

## Polarographic Studies of Basic Triarylmethane Dyes

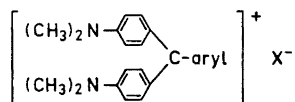
### IV. Polarographic Behaviour of 2-Thiophene Green, *p*-Methoxy Malachite Green, and Crystal Violet in Aqueous Solutions

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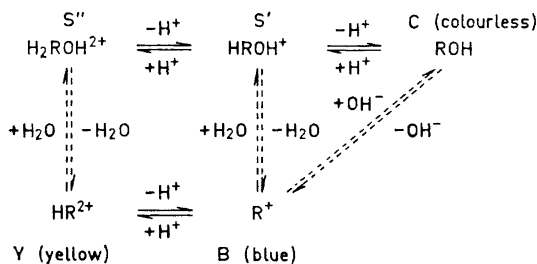
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The polarographic studies of basic triarylmethane dyes<sup>1-3</sup> have been continued by a study of the polarographic behaviour of 2-Thiophene Green (2-TG), *p*-Methoxy Malachite Green (*p*-MeOMG), and Crystal Violet (CV). All three dyestuffs contain each one strongly electron-donating aryl group besides the two dimethylaniline groups common to all the dyestuffs belonging to this group. The similarity between the polarographic behaviour of these dyes is not very pronounced. They are all reducible at the dropping mercury electrode. The full reduction consumes two electrons. There is a tendency towards a splitting of the over-all reduction process into two one-electron steps with increasing depolarizer concentrations and pH-values. This tendency is most pronounced with 2-TG the polarograms of which show two main waves within the whole concentration range and pH-range studied. With *p*-MeOMG and CV the reduction gives rise to one polarographic wave at low depolarizer concentrations and low pH-values. This sole wave is, however, split with increasing depolarizer concentration at sufficiently great pH-values.

In the previous parts of this investigation<sup>1-4</sup> the protolytic equilibria, hydration equilibria, reaction rates, and polarographic behaviour of three basic triarylmethane dyes, namely Methyl Green (MeG), Malachite Green (MG), and 3-Thiophene Green (3-TG) have been studied in aqueous solutions at the temperature 20.0°C and the ionic strength 0.5 M by classical polarography. These dyestuffs can be represented by the generalized structural formula

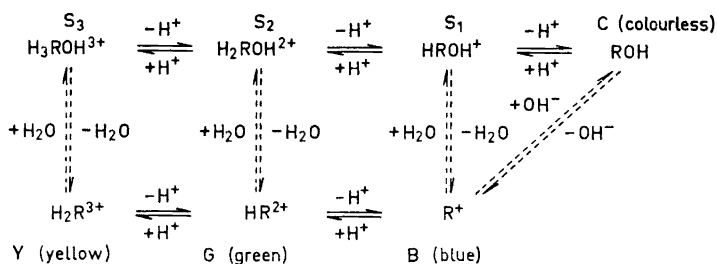


in which the aryl group is different for the different dyestuffs, either being a phenyl group with different substituents or a heterocycle. In order to study further the influence of the aryl group on the polarographic behaviour two derivatives of Malachite Green (*p*-Methoxy Malachite Green and Crystal Violet), the remaining Thiophene analogue of Malachite Green (2-Thiophene Green), and three Pyridine analogues of Malachite Green have been studied by classical polarography. The present paper is devoted to a study of 2-Thiophene Green (2-TG), *p*-Methoxy Malachite Green (*p*-MeOMG), and Crystal Violet (CV).



Scheme I

The equilibria and reaction rates of these dyestuffs have been studied previously by a spectrophotometric method.<sup>5-8</sup> 2-TG and *p*-MeOMG<sup>6</sup> react according to a reaction-equilibrium scheme analogous to the one proposed by Cigén<sup>6</sup> for MG and some of its derivatives (scheme I), but the results of the spectrophotometric measurements in strongly acid solutions indicate that these dyestuffs probably react according to an extended scheme. CV contains three *p*-dimethylaniline groups and reacts according to a more complicated scheme<sup>7</sup> (scheme II).



