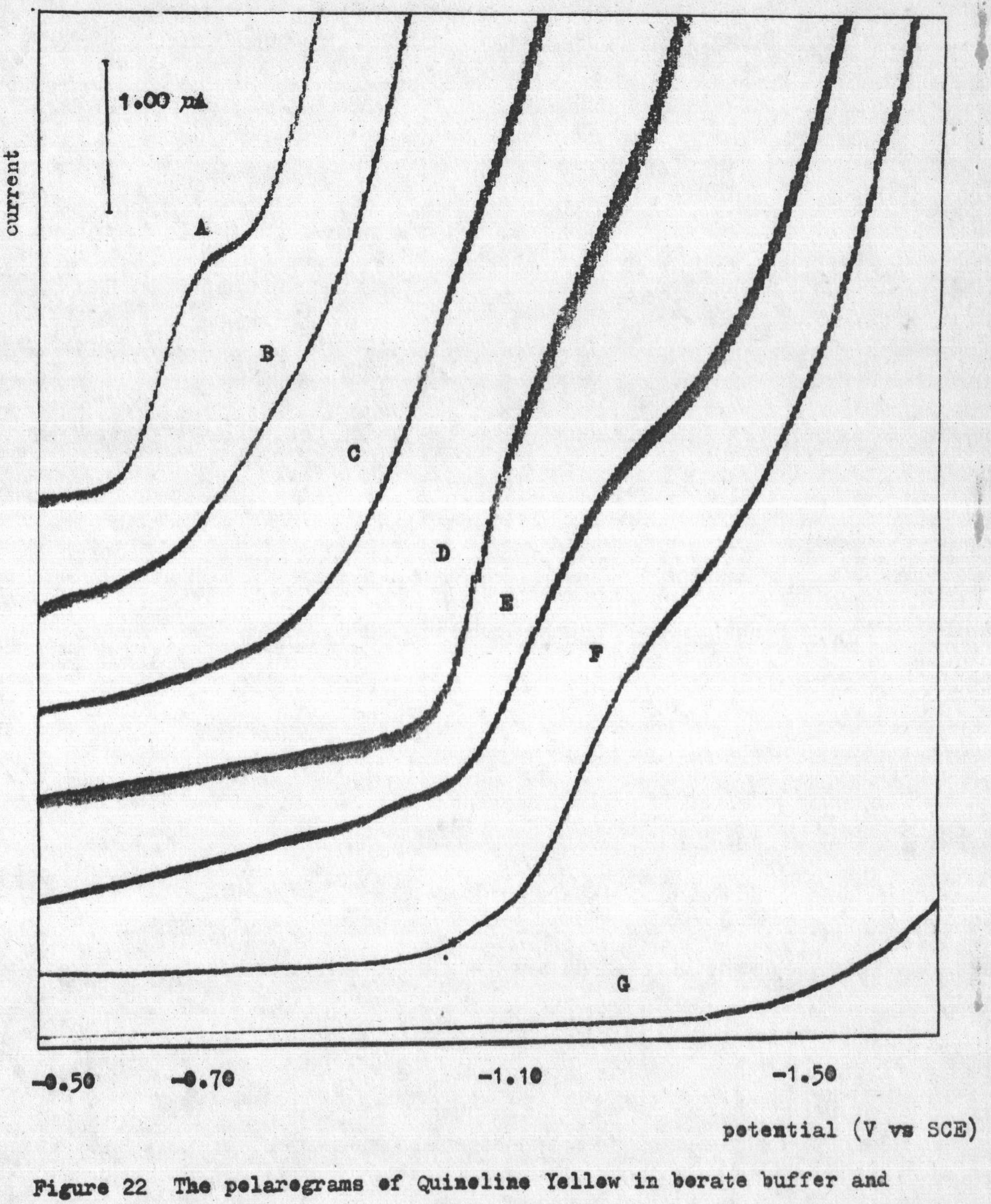


Figure 22 The polarograms of Quinoline Yellow in borate buffer and 0.1 M KCl at pH A) 2.15 , B) 2.82 , C) 4.80 , D) 7.25 , E) 8.13 , F) 11.85 and the polarogram of 0.1 M KCl (G)

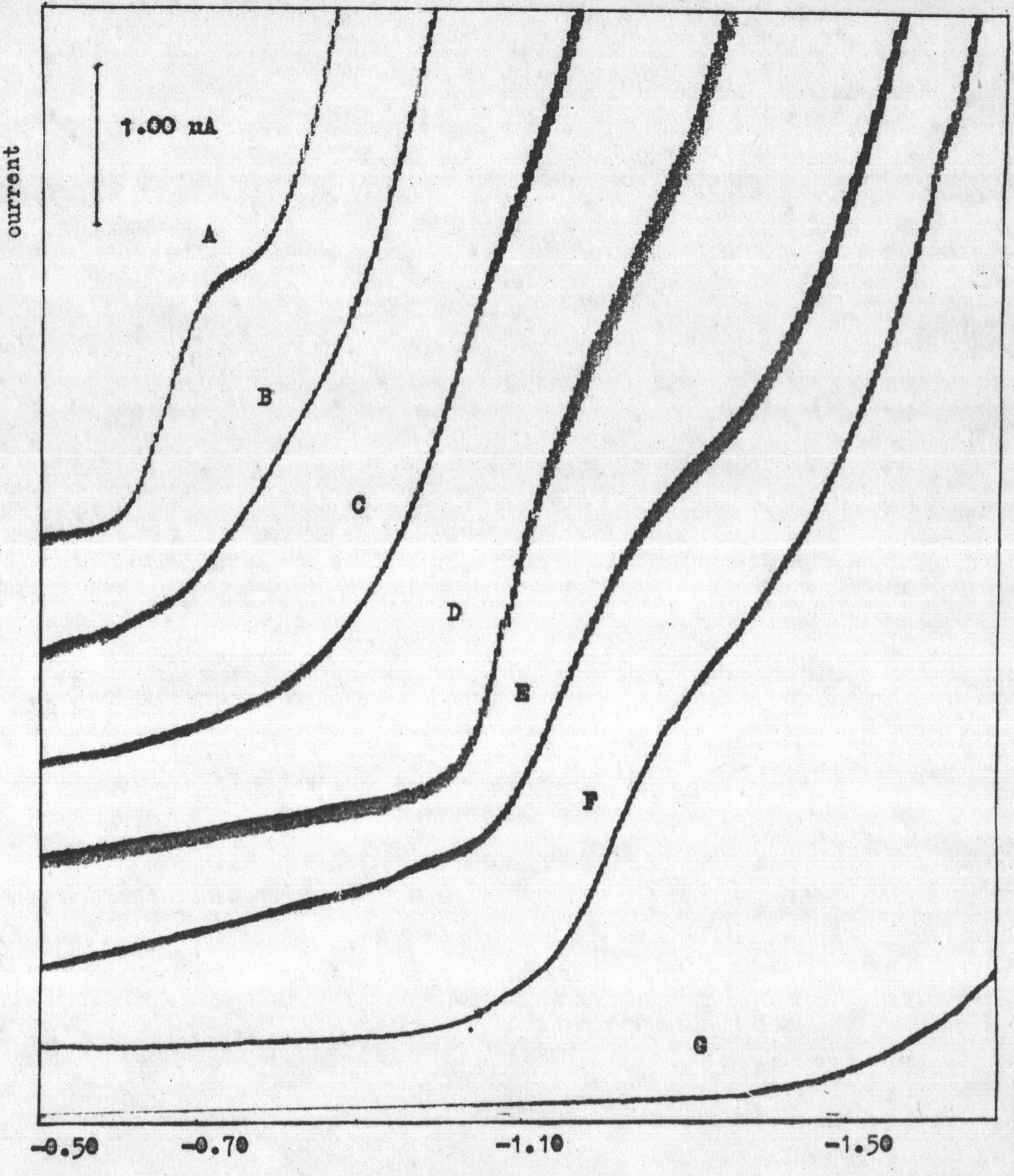


Figure 23 The polarograms of Quinoline Yellow in borate buffer and 0.1 M $KNO_3$ at pH A) 2.13 , B) 2.85 , C) 4.83 , D) 7.20 , E) 8.10 , F) 11.85 and the polarogram of 0.1 M $KNO_3$ (G)

Table 13 Effect of pH on the polarographic wave of Quinoline Yellow in borate buffer and 0.1 M $(C_2H_5)_4NCl$

| pH | $E_{\frac{1}{2}}$ ( V ) | $i_d$ [a] ( µA ) | Remarks |
|---|---|---|---|
| 1.35 | -0.643 | 1.310 | well-defined wave |
| 2.13 | -0.682 | 1.300 | well-defined wave |
| 2.80 | b | b | ill-defined wave |
| 3.80 | b | b | ill-defined wave |
| 4.52 | b | b | ill-defined wave |
| 4.80 | b | b | ill-defined wave |
| 5.61 | b | b | ill-defined wave |
| 5.93 | b | b | ill-defined wave |
| 6.45 | b | b | ill-defined wave |
| 7.22 | b | b | ill-defined wave |
| 8.10 | -1.142 | 1.310 | well-defined wave |
| 8.79 | -1.152 | 1.330 | well-defined wave |
| 9.58 | -1.157 | 1.300 | well-defined wave |
| 10.65 | -1.172 | 1.280 | well-defined wave |
| 11.83 | -1.200 | 0.830 | well-defined wave |

[a] mercury height = 65.0 cm ; $m^{\frac{2}{3}} t^{\frac{1}{6}} = 0.61$

[b] cannot be measured

Table 14 Effect of pH on the polarographic wave of Quinoline Yellow in borate buffer and 0.1 M KCl

| pH | $E_{\frac{1}{2}}$ ( V ) | $i_d^a$ ( μA ) | Remarks |
|---|---|---|---|
| 1.38 | -0.640 | 1.340 | well-defined wave |
| 2.15 | -0.687 | 1.320 | well-defined wave |
| 2.82 | b | b | ill-defined wave |
| 3.83 | b | b | ill-defined wave |
| 4.50 | b | b | ill-defined wave |
| 4.80 | b | b | ill-defined wave |
| 5.51 | b | b | ill-defined wave |
| 5.89 | b | b | ill-defined wave |
| 6.50 | b | b | ill-defined wave |
| 7.25 | b | b | ill-defined wave |
| 8.13 | -1.150 | 1.301 | well-defined wave |
| 8.80 | -1.152 | 1.250 | well-defined wave |
| 9.60 | -1.158 | 1.300 | well-defined wave |
| 10.63 | -1.175 | 1.270 | well-defined wave |
| 11.85 | -1.208 | 0.800 | well-defined wave |

[a] mercury height = 65.0 cm ; $m^{\frac{2}{3}} t^{\frac{1}{6}} = 0.61$

[b] cannot be measured

Table 15 Effect of pH on the polarographic wave of Quinoline Yellow in borate buffer and 0.1 M $KNO_3$

| pH | $E_{\frac{1}{2}}$ ( V ) | $i_d$[a] ( µA ) | Remarks |
|---|---|---|---|
| 1.40 | -0.642 | 1.280 | well-defined wave |
| 2.13 | -0.685 | 1.320 | well-defined wave |
| 2.85 | b | b | ill-defined wave |
| 3.80 | b | b | ill-defined wave |
| 4.56 | b | b | ill-defined wave |
| 4.83 | b | b | ill-defined wave |
| 5.50 | b | b | ill-defined wave |
| 5.90 | b | b | ill-defined wave |
| 6.48 | b | b | ill-defined wave |
| 7.20 | b | b | ill-defined wave |
| 8.10 | -1.148 | 1.310 | well-defined wave |
| 8.83 | -1.155 | 1.260 | well-defined wave |
| 9.61 | -1.160 | 1.305 | well-defined wave |
| 10.65 | -1.178 | 1.280 | well-defined wave |
| 11.85 | -1.203 | 0.780 | well-defined wave |

[a] mercury height = 65.0 ; $m^{\frac{2}{3}} t^{\frac{1}{6}} = 0.61$

[b] cannot be measured

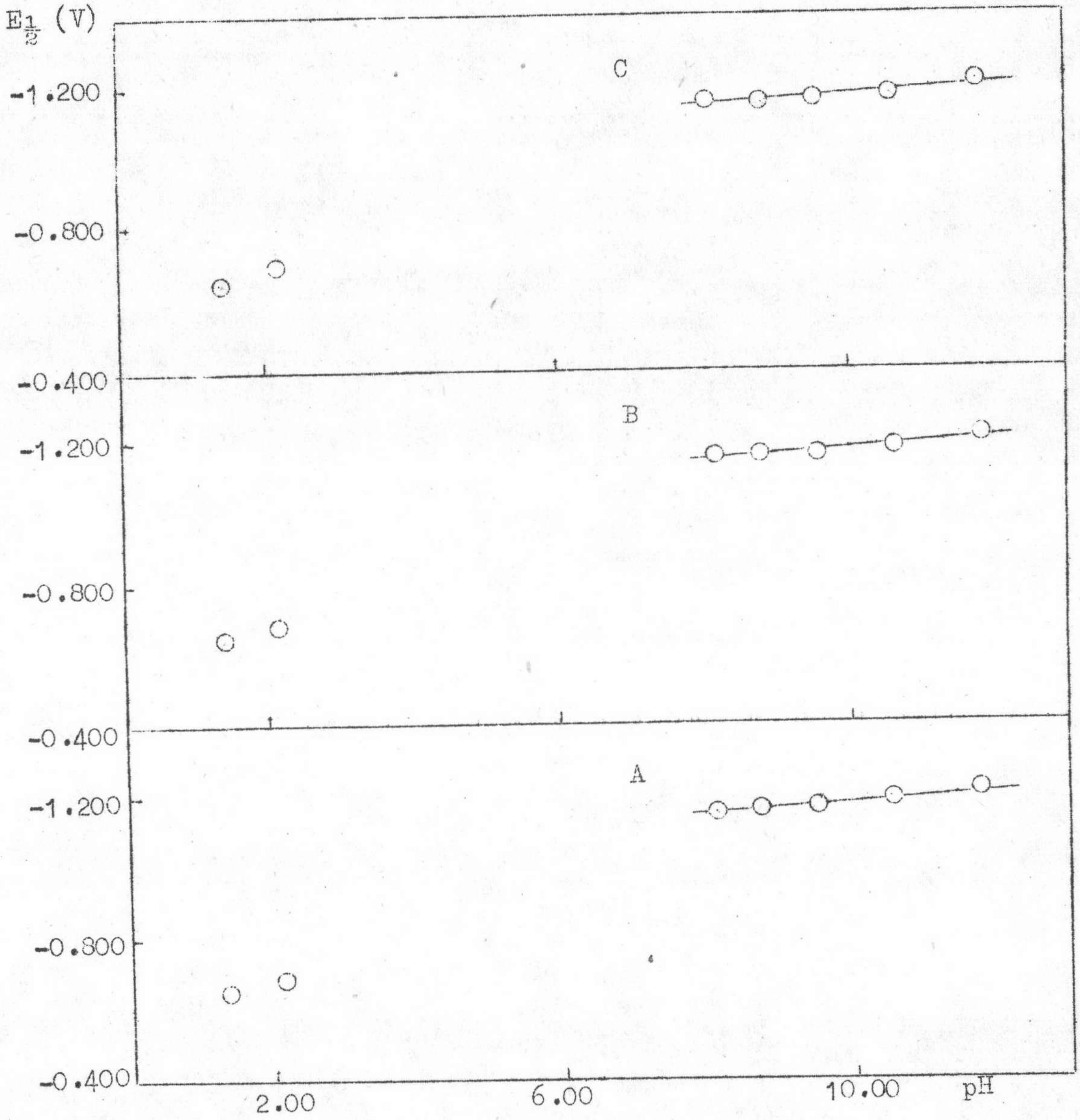


Figure 24 The effects of pH on the half wave potentials of Quinoline Yellow in borate buffer and various supporting electrolytes: A) 0.1M $(C_2H_5)_4NCl$, B) 0.1M KCl and C) 0.1M $KNO_3$

