

results in the formation of a stable 18-electron conjugated ring system, which obeys the Hückel rule ( $N = 4n + 2$ , where  $n = 4$ ).

- Bykov's semi-empirical equations have been used to calculate the  $\pi$ -electron charges of the C-N, C'-C', and C-C' bonds. The phthalocyanine molecule is shown to contain isolated (independent) conjugated systems — the macroring and the benzene rings — which have weak  $\pi$ -electron bonding with one another.
- The main conjugation contour in  $H_2Pc$ , which determines its optical and other properties, is the porphyrane macroring. Calculation of the  $\pi$ -electron charges on the bonds has shown the high (>50%) degree of participation in the conjugation of electrons from unshared pairs on the nitrogen atoms.

## OVERVOLTAGE IN THE ANODIC EVOLUTION OF CHLORINE ON GRAPHITE. I. INFLUENCE OF pH

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The overvoltage attending the evolution of chlorine has been repeatedly investigated. Most workers have used platinum anodes, and their results do not warrant detailed discussion. The only noteworthy contributions among these<sup>1-3</sup> put forward arguments in favour of slow discharge of the  $Cl^-$  ion, and give a detailed study of the inhibition of this process by adsorbed oxygen.

Most of the work on the overvoltage of chlorine on graphite has been of an applied nature, and has not dealt with the mechanism of the electrode reaction: the results of this work are summarised elsewhere<sup>4,5</sup>. Ksenzhek and Stender<sup>6,7</sup> have published a series of papers highly relevant to an understanding of the processes occurring at a graphite anode. Their quantitative discussion of the operation of a porous graphite electrode is based on Ioffe's suggestion<sup>4,8</sup> that the ohmic potential drop in the electrolyte filling the graphite pores can account for a decrease in the true current density deep within the electrode. This investigation was not aimed at the mechanism of chlorine evolution, however. Some other recent papers<sup>9-11</sup> are also not concerned with the mechanism of chlorine evolution. Various other papers<sup>12-17</sup> relate to the oxidation of anodes under conditions where chlorine is preferentially evolved, although they do not deal with measurements of chlorine overvoltage.

Ksenzhek and Stender consider only those processes for which the true current density varies with overvoltage according to the law

$$i = 2i_0 \sinh \frac{\alpha \eta F}{RT}, \quad (1)$$

where  $i_0$  is the exchange current and the other symbols have their usual significance.

Although this is quite a common case, a much more general expression is

$$i = i_0 \left[ \exp \frac{\alpha \eta F}{RT} - \exp \left( \frac{(\lambda - \alpha) \eta F}{RT} \right) \right], \quad (2)$$

in which the expressions for the anodic and the cathodic current are not assumed symmetrical. In Eqn. (2),  $\alpha$  is the transport number, and  $\lambda$  is the number of electrons crossing the electrode-solution interface during the course of one slow event of the reaction.

Following the conclusions of Ksenzhek and Stender<sup>6</sup>, and starting from Eqn. (2), we have obtained the following equation for the polarisation curve:

$$I = \sqrt{\frac{2S i_0 RT}{\rho F}} \left[ \frac{\exp \frac{\alpha \eta F}{RT}}{\alpha} + \frac{\exp \left( -\frac{(\lambda - \alpha) \eta F}{RT} \right)}{\lambda - \alpha} - \frac{1}{\alpha} - \frac{1}{\lambda - \alpha} \right]^{1/2}, \quad (3)$$

where  $S$  is the pore area in  $1 \text{ cm}^3$  of the anode, and  $\rho$  is the specific resistance of the electrolyte in the pores (allowing for pore cross-section and tortuosity).

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At high polarisations the equation becomes

$$\eta = -\frac{2RT}{\alpha F} \ln \sqrt{\frac{2S_0 RT}{\rho \alpha F}} + \frac{2RT}{\alpha F} \ln I = \frac{2RT}{\alpha F} \ln \frac{I}{I_0}, \quad (3')$$

as found earlier by Ksenzhek and Stender<sup>6</sup> the Tafel  $b$  coefficient for a porous electrode is higher than that for a smooth electrode by a factor of 2. The conclusion is true for any real value of  $b$ , not just for  $b = 118$  mV (or  $\lambda = 2.59$  mV), which would correspond to Eqn. (1).

At low polarisations, retaining only the first three terms of the series expansion of the exponentials, we find

$$I = \sqrt{\frac{S_0 F}{RT}} \sqrt{\lambda} \eta. \quad (3'')$$

Eqns. (3)-(3'') are converted into the corresponding equations of Ksenzhek and Stender by putting  $\alpha = \lambda/2$ .