Scheme II

The aryl group of each of the present three dyestuffs is strongly electron-donating, a fact that has a great influence on the chemical properties of these dyestuffs. The chemical properties of these dyes make polarography less suited for the determination of the equilibrium and rate constants of their reactions. Especially the extended reaction schemes would make the calcula-

tion of some of the constants difficult, since polarography cannot distinguish between the different coloured species as can spectrophotometry. It has, however, been shown for the dyestuffs previously studied polarographically that the results of the polarographic measurements agree with the results of the spectrophotometric measurements. It therefore seems possible to use the information obtained by spectrophotometric studies as an aid in the interpretation of the polarographic behaviour. In order to ascertain that there were no major differences in the equilibria and reaction rates, as studied polarographically and spectrophotometrically, a few kinetic measurements were carried out. The over-all rate constants were then compared with those obtained spectrophotometrically at the pH-value in question. Such a comparison is shown in Table 1. Some discrepancies are found, but they are too small to be considered as significant.

Table 1. Comparison between polarographically and spectrophotometrically determined values of the over-all rate constant  $k$ .

| Polarographically<br>$C = 20 \times 10^{-5}$ M |                       | Spectrophotometrically<br>$C = 1 \times 10^{-5}$ M |                       |
|--|-----------------------|--|-----------------------|
| pH   | $k$ min <sup>-1</sup> | pH   | $k$ min <sup>-1</sup> |
| 2-Thiophene Green                              |                       |  |                       |
| 1.00   | 0.066                 | 1.00   | 0.071                 |
| 2.13   | 0.023                 | 2.13   | 0.027                 |
| 3.24   | 0.070                 | 3.24   | 0.049                 |
| 3.72   | 0.112                 | 3.72   | 0.103                 |
| 4.03   | 0.177                 | 4.03   | 0.164                 |
| 4.41   | 0.253                 | 4.41   | 0.230                 |
| 4.76   | 0.294                 | 4.76   | 0.273                 |
| 5.21   | 0.221                 | 5.21   | 0.221                 |
| 5.43   | 0.174                 | 5.43   | 0.175                 |
| <i>p</i> -Methoxy Malachite Green              |                       |  |                       |
| 1.00   | 0.153                 | 1.01   | 0.147                 |
| 1.60   | 0.077                 | 1.53   | 0.092                 |
| 3.75   | 0.219                 | 3.75   | 0.251                 |
| Crystal Violet                                 |                       |  |                       |
| 1.00   | 0.058                 | 1.00   | 0.059                 |

## EXPERIMENTAL

*Dyestuff preparations.* 2-Thiophene Green Perchlorate. The preparation used in the spectrophotometric study<sup>8</sup> was used also in the present study. (Found: C 57.9; H 5.42; N 6.29; Cl 8.18; S 7.5. Calc. for C<sub>21</sub>H<sub>23</sub>O<sub>4</sub>N<sub>2</sub>ClS: C 58.0; H 5.33; N 6.44; Cl 8.15; S 7.37).  $\lambda_{B \max} = 628$  m $\mu$  and 467 m $\mu$ ;  $\epsilon_B = 7.5 \times 10^4$  and  $2.55 \times 10^4$ , respectively.

*p-Methoxy Malachite Green Perchlorate.* A preparation with the following characteristics was used: (Found: C 62.8; H 6.24; N 5.67; O 18.28; Cl 7.21. Calc. for C<sub>24</sub>H<sub>27</sub>O<sub>3</sub>N<sub>2</sub>Cl: C 62.8; H 5.93; N 6.11; O 17.43; Cl 7.73).  $\lambda_{B \max} = 607$  m $\mu$  and 455 m $\mu$ ;  $\epsilon_B = 8.6 \times 10^4$  and  $2.8 \times 10^4$ , respectively.

**Crystal Violet Perchlorate.** Commercial Crystal Violet (Merck's "hydrochlorid") was converted into the perchlorate and recrystallized three times from 25 % acetic acid. Optical constancy was attained.  $\lambda_{B \max} = 590 \text{ m}\mu$ ;  $\epsilon_B = 9.8 \times 10^4$  (cf. Ref. 7).

**Phenolphthalein.** Merck's commercial preparation. ("Indikator"; m.p. 258–261°C) was used without further purification.

Dyestuff solutions were prepared in essentially the manner described previously.<sup>3</sup> The composition of the buffer solutions, the apparatus, and the experimental procedure were the same as those described in Ref. 3. The capillary had the following characteristics: Mercury flow,  $m = 2.18 \text{ mg} \times \text{sec}^{-1}$ ; drop-time  $t_1 = 3.86 \text{ sec}$ , determined in 0.50 M KCl with short-circuited cell.

