Titration of aqueous solutions of phenols and determination of their bromination rate constants by means of ring-disc electrodes

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The use of ring-disc electrodes enables the detection of metacresol, resorcinol, orcinol, phloroglucinol and pyrogallol at concentrations down to 10^{-7} M and generally the titration of these compounds with an accuracy of a few percents when the concentrations are larger than about 5×10^{-6} M. Phenol, ortho- and para-cresol can be titrated at concentrations larger than about 5×10^{-5} M. On the other hand, bromination rate constant determinations have been carried out with phenol, ortho- and meta-cresol.

1. Introduction

The use of ring-disc electrodes may be a convenient method for the titration of compounds which can rapidly react with electrochemicaly generated species. We have applied it to several phenols which can be substituted rapidly by bromine.

Bromine is generated on the disc by oxidation of bromide contained in the solution:

$$(\text{disc}) \ 2\,Br^- \longrightarrow Br_2 + 2e^-.$$

Because of the rotation of the electrode, the nascent bromine reaches the ring which is set at a suitable potential for the complete reduction of bromine:

$$(\text{ring}) \ Br_2 + 2e^- \longrightarrow 2\,Br^-.$$
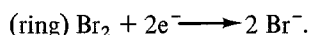
If the solution is free of chemicals which can react with bromine during its transit from disc to ring, the observed ring current I_r is proportional to the monitored disc current I_d. If chemicals such as phenols are present in the solution, bromine reacts before reaching the ring. The shape of the I_r versus I_d titration curves, then, gives two kinds of information: the concentration level of the compound reacting with bromine and the bromination rate.

2. Titrations

If the bromination reaction is very fast, I_r versus I_d curves have the shapes of curves 1 and 2 of Fig. 1. The concentration of the titrated compound C can be easily obtained from the value $I_{d,0}$ of I_d at which the asymptote crosses the I_d axis. Bruckenstein and Johnson [1] have shown that this value is proportional to C, and the ratio between $I_{d,0}$ and C can be either calculated or determined with solutions of known concentration. C can alternatively be obtained by the mathematical analysis of the whole titration curve 2: this second method which eliminates extrapolation uncertainties is assumed to be more accurate than the first one.

If the reaction rate between the titrated compound and the intermediate generated on the disc is not high enough, the slope of the I_r versus I_d curve is different from zero at low values of I_d. As this slope depends on C [3a], titration is still possible. But the slope also depends on the reaction rate which is generally unknown. The easiest way to determine C is therefore to calibrate the I_r versus I_d curves by comparison with those obtained with solutions of known concentration.
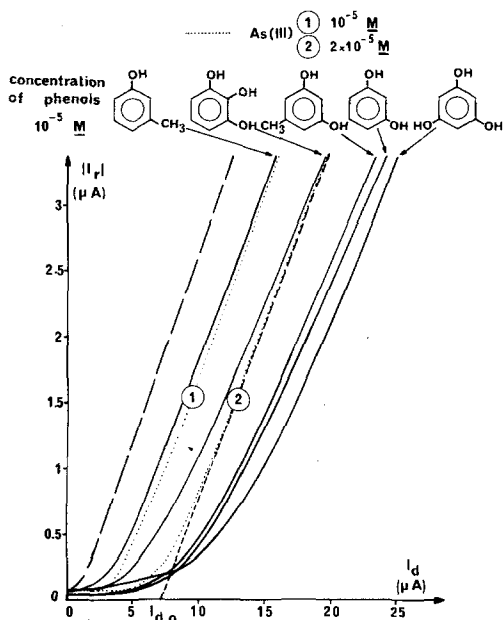
Fig. 1. Titration curves of 10^{-5} M solutions of m.cresol, pyrogallol, orcinol, resorcinol and phloroglucinol; comparison curves (........) with 10^{-5} M (1) and 2×10^{-5} M (2) As (III) solutions. Gold ring-carbon disc electrode (No. 1), H_2SO_4 1 N, Br^- 0·5 M, $W = 28·6$ Hz, 25°C.