Eqns. (3') and (3'') suggest a method for determining the number of electrons consumed in the slow stage of the reaction:

$$\lambda = \left[ \frac{1}{I_0 \left( \frac{d\eta}{dI} \right)_{I \rightarrow 0}} \right]^2 \frac{RT}{F} b. \quad (4)$$

Eqns. (3) and (4) will be used to analyse the experimental results.

## EXPERIMENTAL†

Hydrochloric acid (of "chemically pure" or "analytical reagent" grade) and water were redistilled twice; NaCl of "chemically pure" grade was precipitated from solution in double distilled water by adding concentrated hydrochloric acid of "high purity" grade, and dried at 80–100°C; Na<sub>2</sub>SO<sub>4</sub> of "chemically pure" grade was recrystallised from doubly distilled water and dried. The Fe<sup>3+</sup> ion was introduced into the solutions by anodic dissolution of Armco-iron in a solution of the required composition.

The entire glassware was cleaned by several days' soaking in alkaline permanganate solution, followed by purified hydrochloric acid.

The electrolysis cell is shown diagrammatically in Fig. 1. Its main feature is the absence of separate anodic and cathodic compartments. However, depolarisation of the anode by cathodic products is impossible, since the cathodic reaction is the reverse of the anodic reaction: reduction of Cl<sub>2</sub> to Cl<sup>-</sup>. To exclude H<sub>2</sub> evolution, the cathodic reaction was made to take place at the lowest possible current density — approximately 50 times lower than the anodic current density. Chlorine gas, prepared in an auxiliary U-shaped electrolysis cell, was passed through the solution in a continuous stream in order to keep it saturated with chlorine. The cathode potential remained approximately 1 V more positive than the equilibrium hydrogen potential for the solution, thus showing that hydrogen evolution was not taking place. Before use, the graphite electrodes were cleaned by boiling for several days in frequently renewed purified hydrochloric acid until they ceased to colour the solution, and then in doubly distilled water.

The anode was a graphite rod 8 mm in diameter and several cm long, cut from a saturated "DEZ" electrode

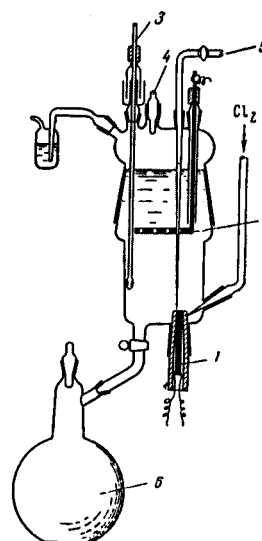


Fig. 1. Diagram of electrolysis cell: 1) anode; 2) cathode; 3) stirrer; 4) opening for introducing auxiliary anode; 5) capillary connection to reference electrode; 6) solution reservoir.

plate. The length of the rod was at least ten times greater than the "effective electrode thickness" for chlorine evolution<sup>6,7</sup>, and therefore Eqns. (3) and (4), which were derived on the assumption of an infinitely thick electrode, can be applied to our experimental results. The anode was tightly held in a Teflon bush, so that its cylindrical surface was insulated. The conical section of the bush fits hermetically into a ground joint provided in the lower part of the cell. Thus, the working surface of the anode is horizontal, which facilitates the detachment of gas bubbles.

The current-carrying lead and the potential-measuring contact to the anode were made from two tantalum tapes, tapered at the ends, tightly inserted into small holes drilled in the anode. (Platinum contacts had proved unsatisfactory in the presence of a chlorine-saturated acidic solution.)

The electrolytic contact consisted of a thin, flexible capillary, 0.3–0.5 mm in diameter, introduced from above and firmly pressed against the anode. The anode potential was measured against that of a saturated calomel electrode. At the end of each polarisation run, the potential was measured under open-circuit conditions, i.e. the equilibrium potential under the conditions of the experiment was determined†. This was subtracted from the potential measured in the presence of anodic current to give the value of the overvoltage.

Before a polarisation run, the solution was purified by electrolysis, using an auxiliary graphite anode. Electrolysis was continued for several days, with mechanical stirring to facilitate the removal of impurities from the

† In some experiments the equilibrium potential was measured both before and after the main measurements, and it was also measured against the other graphite electrode (the cathode) and against an auxiliary platinum electrode. The scatter was usually 2–3 mV, and rarely exceeded 5–6 mV.