The study of CV was complicated by the low solubility of this dyestuff in the buffers used. The solubility of CV was only about  $6 \times 10^{-5} \text{ M}$  within the pH-range 3–9. At lower pH-values it was greater due to the fact that protonated, more soluble species (G, Y, and  $S_3$  of scheme II), dominated at equilibrium. At greater pH-values the carbinol was precipitated. Because of this complication the study of CV could only be fragmentary, and the results obtained for  $C > 5 \times 10^{-5} \text{ M}$  might be of questionable value. By preparing a stock solution of CV in 0.010 M HCl + 0.47 M KCl + 4 % acetone it was, however, possible to carry out reproducible measurements for solutions with the over-all dyestuff concentration  $C = 20 \times 10^{-5} \text{ M}$  at pH = 4.68. When the dye stock solution was mixed with the buffer solution, equilibrium was reached within 2–3 min (cf. Ref 7), and the polarographic curves could be recorded before any precipitation of the dyestuff occurred. The solution was supersaturated with regard to the dyestuff, but it remained stable for a few hours. At pH > 6 the same procedure could not be used since the carbinol C, formed by the rapid reactions  $S_3 \rightleftharpoons S_2 \rightleftharpoons S_1 \rightleftharpoons C$ , was precipitated, when the stock solution was mixed with the buffer solution.

The polarographic behaviour of 2-TG was studied within the concentration range  $1 - 20 \times 10^{-5} \text{ M}$  and the approximate pH-range 1–7. At one pH-value (4.68) the concentration range was extended to  $C = 50 \times 10^{-5} \text{ M}$  but the solutions were probably supersaturated at the highest concentrations. *p*-MeOMG was studied within the same pH and concentration range. The study of CV was carried out within the pH-range 1–12 and the concentration range  $1 - 5 \times 10^{-5} \text{ M}$ . At single pH-values the concentration range was extended to  $20 \times 10^{-5} \text{ M}$  (cf. above).

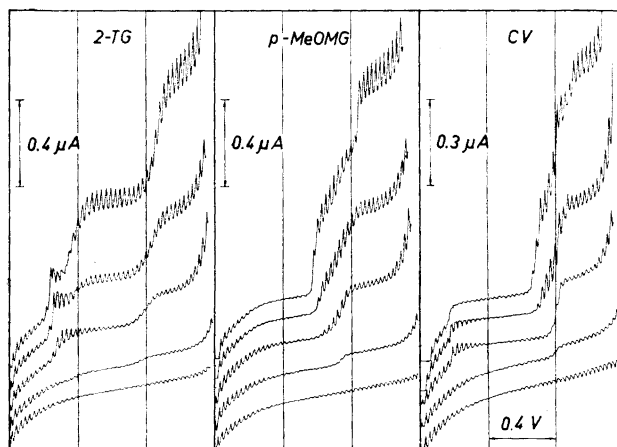


Fig. 1. Polarograms recorded at equilibrium for  $C = 0, 1, 5, \text{ and } 20 \times 10^{-5} \text{ M}$ . pH = 4.68; 0.05 % gelatine. The polarograms start at 0 V vs. SCE.

## RESULTS

*Dependence on the depolarizer concentration.* Fig. 1 shows a few polarograms recorded at different over-all dyestuff concentrations at equilibrium at a constant pH-value (4.68). At this pH-value the concentration of the carbonium species is practically equal to the over-all dyestuff concentration  $C$ .

The reduction of 2-TG proceeds in two steps already at  $C=1 \times 10^{-5}$  M. The first of the waves is, however, rather ill-defined at the lowest concentrations and neither the wave heights nor the half-wave potentials could be evaluated with any reliability. For  $C > 5 \times 10^{-5}$  this first wave splits into two adjacent waves. The height of the first one of these becomes independent of the depolarizer concentration. The two waves found for  $C < 5 \times 10^{-5}$  M are called waves number 1 and 3, respectively. The intermediate wave found at greater concentrations is called wave number 2. The wave heights,  $i_1$ ,  $i_2$ ,  $(i_1+i_2)$ , and  $i_3$  are shown as functions of  $C$  in Fig. 2.