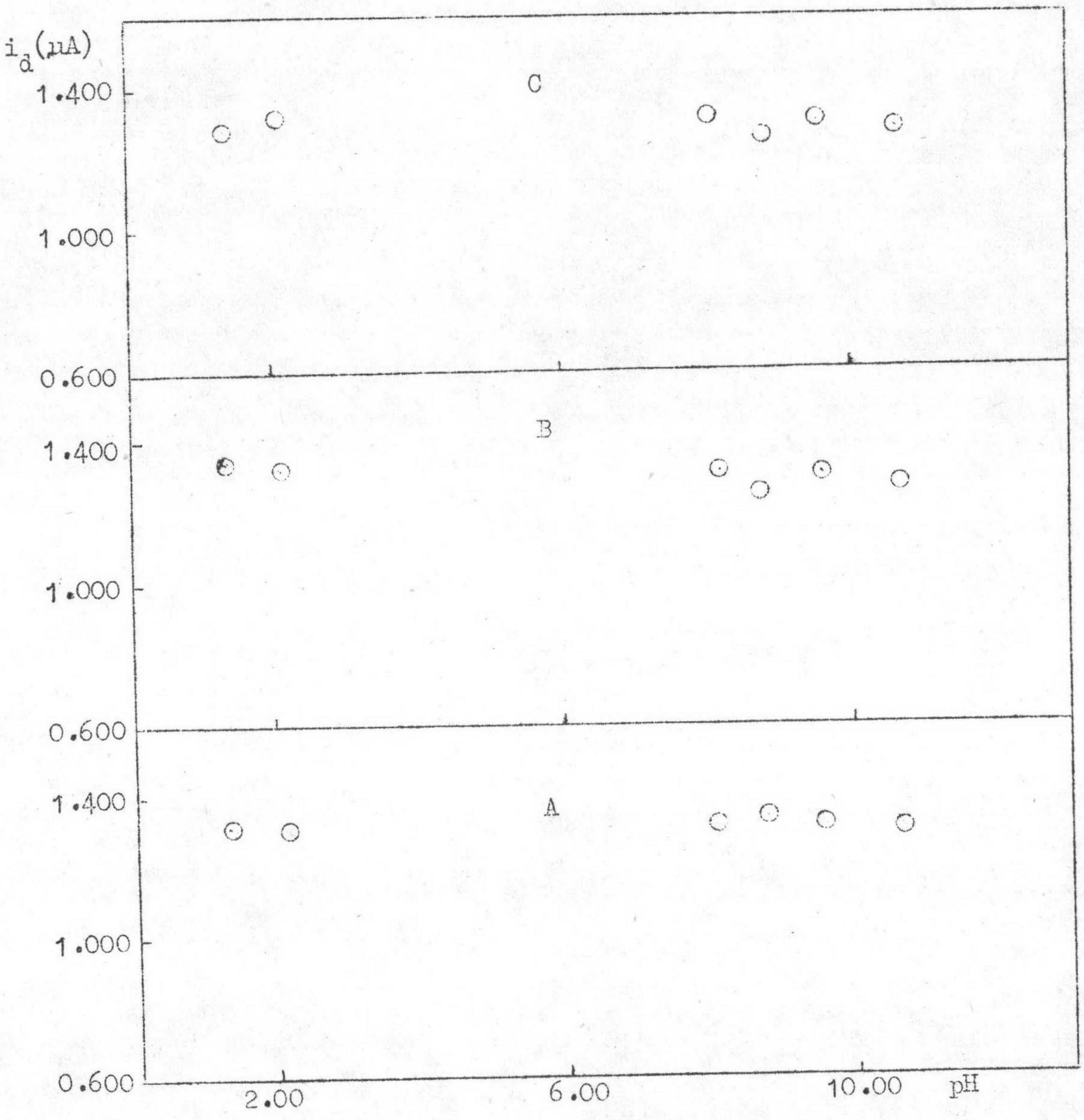


Figure 25 The effects of pH on the diffusion currents of Quinoline Yellow in borate buffer and various supporting electrolytes: A) 0.1M $(C_2H_5)_4NCl$, B) 0.1M KCl and C) 0.1M $KNO_3$

in the phosphate buffer. Two polarographic waves were resulted in this buffer at any pH in the range of 4.60-11.10 (see Figures 26,27 and 28). In 0.1M $(C_2H_5)_4NCl$, the first wave is well-defined at every pH and the second one is ill-defined at the pH of the dye solution lower than 5.50 and the wave becomes well-defined at pH higher than 5.50. In 0.1M KCl and 0.1M $KNO_3$, the same polarographic behaviors of these two waves were obtained, besides pH 11.40 which was less sensitive to the reduction of Quinoline Yellow and the polarographic waves resulted were hard to detect. Data for explaining these effects were listed in Tables 16, 17 and 18. For every electrolyte studied, as pH of the dye solution increases the half wave potentials shift to more negative values. The plots of the half wave potentials of both the first wave and the second one versus pH of the dye solution showed linearities of two sections (see Figure 29). For the first wave, at pH 4.50-8.50 the slopes of -0.070 were obtained in 0.1M $(C_2H_5)_4NCl$ and 0.1M KCl, as well as the slope of -0.066 was yielded in 0.1M $KNO_3$. At pH 9.00-11.10, the slope of -0.010 was resulted in every electrolyte. For the second wave, the slope of -0.060 was resulted in every electrolyte at pH 5.50-8.50 and at pH higher than 8.50 the slope was -0.010.

The dependence of diffusion currents on pH of the dye solution are shown in Figure 30. For the first wave, the diffusion current depended on pH from 4.50 to 8.20 , the maximum diffusion current was obtained at pH 6.00, and it gradually decreased until pH 8.20. At pH higher than 8.50, the diffusion current was constant. For the second wave, as pH of the solution increased the diffusion current gradually increased until pH 8. The diffusion

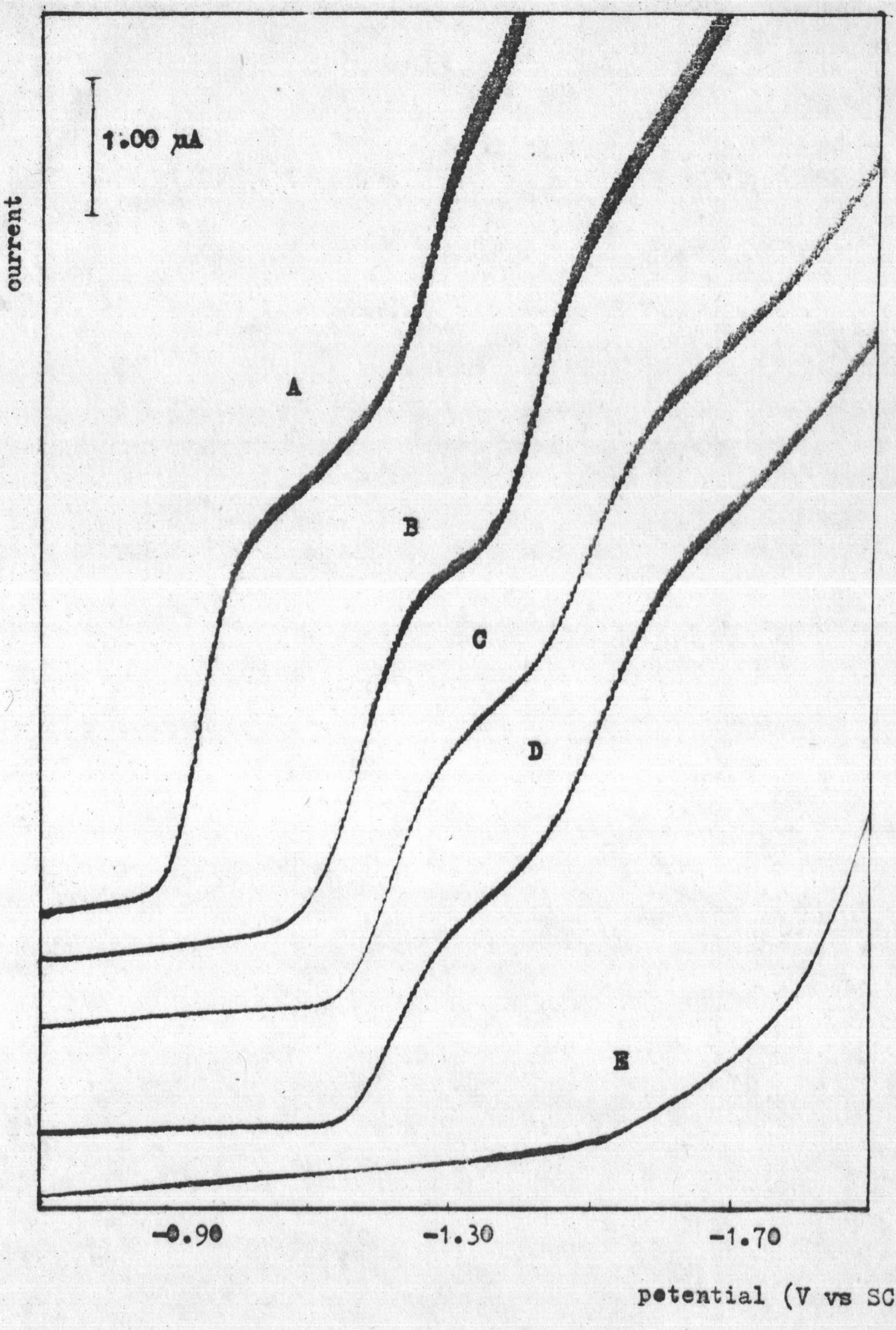


**Figure 26** The polarograms of Quinoline Yellow in phosphate buffer and 0.1 M $(C_2H_5)_4NCl$ at pH A) 5.50 , B, 8.35 , C) 10.15 , D) 11.10 and the polarogram of 0.1 M $(C_2H_5)_4NCl$ (E)

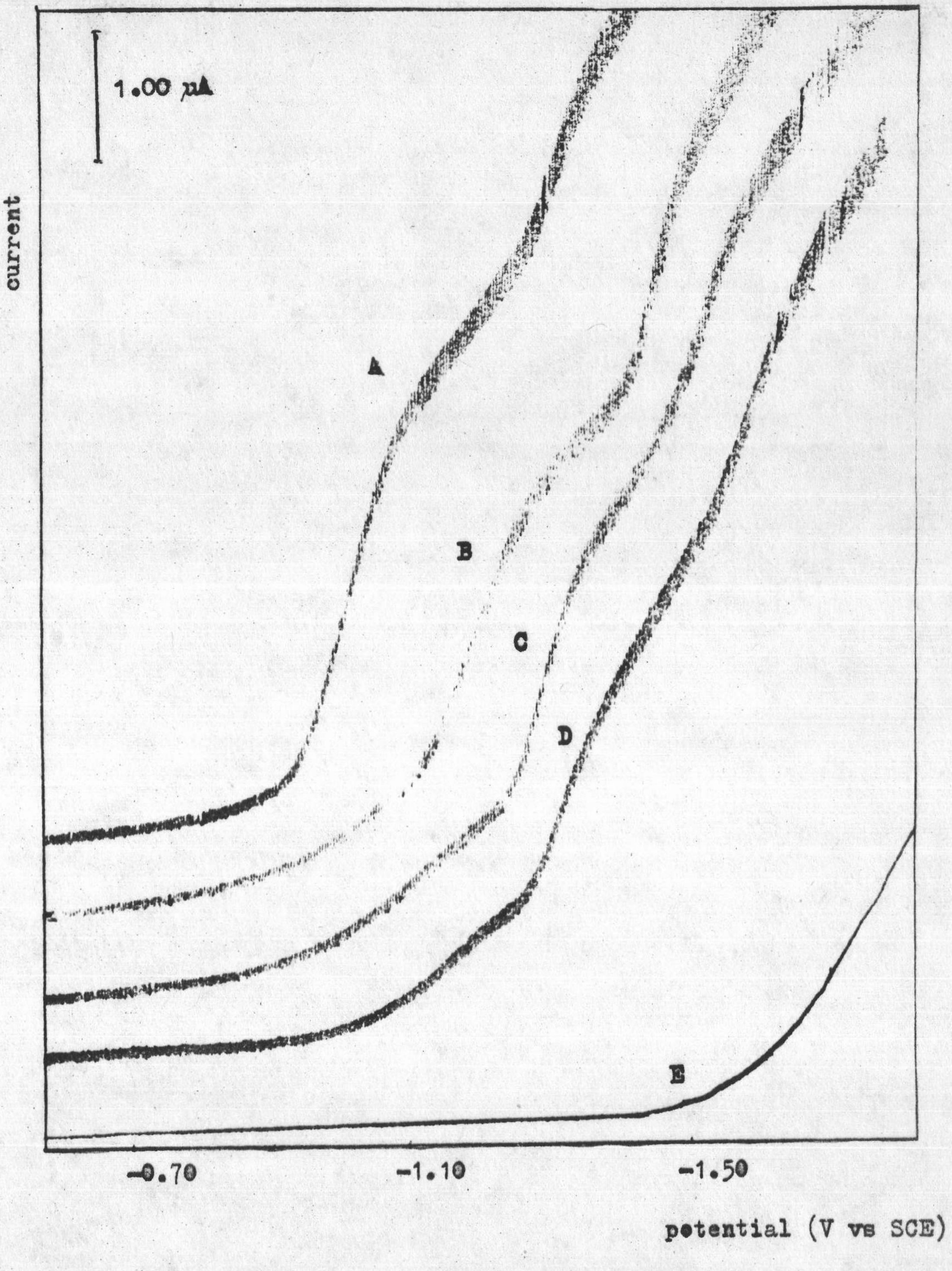


Figure 27 The polarograms of Quinoline Yellow in phosphate buffer and 0.1 M KCl at pH A) 5.10 , B) 8.00 , C) 10.03 , D) 11.42 and the polarogram of 0.1 M KCl (E)

