

Polarographic Studies of Basic Triarylmethane Dyes

II. Kinetics, Equilibria, and Polarographic Behaviour of Malachite Green in Aqueous Solutions

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The polarographic studies of basic triarylmethane dyes^{1,2} have been continued by a study of the chemical reactions and the polarographic behaviour of Malachite Green in aqueous solutions at 20.0°C. The equilibrium and rate constants of the reactions in the reaction-equilibrium scheme proposed by Cigén⁴ for this type of dyestuffs have been determined by classical polarography. The results of the polarographic measurements agree fairly well with the results obtained by Cigén from spectrophotometric measurements.

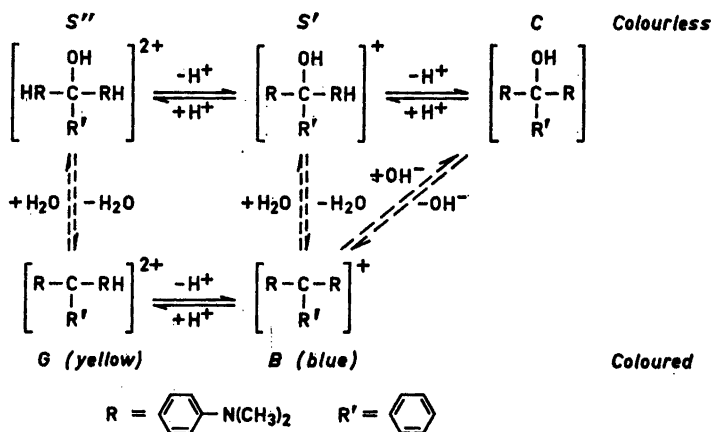
The polarographic behaviour of Malachite Green is complicated. The shapes of the polarographic curves change considerably with the over-all dyestuff concentration and with the pH-values of the solutions. At sufficiently great depolarizer concentrations two "main waves" of approximately equal height are obtained. These are, however, complicated by the appearance of adsorption waves, and at lower depolarizer concentrations the limiting current of the first of these "main waves" does not seem to be entirely diffusion-controlled.

In two previous papers^{1,2} the kinetics, equilibria, and polarographic behaviour of Methyl Green have been studied in aqueous solutions at the temperature 20.0°C and the ionic strength 0.50 M. These investigations have now been continued by a corresponding study of Malachite Green.

The chemical reactions of Malachite Green in aqueous solutions are quite analogous to those of Methyl Green and can be visualized by the following reaction-equilibrium scheme.³⁻⁴

Full drawn arrows denote protolytic reactions proceeding so rapidly to be measured; dashed arrows denote reactions proceeding at a measurable rate.

The reaction rates and the equilibria can be described by a set of rate constants and equilibrium constants which were defined in Ref. 2 (*cf.* also Refs. 3,4).



EXPERIMENTAL

Malachite Green Oxalate. Commercial Malachite Green (Merck's "Malachitgrün, konzentriert, pro analysi") was converted into the carbinol which was isolated and treated with a concentrated aqueous solution of oxalic acid. The solution was evaporated, and Malachite Green Oxalate crystallized as green, leaf-like crystals. The product was recrystallized three times from water. Optical constancy was attained. (Found: C 68.9; H 6.13; N 6.41; O 18.6. Calc. for $\text{C}_{23}\text{H}_{25}\text{N}_2\cdot\text{HC}_2\text{O}_4\cdot\text{H}_2\text{O}$: C 68.8; H 6.47; N 6.42; O 18.3). Optical analysis indicated the molecular weight 434, which is consistent with this formula (molecular weight 436.5).

Dye stock solutions were prepared by dissolving a weighed amount of the dyestuff oxalate in 0.50 M KCl or 0.010 M HCl + 0.49 M KCl. Hydrochloric acid, citric acid-disodium hydrogen phosphate, acetic acid-sodium acetate, and potassium dihydrogen phosphate-disodium hydrogen phosphate were used for the buffer solutions. The buffer concentrations were 0.025–0.250 M, 0.060 M, 0.100 M, and 0.060 M, respectively. Potassium chloride was used to adjust the ionic strength to 0.50 M. The temperature was $20.0 \pm 0.1^\circ\text{C}$. Polarographic maxima were suppressed by 0.03 % gelatine. A conventional dropping mercury electrode was used for the polarographic measurements. Two capillaries were used, with the following characteristics:

Capillary 1: $m = 2.91 \text{ mg sec}^{-1}$; $t_1 = 3.10 \text{ sec}$

Capillary 2: $m = 2.18 \text{ mg sec}^{-1}$; $t_1 = 3.66 \text{ sec}$

m is the mercury flow. t_1 is the drop-time determined in 0.50 M KCl at the potential of the reference electrode. A saturated external calomel electrode served as a reference electrode. The polarographic curves were recorded by a Radiometer PO 4 Polarograph.

Preliminary investigations showed that the polarographic behaviour of Malachite Green is far more complicated than the polarographic behaviour of Methyl Green.² Polarographic maxima were very troublesome within some pH-ranges and concentration ranges, and had to be eliminated by the addition of 0.03 % of gelatine. At low dyestuff concentrations only one wave was observed on the polarographic curves. When the dyestuff concentration was increased, however, this wave split into two to five waves depending on the dyestuff concentration and the pH of the solution. The polarographic behaviour will be discussed more fully later in this paper. The over-all wave heights were evaluated in the manner shown in Fig. 1, which also shows the change of the polarograms with the over-all dyestuff concentration at a constant pH-value. The over-all wave height, evaluated in this manner, is proportional to the over-all dyestuff concentration as can be seen from Fig. 2 where the over-all wave height at equilibrium, i_∞ , is plotted versus the dyestuff concentration C at two different pH-values.