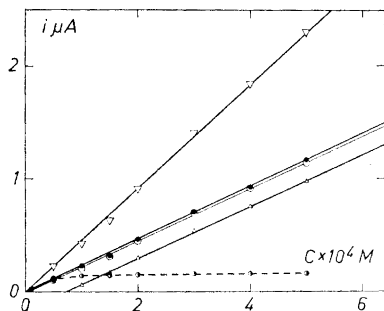


Fig. 2. 2-TG. The wave heights  $i_1$  ●,  $i_2$  △,  $(i_1+i_2)$  ○;  $i_3$  ●, and  $\sum i$  ▽, recorded at equilibrium (pH=4.68), versus the over-all dyestuff concentration  $C$ .

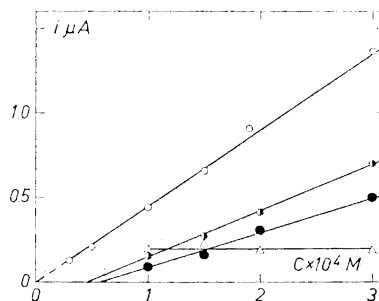


Fig. 3. *p*-MeOMG. The wave heights  $i_1$  ●,  $i_2$  △,  $i_3$  ●, and  $\sum i$  ○, recorded at equilibrium (pH=4.68), versus  $C$ .

The reduction of *p*-MeOMG produces for  $C \leq 5 \times 10^{-5}$  M only one polarographic wave which at greater concentrations splits into two and finally three waves at this pH-value. The waves are numbered in the order of increasing negative potentials as waves number 1, 2, and 3. This does not, however, imply any analogy with the waves of equal numbers with 2-TG. The wave heights  $i_1$ ,  $i_2$ , and  $i_3$  are shown as functions of  $C$  in Fig. 3.

For concentrations below about  $5 \times 10^{-5}$  M only one wave can be seen on the polarographic curves of CV. When the concentration increases a new wave appears at a much less negative potential and on further increase the most negative wave splits into at least three new waves at this pH-value. These waves are rather ill-defined and the separate wave heights could not be evaluated very accurately. They are numbered in the order of increasing negative potential from 1 to 4. The corresponding wave heights are shown in Fig. 4 plotted versus  $C$ .

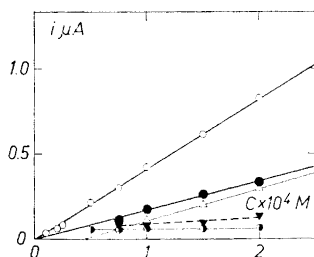


Fig. 4. CV. The wave heights  $i_1$  ●,  $i_2$  △,  $i_3$  ●,  $i_4$  ▼, and  $\sum i$  ○, recorded at equilibrium (pH=4.68), versus  $C$ .

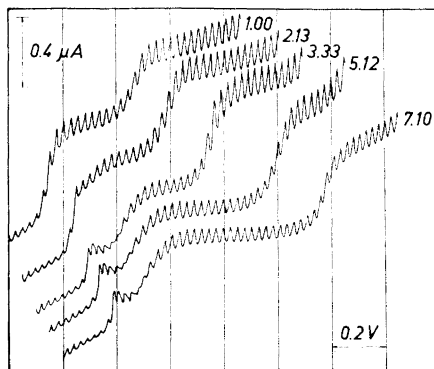


Fig. 5. 2-TG. Polarograms at different pH-values recorded at comparable depolarizer concentrations.  $C=20 \times 10^{-5}$  M; 0.05 % gelatine. All the polarograms start at  $-0.05$  V vs. SCE.

*Dependence on pH.* Some of the polarograms recorded for solutions of 2-TG with comparable depolarizer concentrations but different pH-values are shown in Fig. 5. These polarograms were recorded as soon as possible after the mixing of equal volumes of a dye stock solution ( $C=40 \times 10^{-5}$  M), containing practically all of the dyestuff as coloured species (B and G), and suitable buffer solutions. Both solutions were carefully deaerated before the mixing. An inspection of the figure immediately shows that there are three waves on the polarograms at this depolarizer concentration, when  $\text{pH} > 2$ , and that the position of waves 1 and 2 on the potential axis is almost independent of pH, whereas wave 3 is displaced towards more negative potentials with increasing values of pH within the whole pH-range studied. Wave 2 could not be recognized for  $\text{pH} < 2$ .