Fig. 2. Titration curves of resorcinol. Gold ring-carbon disc electrode (No. 1), H_2SO_4 1 N, Br^- 0·5 M, $W = 28·6$ Hz, 25°C.

2.1. Resorcinol (dihydroxy 1, 3 benzene), phloroglucinol (trihydroxy 1, 3, 5 benzene), orcinol (methyl 5, dihydroxy 1, 3 benzene), pyrogallol (trihydroxy 1, 2, 3 benzene) meta-cresol (methyl 3, phenol)

With these compounds, I_r versus I_d curves (Fig. 1) seem to have the general shape expected for fast reactions, but the mathematical analysis of these curves shows that they cannot be described by the theoretical equations established by Albery, Bruckenstein and Johnson [2]. This is certainly due to a rather low rate of the bromination reaction and/or to the oxidation of the titrated compound on the disc, simultaneously with bromine. We have checked with our electrodes that I_r versus I_d curves obtained with As (III) and allyl-alcohol (compounds previously used to control the method) [2, 4] were in good agreement with the theoretical equations.

With all compounds, the asymptotical part of the curves is reached at a rather high I_d and, therefore, titrations by means of this method of determination of C may not be very accurate. We therefore compared the experimental curves with those
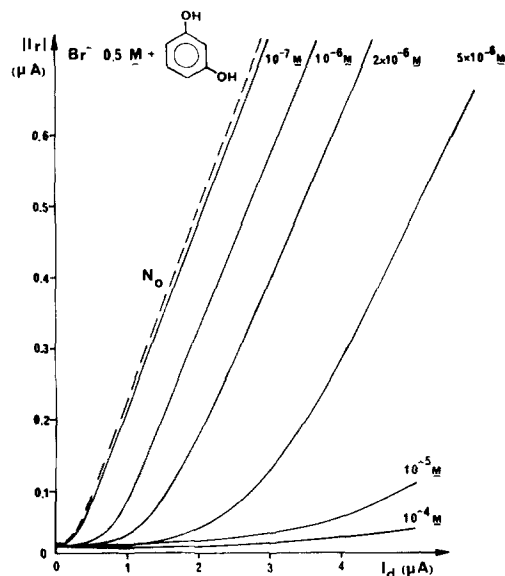
obtained with solutions of known concentration.

2.1.1. Resorcinol, phloroglucinol and orcinol.
These compounds react rather rapidly with bromine because they have substitution sites activated by at least two hydroxy-groups.

The comparison of the I_r versus I_d curves corresponding to these phenols with those obtained with As (III) at the same concentration or at a concentration two times larger shows that these compounds undergo three following rapid brominations (Fig. 1) and perhaps other extra-brominations for resorcinol and phloroglucinol (this last phenol is known to react with six moles of Br_2 when titrated with this compound [5]). With these three phenols, curves start to deviate from the blank straight line when C is larger than about 10^{-7} M; titrations can be achieved with an accuracy of a few per cent when C is larger than about 5×10^{-6} M (Fig. 2).

2.1.2. Pyrogallol.
Pyrogallol also has substitution sites activated by two hydroxy-groups and therefore also reacts rapidly with bromine. The sensitivity of the method is somewhat lower than with resorcinol, orcinol and phloroglucinol because only two brominations occur (Fig. 1), one site being already substituted.
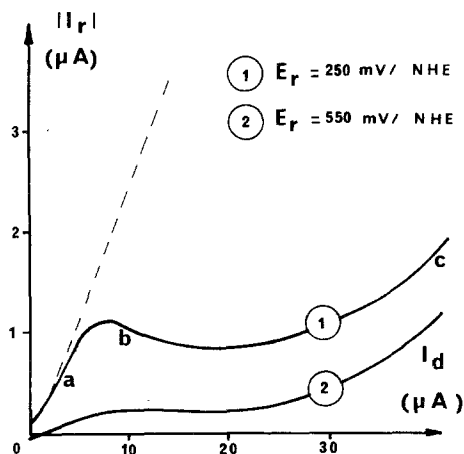
Titration curves may exhibit a peak at low

Fig. 3. I_r versus I_d curves obtained with a solution of pyrogallol 10^{-4} M with two different ring potentials: (1) 0·25 and (2) 0·55 V/N.H.E. Gold ring-carbon disc electrode (No. 1), H_2SO_4 1 N, Br^- 0·5 M, $W = 28·6$ Hz, 25°C.

values of I_d when the ring potential is low enough (Fig. 3, curve 1). This peak results from the interference of two phenomena: (1) the reaction of pyrogallol with the nascent bromine; (2) the oxidation of pyrogallol on the disc and the detection on the ring of its oxidation product.