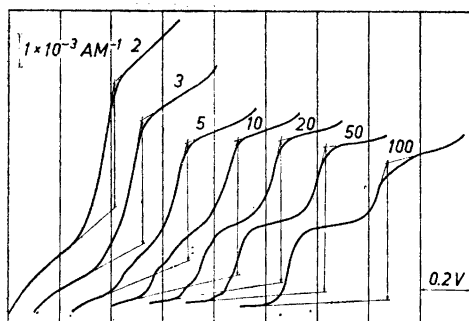


Fig. 1. Polarograms recorded at equilibrium for different over-all dyestuff concentrations. pH = 4.68; Capillary 2. All the polarograms start at -0.25 V vs. SCE. The figures beside the curves represent $C \times 10^5$ M.

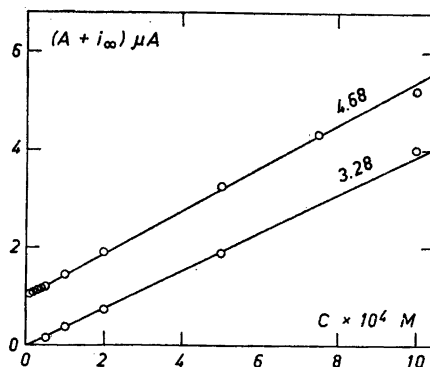


Fig. 2. Calibration curves. pH = 3.28: A = 0; pH = 4.68: A = 1 μ A. Capillary 2.

The over-all wave height represents the sum of the concentrations ($[B] + [G]$) within the pH-range 1–5 as can be seen from Table 1 which shows the over-all wave height, i_0 , immediately after the mixing of equal volumes of a dye stock solution and suitable buffer solutions. When a definite dye stock solution is used, the obtained values of i_0 should be independent of pH, if the over-all wave height represents the sum of the concentrations ($[B] + [G]$). Attempts to find an evaluation principle which would give a constant value of i_0 (for a definite dye stock solution) within the whole investigated pH-range (0.3 – 7.9) were, however, unsuccessful. The observed decrease of i_0 with increasing pH for pH > 5 is probably due to a distortion of the polarographic curves caused by adsorption (*cf.* below).

Table 1. i_0 -values obtained at the dyestuff concentrations $C = 10 \times 10^{-5}$ M and 50×10^{-5} M. Capillary 2.

$C = 10 \times 10^{-5}$ M		$C = 50 \times 10^{-5}$ M	
pH	i_0 μ A	pH	i_0 μ A
1.00	0.37	1.00	2.00
1.60	0.40	1.60	1.99
2.10	0.40	2.10	1.98
2.82	0.41	2.82	2.03
3.28	0.41	3.28	2.02
4.13	0.40	3.74	2.03
4.68	0.40	4.13	2.03
4.88	0.39	4.68	2.03
5.27	0.38	5.27	1.91
5.91	0.37	5.91	1.72
6.32	0.35	6.32	1.69
7.44	0.33	7.47	1.52

The measurements of i_{∞} were carried out in the following manner: Equal volumes of dye stock solution and suitable buffer solutions were mixed and equilibrated at 20.0°C in a thermostat. The polarograms were recorded after 10–30 h. Equilibrium measurements were carried out at the dyestuff concentrations $C = 10 \times 10^{-5}$ M; 20×10^{-5} M, and 50×10^{-5} M.

The kinetic measurements were carried out by recording the over-all current at a constant potential, corresponding to the limiting current, as a function of the time after the mixing of dye stock solution and buffer solution. Within the pH-ranges 0.6–1.6 and 6.5–6.9 a dye stock solution in 0.50 M KCl was used; within the pH-range 2.1–5.2, where the proportion of B + G at equilibrium is great, a partly decolourized dye stock solution in 0.010 M HCl + 0.49 M KCl was used. The solubility of the carbinol C is very low. It was therefore necessary to carry out the kinetic measurements within the pH-range 6.5–6.9 at the dyestuff concentration 2.5×10^{-5} M in spite of the low precision of the measurements at this low concentration. Even then it was not possible to extend the available pH-range above pH \approx 6.9. Within this pH-range polarograms were recorded at suitable time-intervals. The low solubility of the carbinol also set an upper limit to the pH-value at which reliable kinetic measurements could be carried out by using a partially decolourized dye solution. When the pH was increased above pH \approx 5.2, at dyestuff concentrations greater than 5×10^{-5} M, there was a precipitation of the carbinol produced by the rapid reactions $S'' \rightleftharpoons S' + H^+ \rightleftharpoons C + 2 H^+$. At lower dyestuff concentrations the precision of the measurements was greatly decreased due to the increased sensitivity to minor fluctuations of the apparatus and to the presence of small amounts of dissolved oxygen.

Table 2. Experimental values of i_{∞} at different pH-values and different over-all dyestuff concentrations. Capillary 2.