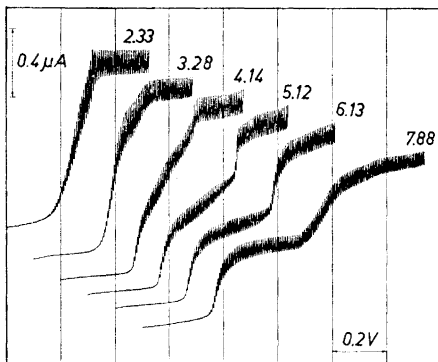


Fig. 6. *p*-MeOMG Polarograms at different pH-values recorded at comparable depolarizer concentrations.  $C=20 \times 10^{-5}$  M; 0.05 % gelatine. All the polarograms start at  $-0.20$  V vs. SCE.

The polarograms of *p*-MeOMG shown in Fig. 6 were recorded in essentially the manner described for the polarograms of 2-TG in Fig. 5 only that a  $1 \times 10^{-2}$  M dye stock solution in acetone had to be used. With *p*-MeOMG there is a more striking change of the general shape of the polarograms with increasing pH-values. In the most acid solutions two adjacent waves can be seen, in an intermediate pH-range there are three waves, and at the greatest pH-values two well-defined and well separated waves of comparable heights can be found. Two main waves of comparable heights might be recognized for  $\text{pH} > 4$ . The position of the first of these on the potential axis is independent of pH within the whole pH-range where it can be observed as a separate wave. The second main wave is displaced towards more negative potentials with increasing pH.

The low solubility of CV made the recording of polarograms in the manner described above for 2-TG and *p*-MeOMG possible only for  $C \leq 5 \times 10^{-5}$  M. The polarograms change but little from  $\text{pH} \approx 1$  to  $\text{pH} \approx 10$ . The half-wave potential of the less negative wave is independent of pH whereas the half-wave potential of the most negative wave is displaced towards more negative values with increasing pH. This second wave is split into three waves for  $\text{pH} > 6$  already at the depolarizer concentration  $5 \times 10^{-5}$  M.

With *p*-MeOMG and CV the splitting of the sole wave found at the lowest depolarizer concentrations occurs at lower concentrations with increasing pH-values.

The sums of the wave heights at equilibrium ( $\sum i$ ) at a few pH-values for 2-TG and *p*-MeOMG are shown in Table 2.

Table 2. The over-all wave heights at equilibrium.  $C = 20 \times 10^{-5}$  M; 0.05 % gelatine.

| 2-TG |  |                      | <i>p</i> -MeOMG |  |                      |
|------|--|----------------------|-----------------|--|----------------------|
| pH   |  | $\sum i \mu\text{A}$ | pH              |  | $\sum i \mu\text{A}$ |
| 1.00 |  | 0.21                 | 1.00            |  | 0.22                 |
| 2.13 |  | 0.53                 | 2.33            |  | 0.74                 |
| 3.33 |  | 0.89                 | 3.28            |  | 0.92                 |
| 4.14 |  | 0.95                 | 4.14            |  | 0.92                 |
| 4.68 |  | 0.91                 | 4.68            |  | 0.91                 |
| 5.12 |  | 0.91                 | 5.12            |  | 0.86                 |
| 6.13 |  | 0.91                 | 6.13            |  | 0.79                 |
| 7.10 |  | 0.39                 |                 |  |                      |

*Estimation of the number of electrons transferred in the over-all electrode reaction.* Two electrons were consumed for the full reduction of all three dyestuffs as estimated by a comparison of the over-all wave heights with the wave height of Phenolphthalein determined under exactly identical conditions. Depolarizer concentration =  $20 \times 10^{-5}$  M; 2 % by volume of acetone; 0.05 % gelatine; ionic strength 0.49 M; acetate buffer with  $\text{pH} = 4.68$ . The results are shown in Table 3.

Table 3. Comparison of the over-all wave heights. Depolarizer concentration =  $20 \times 10^{-5}$  M; 2 % acetone; 0.05 % gelatine; ionic strength = 0.49 M; pH = 4.68.

| Dyestuff                          | $\Sigma i \mu A$ |
|-----------------------------------|------------------|
| Phenolphthalein                   | 0.93             |
| Methyl Green                      | 0.98             |
| Malachite Green                   | 0.88             |
| <i>p</i> -Methoxy Malachite Green | 0.91             |
| Crystal Violet                    | 0.82             |
| 2-Thiophene Green                 | 0.91             |
| 3-Thiophene Green                 | 0.92             |

*Dependence on the mercury pressure.* In order to establish the nature of the different limiting currents the dependence of the wave heights, or sums of wave heights, on the height of the mercury head was studied. Log  $i$  was plotted *versus* log  $P_{\text{corr}}$  ( $P_{\text{corr}}$  = mercury pressure corrected for the back pressure) and the slopes of the approximately straight lines were evaluated. The results are summarized in Table 4, where the exponent  $b$  in the relation  $i \propto P_{\text{corr}}^b$  is shown.

