

INFLUENCE OF SULPHURIC ACID CONCENTRATION ON CURRENT YIELD OF PEROXODISULPHATE

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Overall anodic polarization curves and partial polarization curves of oxygen evolution and formation of peroxosulphates ($S_2O_8^{2-} + SO_5^{2-}$) were measured potentiostatically on a smooth platinum anode in 1–13M- H_2SO_4 at 25°C at a small degree of conversion of SO_4^{2-} to $S_2O_8^{2-}$ ions. The known dependences of the current yield of peroxodisulphate on the total concentration of sulphuric acid at various current densities were substantiated. The found results were used to explain mechanism of formation of $S_2O_8^{2-}$ ions, according to which in contrast to previous explanations the possibility of simultaneous discharging of SO_4^{2-} and HSO_4^- ions is considered with partial rates depending on the reaction conditions. A mathematical formulation of this mechanism is in qualitative agreement with experiments, an evidence for the probability of the mechanism. A correlation of the current yield with the actual concentrations of SO_4^{2-} and HSO_4^- ions at various temperatures helps to further elucidate the negative influence of the temperature on the current yield.

Electrochemical production of concentrated solutions of peroxodisulphuric acid and its ammonium salt as intermediate products in the electrochemical production of hydrogen peroxide^{1–3} maintains its significance in spite of the increasing production by auto-oxidation processes. The technical exploitation of peroxodisulphates and from them derived peroxomonosulphates increases also. The perfecting of the electrolytic manufacture of peroxodisulphates remains therefore actual^{4–12} together with theoretical studies^{13–15}, since certain problems are still unclear. This is understandable since the kinetics and mechanism of the parallel oxygen evolution is also not fully elucidated even at lower anodic potentials where the electrosynthesis of peroxodisulphates does not proceed^{16–19} yet. Measurements with the use of radioisotopes^{20,21} and more detailed kinetic measurements²² showed that peroxodisulphates are formed by discharging directly the SO_4^{2-} or HSO_4^- ions with no relation to oxygen evolution, but there is no unique opinion about the nature of the discharging ions. Some authors^{22–27} attribute the formation of peroxodisulphates to the discharging of HSO_4^- ions according to the conclusions of Efimov and Izgaryshev²³ on the basis of the dependence of the current yield on the actual concentration of SO_4^{2-} and HSO_4^- anions using the older Raman-spectroscopic data²⁸. More recently Smit and Hoogland¹⁴ after a similar correlation with newer Raman-spectroscopic measurements²⁹ arrived at the conclusion that the $S_2O_8^{2-}$ ions are formed by anodic discharge of SO_4^{2-} ions only, whereas the discharge of HSO_4^- leads to the Caro's acid, H_2SO_5 . They did not explain, however, the older observations^{23,30} that at lower than optimum current densities the maximum of the current yield is shifted towards higher concentrations of sulphuric acid at which the content of SO_4^{2-} ions decreases.

The present work is a contribution to this problem area with emphasis to the influence of sulphuric acid concentration on the initial formation rate of peroxo-sulphate ions.

EXPERIMENTAL

Apparatus: All measurements were carried out in a glass H-cell with anode and cathode compartment separated by a fritted glass disc. A smooth platinum anode according to Izgaryshev³¹ was formed by a disc of 0.5 mm thickness and 7 mm diameter whose one side was covered with glass. It was provided with a glass-coated platinum wire of 1 mm diameter as a current lead. In the middle of the disc there was a hole of 0.4 mm diameter serving as an orifice of a Luggin capillary placed on the glass-coated side and leading to a Hg/Hg₂SO₄ reference electrode in 5M-H₂SO₄. The salt bridge was provided with an auxiliary electrode for the measurement of the ohmic potential drop between the anode surface and the tip of the Luggin capillary by the interrupter method³². The electrochemically active surface area of the anode was determined by capacity measurement in the potential range 0.4–0.7 V against hydrogen electrode (R.H.E.) in the same solution. In this way the roughness factor was determined as $f_r = 1.5 \pm 0.07$ in good agreement with literature data for the anode surface treated as given below. The cathode was a platinum sheet of a large surface area (not specially treated).