Current-potential curves obtained with solutions of pyrogallol and bromide show that, at low values of I_d, pyrogallol is oxidized instead of bromide. I_r is different from zero (Fig. 3, part a of curve 1) because the oxidation product of pyrogallol is reducible on the ring. When I_d is larger than the limiting diffusion current of pyrogallol, bromine is generated and reacts with pyrogallol. The number of pyrogallol molecules reaching the disc then decreases, and therefore the number of molecules which results from the oxidation of pyrogallol also decreases. Therefore I_r decreases (Fig. 3, part b of curve 1). When I_d is large enough, bromine is generated in excess and prevents pyrogallol molecules from reaching the disc: the behaviour is then as if pyrogallol could not be oxidized on the disc (Fig. 3, part c of curve 1).

It is possible to remove such a peak from the I_r versus I_d curves by monitoring the ring potential at a value low enough to allow the complete reduction of bromine, but high enough to prevent the oxidation product of pyrogallol from being detected on the ring (Fig. 3, curve 2).

Table 1. Concentration ranges in which various phenols can be titrated at 0°C using the slope N_K of the I_r versus I_d lines

	C_{min} (M)	C_{max} (M)
Anisole	8×10^{-5}	7×10^{-2}
Phenol	7×10^{-6}	6×10^{-3}
Ortho-cresol	2×10^{-6}	2×10^{-3}
Meta-cresol	$1·5 \times 10^{-7}$	$1·5 \times 10^{-4}$

Concentration limits determined by $0·1 N_0 < N_K < 0·9 N_0$ for platinum-platinum ring-disc electrode No. 2 and for a rotation speed range 4–80 Hz.

2.1.2. Meta-cresol. The detection limits are somewhat higher than with the previous phenols, for this compound undergos only one rapid bromination in the time scale of the transit time from disc to ring (Fig. 1). This confirms that the mesomer effect of the OH-entity is larger than the inductive effect of the CH_3-group.

2.2. Phenol, ortho- and para-cresol

These compounds react more slowly with bromine than the previous ones. This is the reason why the slopes of the I_r versus I_d curves are different from zero even when C is as large as 10^{-4} M and when the rotation speed W of the electrode is low (Fig. 4). The relative positions of the curves shows that the bromination rate increases according to:

phenol < para-cresol < ortho-cresol.
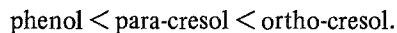
In the next paragraph we give an estimate of these reaction rates.

Even in very acidic media, these phenols are oxidized on solid electrodes at potentials which are very near the oxidation potential of bromine. As their oxidation products spoil the surfaces of the electrode [6], no reproducible curves can be obtained when I_d is too large. Thus it is generally not possible to reach the asymptotical parts of the curves. This does not occur with metacresol which reacts at least ten times more rapidly with bromine (see later) because in this case bromine prevents molecules of meta-cresol from reaching the disc and interfering with the desired reaction.