Table 4. The exponent  $b$  in the relation  $i \propto P_{\text{corr}}^b$ .

| Dyestuff        | $C \times 10^5$ M | pH   | $i$         | $b$  |
|-----------------|-------------------|------|-------------|------|
| 2-TG            | 20                | 4.68 | $i_1$       | 1.04 |
|                 |                   |      | $i_1 + i_2$ | 0.52 |
|                 |                   |      | $i_3$       | 0.52 |
|                 |                   |      | $\Sigma i$  | 0.52 |
| <i>p</i> -MeOMG | 20                | 4.68 | $i_1$       | 0.32 |
|                 |                   |      | $i_1 + i_2$ | 0.43 |
|                 |                   |      | $\Sigma i$  | 0.47 |
|                 | 20                | 6.13 | $i_1$       | 0.35 |
|                 |                   |      | $i_2 + i_3$ | 0.56 |
| $\Sigma i$      | 0.45              |      |             |      |
| CV              | 20                | 4.68 | $i_1$       | 1.0  |
|                 |                   |      | $i_1 + i_2$ | 0.4  |
|                 |                   |      | $i_3 + i_4$ | 0.6  |
|                 |                   |      | $\Sigma i$  | 0.50 |

*Electrocapillary curves.* Fig. 7 shows four electrocapillary curves for each of the three dyestuffs, determined at  $C = 0, 1, 5, 20 \times 10^{-5}$  M, and pH = 4.68 in the presence of 0.05 % gelatine. For all three dyestuffs the curves for the lowest concentration coincide, within the experimental error, with that of the pure buffer solution. The dyestuff concentrations have to exceed about  $2 \times 10^{-5}$  M for any noticeable effect to appear. Above this value, however, the



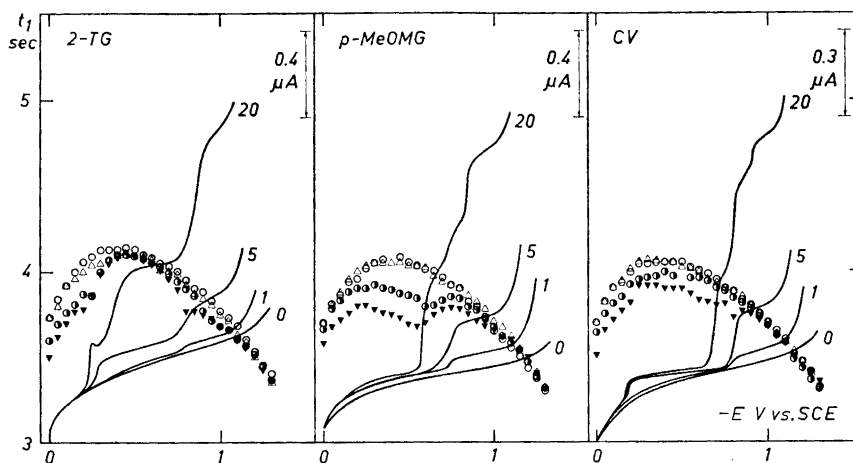


Fig. 7. Electrocapillary curves.  $\circ$   $C=0$ ;  $\triangle$   $C=1 \times 10^{-5}$  M;  $\bullet$   $C=5 \times 10^{-5}$  M;  $\blacktriangledown$   $C=20 \times 10^{-5}$  M. The figures beside the polarograms denote  $C \times 10^5$  M. pH=4.68; 0.05 % gelatine.

drop-times are lowered as compared to the pure buffer solution within wide-potential ranges for all three dyestuffs. With 2-TG the depressions coincide with the rise of waves 1 and 3 but are else small. Within the potential range where depressions of the electrocapillary curves occur, the drop-times at a constant potential decrease at first rather rapidly with increasing dyestuff concentrations above  $2 \times 10^{-5}$  M but then they tend towards a limiting value which is not, however, reached within the studied concentration range.