Preparation of anode and electrolyte: Mechanical polishing was combined with electrochemical treatment. Lapping papers of No 0/0 to 8/0 were used with subsequent polishing with an emulsion of alumina No 3 on a cloth. After washing with distilled water, the electrode was polarised in the same solution as used in the measurement first at -0.1 V against R.H.E. for 30 min and then at $+2.1$ V for 30 min with the aid of a Wenking ST 72 potentiostat. Afterwards the solution was replaced by a fresh one and the measurement commenced.

Solutions of H₂SO₄ were prepared by diluting concentrated acid of reagent grade with distilled water without preelectrolysis, which was sufficient to attain reproducible results within the limits of experimental accuracy^{33,34}.

Measurement: After preparation of the anode and replacement of the electrolyte, the initial anode potential was set to 2.1 V (R.H.E.) and the current was measured. The current yields of both main anodic reactions, formation of oxygen and S₂O₈²⁻ ions, were determined both by chemical analysis of the anolyte (mainly at lower currents) and by measuring the anode gas volume (at higher currents). The rate of ozone formation was according to the previous work³⁵ considered negligible. The gas volume was measured both immediately after setting the chosen potential and after 15 min when a stationary value of the current was reached (the average from three subsequent measurements was taken). For a sufficient accuracy of the chemical analysis it was necessary to maintain the chosen potential at smaller currents for several hours. After taking a sample, the anode potential was increased to a further chosen value and the measurement was continued until a current of 1–2 A was reached. To check the reproducibility, in some cases the measurement of the polarization curve continued backwards. During the whole measurement, the electrolysed solution was quickly exchanged for several times without interrupting the polarization in order to keep the conversion of SO₄²⁻ to S₂O₈²⁻ ions and hence its influence on the current yield very small³⁶. The correction for the ohmic potential drop between the orifice of the Luggin capillary and the anode surface was determined by the interrupter method³² with the given solutions without awaiting the stationary value of the current. The measured anode potential included the liquid junction potential, E_j , between the measured solution (xM-H₂SO₄) and the reference electrode (5M-H₂SO₄). This was eliminated by measuring the poten-

tial difference between the reference and hydrogen electrode in various solutions of sulphuric acid, involving also the diffusion potential E_j . In this way the anode potential could be expressed against hydrogen electrode in the same solution (R.H.E.), as given in the present work. Small differences in the composition of the electrolysed solutions at a small conversion of SO_4^{2-} to $\text{S}_2\text{O}_8^{2-}$ were negligible as they were within the limits of accuracy of the measurement.

The current densities are referred to the working surface area of the platinum anode. The content of Caro's acid in the anolyte was with respect to the low degree of conversion not determined, hence the polarization curves of peroxodisulphates correspond to the formation of $\text{S}_2\text{O}_8^{2-} + \text{SO}_3^{2-}$. The temperature of measurement was $25 \pm 0.1^\circ\text{C}$.

RESULTS

The measured equilibrium potential differences of the cell with transference, $\text{Pt} | \text{Hg} | \text{Hg}_2\text{SO}_4 | \text{H}_2\text{SO}_4(5\text{M}) : (\text{H}_2\text{SO}_4(x\text{M}) | \text{H}_2 | \text{Pt}$, for various values of x are shown in Fig. 1 (curve 1); curve 2 represents the theoretical concentration dependence of the potential difference of the same cell but without transference calculated with the use of the published mean activity coefficients of sulphuric acid^{37,38} (the older data³⁹ valid up to a concentration of 17 m or about 9M are according to Covington and co-workers³⁷ not quite reliable). The difference of both curves gives the value of E_j .

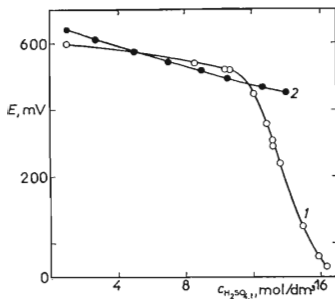


FIG. 1

Equilibrium Potential Difference of the Cell $\text{Pt} | \text{Hg} | \text{Hg}_2\text{SO}_4 | 5\text{M}\cdot\text{H}_2\text{SO}_4 : x\text{M}\cdot\text{H}_2\text{SO}_4 | \text{H}_2 | \text{Pt}$ as Function of x at 25°C