$C = 50 \times 10^{-5}$ M		$C = 20 \times 10^{-5}$ M		$C = 10 \times 10^{-5}$ M	
pH	i_{∞} μ A	pH	i_{∞} μ A	pH	i_{∞} μ A
2.13	0.476	2.10	0.189	2.09	0.093
2.33	0.680	2.31	0.251	2.29	0.129
2.53	0.980	2.56	0.366	2.53	0.182
2.82	1.351	2.81	0.509	2.80	0.241
3.28	1.895	3.28	0.752	3.28	0.375
3.55	2.078	3.56	0.820	3.43	0.399
3.74	2.150	3.75	0.846	3.55	0.414
3.90	2.193	4.13	0.869	3.65	0.412
4.13	2.240	4.68	0.885	3.73	0.419
4.68	2.249	5.44	0.832	3.89	0.428
5.38	1.941	5.91	0.751	4.13	0.420
				4.49	0.425
				4.68	0.416
				4.86	0.419
				5.10	0.393
				5.45	0.399
				5.74	0.389

Table 3. Experimental values of the over-all rate constant k .

pH	$k \text{ min}^{-1}$	pH	$k \text{ min}^{-1}$
$C = 10 \times 10^{-5} \text{ M}$; No added gelatine		$C = 2.5 \times 10^{-5} \text{ M}$; No added gelatine	
0.60	0.152	6.52	0.032
0.70	0.147	6.69	0.024
0.82	0.139	6.78	0.019
1.00	0.129	6.89	0.016
1.10	0.123		
1.22	0.111	$C = 10 \times 10^{-5} \text{ M}$; 0.03 % gelatine	
1.30	0.108		
3.05	0.0228		
3.17	0.0274	1.00	0.138
3.27	0.0281	1.60	0.0817
3.43	0.0348	3.74	0.0539
3.55	0.0456		
3.76	0.0578	$C = 50 \times 10^{-5} \text{ M}$; 0.03 % gelatine	
3.89	0.0722		
3.98	0.0813		
4.23	0.116	1.00	0.140
4.41	0.150	1.60	0.0815
4.51	0.170	2.10	0.0388
4.61	0.177	2.33	0.0303
4.77	0.182	2.82	0.0228
5.03	0.183	4.13	0.099
5.18	0.177		

The kinetic measurements from which the constants were calculated (within the pH-range 0.6—5.2) were carried out at the dyestuff concentration $C = 10 \times 10^{-5} \text{ M}$ in the absence of gelatine. Calibration curves showed that the current at a constant potential is a linear function of C both in the presence and the absence of gelatine. Isolated measurements were carried out in the presence of 0.03 % of gelatine at $C = 10 \times 10^{-5} \text{ M}$ and $50 \times 10^{-5} \text{ M}$. The results agreed within narrow limits with the results obtained without added gelatine.

The pH-values of the solutions were determined titrimetrically and potentiometrically in the manner described in Ref. 2.

EQUATIONS, CALCULATIONS, AND RESULTS

The following symbols and notations are defined:

- i_B the over-all wave height (*cf.* Fig. 1) in a solution where the dyestuff is present only as carbonium species, *i.e.* B or G.
- i_0 the over-all wave height at a moment immediately after mixing a dye stock solution and an appropriate buffer solution.
- i_t the over-all wave height at the time t after mixing.
- i_∞ the over-all wave height at equilibrium.

- $I_{t=0}$ the total current at a given potential at a moment immediately after mixing a dye stock solution and a buffer solution.
 I the total current at a given potential at the time t after mixing.
 $I_{t=\infty}$ the total current at a given potential at equilibrium.

The latter three notations were used only in the kinetic measurements, in which the change of the total current at a constant potential for each pH-value was measured as a function of the time t .

$$h = [H^+]; oh = [OH^-].$$

The following two non-approximated equations can be derived for the over-all wave height at equilibrium, i_∞ , and the measured over-all rate constant k (cf. Refs. 2,4):

$$i_\infty = \frac{i_B (1 + hK_1)}{1 + 1/K_6 + hK_1(1 + K_2) + K_4/K_6h} \quad (1)$$

$$k = \frac{1}{t} \ln \frac{I_{t=0} - I_{t=\infty}}{I - I_{t=\infty}} = \frac{hk_1K_1 + k_3 + k_5oh}{1 + hK_1} + \frac{h^2k_2 + hk_4K_3 + k_6K_3K_4}{h^2 + hK_3 + K_3K_4} \quad (2)$$

By using these two equations the constants can be calculated from experimental values of I , $I_{t=\infty}$, i_∞ , h , and t . The equations can be approximated, since the concentrations of some of the species and the contributions from some of the reaction paths to the over-all reaction rate can be neglected within some pH-ranges. When the approximations which would give simple relations are too rough, it is possible to proceed by successive approximations to obtain more accurate results. The approximate values obtained in preceding calculations are then used in correction terms in succeeding calculations.

Eqn. (2) is transformed to

$$k = \frac{k_1hK_1}{1 + hK_1} + \frac{k_2h^2}{h^2 + hK_3 + K_3K_4} + \frac{k_3}{1 + hK_1} + \frac{k_4hK_3}{h^2 + hK_3 + K_3K_4} + \frac{k_5oh}{1 + hK_1} + \frac{k_6K_3K_4}{h^2 + hK_3 + K_3K_4} \quad (3)$$

which can be written

$$k = \sum_{i=1}^6 f_i \quad (4)$$

where

$$f_1 = \frac{k_1hK_1}{1 + hK_1}; f_2 = \frac{k_2h^2}{h^2 + hK_3 + K_3K_4} \text{ etc.}$$

Thus every f_i denotes the contribution to k from the reaction path in question.