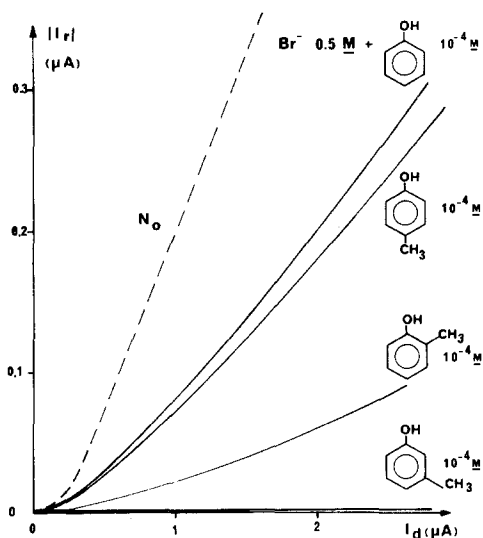However, for low I_d, I_r versus I_d curves are

Fig. 4. I_r versus I_d curves obtained with 10^{-4} M solutions of phenol, para-, ortho-, and meta-cresol. Gold ring-carbon disc electrode (No. 1), H_2SO_4 1 N, Br^- 0·5 M, $W = 28·6$ Hz, 25°C.

reproducible and depend on C. Titrations are therefore possible but the slope N_K at $I_d = 0$, which depends also on W and the bromination kinetics, must be significantly different from zero and from N_0. Table 1 presents, for one of our electrodes, the concentration ranges of these phenols which give

$$0·1\, N_0 < N_K < 0·9\, N_0,$$

W being taken in the range 4–80 Hz. In these conditions, the accuracy of the titrations is about 10–20%, when the I_r versus I_d curves are linear enough i.e. when C is larger than about 2×10^{-6} M.

2.3. Hydroquinone.

I_r versus I_d curves have the usual shapes of the titration curves obtained with chemicals which react very rapidly with bromine, but the value $I_{d,0}$ of I_d at which the asymptotical part of the curve crosses the I_d axis is much smaller than predicted by the theory, and the slope of the curves near the origin may not be equal to zero. In fact, the shape of the curves is not related to the bromination of hydroquinone (the rate of which is not high enough though the reaction seems instantaneous when solutions of these compounds are mixed), but to its oxidation on the disc prior to the oxidation of bromide. This appears clearly on the

current-potential curves of solutions of both hydroquinone and bromine: at low I_d, hydroquinone is oxidized instead of bromine and the limiting diffusion-current has approximately the same value as $I_{d,0}$. As I_r versus I_d curves depend on C, titrations are still possible, but the detection limits and the accuracy of the method are those of simple voltammetry on a rotating disc electrode.

The slopes of the I_r versus I_d curves may not be equal to zero when I_d is smaller than $I_{d,0}$ because, as with pyrogallol, the oxidation product of hydroquinone may be detected on the ring.

3. Bromination rate constant determinations

3.1. Theory

When the intermediate species generated on the disc reacts by a first-order or a second-order reaction, the reaction rate constant may be calculated [3a, b].

3.1.1. First-order bromination reactions. When the concentration level of the electrochemically generated species is low enough in comparison with C near the electrode, second order reactions, the rate of which can be written

$$-\frac{d(Br_2)}{dt} = k_2(Br_2)\,C$$

become apparent first-order reactions, $k_2 C$ being constant. With low values of I_d, I_r versus I_d plots are straight lines, the slopes of which, N_K, depend on the rotation speed W, on k_2, on C, and on the characteristics of the electrode. But the curve N_K versus K with

$$K = 0·499,\, \nu^{\frac{1}{6}} D^{-\frac{1}{6}} k_2^{\frac{1}{2}} C^{\frac{1}{2}} W^{-\frac{1}{2}}$$

depends only on the geometrical parameters of the electrode. Then the comparison of the experimental curve N_K versus $C^{\frac{1}{2}} W^{-\frac{1}{2}}$ with the theoretical N_K versus K curve calculated for the electrode gives k_2 when ν and D are known.