† G. L. Melikova helped to devise the procedure.

solution. A fresh aliquot of the solution was purified in the absence of the working electrode. A series of polarisation curves was usually measured in one of the solutions, with further (16–18 h) electrolytic purification of the solution after each curve. As a rule, the additional purification had no effect on the results.

Potentials were measured on a PPTV-1 potentiometer, currents on an M-104 multirange ammeter. For the lowest ranges, an MA750/5 microammeter was used. (Both instruments were of the 0.5 precision class.) The curves were explored both from high to low current densities and vice-versa. The discrepancy between the curves for increasing and decreasing current was quite random, and was seldom greater than 5–10 mV. The electrode was kept at each current density for 20–40 min (1.5–2 h at the beginning of the plot), and a constant potential was observed for at least 20 min.

It follows from the theory of the operation of a porous electrode that the distribution of current density in the depth of the anode is a function of the electrical conductivity of the electrolyte. Therefore, it is more correct to compare polarisations in different solutions at overall current densities proportional to the square root of the solution conductivity [see Eqn. (3)]. In order to introduce the required corrections, we have measured the electrical conductivity of acidified NaCl solutions of different compositions by a constant-current four-terminal method<sup>18</sup>. Our results are in satisfactory agreement with published data<sup>4</sup> for weakly acid solutions.

## DISCUSSION

Fig. 2 shows the polarisation curves obtained with three different specimens of graphite in a strongly acid NaCl solution ( $\kappa_{\text{Cl}^-} = 4.4$ ,  $\kappa_{\text{H}^+} = 1.5$ ), i.e. under conditions which effectively preclude oxygen evolution. The first curve for a given graphite specimen (curve 1) lies somewhat below the subsequent curves. When the next curve is plotted, the overvoltage rises, but eventually it reaches a value which stays practically constant even after 30 hours' electrolysis. The final overvoltage values for different graphite specimens are fairly close to each other (curves 2–4) and in satisfactory agreement with published data<sup>6</sup> for DEZ anodes<sup>8</sup>.

Since the anode suffers considerable oxidation in the industrial electrolytic process, it was thought desirable to investigate the kinetics of chlorine evolution also on a similarly oxidised surface. To this end, the graphite specimen used to measure curves 1 and 2 was anodised for a certain time in a weakly acid solution, which is known to cause oxygen evolution. The same anode was then used to measure polarisation curves in a strongly acid solution (curves 5–7). As the figure shows, anodic oxidation of the surface produced a very significant change in the kinetics of chlorine evolution: there was a drop in overvoltage, and the slope of the polarisation curves became appreciably lower. Relatively short oxidation times produced an intermediate behaviour (curve 5), but after some time the anode developed a steady-state polarisation which was practically unaffected by very much longer oxidation (curves 6 and 7). This shows that the decrease in overvoltage is associated with a change in the nature of the

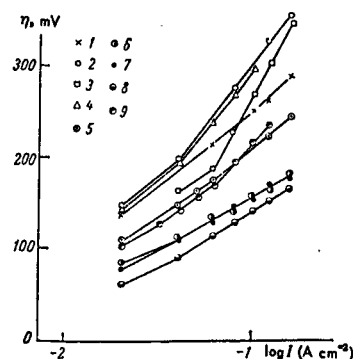


Fig. 2. Effect of graphite treatment on chlorine overvoltage in strongly acid solution:

- 1) electrode not oxidised anodically, specimen No.1;
- 2) ditto, final overvoltage values;
- 3) ditto, specimen No.2;
- 4) ditto, specimen No.3;
- 5) specimen No.1 after operation in a weakly acid solution ( $2300 \text{ C cm}^{-2}$  passed);
- 6) ditto ( $7000 \text{ C cm}^{-2}$  passed);
- 7) ditto ( $19400 \text{ C cm}^{-2}$  passed);
- 8) specimen No.2 after prolonged operation in a weakly acid solution;
- 9) specimen No.3 after careful cathodic reduction ( $6 \text{ C cm}^{-2}$  passed).

surface rather than with a gradual increase in true surface area.

It must not be thought, however, that an oxidised anode is covered with adsorbed oxygen whereas a fresh electrode is bare: we know that oxidation of a graphite surface in contact with air is unavoidable<sup>19–21</sup>. The difference in behaviour of the anode in the two cases can be explained by assuming that surface oxides of a different nature are produced by anodic oxidation and by high-temperature oxidation by atmospheric oxygen during manufacture of the anode. Anodic oxidation causes slow combustion of the surface layers of carbon with formation of  $\text{CO}_2$ . This must also remove the thermal oxides initially present on the graphite surface. As the oxidation proceeds, a stationary state is set up as soon as the layers of "anodic" oxide removed from the surface are replaced by new layers with identical properties. The profound influence upon the overvoltage of a change in the nature of the surface oxides present on a new electrode is made clear also by the following experiment. Anode No. 3 (curve 4) was subjected to thorough cathodic reduction. This caused a significant lowering of the overvoltage (curve 9), to a level close to that of anodically oxidised graphite.