Determination of k_1 and K_1 . In strongly acid solutions (pH < 2) f_1 and f_2 in eqn. (4) dominate. The equilibrium wave heights are, however, very low

within this pH-range, and it can therefore be assumed that $k_2 = k_1/K_2$, and thus f_2 , is small. We therefore put $k \approx f_1$ as a first rough approximation. We have

$$\frac{h}{f_1} = \frac{1}{k_1 K_1} + \frac{h}{k_1} \quad (5)$$

and thus

$$\frac{h}{k} = \frac{1}{k_1 K_1} + \frac{h}{k_1} \quad (6)$$

When h/k is plotted *versus* h an approximately straight line is obtained. From the intercept on the ordinate-axis and the slope of this line approximate values of k_1 and K_1 are obtained.

Determination of K_2 and k_2 . When $h \gg K_4$, [C] can be neglected and eqn. (1) is approximated and rewritten as

$$\frac{1 + hK_1}{i_\infty} = \frac{1 + 1/K_6}{i_B} + \frac{K_1(1 + K_2)}{i_B} h \quad (7)$$

Within the pH-range 2.1–4.5 hK_1 is only a correction term which amounts to less than 0.25. Thus the previously obtained approximate value of K_1 can be used for the calculation of $(1 + hK_1)/i_\infty$. From the intercept on the ordinate-axis and the slope of the straight line that is obtained, when $(1 + hK_1)/i_\infty$ is plotted *versus* h , the quantities $i_B/(1 + 1/K_6)$ and $K_1(1 + K_2)/(1 + 1/K_6)$ are obtained. The fact that i_∞ is almost constant within a wide pH-range indicates that $K_6 \gg 1$, and therefore $1/K_6$ can be neglected as a first approximation. Since K_1 is known, an approximate value of K_2 can be calculated. An estimation of $k_2 = k_1/K_2$ can also be made.

Estimation of k_3 . Within a rather broad pH-range around pH = 5 the reaction paths $B + H_2O \rightleftharpoons S'$ dominate and eqn. (2) can be approximated to

$$k = k_3 + \frac{k_4 h K_3}{h^2 + hK_3 + K_3 K_4} \quad (8)$$

At sufficiently great pH-values k changes almost linearly with h . An extrapolation to $h = 0$ gives k_3 as the intercept on the ordinate-axis.

Determination of k_4 and K_3 . These constants were determined by kinetic measurements in acetate buffers, pH = 3.8–4.5.

The relation

$$f_4 = \frac{k_4 h K_3}{h^2 + hK_3 + K_3 K_4} \quad (9)$$

can be rearranged to

$$\frac{1}{f_4} - \frac{K_4}{k_4 h} = \frac{1}{k_4} + \frac{h}{k_4 K_3} \quad (10)$$

Within the used pH-range the term $K_4/k_4 h$ is only a correction term and can be neglected in the first calculation. Furthermore, f_1 , f_2 , and f_3 are small compared to k within this pH-range, and the previously determined approxi-

mate values of k_1 , k_3 , and K_1 can be used for the first calculation of $f_4 = k - \sum_{i \neq 4} f_i$. In the first calculation f_2 has to be neglected. f_5 and f_6 could not be determined due to the low solubility of the carbinol and are neglected throughout the calculations. From the almost straight line $1/(k - f_1 - f_3)$ versus h approximate values of k_4 and K_3 are obtained.

Estimation of K_4 . Differentiation of eqn. (8) with regard to h and putting the derivative equal to zero shows that k has a maximum for $h = \sqrt{K_3 K_4}$. When K_3 is known, it is possible to calculate K_4 from the graphically determined pH-value at which k is maximum. Since it was not possible to obtain reliable values of k for $\text{pH} > 5.2$, the obtained value of K_4 is very unreliable.

The hydration-equilibrium constant $K_6 = [B]_\infty/[S']_\infty$ could not be determined by direct measurements but was calculated from the relation

$$K_1 K_2 K_3 K_6 = 1 \quad (11)$$

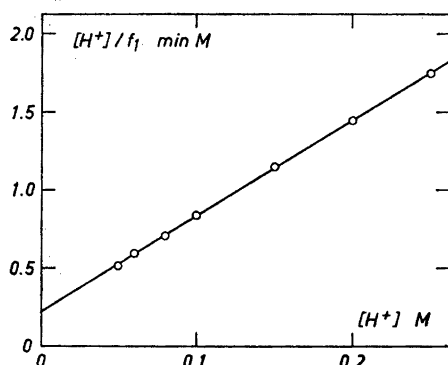


Fig. 3. $[H^+]/f_1$ versus $[H^+]$ for the determination of k_1 and K_1 .

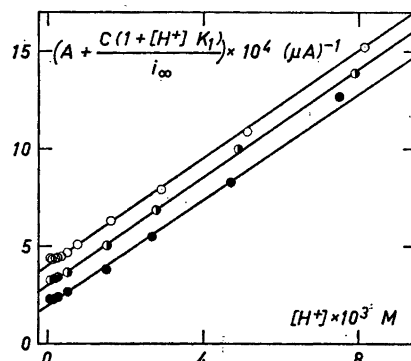


Fig. 4. $A + C(1 + [H^+]K_1)/i_\infty$ versus $[H^+]$ for the determination of K_2 . \bullet $C = 50 \times 10^{-5}$ M; $A = 0$. \blacksquare $C = 20 \times 10^{-5}$ M; $A = 1.00$ $(\mu A)^{-1}$. \circ $C = 10 \times 10^{-5}$ M; $A = 2.00$ $(\mu A)^{-1}$.