In fact, N_K versus $C^{\frac{1}{2}} W^{-\frac{1}{2}}$ curves (Fig. 5) were compared with only a part of the theoretical one, an approximate expression of which is

$$\mathrm{Log}\, N_k = \mathrm{Log}\, N_0 - aK + b - \mathrm{Log}\left(1 + \frac{1}{K+c}\right)$$

$$[3a]$$

Table 2. *Geometrical characteristics of ring-disc electrodes used – calculated and measured collection efficiency N_0 – values of coefficients a, b and c used in the analytical expression of N_K as a function of K*

	Gold-ring carbon-disc electrode (No. 1)	Platinum-ring platinum-disc electrode (No. 2)
r_1 (radius of disc electrode)	1.37 ± 0.04 mm	3.56 ± 0.06 mm
r_2 (inner radius of ring electrode)	1.65 ± 0.04 mm	3.73 ± 0.06 mm
r_3 (outer radius of ring electrode)	1.91 ± 0.04 mm	4.77 ± 0.05 mm
Calculated[†] N_0	0.269 ± 0.020	0.398 ± 0.015
Observed N_0	$0.280^* \pm 0.006$	$0.401[‡] \pm 0.011$
a	–	2.08
b	–	1.74
c	–	-0.18

* Average of eight experiments at $W = 28.6$ Hz, Br^- 0.5 M and ring-potential $+0.45$ V/N.H.E. with Br_2/Br^- system.

[†] Theoretical equation from [3d]

[‡] Average of eight experiments at various W, (Br^-), and ring-potential $+0.2$ V/N.H.E., with Br_2/Br^- system.
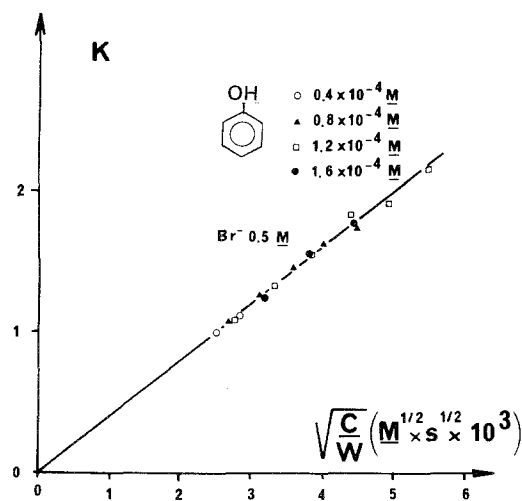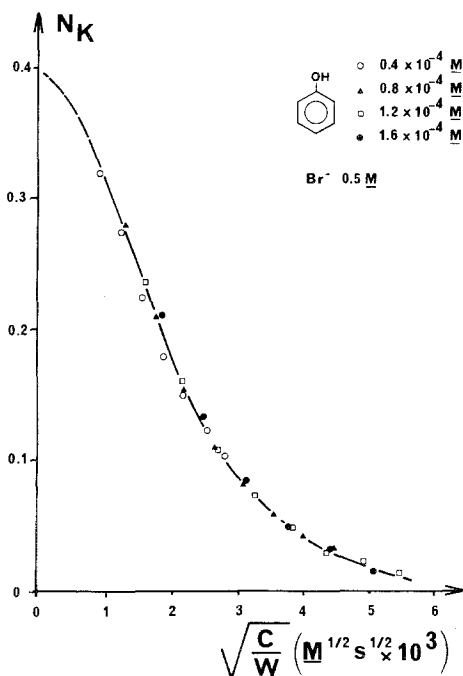

Fig. 5 and 6. Apparent first-order rate constant determination: bromination of phenol. W range 4–50 Hz. Platinum ring-platinum disc electrode (No. 2), H_2SO_4 1 N, Br^- 0.1 M, 25°C.
Fig. 5. Experimental slope N_K versus $C^{\frac{1}{2}} W^{-\frac{1}{2}}$.
Fig. 6. K versus $C^{\frac{1}{2}} W^{-\frac{1}{2}}$ respectively calculated and measured for observed N_K values.

where a, b and c are numerical constants which have been calculated as a function of the geometrical parameters of the electrode [3c]

(Table 2). Values of K, plotted against $C^{\frac{1}{2}} W^{-\frac{1}{2}}$ for various N_K give a straight line, the slope of which is related to k_2 (Fig. 6).