1 With transference; 2 without transference.

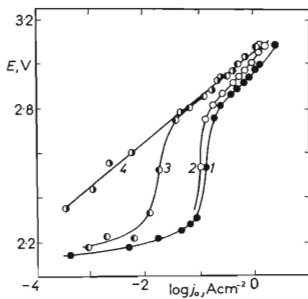


FIG. 2

Anodic Polarization Curves on Smooth Platinum in $5\text{M}\cdot\text{H}_2\text{SO}_4$ at 25°C

1 Overall anodic polarization curve; 2 partial anodic curve for oxygen evolution; 3 same for formation of peroxosulphates ($\text{S}_2\text{O}_8^{2-} + \text{SO}_3^{2-}$) from short-time gas analysis; 4 as 3 but from chemical analysis of anolyte after long-time polarization.

In the range of 1–6M-H₂SO₄ the E_j values are in the range from –40 to +12 mV and increase still somewhat with further increasing concentration of the acid. Beginning from about 10.5M-H₂SO₄, the difference between curves 1 and 2 becomes gradually smaller, at 11.7M attains zero and at still higher concentrations drops markedly. Hence it follows that although the polarization curves of peroxodisulphate formation are relatively less reproducible, the liquid junction potential between the measured solution and reference electrode must be taken into account. This was, however, disregarded in earlier works, causing possibly some disagreement among the experimental data of different authors.

Fig. 2 shows the overall anodic polarization curve 1 together with the partial polarization curve 2 of oxygen evolution and formation of peroxosulphates $S_2O_8^{2-} + SO_3^{2-}$ determined by gasometric measurements of relatively short duration (curve 3) and chemical analysis of the anolyte (curve 4). Differences between the last two curves are mainly in the potential region up to about 2.6 V and during measurement in the increasing order of potentials. Here besides the common surface oxide I (about one monolayer of Pt-O₂) a multilayer phase oxide II with different electrocatalytic properties with respect to oxygen evolution^{33,34} is formed at a rate lower by several orders of magnitude. If the duration of anodic polarization during gasometric evaluation of the current yield was so short that the amount of the formed oxide II was small or negligible, the formation of $S_2O_8^{2-}$ ions proceeded according to curve 3 which is similar in form to the overall curve and to the partial polarization curve of oxygen evolution as well. With increasing duration of polarization, the amount of the multilayer oxide II increased and a reorientation of the oxide I took place so that the surface of the platinum anode became gradually energetically stabilized^{40,41} and hence the polarization curve of persulphate formation changed in accord with the curve 4. In the nearly whole measured range of potentials it obeys the Tafel relation and at potentials higher than 2.6 V fuses with curve 3 obtained gasometrically after short-time polarization. Therefore, the form of curve 3 can be attributed to an energetically not quite stabilized surface of the platinum anode during short-time measurement in the increasing order of potentials, whereas curve 4 represents the studied process on a more stabilized anode surface. This is in the region up to about 2.6 V formed by a combination of oxide films I and II (or α and β according to the notation of other authors⁴²), and at still higher potentials by the energetically more stabilized monolayer oxide I. During measurement in the decreasing order of potentials there is a satisfactory agreement between the partial polarization curves of formation of $S_2O_8^{2-}$ ions found gasometrically and by chemical analysis. Therefore, the evaluation proper was based only on the partial curves corresponding to more stabilized surface according to curve 4.

A survey of the complete polarization curves and partial curves of peroxosulphate formation in 1–13M-H₂SO₄ is given in Fig. 3 (the partial curves of oxygen evolu-

tion were omitted to simplify the diagram). It is seen that both the complete and partial polarisation curves are shifted to higher anodic potentials with increasing concentration of the acid, which agrees with earlier results^{23,24}. We also confirmed the previous findings^{22,43} that whereas the complete and partial polarization curves of oxygen evolution show marked transition regions in which the Tafel equation does not hold, the partial polarization curves of peroxodisulphate formation can be expressed by this equation in a rather broad range of current densities. Only in solutions above about 6M-H₂SO₄ the polarization curves were at higher potentials bent toward still higher potentials as was similarly observed in the preceding work³⁴. It is also apparent from Fig. 3 that the Tafel slope, *b*, of the linear part of the polarization curve of peroxodisulphate formation increases from 0.2 to 0.3 with the acid concentration increasing from 2 to 13M. The polarization curve for this reaction in 13M-H₂SO₄ can no longer be expressed by the Tafel equation in a larger range of current densities.