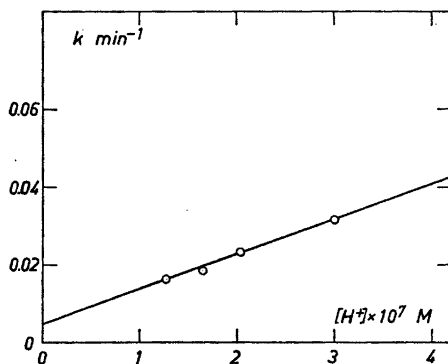


Fig. 5. k versus $[H^+]$ for the estimation of k_3 .

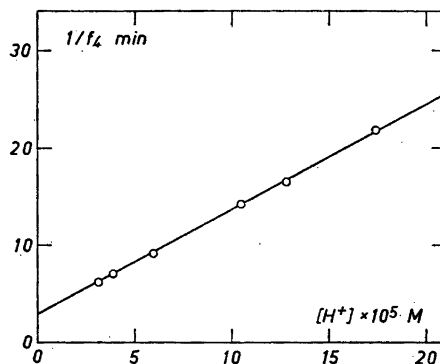


Fig. 6. $1/f_4$ versus $[H^+]$ for the determination of k_4 and K_3 .

Refined calculations. By the first series of calculations only approximate values of the constants were obtained. The values of some of the constants could, however, be refined by repeating the calculations. The previously obtained values were used for the calculation of correction terms. These calculations were repeated until further recalculations did not change the values of the constants noticeably.

Figs. 3–6 show h/f_1 versus h (pH = 0.6–1.3), $C(1 + hK_1)/i_\infty$ versus h at three different values of C (pH = 2.1–4.7), k versus h (pH = 6.5–6.9); and $1/f_4$ versus h (pH = 3.8–4.5), respectively. The experimental values of the over-all wave height at equilibrium, i_∞ and the over-all rate constant k at different pH-values are shown in Tables 2 and 3, respectively. The obtained values of the constants are shown in Table 4 compared to the values obtained spectrophotometrically by Cigén.⁴ The errors of the polarographically determined constants are the maximum random errors estimated from the reproducibility of different series of measurements and from the estimated errors of the graphical evaluations. Fig. 7 shows k as a function of pH within the pH-range 0.3–7. The symbols denote experimental values, and the full drawn curve has been calculated with eqn. (2) using the values of the constants shown in Table 4.

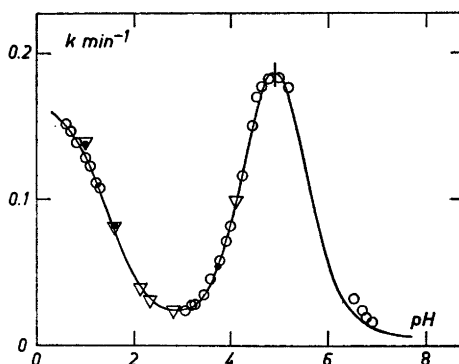
POLAROGRAPHIC BEHAVIOUR

The polarographic behaviour of Malachite Green in aqueous solutions is complicated and not fully understood. The application of classical polarography does not seem to be sufficient for the full clarification of the polarographic behaviour. The dyestuff is reduced at the dropping mercury electrode within the whole investigated pH-range (0.3–7.9), the carbonium species being the electro-active species. At dyestuff concentrations below about 2×10^{-5} M the reduction produces one polarographic wave. At greater dyestuff concentrations, however, this wave splits into 2–5 new waves (*cf.* Fig. 1). The

Table 4. Comparison between spectrophotometrically and polarographically determined values of the equilibrium and rate constants.

	Polarographically	Spectrophotometrically
$1/K_1$ M	0.036 ± 0.003	0.036
K_2	24 ± 4	22
$K_3 \times 10^5$ M	2.6 ± 0.4	2.7 ± 0.1
$K_4 \times 10^6$ M	6	5.8 ± 0.2
$1/K_5$	0.018	0.0149 ± 0.0003
k_1 min ⁻¹	0.164 ± 0.004	0.168
k_2 min ⁻¹	0.007 ± 0.001	0.0078
k_3 min ⁻¹	0.005	0.0065 ± 0.0002
k_4 min ⁻¹	0.35 ± 0.04	0.44 ± 0.01
k_5 min ⁻¹ M ⁻¹	—	31.7
k_6 min ⁻¹	—	4.6×10^{-6}

Fig. 7. The over-all rate constant k versus pH. \circ $C = 10 \times 10^{-5}$ M, no added gelatine; \circ $C = 2.5 \times 10^{-5}$ M, no added gelatine; \bullet $C = 10 \times 10^{-5}$ M, 0.03 % gelatine; ∇ $C = 50 \times 10^{-5}$ M, 0.03 % gelatine.



number of waves and the differences of the half-wave potentials between some of them depend on pH and on the depolarizer concentration. There is a spreading out of the waves over a wider potential range with increasing pH-values, and also with increasing dyestuff concentration at a constant pH-value. 0.03 % of gelatine had to be added to eliminate polarographic maxima which were very troublesome below $\text{pH} \approx 4$, when $C > 2 \times 10^{-5}$ M. In the absence of gelatine the limiting currents were less well-defined, and the evaluations of some of the wave heights could not be carried out within some pH-ranges and concentration ranges (cf. Fig. 8).