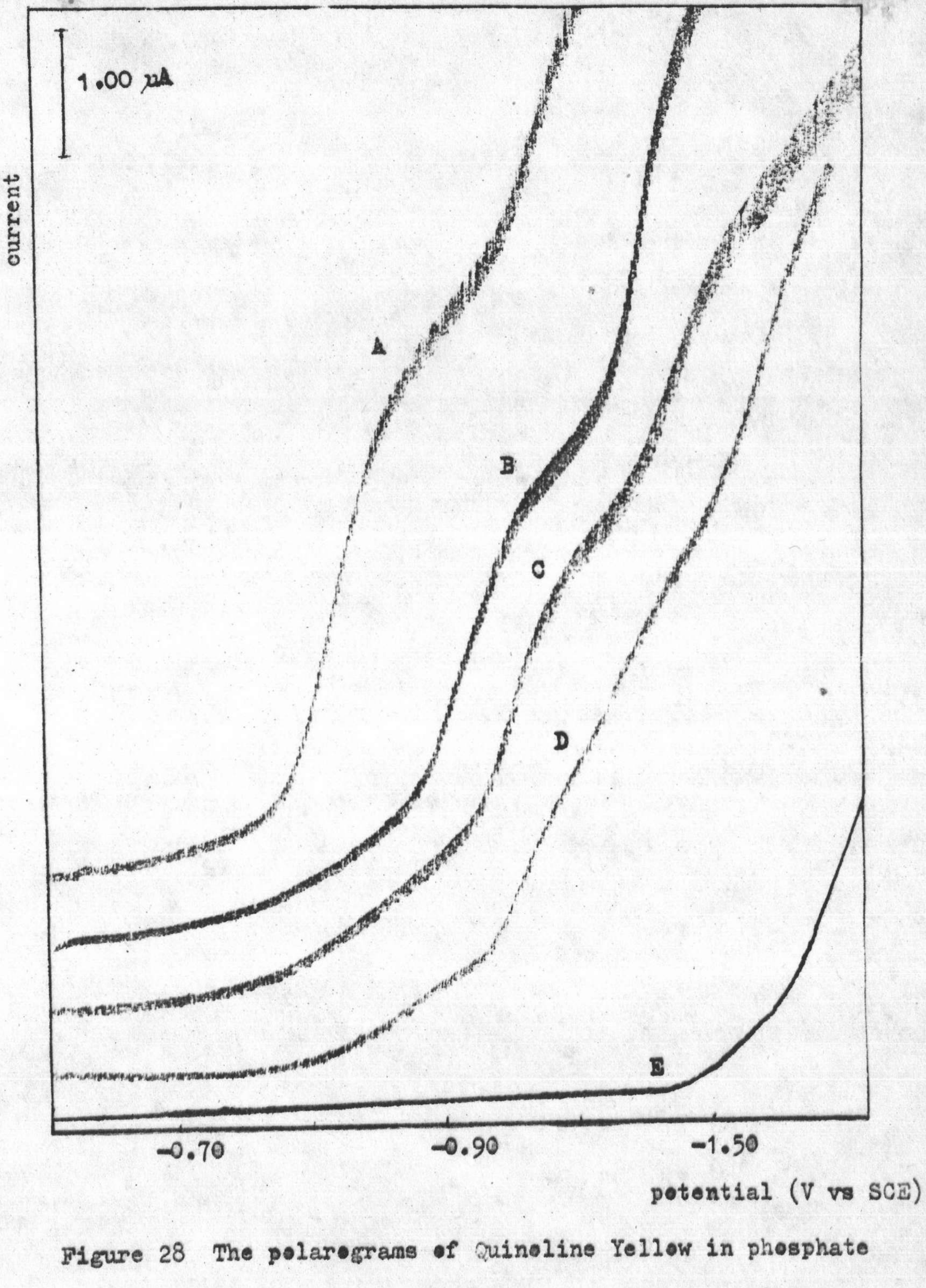


Figure 28 The polarograms of Quinoline Yellow in phosphate buffer and 0.1 M $KNO_3$ at pH A) 5.00 , B) 8.30 , C) 10.80 , D) 11.40 and the polarogram of 0.1 M $KNO_3$ (E)

Table 16 Effects of pH on the polarographic waves of Quinoline Yellow in phosphate buffer and 0.1M $(C_2H_5)_4NCl$.

| pH | First wave | | | Second wave | | |
|---|---|---|---|---|---|---|
| | $E_{\frac{1}{2}}$ (V) | $i_d^a$ (μA) | Remarks | $E_{\frac{1}{2}}$ (V) | $i_d^a$ (μA) | Remarks |
| 4.60 | -0.905 | 2.230 | well-defined wave | b | b | ill-defined wave |
| 5.05 | -0.942 | 2.230 | well-defined wave | b | b | ill-defined wave |
| 5.50 | -0.968 | 2.230 | well-defined wave | -1.310 | 0.420 | well-defined wave |
| 6.50 | -1.050 | 2.340 | well-defined wave | -1.360 | 0.600 | well-defined wave |
| 6.90 | -1.082 | 2.220 | well-defined wave | -1.392 | 0.860 | well-defined wave |
| 7.50 | -1.120 | 1.850 | well-defined wave | -1.423 | 0.960 | well-defined wave |
| 7.90 | -1.143 | 1.600 | well-defined wave | -1.440 | 1.000 | well-defined wave |
| 8.35 | -1.165 | 1.560 | well-defined wave | -1.476 | 0.980 | well-defined wave |
| 9.00 | -1.190 | 1.300 | well-defined wave | -1.500 | 0.860 | well-defined wave |
| 9.50 | -1.200 | 1.300 | well-defined wave | -1.505 | 0.800 | well-defined wave |
| 10.15 | -1.210 | 1.300 | well-defined wave | -1.508 | 0.800 | well-defined wave |
| 11.10 | -1.220 | 1.100 | well-defined wave | -1.518 | 0.780 | well-defined wave |

[a] mercury height = 65.0 cm ; $m^{\frac{2}{3}} t^{\frac{1}{6}} = 0.61$

[b] cannot be measured accurately

Table 17 Effects of pH on the polarographic waves of Quinoline Yellow in phosphate buffer and 0.1M KCl

| pH | First wave | | | Second wave | | |
|---|---|---|---|---|---|---|
| | $E_{\frac{1}{2}}$ (V) | $i_d^a$ (μA) | Remarks | $E_{\frac{1}{2}}$ (V) | $i_d^a$ (μA) | Remarks |
| 4.50 | -0.956 | 2.350 | well-defined wave | b | b | ill-defined wave |
| 5.10 | -0.998 | 2.500 | well-defined wave | b | b | ill-defined wave |
| 5.60 | -1.013 | 2.350 | well-defined wave | -1.310 | 0.550 | well-defined wave |
| 6.02 | -1.041 | 2.470 | well-defined wave | -1.338 | 0.600 | well-defined wave |
| 6.52 | -1.088 | 2.500 | well-defined wave | -1.363 | 0.600 | well-defined wave |
| 7.01 | -1.105 | 2.200 | well-defined wave | -1.395 | 0.750 | well-defined wave |
| 7.55 | -1.130 | 1.700 | well-defined wave | -1.425 | 0.850 | well-defined wave |
| 8.00 | -1.145 | 1.500 | well-defined wave | -1.453 | 1.000 | well-defined wave |
| 8.55 | -1.213 | 1.200 | well-defined wave | -1.481 | 0.950 | well-defined wave |
| 9.00 | -1.215 | 1.150 | well-defined wave | -1.500 | 0.900 | well-defined wave |
| 9.51 | -1.218 | 1.150 | well-defined wave | -1.506 | 0.850 | well-defined wave |
| 10.03 | -1.225 | 1.150 | well-defined wave | -1.506 | 0.920 | well-defined wave |
| 11.42 | b | b | ill-defined wave | b | b | ill-defined wave |

[a] mercury height = 65.0 cm; $m^{\frac{2}{3}} t^{\frac{1}{6}} = 0.61$

[b] cannot be measured accurately

Table 18 Effects of pH on the polarographic waves of Quinoline Yellow in phosphate buffer and 0.1M $KNO_3$

| pH | First wave | | | Second wave | | |
|---|---|---|---|---|---|---|
| | $E_{\frac{1}{2}}$ (V) | $i_d$[a] (uA) | Remarks | $E_{\frac{1}{2}}$ (V) | $i_d$[a] (uA) | Remarks |
| 4.58 | -0.943 | 2.400 | well-defined wave | b | b | ill-defined wave |
| 5.00 | -0.962 | 2.470 | well-defined wave | b | b | ill-defined wave |
| 5.50 | -1.005 | 2.580 | well-defined wave | b | b | ill-defined wave |
| 6.00 | -1.039 | 2.700 | well-defined wave | -1.328 | 0.510 | well-defined wave |
| 6.50 | -1.071 | 2.550 | well-defined wave | -1.358 | 0.600 | well-defined wave |
| 7.00 | -1.090 | 2.300 | well-defined wave | -1.390 | 0.820 | well-defined wave |
| 7.50 | -1.095 | 1.900 | well-defined wave | -1.418 | 0.930 | well-defined wave |
| 8.30 | -1.161 | 1.300 | well-defined wave | -1.458 | 1.150 | well-defined wave |
| 8.80 | -1.190 | 1.050 | well-defined wave | -1.462 | 0.850 | well-defined wave |
| 9.40 | -1.192 | 1.080 | well-defined wave | -1.460 | 0.800 | well-defined wave |
| 10.80 | -1.210 | 1.030 | well-defined wave | -1.460 | 0.800 | well-defined wave |
| 11.40 | b | b | ill-defined wave | b | b | ill-defined wave |

[a] mercury height = 65.0 cm; $m^{\frac{2}{3}}t^{\frac{1}{6}} = 0.61$

[b] cannot be measured accurately

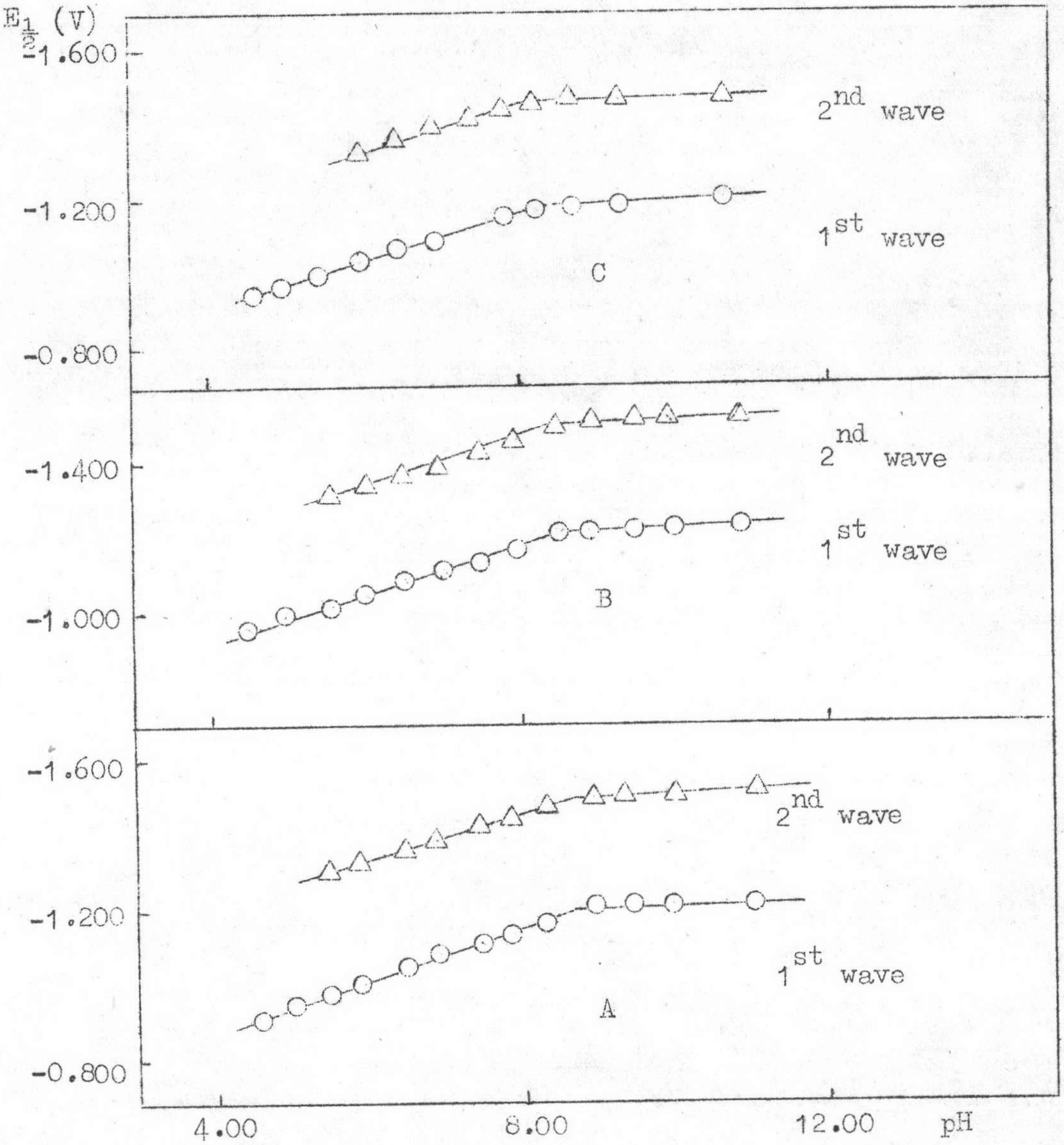


Figure 29 The effects of pH on the half wave potentials Quinoline Yellow in phosphate buffer and variuos supporting electrolytes: A) 0.1M $(C_2H_5)_4NCl$, B) 0.1M KCl and C) 0.1M $KNO_3$