*Half-wave potentials.* Fig. 8 shows the dependence of the half-wave potentials of 2-TG on the over-all dyestuff concentration at a constant pH-value. The complicated behaviour of *p*-MeOMG and CV makes a corresponding figure for these dyestuffs of little value. The half-wave potentials of the sole wave found at lower concentration of these dyes is, however, practically independent of the dyestuff concentration. With 2-TG two waves are found already at the lowest over-all dyestuff concentrations. The half-wave potentials of these two waves, and of the third wave found at greater concentrations, all change with  $C$ . The change is most pronounced within the concentration range  $1-10 \times 10^{-5}$  M.

The half-wave potentials shown in Fig. 9 plotted against pH were determined at the depolarizer concentration  $1 \times 10^{-5}$  M with and without added gelatine. They were determined as soon as possible after the mixing of equal volumes of buffer solution and a dye stock solution containing practically all of the dyestuff as coloured species. The first wave of 2-TG could hardly be distinguished from the residual current at this low concentration. The precision of the determined half-wave potentials was thus very low and only the values of the second wave are shown in Fig. 9.

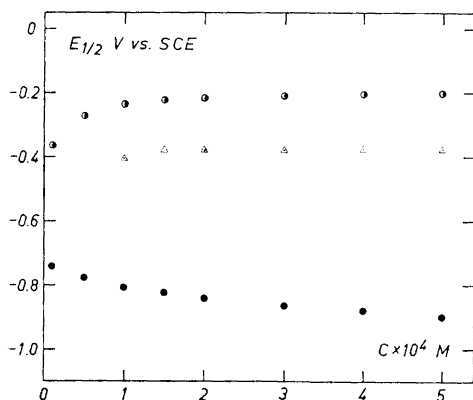


Fig. 8. 2-TG. The half-wave potentials  $(E_{1/2})_1$  (●),  $(E_{1/2})_2$  (△),  $(E_{1/2})_3$  (●) versus the over-all dyestuff concentration  $C$ . pH = 4.68; 0.05 % gelatine.

### DISCUSSION

The complete discussion of the polarographic behaviour of the basic triarylmethane studied will be postponed until all the experimental material now available has been reported. A few aspects can, however, be considered already at this stage of the investigations.

All three dyestuffs studied in this paper contain one strongly electron-donating aryl group besides the two dimethylaniline groups common to all the dyestuffs belonging to this group. The electron-donating character of the aryl group has been found to have a great influence on the hydration equilibria, and also on the rates of the hydration and dehydration reactions, stabilizing the coloured carbonium ions, and with 2-TG and *p*-MeOMG probably also facilitating the addition of a second proton to the carbonium species G (*cf.* Ref. 8). The trend in the polarographic behaviour observed when going from MeG, with a strongly electron-attracting aryl group, to MG and 3-TG, with weakly electron-donating aryl groups, indicates that there exists a similar relation between the polarographic behaviour and the nature of the aryl group. It might therefore be expected that 2-TG, *p*-MeOMG, and CV should exhibit similar polarographic behaviours. The similarity between these three dyestuffs is not, however, more pronounced than the similarity between any three of the dyestuffs studied hitherto. They are all reducible at the dropping mercury electrode, the carbonium species being the electroactive species. The full reduction consumes two electrons, and there is a tendency towards a splitting of the polarographic curve into two main waves of comparable heights which indicates that the reduction proceeds in two one-electron steps with the intermediate formation of a semiquinone.<sup>9,10</sup> This splitting of the over-all polarographic curve into two main waves is observed already at  $C = 1 \times 10^{-5}$  M with 2-TG but only at greater depolarizer concentrations with *p*-MeOMG and CV. The polarographic curve as a whole is spread over a wider potential range with increasing depolarizer concentration at a constant pH-value, and also with increasing values of pH. With all three dyestuffs the adsorption of the dyestuff and its reduction products manifests itself by the

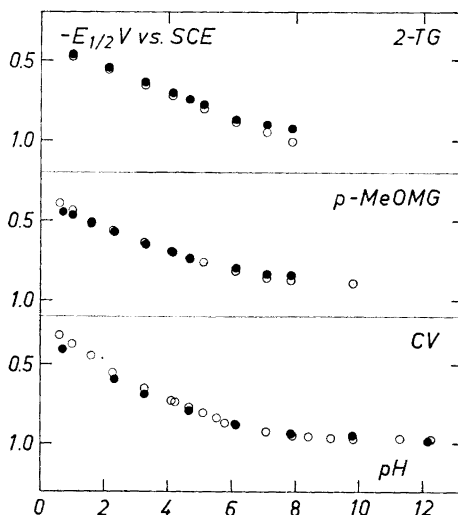


Fig. 9. The half-wave potential *versus* pH.  $C = 1 \times 10^{-5}$  M. ○ without added gelatine; ● 0.05 % gelatine.

appearance of adsorption waves, and depressions of the electrocapillary curves.