Table 3. Overall bromination rates of some compounds. Platinum-platinum ring-disc electrode (No. 2)

Compound	T (°C)	(Br^-) (M)	(H^+) (M)	k (M^{-1} × s^{-1})	Reaction order
Anisole	0	0·2	10^{-3}	$1·4 \times 10^3$	1
m-cresol	0	0·5	2	$6·8 \times 10^5$	1
o-cresol	0	0·5	2	$4·6 \times 10^4$	1
Phenol	0	0·5	2	$1·5 \times 10^4$	1
	25	0·1	1	$6·4 \times 10^4$	1
	25	*	0·2	$1·8 \times 10^5$ (10)	
Allyl-alcohol	20	0·1	$5·6 \times 10^{-4}$	2×10^5	2
	25	0·1	$5·64 \times 10^{-4}$	$7·2 \times 10^5$ (3b)	2

* extrapolation to $(Br^-) = 0$

3.1.2. Second-order bromination reactions.

When k_2 is very high, the reacting compounds cannot exist simultaneously outside of a narrow volume at the border of two regions: one where bromine alone is present and one where the compound reacting with bromine alone is present. (Br_2) and C vary around the electrode and the reaction is really second-order.

I_r versus I_d curves present the usual shape observed with As (III) and polyphenols and the determination of k_2 is related to the measure of the ring current $I_{r,k}$ at which the reaction zone just reaches the ring [3b].

3.2. Results

3.2.1. First-order bromination reactions.

With anisole, I_r versus I_d plots are straight lines as found by Albery, Hitchman and Ulstrup [7]. With phenol, ortho- and meta-cresol, I_r versus I_d traces are slightly curved even at high recording sensitivities, due to the too high bromination rates of these compounds. Nevertheless, we applied first-order kinetics theory, using the slopes of the curves at the origin.

Table 3 gives the bromination constants k_g observed for anisole, phenol, ortho and meta-cresol. These are overall constants taking into account bromination by Br_2 and Br_3^-:

$$k_g = \frac{k_2^{Br_2} + k_2^{Br_3^-} \times k \times (Br^-)}{1 + k \times (Br^-)}$$

with

$$k = \frac{(Br_3^-)}{(Br_2) \times (Br^-)} = 20\ M^{-1}\ \text{at } 0°C. \quad (10)$$
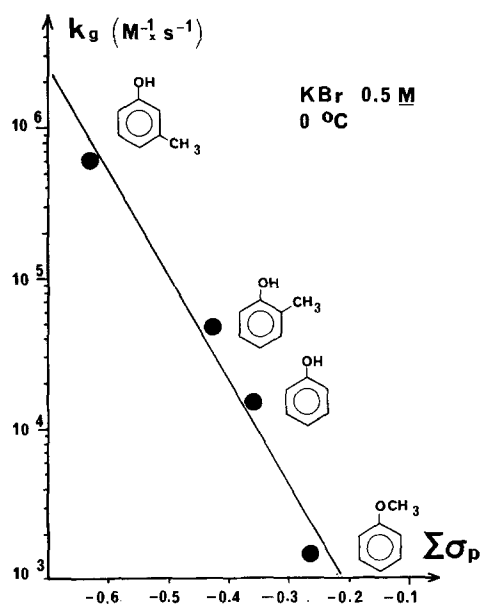

Fig. 7. Correlation between bromination constants and σ_p coefficients (8, 9) for m-cresol, o-cresol, phenol and anisole. Apparent first order bromination rate constant. Platinum ring-platinum disc electrode (No. 2), H_2SO_4 2 M, Br^- 0·5 M (except for anisole: $HClO_4$ 10^{-3} N, Br^- 0·2 M).

In Fig. 7, we have plotted k_g observed for several phenols versus Hammet [8] and Jaffe [9] coefficients for a para bromination. A straight line is observed showing that bromination occurs mainly in the para-position and that the σ_p used are suitable to take into account the effects of substituents on the overall reactivity with bromine.

3.2.2. Second-order bromination reaction.

Though we have checked the method with allyl-alcohol and recovered data already published [3b]

(Table 3), no determination of k_2 was possible for resorcinol, phloroglucinol and orcinol because curves obtained with these phenol differ significantly from the theoretical ones.