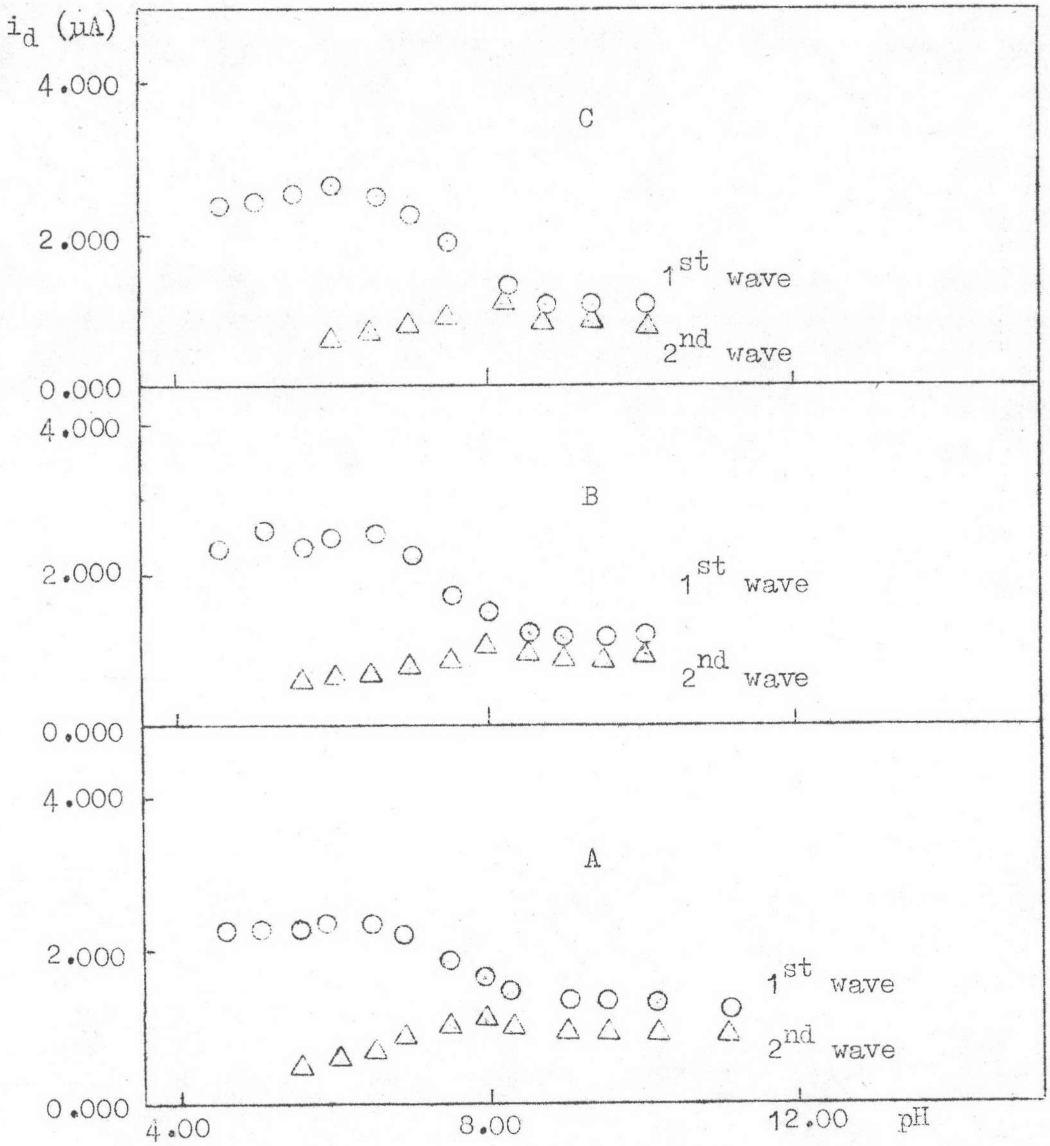


Figure 30 The effects of pH on the diffusion currents of Quinoline Yellow in phosphate buffer and various supporting electrolytes: A) 0.1M $(C_2H_5)_4NCl$, B) 0.1M KCl and C) 0.1M $KNO_3$

current obtained at pH higher than 8 is almost constant. Thus, the diffusion current of the second wave of Quinoline Yellow is independent on pH at pH higher than 8.00 (see Figure 30).

### 4.2.3 Reversibility

The electrode reactions of Tartrazine, Brilliant Blue FCF and Quinoline Yellow were investigated from the polarograms of well-defined waves. For a reversible process, the plot of the working electrode potential against log i/id-i gives a straight line of slope $\left|2.303RT/nF\right|$ V or $\left|\frac{60}{n}\right|$ mV at 30° C. If the electrode process is irreversible the slope is larger than $\left|\frac{60}{n}\right|$ mV since the wave is more drawn out. Another simpler method, although less exact, is to determine the $\left|E_{\frac{1}{4}} - E_{\frac{3}{4}}\right|$ value of the wave. For a reversible process, the $\left|E_{\frac{1}{4}} - E_{\frac{3}{4}}\right|$ value equals to $\left|\frac{57}{n}\right|$ mV at 30°C and for an irreversible wave, the $\left|E_{\frac{1}{4}} - E_{\frac{3}{4}}\right|$ value is greater than $\left|\frac{57}{n}\right|$ mV.

Results of these investigations are listed in Table 19 for Tartrazine, Table 20 for Brilliant Blue FCF and Table 21 for Quinoline Yellow. Polarographic reduction of Tartrazine in every electrolyte informed that the electrode reaction was irreversible at pH lower than 4.00 but it was reversible at pH higher than 4.00 ( see Table 19 ). The first reduction wave of Brilliant Blue FCF in every electrolyte and pH studied was irreversible. The second wave was reversible in pH 1.50-2.20 but in other pH it was irreversible ( see Table 20 ). Polarographic reduction of Quinoline Yellow in every electrolyte and every pH studied provided irreversible process ( see Table 21 ).

From this study, it can be seen that the electrode

Table 19 Tests for reversibilities of Tartrazine in various electrolytes

| pH | slope of $-E_{de}$ vs $\log i/i_d-i$ | $\lvert E_{\frac{1}{4}} - E_{\frac{3}{4}} \rvert$ | Electrode Reaction |
|---|---|---|---|
| in 0.1M $(C_2H_5)_4NCl$ | | | |
| 1.50 | 0.027 | 0.025 | irreversible |
| 2.20 | 0.027 | 0.025 | |
| 3.00 | 0.027 | 0.025 | |
| 3.85 | 0.027 | 0.025 | |
| 4.58 | 0.030 | 0.028 | reversible |
| 5.15 | 0.030 | 0.028 | |
| 5.60 | 0.030 | 0.028 | |
| 6.18 | 0.030 | 0.028 | |
| 6.55 | 0.030 | 0.028 | |
| 6.98 | 0.030 | 0.028 | |
| 8.22 | 0.031 | 0.029 | |
| 9.00 | 0.031 | 0.029 | |
| 9.65 | 0.030 | 0.028 | |
| 10.25 | 0.030 | 0.028 | |
| 11.82 | 0.030 | 0.028 | |
| in 0.1M KCl | | | |
| 1.31 | 0.026 | 0.024 | irreversible |
| 2.20 | 0.026 | 0.024 | |
| 3.00 | 0.026 | 0.024 | |
| 4.02 | 0.026 | 0.024 | |
| 4.60 | 0.030 | 0.028 | reversible |
| 5.20 | 0.030 | 0.028 | |
| 5.52 | 0.030 | 0.028 | |
| 6.02 | 0.031 | 0.029 | |
| 6.50 | 0.031 | 0.029 | |
| 6.80 | 0.031 | 0.029 | |
| 7.00 | 0.030 | 0.028 | |
| 8.02 | 0.030 | 0.028 | |
| 8.98 | 0.030 | 0.028 | |
| 9.72 | 0.030 | 0.028 | |
| 10.60 | 0.030 | 0.028 | |

Table 19 (continued)

| pH | slope of $-E_{de}$ vs log $i/i_d-i$ | $E_{\frac{1}{4}} - E_{\frac{3}{4}}$ | Electrode Reaction |
|---|---|---|---|
| in 0.1M $KNO_3$ | | | |
| 1.30 | 0.027 | 0.025 | irreversible |
| 2.30 | 0.027 | 0.025 | |
| 3.10 | 0.027 | 0.025 | |
| 4.10 | 0.027 | 0.025 | |
| 4.55 | 0.030 | 0.028 | reversible |
| 5.25 | 0.030 | 0.028 | |
| 5.58 | 0.030 | 0.028 | |
| 6.15 | 0.030 | 0.028 | |
| 6.82 | 0.030 | 0.028 | |
| 7.25 | 0.030 | 0.028 | |
| 8.20 | 0.031 | 0.029 | |
| 9.05 | 0.030 | 0.028 | |
| 9.39 | 0.030 | 0.028 | |
| 10.10 | 0.030 | 0.028 | |

Table 20 Tests for reversibilities of Brilliant Blue FCF in various electrolytes

| pH | First wave |  |  | Second wave |  |  |
|---|---|---|---|---|---|---|
|  | slope of $-E_{d.e.}$ vs log $i/i_d-i$ | $E_{\frac{1}{4}} - E_{\frac{3}{4}}$ | Electrode Reaction | slope of $-E_{d.e}$ vs log $i/i_d-i$ | $E_{\frac{1}{4}} - E_{\frac{3}{4}}$ | Electrode Reaction |
| in 0.1 M $(C_2H_5)_4NCl$ |  |  |  |  |  |  |
| 1.50 | 0.045 | 0.043 | irreversible | 0.031 | 0.029 | reversible |
| 2.20 | 0.045 | 0.043 |  | 0.031 | 0.029 |  |
| 3.02 | 0.045 | 0.043 |  | 0.047 | 0.045 | irreversible |
| 4.15 | 0.045 | 0.043 |  | 0.047 | 0.045 |  |
| 4.58 | 0.055 | 0.053 |  | 0.055 | 0.053 |  |
| 5.19 | 0.055 | 0.053 |  | 0.055 | 0.053 |  |
| 5.60 | 0.055 | 0.053 |  | 0.055 | 0.053 |  |
| 6.12 | 0.055 | 0.053 |  | 0.055 | 0.053 |  |
| 6.80 | 0.067 | 0.065 |  | 0.071 | 0.069 |  |
| 7.20 | 0.067 | 0.065 |  | 0.071 | 0.069 |  |
| 8.20 | 0.067 | 0.065 |  | 0.071 | 0.069 |  |
| 8.98 | 0.067 | 0.065 |  | 0.071 | 0.069 |  |
| 9.70 | 0.067 | 0.065 |  | 0.071 | 0.069 |  |
| 10.30 | 0.067 | 0.065 |  | 0.071 | 0.069 |  |
| 11.80 | 0.067 | 0.065 |  | 0.071 | 0.069 |  |
| in 0.1 M KCl |  |  |  |  |  |  |
| 1.30 | 0.048 | 0.046 | irreversible | 0.031 | 0.029 | reversible |
| 2.17 | 0.048 | 0.046 |  | 0.031 | 0.029 |  |
| 2.70 | b | b |  | b | b | irreversible |
| 3.95 | b | b |  | b | b |  |
| 4.30 | 0.048 | 0.046 |  | 0.058 | 0.056 |  |
| 4.90 | 0.058 | 0.056 |  | 0.058 | 0.056 |  |

Table 20 continued

| pH | First wave |  |  | Second wave |  |  |
|---|---|---|---|---|---|---|
|  | slope of $-E_{d.e}$ vs log $i/i_d-i$ | $E_{\frac{1}{4}} - E_{\frac{3}{4}}$ | Electrode Reaction | slope of $-E_{d.e}$ vs log $i/i_d-i$ | $E_{\frac{1}{4}} - E_{\frac{3}{4}}$ | Electrode Reaction |
| in 0.1 M KCl |  |  |  |  |  |  |
| 5.60 | 0.058 | 0.056 | irreversible | 0.058 | 0.056 | irreversible |
| 6.00 | 0.058 | 0.056 |  | 0.058 | 0.056 |  |
| 6.50 | 0.068 | 0.066 |  | 0.058 | 0.056 |  |
| 7.00 | 0.068 | 0.066 |  | 0.071 | 0.069 |  |
| 8.17 | 0.068 | 0.066 |  | 0.071 | 0.069 |  |
| 8.85 | 0.068 | 0.066 |  | 0.071 | 0.069 |  |
| 9.20 | 0.068 | 0.066 |  | 0.071 | 0.069 |  |
| 9.70 | 0.068 | 0.066 |  | 0.071 | 0.069 |  |
| 11.30 | 0.068 | 0.066 |  | 0.071 | 0.069 |  |
| in 0.1 M $KNO_3$ |  |  |  |  |  |  |
| 1.31 | 0.048 | 0.046 | irreversible | 0.031 | 0.029 | reversible |
| 2.18 | 0.048 | 0.046 |  | 0.031 | 0.029 |  |
| 2.71 | b | b |  | b | b |  |
| 3.97 | b | b |  | b | b |  |
| 4.31 | 0.048 | 0.046 |  | 0.058 | 0.056 | irreversible |
| 4.90 | 0.058 | 0.056 |  | 0.058 | 0.056 |  |
| 5.62 | 0.058 | 0.056 |  | 0.058 | 0.056 |  |
| 6.02 | 0.058 | 0.056 |  | 0.058 | 0.056 |  |
| 6.53 | 0.068 | 0.066 |  | 0.058 | 0.056 |  |
| 7.03 | 0.068 | 0.066 |  | 0.071 | 0.069 |  |
| 8.20 | 0.068 | 0.066 |  | 0.071 | 0.069 |  |
| 8.87 | 0.068 | 0.066 |  | 0.071 | 0.069 |  |
| 9.73 | 0.068 | 0.066 |  | 0.071 | 0.069 |  |
| 11.32 | 0.068 | 0.066 |  | 0.071 | 0.069 |  |