Fig. 9 shows two typical polarograms recorded for solutions with $C = 50 \times 10^{-5}$ M and $\text{pH} = 3.28$ and 4.68. This figure also shows the notations used for the different waves. Some of the waves coincide, when pH is decreased,

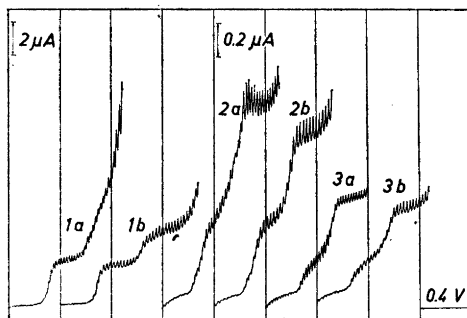


Fig. 8. A comparison between polarograms recorded with (b) and without (a) added gelatine. 1. $C = 100 \times 10^{-5}$ M; 2. $C = 20 \times 10^{-5}$ M; 3. $C = 10 \times 10^{-5}$ M. $\text{pH} = 4.68$. All the polarograms start at -0.20 V vs. SCE.

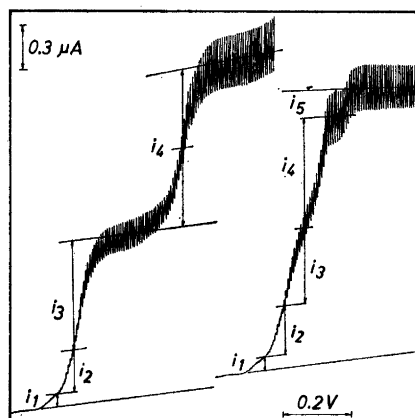


Fig. 9. Typical polarograms at $\text{pH} = 4.68$ (left) and 3.28 (right). $C = 50 \times 10^{-5}$ M; Capillary 2. Both polarograms start at -0.25 V vs. SCE.

and in the most acid solutions only two waves can be seen on the polarograms at this depolarizer concentration. A few polarograms recorded at different pH-values, but comparable depolarizer concentrations are shown in Fig. 10. These polarograms were recorded as soon as possible after the mixing of a dye stock solution and suitable buffer solutions.

The dependence of the over-all wave height at equilibrium, i_{∞} , on the dyestuff concentration at a constant pH-value has been considered in connection with the study of the chemical reactions of Malachite Green, and it was found that i_{∞} is proportional to C . i_{∞} is also proportional to the square root of the height of the mercury reservoir within the whole investigated concentration range (1×10^{-5} – 100×10^{-5} M) and pH-range.

The wave heights i_1 and i_5 are independent of the dyestuff concentration as soon as the latter is great enough for these wave heights to be evaluated with a reasonable precision. They are also approximately proportional to the height of the mercury reservoir, and the corresponding waves can therefore be classified as adsorption waves. The nature of wave 2 is uncertain. This wave is so ill-defined that it cannot be evaluated accurately. Approximate evaluations indicated, however, that also wave 2 might be an adsorption wave.

As can be seen from Figs. 1, 9, and 10, two "main waves" can be recognized on the polarographic curves, when the depolarizer concentration is greater than about 20×10^{-5} M. The sum of the wave heights ($i_1 + i_2 + i_3$) represents the over-all wave heights of the first of these "main waves" whereas ($i_4 + i_5$) represents the second one. The sum ($i_1 + i_2 + i_3$) increases almost linearly with C at a constant pH-value, but the line cuts the C -axis to the right of the origin (Fig. 11). The dependence of this sum of wave heights on the height of the mercury reservoir is complicated. For solutions with a depolarizer

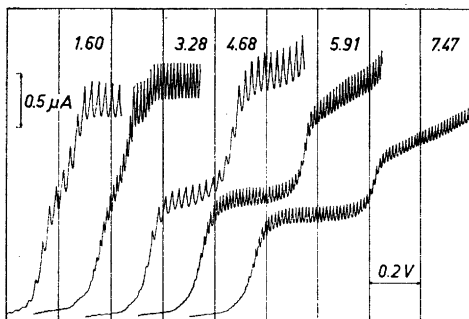


Fig. 10. Polarograms recorded at comparable depolarizer concentrations. $C = 50 \times 10^{-5}$ M; Capillary 2. All the polarograms start at -0.25 V vs. SCE.

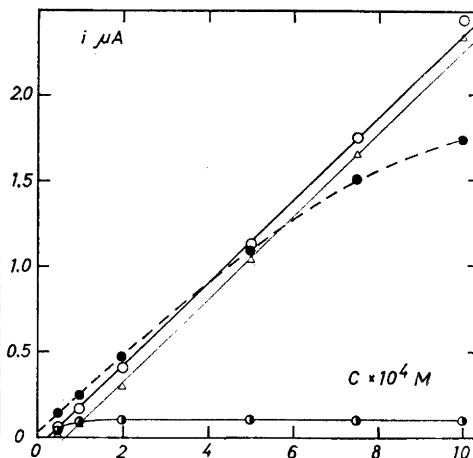


Fig. 11. The wave heights i_1 ●, ($i_2 + i_3$) △, ($i_1 + i_2 + i_3$) ○, and i_4 ●, determined at equilibrium versus the over-all dyestuff concentration C . pH = 4.68; Capillary 2.

concentration equal to or above 50×10^{-5} M ($i_1 + i_2 + i_3$) is approximately proportional to the square root of the mercury pressure (P_{corr}), corrected for the back pressure, indicating a limiting current controlled by the rate of diffusion. For depolarizer concentrations below about 20×10^{-5} M $\log(i_1 + i_2 + i_3)$ versus $\log P_{\text{corr}}$ is not, however, quite linear but is convex upwards.