The dependence of the different wave heights on the depolarizer concentration and on the mercury pressure is a little more complicated than might be expected from this simple picture of a reduction proceeding in two one-electron steps. A reduction proceeding with the intermediate formation of a semiquinone would give two main waves of approximately equal heights with diffusion current characteristics. This condition is fulfilled with 2-TG at  $C > 20 \times 10^{-5}$  M but not completely at lower  $C$ -values. A similar behaviour was observed with *p*-MeOMG and CV. The limiting current of the first main wave seems to be influenced also by the rate of a preceding chemical reaction. An analogous behaviour was observed with MG and 3-TG at  $C \leq 20 \times 10^{-5}$  M. With MG the first main wave became, however, entirely diffusion controlled for  $C \geq 50 \times 10^{-5}$  M (*cf.* Ref. 3). With *p*-MeOMG, and CV the concentration range could not be extended to much greater values than  $20 \times 10^{-5}$  M so it could not be established whether they behave in a similar way. The nature of the chemical reaction influencing the limiting current of the first main wave is still unknown. The observed complication does not, however, constitute a serious objection to the proposed electrode reaction.

Waves number 1 of 2-TG and CV both have the characteristics of adsorption waves. The wave heights attain constant values at sufficiently great depolarizer concentrations, and they are also proportional to the height of the mercury head (*cf.* Table 3). The limiting currents of wave 3 with CV and wave 2 with *p*-MeOMG (observed only within the approximate pH-range 4–5) might be due to an inhibition of the electrode reaction.

The half-wave potential of the sole wave of *p*-MeOMG and CV found at low depolarizer concentrations is almost independent of  $C$  at a constant

pH-value. The half-wave potentials of the waves found at greater depolarizer concentration change, however, with  $C$ . The first main wave is displaced towards less negative potentials and the second main wave towards more negative potentials with increasing  $C$ . The half-wave potentials of the two waves found with 2-TG already at low  $C$ -values change considerably with  $C$  in the same directions as the main waves of  $p$ -MeOMG and CV. The half-wave potential of wave 2 of 2-TG, appearing for  $C \geq 5 \times 10^{-5}$  M changes in the same direction with  $C$  as the half-wave potential of wave 1. This change is, however, rather small. The transition from a reduction process yielding one two-electron wave to one yielding essentially two one-electron waves with increasing depolarizer concentrations might indicate a dimerization of the semiquinone. Such a dimerization reaction is indicated also by the change of the "half-wave potentials" of the main waves with  $C$ .

Since there is a splitting of the polarographic waves with increasing depolarizer concentration and the effect of the adsorption also increases with increasing concentrations within some concentration ranges, it is desirable to carry out the determination of the halfwave potentials as a function of pH at such a low depolarizer concentration that only one wave is found on the polarograms and the adsorption effects are of minor importance. The determinations were therefore carried out at the depolarizer concentration  $1 \times 10^{-5}$  M (as nearly as possible). At this depolarizer concentration it is still possible to estimate the half-wave potentials with a reasonable precision, and the adsorption effects are rather small as seen from the electrocapillary curves. With 2-TG there are, however, still two waves on the polarographic curves within the whole investigated pH-range, and the results of this dyestuff cannot therefore be compared with the results of the other dyestuffs. With  $p$ -MeOMG and CV the half-wave potentials (Fig. 9), at this depolarizer concentration become more negative with increasing values of pH, and at sufficiently great pH-values they become independent of pH. With 2-TG only the half-wave potentials of the second wave could be determined with a reasonable precision. The change is most clearly shown for CV where the extension of the wave over a wider potential range observed with the other dyestuffs at greater pH-values was smaller. The effect of gelatine on the half-wave potentials is demonstrated also for these dyestuffs and seems to be analogous with the effects observed previously (*cf.* Refs. 3 and 4).

CV has been the subject of previous studies at the dropping mercury electrode.<sup>11,12</sup> The study of Kaye and Stonehill was carried out in 50% ethanol-water solutions and is not comparable to the present one. The study of Kemula and Axt-Zak was, however, carried out under comparable conditions. The results of my study agree in the essential parts with those of the latter authors. The chief difference seems to be the adsorption wave number 1, which was not observed by these authors.

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