$^b$cannot be measured accurately

Table 21 Tests for reversiblities of Quinoline Yellow in phosphate buffer and various electrolytes

| pH | First wave |  |  | Second wave |  |  |
|---|---|---|---|---|---|---|
|  | slope of $-E_{de}$ vs $\log i/i_d - i$ | $\lvert E_{\frac{1}{4}} - E_{\frac{3}{4}} \rvert$ | Electrode Reaction | slope of $-E_{de}$ vs $\log i/i_d - i$ | $\lvert E_{\frac{1}{4}} - E_{\frac{3}{4}} \rvert$ | Electrode Reaction |
| in 0.1M $(C_2H_5)_4NCl$ |  |  |  |  |  |  |
| 4.60 | 0.058 | 0.056 | irreversible | b | b |  |
| 5.05 | 0.058 | 0.056 |  | b | b |  |
| 5.50 | 0.058 | 0.056 |  | 0.058 | 0.056 | irreversible |
| 5.90 | 0.058 | 0.056 |  | 0.058 | 0.056 |  |
| 6.50 | 0.058 | 0.056 |  | 0.058 | 0.056 |  |
| 6.90 | 0.058 | 0.056 |  | 0.058 | 0.056 |  |
| 7.50 | 0.058 | 0.056 |  | 0.058 | 0.056 |  |
| 7.90 | 0.058 | 0.056 |  | 0.058 | 0.056 |  |
| 8.35 | 0.058 | 0.056 |  | 0.058 | 0.056 |  |
| 9.00 | 0.058 | 0.056 |  | 0.058 | 0.056 |  |
| 9.50 | 0.058 | 0.056 |  | 0.058 | 0.056 |  |
| 10.15 | 0.058 | 0.056 |  | 0.058 | 0.056 |  |
| 11.10 | 0.058 | 0.056 |  | 0.058 | 0.056 |  |

[b] cannot be measured accurately

Table 21 (continued)

| pH | First wave | | | Second wave | | |
|---|---|---|---|---|---|---|
| | slope of $-E_{de}$ vs log $i/i_d-i$ | $\lvert E_{\frac{1}{4}} - E_{\frac{3}{4}} \rvert$ | Electrode Reaction | slope of $-E_{de}$ vs log $i/i_{d-i}$ | $\lvert E_{\frac{1}{4}} - E_{\frac{3}{4}} \rvert$ | Electrode Reaction |
| in 0.1M KCl | | | | | | |
| 4.50 | 0.060 | 0.058 | irreversible | b | b | |
| 5.10 | 0.060 | 0.058 | | b | b | |
| 5.60 | 0.060 | 0.058 | | 0.060 | 0.058 | irreversible |
| 6.02 | 0.060 | 0.058 | | 0.060 | 0.058 | |
| 6.52 | 0.060 | 0.058 | | 0.060 | 0.058 | |
| 7.01 | 0.060 | 0.058 | | 0.060 | 0.058 | |
| 7.55 | 0.060 | 0.058 | | 0.060 | 0.058 | |
| 8.00 | 0.060 | 0.058 | | 0.060 | 0.058 | |
| 8.55 | 0.060 | 0.058 | | 0.060 | 0.058 | |
| 9.00 | 0.060 | 0.058 | | 0.060 | 0.058 | |
| 9.51 | 0.060 | 0.058 | | 0.060 | 0.058 | |
| 10.03 | 0.060 | 0.058 | | 0.060 | 0.058 | |
| 10.95 | 0.060 | 0.058 | | 0.060 | 0.058 | |
| 11.42 | b | b | | b | b | |

[b] cannot be measured accurately

Table 21 (continued)

| pH | First wave |  |  | Second wave |  |  |
|---|---|---|---|---|---|---|
|  | slope of $-E_{de}$ vs log $i/i_{d}-i$ | $E_{\frac{1}{4}} - E_{\frac{3}{4}}$ | Electrode Reaction | slope of $-E_{de}$ vs log $i/i_{d}-i$ | $E_{\frac{1}{4}} - E_{\frac{3}{4}}$ | Electrode Reaction |
| in 0.1M $KNO_3$ |  |  |  |  |  |  |
| 4.58 | 0.060 | 0.058 | irreversible | b | b |  |
| 5.00 | 0.060 | 0.058 |  | b | b |  |
| 5.50 | 0.060 | 0.058 |  | b | b |  |
| 6.00 | 0.060 | 0.058 |  | 0.060 | 0.058 | irreversible |
| 6.50 | 0.060 | 0.058 |  | 0.060 | 0.058 |  |
| 7.00 | 0.060 | 0.058 |  | 0.060 | 0.058 |  |
| 7.50 | 0.060 | 0.058 |  | 0.060 | 0.058 |  |
| 7.90 | 0.060 | 0.058 |  | 0.060 | 0.058 |  |
| 8.30 | 0.060 | 0.058 |  | 0.060 | 0.058 |  |
| 8.80 | 0.060 | 0.058 |  | 0.060 | 0.058 |  |
| 9.40 | 0.060 | 0.058 |  | 0.060 | 0.058 |  |
| 10.80 | 0.060 | 0.058 |  | 0.060 | 0.058 |  |
| 11.40 | b | b |  | b | b |  |

[b] cannot be measured accurately

reactions of Tartrazine, Brilliant Blue FCF and Quinoline Yellow were not affected by the supporting electrolytes : $(C_2H_5)_4NCl$, KCl and $KNO_3$ , but they were controlled by the pH of solution.

### 4.2.4 Electron transfer and proton transport values

In this study, the numbers of electron transfer (n) and proton transport (**m**) in the polarographic reduction of the dye were determined from the reversible wave as well as the value of the product of electron transfer coefficient and electron transfer ($\alpha n$) and **m** were calculated for the irreversible wave. Data from the present study were insufficient to calculate the number of electron transfer of the irreversible wave. The number of electron transfer for the irreversible process can be determined by a coulometric analysis at a fixed potential that is 0.2 volt more negative than the half wave potential. For a reversible wave the number of electron transfer was determined from the slope of a plot of the electrode potential against its corresponded $\log i/i_d-i$ and proton transport value was calculated by equation 9 (see page 15). Data for number of electron transfer, product of transfer coefficient and electron transfer and proton transport of Tartrazine, Brilliant Blue FCF and Quinoline Yellow are listed in Tables **22,** 23 and 24. Table 22 indicated that at pH higher than 4.50 the number of electrons transferred in the reduction of Tartrazine are 2 and the number of protons consumed by Tartrazine are also 2. For Brilliant Blue FCF, the first wave is irreversible and the values of $\alpha n$ and m are listed in Table 23. The second wave for the reduction of Brilliant Blue FCF is reversible at pH 1.50-2.20 and its number of electrons transferred are 2 and protons transported are 4 when the pH is higher than 2.20 the wave becomes irreversible and the values of $\alpha n$ and m

Table 22 Numbers of electron transfer, product of transfer coefficient and electron transfer and proton transport for the polarographic reduction of Tartrazine in various electrolytes

| pH | αn | n | m | pH | αn | n | m | pH | αn | n | m |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.1 M ( $C_2H_5)_4NCl$ | | | | 0.1 M KCl | | | | 0.1 M $KNO_3$ | | | |
| 1.50 | 2.2 | - | 3.7 | 1.31 | 2.3 | - | 3.5 | 1.30 | 2.2 | - | 3.7 |
| 2.20 | 2.2 | - | 3.7 | 2.20 | 2.3 | - | 3.5 | 2.30 | 2.2 | - | 3.7 |
| 3.00 | 2.2 | - | 3.7 | 3.00 | 2.3 | - | 3.5 | 3.10 | 2.2 | - | 3.7 |
| 3.85 | 2.2 | - | 3.7 | 4.02 | 2.3 | - | 3.5 | 4.10 | 2.2 | - | 3.7 |
| 4.58 | - | 2.0 | 2.0 | 4.60 | - | 2.0 | 2.1 | 4.55 | - | 2.0 | 2.0 |
| 5.15 | - | 2.0 | 2.0 | 5.20 | - | 2.0 | 2.1 | 5.25 | - | 2.0 | 2.0 |
| 5.60 | - | 2.0 | 2.0 | 5.52 | - | 2.0 | 2.1 | 5.58 | - | 2.0 | 2.0 |
| 6.18 | - | 2.0 | 2.0 | 6.02 | - | 1.9 | 2.0 | 6.15 | - | 2.0 | 2.0 |
| 6.55 | - | 2.0 | 2.0 | 6.50 | - | 1.9 | 2.0 | 6.82 | - | 2.0 | 2.0 |
| 6.98 | - | 2.0 | 2.0 | 7.00 | - | 2.0 | 2.1 | 7.25 | - | 2.0 | 2.0 |
| 8.22 | - | 1.9 | 1.9 | 8.02 | - | 2.0 | 2.1 | 8.20 | - | 1.9 | 1.9 |
| 9.00 | - | 1.9 | 1.9 | 8.98 | - | 2.0 | 2.1 | 9.05 | - | 2.0 | 2.0 |
| 9.65 | - | 2.0 | 2.0 | 9.72 | - | 2.0 | 2.1 | 9.39 | - | 2.0 | 2.0 |
| 10.25 | - | 2.0 | 2.0 | 10.60 | - | 2.0 | 2.1 | 10.10 | - | 2.0 | 2.0 |

Table 23 Numbers of electron transfer, product of transfer coefficient and electron transfer and proton transport for the polarographic reduction of Brilliant Blue FCF in various electrolytes

| pH | First wave | | Second wave | | |
|---|---|---|---|---|---|
| | $\alpha n$ | m | n | $\alpha n$ | m |
| 0.1M $(C_2H_5)_4NCl$ | | | | | |
| 1.50 | 1.3 | 2.3 | 2.0 | - | 4.0 |
| 2.20 | 1.3 | 2.3 | 2.0 | - | 4.0 |
| 3.02 | 1.3 | 2.3 | - | 1.3 | 2.2 |
| 4.15 | 1.3 | 2.3 | - | 1.3 | 2.2 |
| 4.58 | 1.1 | 0.2 | - | 1.1 | 1.8 |
| 5.19 | 1.1 | 0.2 | - | 1.1 | 1.8 |
| 5.60 | 1.1 | 0.2 | - | 1.1 | 1.8 |
| 6.12 | 1.1 | 0.2 | - | 1.1 | 1.8 |
| 6.80 | 0.9 | 0.2 | - | 0.9 | 0.3 |
| 7.20 | 0.9 | 0.2 | - | 0.9 | 0.3 |
| 8.20 | 0.9 | 0.2 | - | 0.9 | 0.3 |
| 8.98 | 0.9 | 0.2 | - | 0.9 | 0.3 |
| 9.70 | 0.9 | 0.2 | - | 0.9 | 0.3 |
| 10.30 | 0.9 | 0.2 | - | 0.9 | 0.3 |
| 11.80 | 0.9 | 0.2 | - | 0.9 | 0.3 |
| 0.1M KCl | | | | | |
| 1.30 | 1.3 | 2.1 | 2.0 | - | 4.0 |
| 2.17 | 1.3 | 2.1 | 2.0 | - | 4.0 |
| 2.70 | b | b | | b | b |
| 3.95 | b | b | | b | b |
| 4.30 | 1.3 | 2.1 | - | 1.1 | 1.7 |
| 4.90 | 1.1 | 0.2 | - | 1.1 | 1.7 |
| 5.60 | 1.1 | 0.2 | - | 1.1 | 1.7 |
| 6.00 | 1.1 | 0.2 | - | 1.1 | 1.7 |
| 7.00 | 0.9 | 0.1 | - | 0.9 | 0.2 |
| 8.17 | 0.9 | 0.1 | - | 0.9 | 0.2 |
| 8.85 | 0.9 | 0.1 | - | 0.9 | 0.2 |
| 9.20 | 0.9 | 0.1 | - | 0.9 | 0.2 |
| 9.70 | 0.9 | 0.1 | - | 0.9 | 0.2 |
| 11.30 | 0.9 | 0.1 | - | 0.9 | 0.2 |

Table 23 (continued)

| pH | First wave | | Second wave | | |
|---|---|---|---|---|---|
| | $\alpha n$ | m | n | $\alpha n$ | m |
| $0.1M\ KNO_3$ | | | | | |
| 1.31 | 1.3 | 2.3 | 2.0 | - | 4.0 |
| 2.18 | 1.3 | 2.3 | 2.0 | - | 4.0 |
| 2.71 | b | b | - | b | b |
| 3.97 | b | b | - | b | b |
| 4.31 | 1.3 | 2.3 | - | 1.1 | 1.8 |
| 4.90 | 1.1 | 0.3 | - | 1.1 | 1.8 |
| 5.62 | 1.1 | 0.3 | - | 1.1 | 1.8 |
| 6.02 | 1.1 | 0.3 | - | 1.1 | 1.8 |
| 6.53 | 0.9 | 0.2 | - | 1.1 | 1.8 |
| 7.03 | 0.9 | 0.2 | - | 0.9 | 0.2 |
| 8.20 | 0.9 | 0.2 | - | 0.9 | 0.2 |
| 8.87 | 0.9 | 0.2 | - | 0.9 | 0.2 |
| 9,22 | 0.9 | 0.2 | - | 0.9 | 0.2 |
| 9.73 | 0.9 | 0.2 | - | 0.9 | 0.2 |
| 11.32 | 0.9 | 0.2 | - | 0.9 | 0.2 |