4. Discussion

Compounds which react rapidly with bromine (resorcinol, orcinol, pyrogallol, phloroglucinol, meta-cresol) can be detected and titrated in very dilute solutions, using ring-disc electrodes. However, these bromination reactions are very complex, especially with dihydroxy 1, 3 phenols which undergo several following brominations at different rate-constants, and it is not possible to directly determine the concentration level from the mathematical analysis of the I_r versus I_d curves: this is only possible in the case of a fast bimolecular reaction. Besides, the electrochemical oxidation of the titrated compound on the disc and the detection of its oxidation product on the ring may sometimes interfere with the bromination reaction. So, for these two reasons, titrations should be carried out by comparison of the experimental curves with those obtained with solutions of known concentration.

With phenol, ortho and para-cresol, which react less rapidly with bromine, the sensitivity is somewhat lower and difficulties arise from the oxidation products of these phenols which interfere with the disc-surface when the disc-current is too high.

To conclude; in spite of these difficulties, we think that the use of ring-disc electrodes may be a convenient method for the titration of very dilute solutions of phenols. For example, this method could be used to detect phenolic compounds as pollutants in rivers or in industrial wastes in which they are very often found.

Moreover, we think that ring-disc electrode techniques could lead to the definition of new water pollution criteria such as, for example, an amount of substances reacting rapidly with bromine. Sulphides, thiols, alkyl sulphides and disulphides can be similarly titrated by this method [11].

5. Experimental

5.1. Reagents

Water was distilled in a glass vessel. Unless otherwise specified, all chemicals used were Prolabo compounds. The following compounds have been used without further purification: sulphuric acid (RP), potassium bromide (RP), triarsenic oxide (RP), resorcinol (RP), orcinol (crystallised), phloroglucinol (RP), pyrogallol (Fluka, pure), hydroquinone (Touzart et Matignon, pure). The following compounds have been distilled under atmospheric pressure: ortho-, meta-, and para-cresol, anisole, allyl alcohol (for scientific use).

5.2. Materials

A Tacussel bipotentiostat (Bipad type), and a Tacussel monitor (Servovit type) enable linear sweeps of the disc-potential or the disc-current (the ring being set at a constant potential) or linear sweeps of the ring potential (the disc-potential or the disc-current being constant) to be made. The disc- or the ring-potential is measured with respect to a Ag/AgCl, saturated KCl electrode (Tacussel, AgCl 10) with an electronic millivoltmeter (Tacussel S 6 N). A Servogor XY Goertz enables the simultaneous recording of two variables among: ring- and disc-current, ring- and disc-potential.

A gold ring-carbon disc electrode (No. 1) was purchased from Tacussel whereas platinum-platinum ring-disc electrodes (No. 2) were constructed by Coquelet (Electricité de France).

Table 2 indicates the characteristics of the ring-disc electrodes. Diameters have been measured from photographic enlargements where a length reference also appeared (slide calipers opened at 1 ± 0.05 cm).

The rotation speed of the direct-current motor which drove the electrode was monitored by a Tacussel Asservitex, between 4 and 80 Hz. The rotation speed was checked with a Jaquet revolution counter.

The 350 cm^3 cell used was generally thermostated at $25.0 \pm 0.2°$C.

5.3. Procedure

The ring-disc electrode surfaces were polished using emery papers before every sequence of recordings, and were submitted to repeated sweeps of potential or current until a reproducible blank was obtained with a solution of potassium bromide. The current or the potential sweep rate was chosen so that scans in the cathodic or the anodic directions agreed with one another (usually 100 s per sweep). When the disc was monitored for current, the ring-potential was adjusted at a suitable value to obtain a low ring-current background when $I_d = 0$. The ring-potential was always low enough to allow the complete reduction of bromide. Under these conditions, the calculated N_0 is in very good agreement with the observed N_0 (Table 2). I_r versus I_d blank straight lines may be curved near the origin. This behaviour is more important with the gold-carbon electrode than with the platinum-platinum electrode. With these latter electrodes, this phenomenon is negligible at room temperature but appears clearly at $0°C$.

Acknowledgments

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