Electrocapillary curves measured at different dyestuff concentrations at a constant pH-value, and also at different pH-values provide a further evidence that adsorption of the dyestuff and its reduction product on mercury occurs (cf. Fig. 12). For $C = 1 \times 10^{-5}$ M the electrocapillary curves coincide with that of the pure buffer solutions (containing 0.03 % of gelatine). For greater dyestuff concentrations, however, there is a decrease of the drop-time as compared to the pure buffer solution already at the potential of the reference electrode and to about -1.2 V vs. SCE, indicating a specific adsorption of both the depolarizer and its reduction product on mercury. These electrocapillary curves pass through a maximum at $E \approx -0.3$ V vs. SCE, then through a minimum, and finally through a second maximum at more negative potentials. The heights of both maxima decrease at first with increasing dyestuff concentration and then become almost constant. The minimum of the electrocapillary curves corresponds roughly to the rise of the first "main wave". The drop-times at potentials corresponding to the total limiting current are lower in the dye solutions ($C > 2 \times 10^{-5}$ M) than in the pure buffer solution. This fact indicates an adsorption of the reduction product. No thorough study of the electrocapillary curves in the absence of gelatine was carried out. The obtained results indicated, however, that the curves are in the essential parts analogous to the curves obtained in the presence of gelatine.

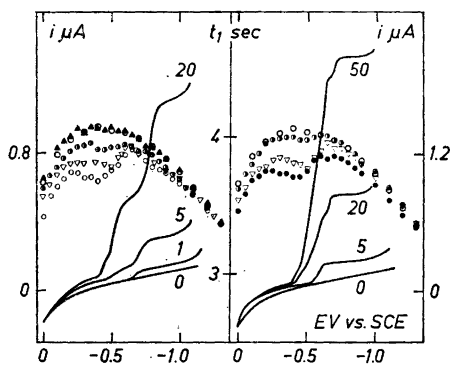


Fig. 12. Electrocapillary curves and the corresponding polarograms at pH = 4.68 (left) and 3.28 (right). Different symbols denote different over-all dyestuff concentrations. \circ 0; \blacktriangle 1×10^{-5} M; \circ 5×10^{-5} M; ∇ 20×10^{-5} M; \bullet 50×10^{-5} M; \circ 100×10^{-5} M. The figures beside the polarograms denote the dyestuff concentrations multiplied by 10^{-5} . Capillary 2.

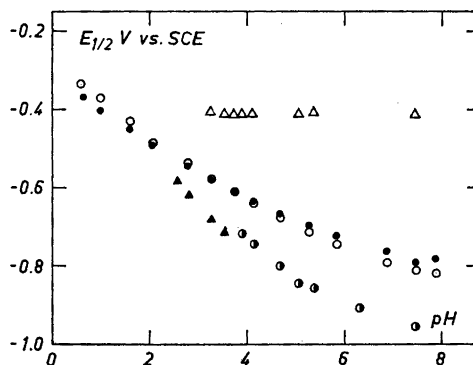


Fig. 13. Half-wave potentials versus pH. $C = 1 \times 10^{-5}$ M; \circ without gelatine; \bullet 0.03 % gelatine. $C = 50 \times 10^{-5}$ M; 0.03 % gelatine; \triangle ($E_{1/2}$)₁; \bullet ($E_{1/2}$)₄; \blacktriangle ($E_{1/2}$)₅.

The number of electrons transferred in the reduction process was estimated by a comparison of the wave heights obtained for Methyl Green with the same dropping mercury electrode. The wave heights obtained at equal depolarizer concentrations agreed within a few per cent, so it was concluded that two electrons are consumed for the full reduction of Malachite Green. The reduction product was not identified. The reduction seems to be polarographically irreversible, since the chemical reduction of the depolarizer and after that recording of a polarogram does not give rise to any anodic wave within the available potential range.

Fig. 13 shows the dependence of some of the half-wave potentials on pH at the dyestuff concentrations $C = 1 \times 10^{-5}$ M and 50×10^{-5} M. These half-wave potentials were determined by slow recording of the polarograms in two directions. The mean value was accepted as the half-wave potential at the pH-value in question. Since the half-wave potentials change with the depolarizer concentration (*cf.* below), it was essential to record the polarograms at as nearly as possible equal depolarizer concentrations. They were therefore recorded as soon as possible after the mixing of a certain dye stock solution and the buffer solution in question. At low pH-values there was, however, a considerable change of the depolarizer concentration during the time necessary for the recording of the polarograms (*cf.* Table 3). The half-wave potentials change, however, but little with the depolarizer concentration just around the concentrations represented in Fig. 13.

At the lower depolarizer concentration only one wave is obtained on the polarographic curves, and no depression of the drop-times is found on the electrocapillary curves. It is therefore reasonable to assume that this wave represents the pure reduction process without adsorption phenomena. The half-wave potentials at this depolarizer concentration were determined both with and without added gelatine. The half-wave potential is shifted towards more negative values with increasing pH within the whole investigated pH-range. The slope of the $E_{1/2}$ -pH-plot is decreased by the addition of 0.03 % of gelatine. The curves obtained with and without gelatine are else analogous and cross at $\text{pH} \approx 3.6$. The wave becomes more drawn out in the presence of gelatine. This effect increases with increasing pH with a consequent decrease of the precision of the determinations of the half-wave potentials.