[b] cannot be calculated

Table 24 Product of transfer coefficient and electron transfer and proton transport for the reduction of Quinoline Yellow in phosphate buffer and various supporting electrolytes

| pH | First wave | | Second wave | |
|---|---|---|---|---|
| | $\alpha n$ | m | $\alpha n$ | m |
| 0.1M $(C_2H_5)_4NCl$ | | | | |
| 4.60 | 1.1 | 1.1 | b | b |
| 5.05 | 1.1 | 1.1 | b | b |
| 5.50 | 1.1 | 1.1 | 1.1 | 1.1 |
| 5.90 | 1.1 | 1.1 | 1.1 | 1.1 |
| 6.50 | 1.1 | 1.1 | 1.1 | 1.1 |
| 6.90 | 1.1 | 1.1 | 1.1 | 1.1 |
| 7.50 | 1.1 | 1.1 | 1.1 | 1.1 |
| 7.90 | 1.1 | 1.1 | 1.1 | 1.1 |
| 8.35 | 1.1 | 1.1 | 1.1 | 1.1 |
| 9.00 | 1.1 | 0.2 | 1.1 | 0.2 |
| 9.50 | 1.1 | 0.2 | 1.1 | 0.2 |
| 10.15 | 1.1 | 0.2 | 1.1 | 0.2 |
| 11.10 | 1.1 | 0.2 | 1.1 | 0.2 |
| 0.1M KCl | | | | |
| 4.50 | 1.1 | 1.1 | b | b |
| 5.10 | 1.1 | 1.1 | b | b |
| 5.60 | 1.1 | 1.1 | 1.1 | 1.1 |
| 6.02 | 1.1 | 1.1 | 1.1 | 1.1 |
| 6.52 | 1.1 | 1.1 | 1.1 | 1.1 |
| 7.01 | 1.1 | 1.1 | 1.1 | 1.1 |
| 7.55 | 1.1 | 1.1 | 1.1 | 1.1 |
| 8.00 | 1.1 | 1.1 | 1.1 | 1.1 |
| 8.55 | 1.1 | 1.1 | 1.1 | 1.1 |
| 9.00 | 1.1 | 0.2 | 1.1 | 0.2 |
| 9.51 | 1.1 | 0.2 | 1.1 | 0.2 |
| 10.03 | 1.1 | 0.2 | 1.1 | 0.2 |
| 11.42 | b | b | b | b |

Table 24 (continued)

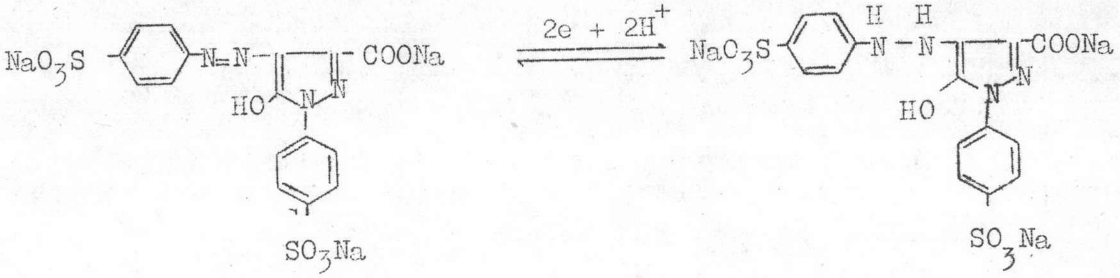
| pH | First wave | | Second wave | |
|---|---|---|---|---|
| | $\alpha n$ | m | $\alpha n$ | m |
| 0.1M $KNO_3$ | | | | |
| 4.58 | 1.1 | 1.1 | b | b |
| 5.00 | 1.1 | 1.1 | b | b |
| 5.50 | 1.1 | 1.1 | b | b |
| 6.00 | 1.1 | 1.1 | 1.1 | 1.1 |
| 6.50 | 1.1 | 1.1 | 1.1 | 1.1 |
| 7.00 | 1.1 | 1.1 | 1.1 | 1.1 |
| 7.50 | 1.1 | 1.1 | 1.1 | 1.1 |
| 7.90 | 1.1 | 1.1 | 1.1 | 1.1 |
| 8.30 | 1.1 | 1.1 | 1.1 | 1.1 |
| 8.80 | 1.1 | 0.2 | 1.1 | 0.2 |
| 9.40 | 1.1 | 0.2 | 1.1 | 0.2 |
| 10.80 | 1.1 | 0.2 | 1.1 | 0.2 |
| 11.40 | b | b | b | b |

[b] cannot be calculated

are calculated and listed in Table 23. For Quinoline Yellow both reduction waves are irreversible and their $\alpha n$ and m are listed in Table 24.

### 4.2.5 Reduction mechanism

Corresponding to the polarographic behavior of Tartrazine as mentioned above and its -N=N-, the reduction of Tartrazine should be

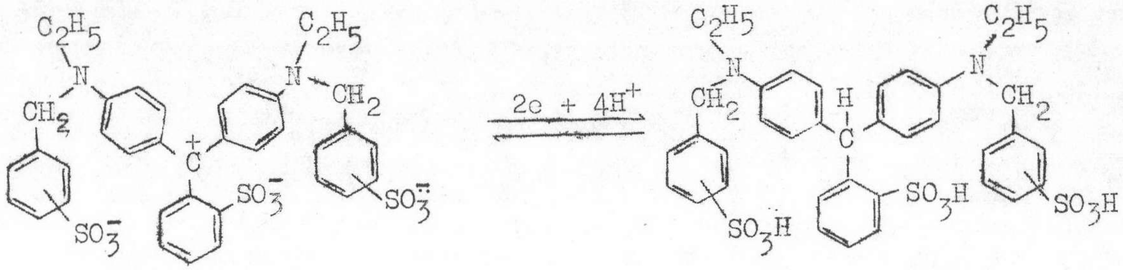


This mechanism confirmed the reduction of azo compounds which **took** place at -N=N- , giving hydrazo derivative( 16,23,38). The reduction of Tartrazine **was** quite fast since the electrode reaction resulted in .. reversible process.

The polarographic reduction of Brilliant Blue FCF in 0.1M $(C_2H_5)_4NCl$, 0.1M KCl or 0.1M $KNO_3$ provided two reduction waves. These waves were irrevsible except at pH 1.50-2.20. The irreversibility indicated that the rates of electron transfer for the reduction were slow.
At pH 1.50-2.20, the second wave was reversible. The polarographic reduction of triarylcarbonium ion in aprotic medium involved a 2-electron wave to triarylmethane but in the presence of water, two reduction waves were reported and the free radical was observed (35).

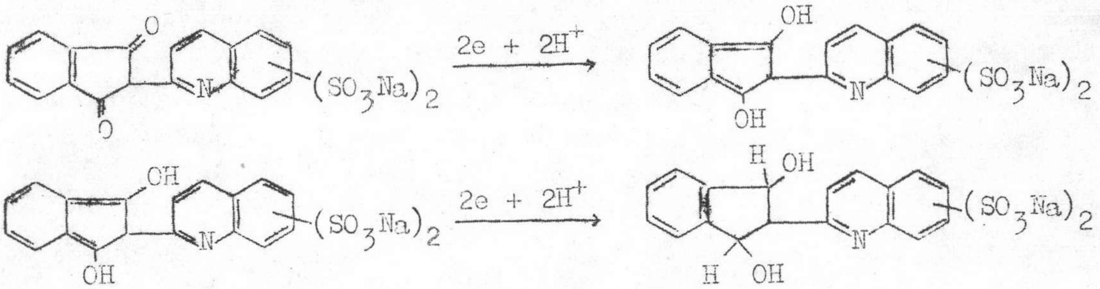
$$(C_6H_5)_3C^+ \quad + \quad e \rightleftharpoons (C_6H_5)_3C^{\cdot} \xrightarrow[H^+]{e} (C_6H_5)_3CH$$

Brilliant Blue FCF is a triarylcarbonium ion and two reduction waves were observed in aqueous solution. At some pH, 2.70-4.30, these two waves overlapped in 0.1M KCl and 0.1M $KNO_3$..Thus the reduction of Brilliant Blue FCF **was** possible to give triarylmethane and the mechanism could be



The electrode processes for reduction of Quinoline Yellow in phosphate buffer and 0.1M $(C_2H_5)_4NCl$, 0.1M KCl or 0.1M $KNO_3$ **were** irreversible. This was meant that the rates of electron transfer and proton transport in the reduction reaction were quite slow. The reduction of **1,3-indandione** usually **took** place at its carbonyl groups and the two 2-electron waves were reported (20).

Corresponding to Table 24 the reduction of Quinoline Yellow gave two reduction steps and the $\alpha$n values of these steps were equal as well as the number of proton consumed **was** equal to the $\alpha$n value in each step. Thus, Quinoline Yellow could be reduced at $-\overset{|}{C}=O$ to diendiol and followed to be the diol as shown below



### 4.2.6 Sensitivities

From the previous study, one well-defined polarographic wave of Tartrazine in 0.1 M $(C_2H_5)_4NCl$, 0.1 M KCl or 0.1 M $KNO_3$ was obtained in pH 1-11. The diffusion current of Tartrazine is independent on pH between pH 1.5-8.2. Thus, Tartrazine at any pH in this range was taken to study for the sensitivity. The concentrations of the dye studied were in the range $10^{-4}$ M and as low as possible to detect. The relationship between the concentration and the diffusion current of Tartrazine is listed in Table 25 and shown in Figure 31. It provided a linearity in the range of $1.5 \times 10^{-5}$-$8.0 \times 10^{-4}$ M. Thedetection limit of Tartrazine was found to be $1.5 \times 10^{-5}$ M.

The relationships between concentrations and the diffusion currents were studied at pH 1.35 for Brilliant Blue FCF and at pH 7.50 for Quioline Yellow since the polarographic waves in these pH values were well separated. The linearities were obtained in the range of $1.0 \times 10^{-5}$ - $1.0 \times 10^{-4}$ M for Brilliant Blue FCF and in the range of $2.0 \times 10^{-5}$ - $8.0 \times 10^{-4}$ M for Quinoline Yellow. The limits of detection of the first wave of Brilliant Blue FCF was $1.0 \times 10^{-5}$ M and of the second wave was $7.0 \times 10^{-5}$ M. For Quinoline Yellow the detection limits were found to be $2.0 \times 10^{-5}$ M for the first wave and $2.0 \times 10^{-4}$ M for the second wave. Therefore, the first reduction waves of Brilliant Blue FCF and Quinoline Yellow provided higher sensitivity for quantitative analysis than the second waves.

Table 25 The relationships between the concentrations and the diffusion currents of Tartrazine, Brilliant Blue FCF and Quinoline Yellow

| Tartrazine | | Brilliant Blue FCF | | | Quinoline Yellow | | |
|---|---|---|---|---|---|---|---|
| $10^5$ x conc (M) | $i_d$ (μA) | $10^5$ x conc. (M) | $i_{d_1}$ (μA) | $i_{d_2}$ (μA) | $10^5$ x conc. (M) | $i_{d_1}$ (μA) | $i_{d_2}$ (μA) |
| 0.90 | c | 0.90 | c | c | 1.00 | c | c |
| 1.00 | c | 1.00 | 0.030 | c | 2.00 | 0.170 | c |
| 1.50 | 0.150 | 3.00 | 0.060 | c | 3.00 | 0.180 | c |
| 3.00 | 0.430 | 5.00 | 0.095 | c | 5.00 | 0.220 | c |
| 5.00 | 0.600 | 7.00 | 0.120 | 0.030 | 7.00 | 0.360 | c |
| 7.00 | 0.800 | 9.00 | 0.135 | 0.058 | 10.00 | 0.400 | c |
| 9.00 | 0.952 | 10.00 | 0.150 | 0.100 | 20.00 | 0.800 | 0.300 |
| 10.00 | 1.000 | 20.00 | 0.300 | 0.360 | 30.00 | 1.100 | 0.500 |
| 20.00 | 2.010 | 30.00 | 0.452 | 0.550 | 40.00 | 1.450 | 0.700 |
| 30.00 | 2.800 | 40.00 | 0.580 | 0.680 | 50.00 | 1.800 | 0.830 |
| 40.00 | 3.962 | 50.00 | 0.740 | 0.800 | 60.00 | 2.180 | 1.020 |
| 50.00 | 4.405 | 60.00 | 0.920 | 1.070 | 70.00 | 2.600 | 1.150 |
| 60.00 | 5.180 | 70.00 | 1.120 | 1.200 | 80.00 | 3.020 | 1.440 |
| 70.00 | 6.050 | 80.00 | 1.220 | 1.530 | 90.00 | 3.810 | 1.800 |
| 80.00 | 7.000 | 90.00 | 1.510 | 1.920 | 100.00 | 4.500 | 2.550 |
| 90.00 | 8.400 | 100.00 | 1.700 | 2.320 | | | |
| 100.00 | 8.800 | | | | | | |