The experiments described below were made with electrodes which had been pre-anodised in weakly acid solutions.

Fig. 3 shows the variation of overvoltage with solution acidity at constant current density<sup>†</sup>. There is a range of pH over which the overvoltage is practically constant,

<sup>†</sup> This includes the correction for electrical conductivity, mentioned above. The correction is appreciable only at high acidities, since the electrical conductivity of our solutions is practically constant at  $\text{pH} > 1$ .

<sup>§</sup> These workers also carried out anodic pretreatment of their specimens in a fairly acid solution of NaCl.

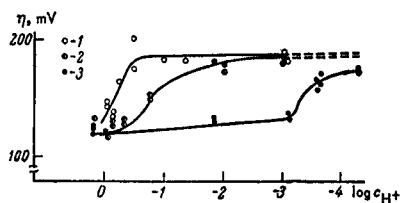


Fig. 3. Variation of overvoltage with acidity at the following chloride concentrations:

1) 1.5 N; 2) 3 N; 3) 4.4 N.

followed by a fairly sharp rise to a new stable level. The lower the chloride concentration, the lower the pH at which the inflection is observed.

This type of behaviour can be explained by assuming that at a given pH oxygen evolution sets in, as well as chlorine evolution, and that this inhibits the discharge of  $\text{Cl}^-$  (as reported for platinum anodes<sup>1-3</sup>). The evolution of oxygen is favoured by low chloride concentrations, which shift the potential of the chlorine electrode towards more positive values†.

This interpretation is supported also by the following observations. Addition of  $\text{SO}_4^{2-}$  ions, which is known to intensify the oxidation of graphite<sup>16,17</sup>, shifts the inflection to a much lower pH (see Fig. 4). We had previously suggested<sup>16</sup> that the effect of sulphate stems from the specific adsorption of this ion<sup>17</sup>, which causes a negative shift in  $\psi_1$  potential. On this model, addition of a specifically adsorbed cation could be expected to produce the opposite effect. The  $\text{Fe}^{3+}$  ion was chosen‡ as a typical cation showing specific adsorption. The results of Fig. 5 show that in the presence of  $\text{Fe}^{3+}$  the inflection occurs at a higher pH, i.e. the effect is opposite to that of sulphate. It is interesting to note that the addition of salts of another metal of the iron group (cobalt) has been proposed<sup>24</sup> for reducing anode deterioration in chlorine electrolysis. We

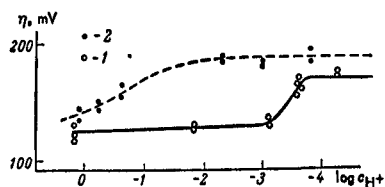


Fig. 4. Variation of overvoltage with acidity at 4.4 M concentration of chloride:

1) in the absence of sulphate;  
2) in the presence of 0.25 M  $\text{Na}_2\text{SO}_4$ .

† Another possibility is inhibition of oxygen evolution by  $\text{Cl}^-$  ions, since the critical pH increases with chloride concentration faster than required by the change in equilibrium potential only.

‡ Although we have no definite data on the adsorption of  $\text{Fe}^{3+}$ , we may assume that this ion is adsorbed on graphite, since most multiply charged ions show some surface activity<sup>22</sup>, and also because of the report<sup>23</sup> that graphite swells very considerably in ferric chloride.

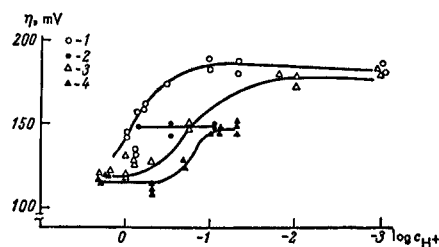


Fig. 5. Variation of overvoltage with composition in solutions of composition:

1) 1.5 g-ion litre<sup>-1</sup>  $\text{Cl}^-$ ;  
2) 1.5 g-ion litre<sup>-1</sup>  $\text{Cl}^-$ , 0.2 g-ion litre<sup>-1</sup>  $\text{Fe}^{3+}$ ;  
3) 3 g-ion litre<sup>-1</sup>  $\text{Cl}^-$ ;  
4) 3 g-ion litre<sup>-1</sup>  $\text{Cl}^-$ , 0.2 g-ion litre<sup>-1</sup>  $\text{Fe}^{3+}$ .

checked the effect of  $\text{Co}^{2+}$  on anode consumption by a method which we have previously described<sup>16</sup>, and found that addition of  $\text{Co}^{2+}$  to the electrolyte ( $3 \times 10^{-4}$  M) decreases anode consumption by a factor of  $\sim 1.5$  (acidity of anolyte 0.085 N, current density  $8 \times 10^{-2}$  A cm<sup>-2</sup>, temperature 80°C).

Increase of electrolyte temperature is often found to intensify the oxidation of anodes. The results of Fig. 6 show that the pH at which the inflection occurs (i.e. the pH of incipient oxygen evolution) is sharply decreased by increase of temperature. At 80°C it was usually impossible to find a region of pH where oxygen was not evolved.

Lastly, a direct proof of the appreciable oxygen evolution above the inflection pH can be obtained by measuring the acidity of the solution: as the experiment proceeds, the acidity increases significantly, but it remains constant when the pH is below the point of inflection.

We can conclude, therefore, that a single electrode process — chlorine evolution — occurs in the pH region below the critical value, and that oxygen evolution either does not occur or is so slow as to have practically no effect on the state of the surface over long periods. At higher pH values, appreciable amounts of oxygen are evolved in addition to chlorine: this alters the state of the surface in the sense of inhibiting chlorine evolution. The resulting surface oxides are labile, since the overvoltage returns to its initial low value on restoring the high solution acidity.

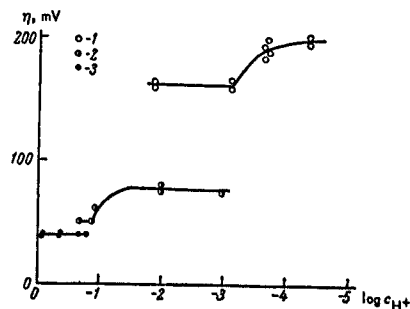


Fig. 6. Variation of overvoltage with acidity at different temperatures:

1) 25°C; 2) 60°C; 3) 80°C.

The mechanism by which oxygen affects the chlorine overvoltage may be twofold: a negative shift of the  $\psi_1$  potential or a decrease in the adsorption energy of chlorine. These two effects will be displayed to different degrees in different mechanism of chlorine evolution.

The similarity between the effects of oxygen upon chlorine evolution on graphite and on platinum has already been pointed out. There is one important difference between the two, however: on platinum the overvoltage increases monotonically with pH, pointing to an increase in the amount of oxygen on the anode surface<sup>1,2</sup>. On graphite, on the other hand, the overvoltage becomes constant and practically independent of pH after a sharp increase. Evidently, the concentration of oxygen adsorbed on graphite does not increase appreciably with pH, even though the oxygen evolution current increases<sup>16</sup>: practically the whole of the oxygen is evolved as CO<sub>2</sub>.

### SUMMARY

The variation of the overvoltage for chlorine evolution with solution acidity has been studied at various chloride concentrations in the presence of sulphate and of ferric ions and at different temperatures. Two pH regions in which the chlorine overvoltage is substantially different have been identified: the overvoltage is lower in the lower pH region, and vice versa. The increase in overvoltage is caused by the simultaneous evolution of oxygen and discharge of chlorine. Within each of these regions the overvoltage is practically independent of pH.

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### CRYOSCOPIC DETERMINATION OF THE MOLECULAR WEIGHTS OF BINARY LIQUID SYSTEMS WITH IMMISCIBILITY: GLYCEROL-NITROMETHANE, GLYCEROL-n-PENTANOL, AND n-PENTANOL-NITROMETHANE

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Our knowledge of the physicochemical relationship between the components of binary liquid systems exhibiting immiscibility is very inadequate. It is mainly confined to observations of the binodal curve, which separates the two-phase liquid region from the region of homogeneous solutions. Such empirical data, however, give only a qualitative picture of the solubility of liquid phases, and do not tell us whether the systems contain products of the mutual association of the component molecules, or what their composition is. To answer these questions, other methods of investigating liquid-phase systems must be brought to bear.

Studies of the solubility of liquid and solid phases, and of complete phase diagrams, have shown that interaction between the components can occur in binary systems exhibiting incomplete miscibility, since separation is observed