Fig. 13 also shows the dependence of the half-wave potentials for waves number 1, 4, and 5 on pH at the over-all dyestuff concentration $C = 50 \times 10^{-5}$ M. These half-wave potentials could be determined only in the presence of gelatine. $(E_{1/2})_4$ and $(E_{1/2})_5$ are both shifted towards more negative values with increasing pH, whereas $(E_{1/2})_1$ is independent of pH within the pH-range where wave 1 can be observed. $(E_{1/2})_2$ and $(E_{1/2})_3$ could not be determined very accurately and are therefore omitted in the figure. The position of both these waves on the potential axis seems, however, to be independent of pH within the pH-range (3–8) where they can be found as separate waves.

The half-wave potentials of all the waves change with the depolarizer concentration (Fig. 14). $(E_{1/2})_1$ is displaced towards less negative potentials with increasing values of C at a constant pH-value, and so are probably $(E_{1/2})_2$ and $(E_{1/2})_3$. $(E_{1/2})_4$ is displaced towards more negative potentials. All the half-wave potentials in Fig. 14 were determined in the presence of gelatine

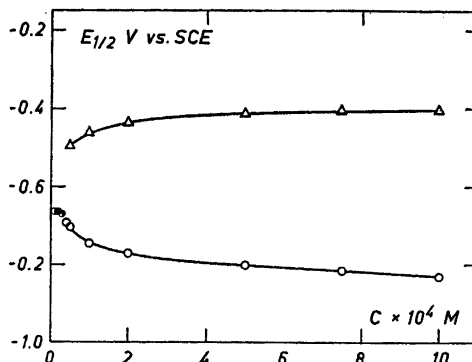


Fig. 14. $E_{1/2}$ versus C . 0.03 % gelatine. pH = 4.68. Capillary 2. Δ ($E_{1/2}^1$); \circ ($E_{1/2}^2$); \bullet $E_{1/2}^3$ for the sole wave found at $C < 3 \times 10^{-5}$ M.

and after the solutions had reached chemical equilibrium. The changes of the half-wave potentials are most pronounced within the concentration range $3 \times 10^{-5} - 10 \times 10^{-5}$ M but are rather small around $C = 1 \times 10^{-5}$ M and 50×10^{-5} M (cf. above).

DISCUSSION

A comparison between the polarographically determined values of the equilibrium and rate constants of Malachite Green with the corresponding values obtained by Cigén⁴ by a spectrophotometric method shows a rather good agreement (Table 4). The observed differences between some of the constants are not greater than might be accounted for by the fact that different experimental methods have been applied and the lower precision of the polarographic measurements. As with Methyl Green^{1,2} it is found that an increase of the over-all dyestuff concentration has but little effect on the values of the constants. This was further supported by the agreement between the results of the polarographic measurements at different dyestuff concentrations.

A detailed discussion of the polarographic behaviour of Malachite Green in aqueous solutions will be postponed until the corresponding studies of a few other basic triarylmethane dyes with slightly different chemical properties have been completed. A few aspects will, however, be considered already in this paper.

The reduction of Malachite Green at the dropping mercury electrode in aqueous solutions produces at low depolarizer concentrations one two-electron wave on the polarographic curves. At greater depolarizer concentrations this wave splits into several waves. At depolarizer concentrations between about 20×10^{-5} M and 75×10^{-5} M two "main waves" of comparable heights can be distinguished. This shape of the polarograms might be interpreted as due to the dyestuff being reduced in two one-electron steps with the intermediate formation of a semiquinone^{5,6} the stability of which increases with increasing pH. This interpretation is supported by the approximately equal heights of the "main waves" and the fact that the limiting currents of both these waves are diffusion controlled, when $C \geq 50 \times 10^{-5}$ M. The fact that

the sole wave found at low depolarizer concentrations splits, when the concentration is increased, might be explained by dimerisation of the semiquinone.⁵ There is not, however, a splitting at the midpoint of the original wave but rather an extension of the lower part of the wave. Furthermore, the wave height of the first "main wave" has a P_{corr} -dependence with an n -value that is not constant and < 0.5 at depolarizer concentrations below about 20×10^{-5} M. This fact indicates that the limiting current of this wave is not entirely diffusion-controlled at lower concentrations.

The "main waves" are subdivided into two or more waves within some pH-ranges and concentration ranges. The adsorption character of two of these waves (1 and 5) has been established, whereas the adsorption character of a third wave (2) is uncertain. Wave 1 appears as a pre-wave which disappears, when pH becomes less than about 3. Wave 5 has the character of a post-wave, probably caused by the inhibition of the electrode reaction by an adsorbed layer of the final reduction product (*cf.* Ref. 7). This wave is found as an easily recognizable wave only within a limited concentration and pH-range, but the inhibition might be the cause of the steeper slope of the limiting current plateau found at greater dyestuff concentrations, when pH is increased (*cf.* also Fig. 11). This latter effect might also be the explanation of the fact that i_0 obtained for a definite dye stock solution decreases for $\text{pH} > 5$ (*cf.* Table 1).

The fact that $E_{\frac{1}{2}}$ at $C = 1 \times 10^{-5}$ M changes with pH within the pH-range 0.6–7 (*cf.* Fig. 13) indicates that at least one hydrogen ion participates in the electrode process. Since the uptake of the proton probably precedes the reduction,⁸ this would mean that the species G is the electro-active species. The dependence of the half-wave potentials on pH at greater depolarizer concentrations is, however, more complicated.

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