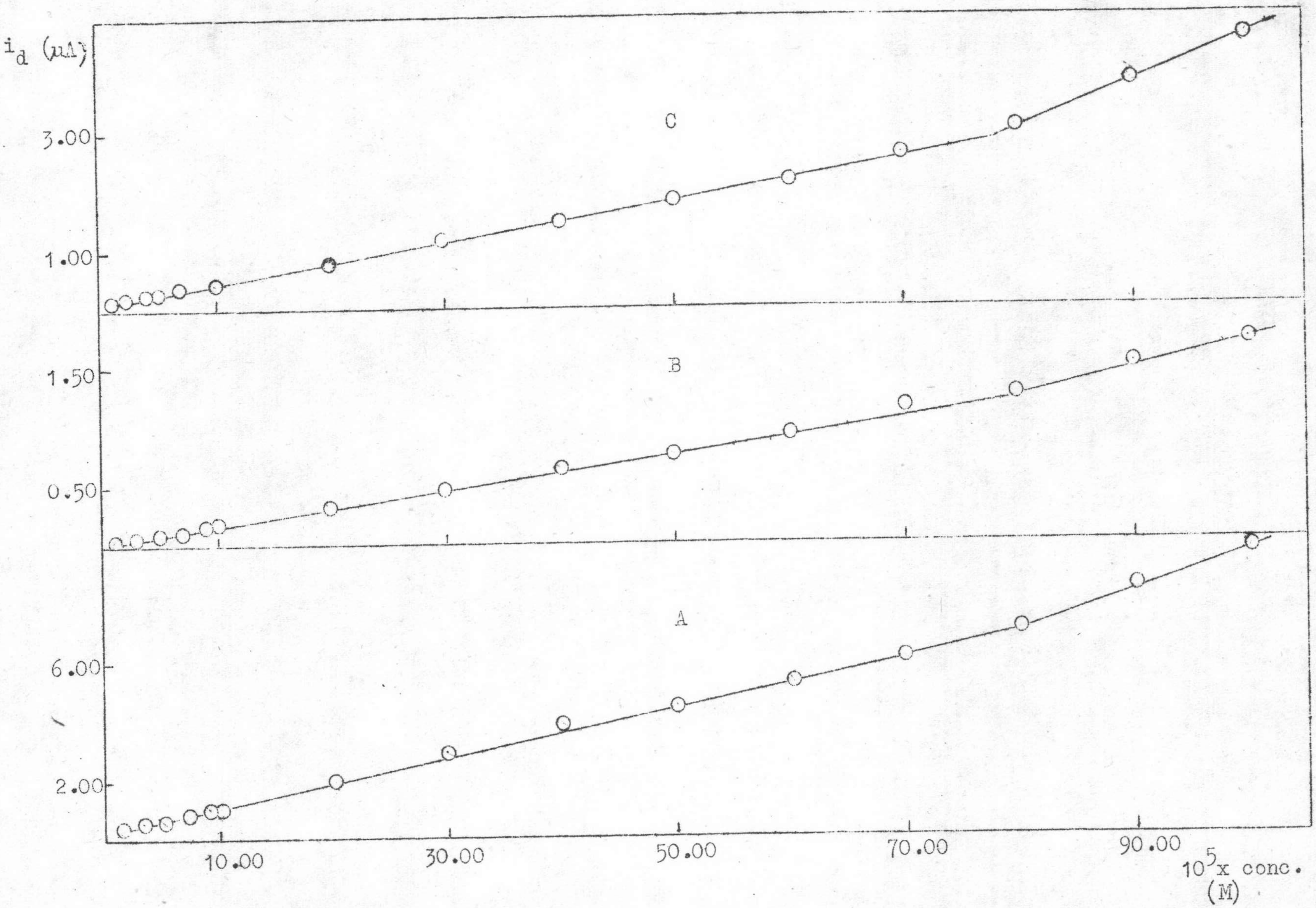


Figure 31A-C The relationships between the concentrations and the diffusion currents in 0.1M $(C_2H_5)_4NCl$ of A) Tartrazine at pH 2.20, B) the first wave of Brilliant Blue FCF at pH 1.35 and C) the first wave of Quinoline yellow at pH 7.50

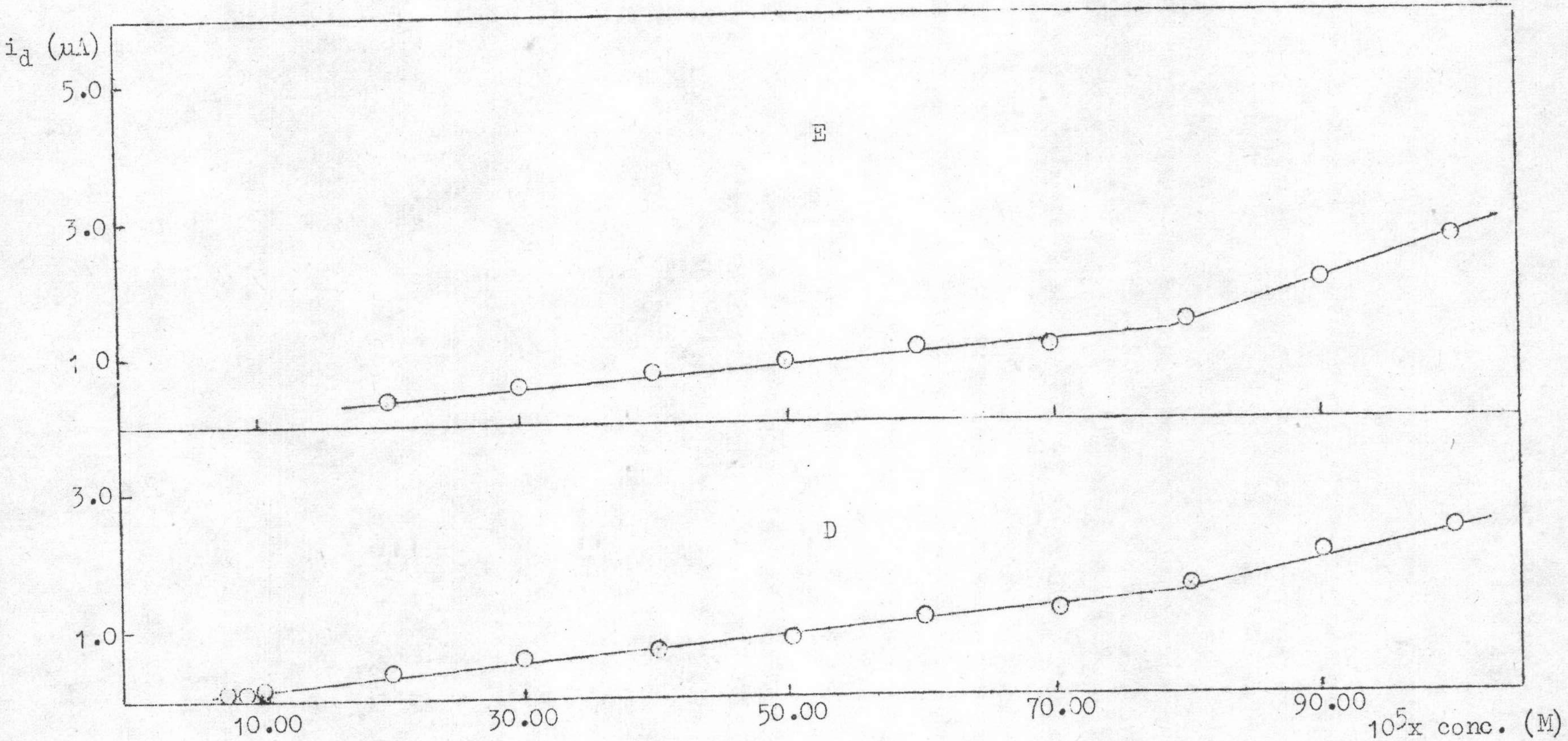


Figure 31D-E The relationships between the concentrations and the diffusion currents in 0.1M $(C_2H_5)_4NCl$ of D) the second wave of Brilliant Blue FCF at pH 1.35 and E) the second wave of Quinoline Yellow at pH 7.50

## 4.3 Mixture of Tartrazine and Brilliant Blue FCF

Another food(additive)color interested is the green color which is a mixture of Tartrazine and Brilliant Blue FCF . These two dyes **are** permitted for food additive by FAO.

### 4.3.1 Composition of the mixture

Concentrations of Tartrazine and Brilliant Blue FCF in the mixture were varied to provide various shades of green color. Ratios of Tartrazine to Brilliant Blue FCF in this study were 1:4 , 3:2 , 1:1 , 2:3 and 4:1 and the initial concentration of Tartrazine was $1 \times 10^{-4}$ M . Paper chromatographic and polarographic data including the shade observed for these mixtures were listed in Table 26 . Paper chromatograms of these mixtures showed two well-defined spots . The $R_f$ values of these spots pointed to the $R_f$ values of Tartrazine and Brilliant Blue FCF ( see Table 26 ) . The polarogram of each mixture in 0.1 M KCl at pH 1.35 provided one distorted and one well-defined waves. The comparison of polarograms between the mixture and the single dyes ( Tartrazine and Brilliant Blue FCF ) indicated that the distorted wave belonged to Tartrazine and the well-defined wave belonged to Brilliant Blue FCF ( see Figure 32 ) . The distortion of Tartrazine wave might be resulted from intermolecular bonding between the dyes in aqueous solution .

### 4.3.2 Effect of pH on the polarographic wave

According to the polarogram of the reduction of each mixture composition provided the same characteristic , the dye mixture of ratio 1:1 ( Tartrazine : Brilliant Blue FCF ) which produced green shade was selected for this study . Polarographic reduction of the mixture

Table 26 The paper chromatograms and polarograms of the mixtures including the shade observed

| Conc. ratio Tart.:B.B. | shade of color | Paper chromatogram[a] $R_f$ | Polarogram[b] $E_{\frac{1}{2}}$,V Tart. wave | 2nd wave of B.B. |
|---|---|---|---|---|
| 1 : 4 | green-yellow | 0.19, 0.51 | distorted wave | -0.651 |
| 2 : 3 | green-yellow | 0.19, 0.51 | distorted wave | -0.653 |
| 1 : 1 | green | 0.19, 0.51 | distorted wave | -0.652 |
| 3 : 2 | yellow-green | 0.19, 0.51 | distorted wave | -0.653 |
| 4 : 1 | yellow-green | 0.19, 0.50 | distorted wave | -0.653 |

Tart. = Tartrazine ; B.B. = Brilliant Blue FCF

[a] Paper chromatogram in solvent system II; $R_f^{(32)}$ Tart. = 0.20

$R_f^{(32)}$ B.B. = 0.50

[b] Polarogram in 0.1 M KCl at pH 11.35

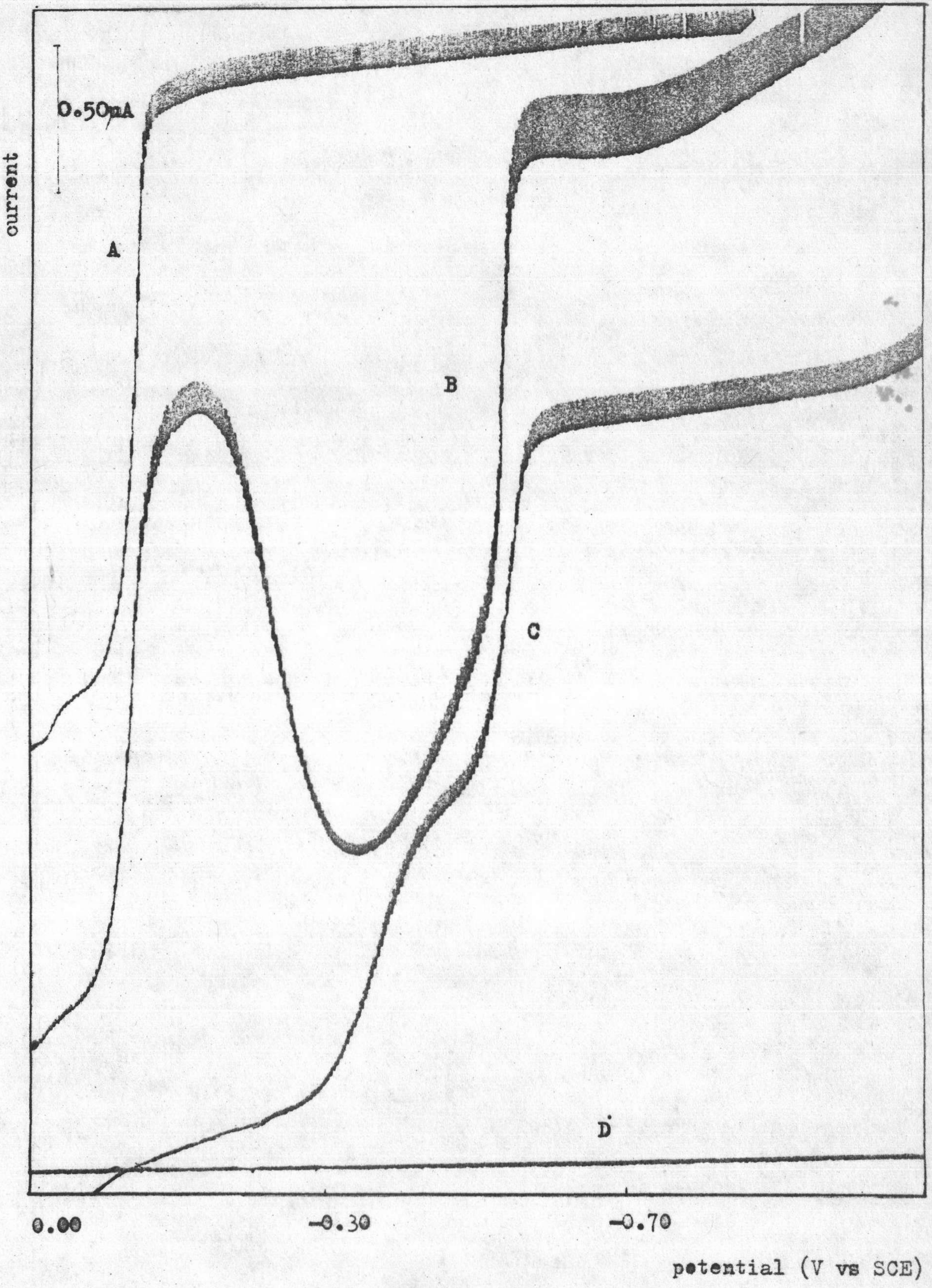


Figure 32 The polarograms of A) Tartrazine , B) Mixture , C) Brilliant Blue FCF in 0.1 M KCl and D) the polarogram of 0.1 M KCl.

in 0.1 M ( $C_2H_5)_4NCl$ , 0.1 M KCl or 0.1 M $KNO_3$ was studied in various pH between 1 - 12 . The effect of pH on the polarographic waves of the mixture was illustrated in Figures 33, 34 and 35 . At pH 1-3 , the distorted wave of Tartrazine in the mixture was observed , the first wave of Brilliant Blue FCF was suppressed by this distorted wave and the second reduction wave of Brilliant Blue FCF was shown . At pH 4-12 , the half wave potentials of these two single dyes , the first and second waves of Brilliant Blue FCF and Tartrazine wave were quite closed ( see Tables 7, 8, 9, 10, 11 and 12 ) . Thus, the polarogram of the dye mixture provided only one well-defined wave . However, at pH higher than 7.0 , the polarogram of the mixture showed two well-defined waves , the overlapped wave of Tartrazine and the first wave of Brilliant Blue FCF and the second wave of Brilliant Blue FCF since their half wave potentials were far apart.

Therefore, the polarographic reduction of the green color which composed of Tartrazine and Brilliant Blue FCF was not suggested to use for quantitative analysis of the dye .

### 4.4 Food colors in some beverages

The common color shades used in beverages are yellow,green, orange and red. Only yellow and green shades of beverages were selected to study and analyze for Tartrazine, Brilliant Blue FCF and Quinoline Yellow .

#### 4.4.1 Identification of dyes

Color additives in Fanta ( yellow and green color ) and Union ( green color ) were identified by paper chromatographic and visible spectrophotometric methods as mentioned in 3.3.1 and 3.3.2.1 ,

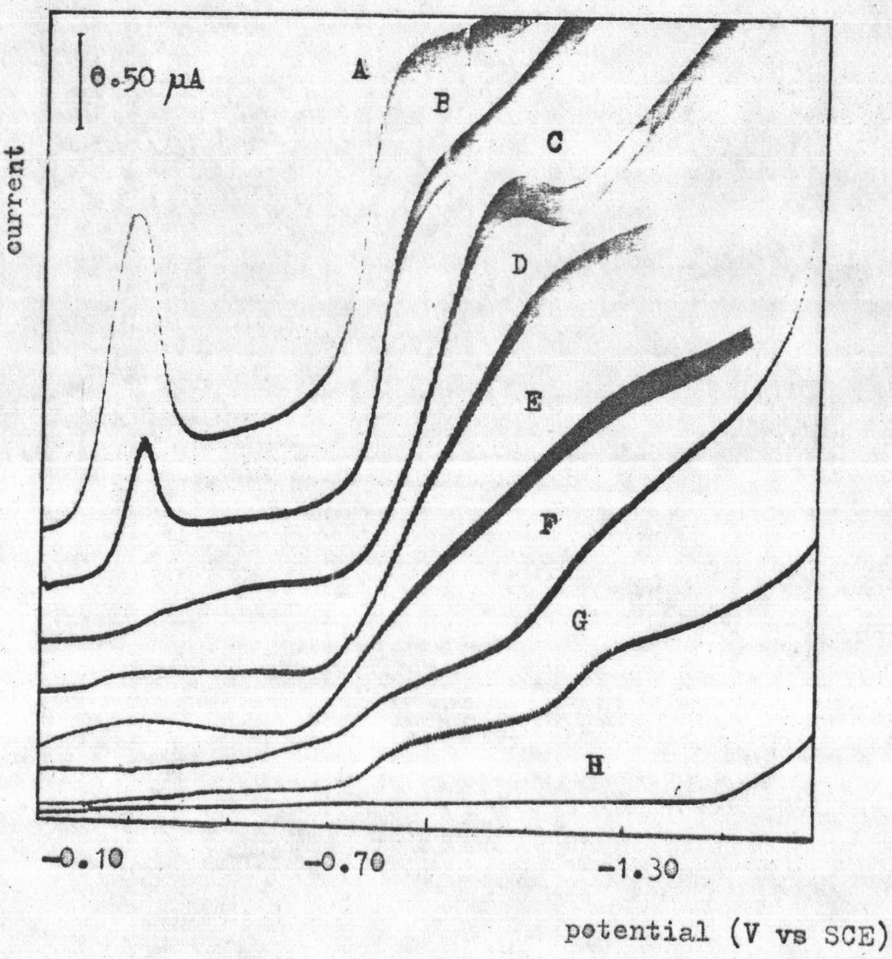


Figure 33 The polarograms of the mixture in 0.1 M $(C_2H_5)_4NCl$ at pH A) 2.20 , B) 3.00 , C) 4.00 , D) 5.70 E) 7.00 F) 9.70 , G) 11.80 and the polarogram of 0.1 M $(C_2H_5)_4NCl$ (H)

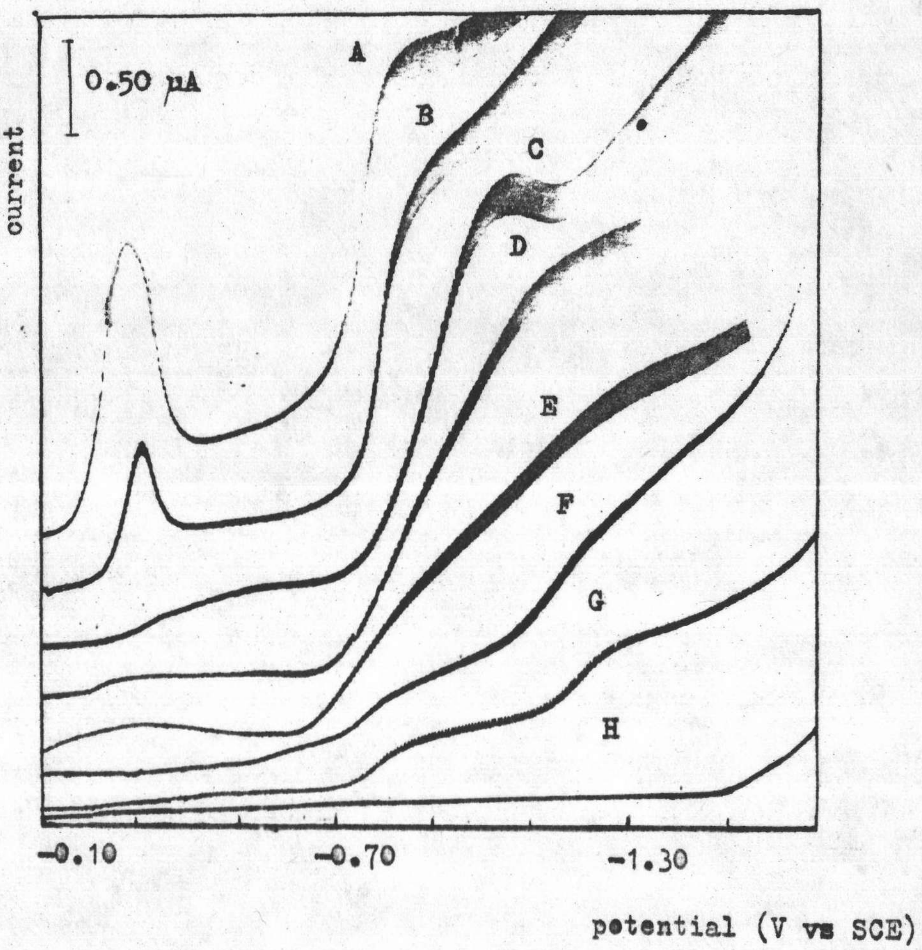


Figure 34 The polarograms of the mixture in 0.1 M KCl at pH A) 2.40 , B) 3.00 , C) 3.80 , D) 5.55 , E) 7.00 , F) 9.78 , G) 12.05 and the polarogram of 0.1 M KCl (H)

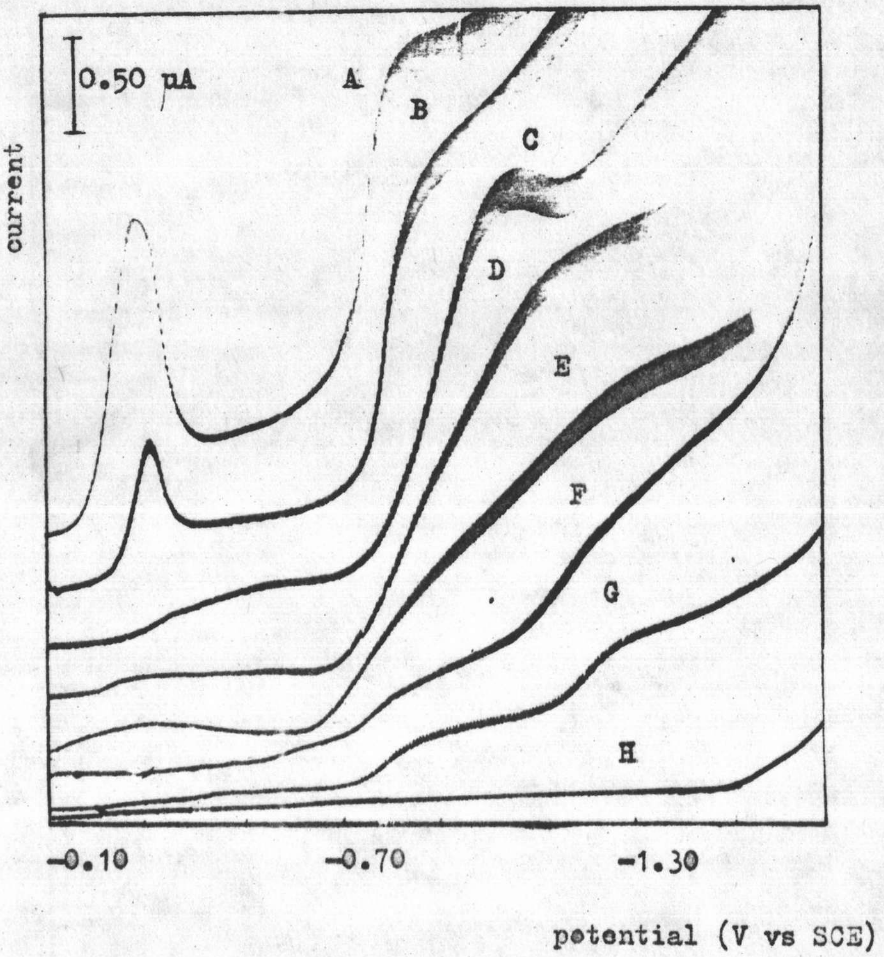


Figure 35 The polarograms of the mixture in 0.1 M $KNO_3$ at pH A) 2.20 , B) 3.00 , C) 4.05 , D) 5.70 E) 7.00 , F) 9.70 , G) 12.00 and the polarogram of 0.1 M $KNO_3$ (H)

respectively. Their $R_f$ values **are** listed in Table 27 . The $R_f$ value of yellow color in Fanta was equal to the $R_f$ value of Tartrazine. One of the $R_f$ values of the green color in Fanta and Union beverages was identified to be that of Tartrazine (see Table 27 ).

The comparison between the maximum absorption wavelengths of the yellow and green colors in Fanta, green color in Union and Tartrazine was resulted in the same value ( see Table 28 ) .

### 4.4.2 Determination of dyes in beverages

Since the identification in 4.4.1 indicated that the green color in Fanta and Union was composed of Tartrazine and other dye, the quantitative analysis by polarography for the green color was not **performed.**

Therefore, only yellow color in Fanta was graphically determined by standard addition method . A series of the standard dye solutions of concentration 0-12.84 mg/dm$^3$ were added to the beverages and the polarographic analysis of the dye in the beverages was performed in 0.1 M $(C_2H_5)_4NCl$ at pH 5.60 . The yellow color in Fanta was analyzed for Tartrazine . Three samples of each beverage , one week difference in buying , were analyzed and three trials were performed for each sample . Graphical determination of Tartrazine in Fanta is illustrated in Figure 36 . The contents of Tartrazine in Fanta bottle A was 4.70 ± 0.15 mg/dm$^3$ , bottle B was 4.81 ± 0.13 mg/dm$^3$ and bottle C was 3.99 ± 0.22 mg/dm$^3$ .

Table 27 $R_f$ values of the yellow and green colors in some beverages

| Beverage | Solvent system I | Solvent system II |
|---|---|---|
| Fanta (yellow) | 0.29 (0.28, Tartrazine) | 0.18 (0.19, Tartrazine) |
| Fanta (green) | 0.29 (0.28, Tartrazine) | 0.18 (0.19, Tartrazine) |
| | 0.78 | 0.70 |
| Union (green) | 0.29 (0.28, Tartrazine) | 0.19 (0.19, Tartrazine) |
| | 0.76 | 0.67 |

[32] Solvent system I Quinoline Yellow $R_f = 0.50$

[32] Solvent system II Brilliant Blue FCF $R_f = 0.50$

Table 28 The maximum absorption wavelengths of the dyes in some beverages in acid solution

| Beverage | $\lambda$ max. (nm) |
|---|---|
| Fanta (yellow) | 432 (432 for Tartrazine) |
| Fanta (green) | 430 (432 for Tartrazine) |
| Union (green) | 430 (432 for Tartrazine) |

Data in the brackets are from reference 33 .

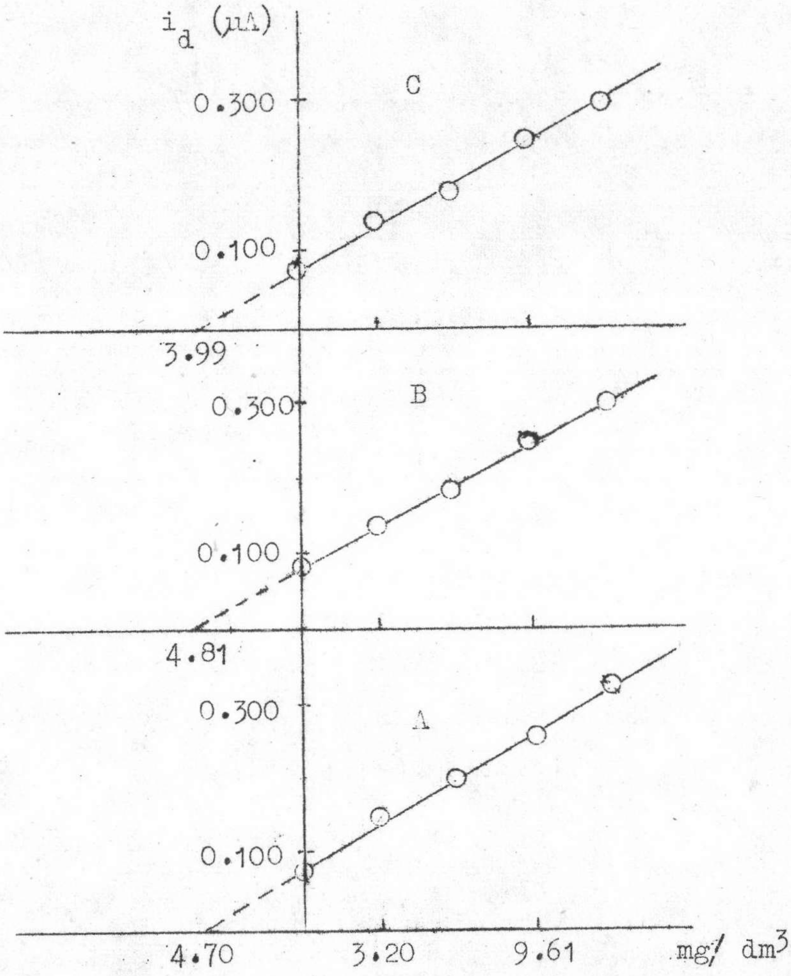


Figure 36 Graphical determinations of Tartrazine in Fanta (pineapple flavor): A) bottle A, B) bottle B and C) bottle C