In Fig. 4 is shown the dependence of initial current yield of peroxosulphates on total current density at various concentrations of the electrolyzed solutions. This dependence passes in most cases through a maximum which shifts with increasing concentration toward lower current densities. The highest current yield was obtained during electrolysis of 8M-H₂SO₄ at 0.35–0.40 A/cm² (i.e., 0.52–0.60 A/cm² of geo-

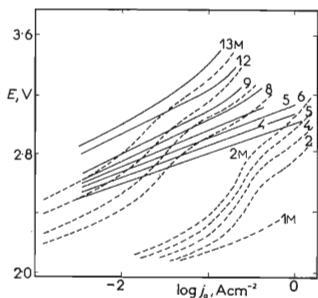


FIG. 3

Overall Anodic Polarization Curves (dashed) and Partial Polarization Curves for Peroxosulphate Formation (solid lines) on Smooth Platinum at 25°C in Various Solutions of H₂SO₄

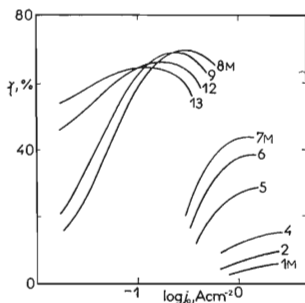


FIG. 4

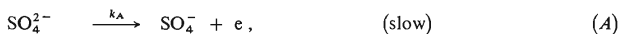
Dependence of Current Yield of Peroxosulphates ($S_2O_8^{2-} + SO_3^{2-}$) on Current Density in Various Solutions of H₂SO₄

metric surface area). The maximum current yield during electrolysis of 7, 9, and 12–13M-H₂SO₄ was attained at a total current density of 1.0, 0.3, and 0.1 A/cm² respectively.

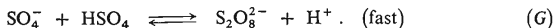
DISCUSSION

Two points of view exist at present, according to which S₂O₈²⁻ ions are formed by discharging either SO₄²⁻ (ref.¹⁴) or HSO₄⁻ ions^{22–27}, but not both simultaneously (although Bancroft⁴⁴ admitted this possibility). Interestingly enough, these different conclusions are based on the same correlation of the total current yield of peroxodisulphate on the actual content of sulphate and bisulphate ions at various concentrations of sulphuric acid. Their first, obviously not much accurate determination by Raman spectroscopy²⁸ led Efimov and Izgaryshev²³ to the idea of the primary discharge of HSO₄⁻ ions, which was accepted by other authors^{22,24–27}. Smit and Hoogland¹⁴, on the other hand, based their correlation on the newer measurements of Young and coworkers²⁹ which led them to the conclusion about formation of S₂O₈²⁻ ions by discharging only sulphate ions. However, neither by the first nor by the second mechanism it is possible to explain the mentioned observation^{23,30}, substantiated by our results (Fig. 5), that the maximum of the current yield is at lower than optimum current densities shifted toward higher concentrations of sulphuric acid, where the content of sulphate ions still decreases.

We therefore consider the concept that more probably both anions participate by their discharge in the formation of S₂O₈²⁻ ions:



The following recombination reaction is also not excluded:



The standard potentials⁴⁶ of both parallel reactions (C) and (F) suggest that the discharge of SO₄²⁻ ions is thermodynamically more feasible. The available kinetic

results show again that their discharge is more rapid than that of HSO_4^- ions. This is evidenced by the mentioned fact that the dependence of the maximum current yield of $\text{S}_2\text{O}_8^{2-}$ ions at the optimum current density on the total acid concentration is similar to the dependence of the actual content of SO_4^{2-} and not HSO_4^- ions on the acid concentration, although the latter ions are the prevailing form. This, of course, does not mean that the discharge of HSO_4^- ions does not participate in the formation of peroxydisulphate, especially at current densities smaller than the optimum.

Since the anodic processes (C) and (F) are according to the accepted view controlled by the electron transfer reactions (A) and (D), it is possible to express their rate as

$$j_C = 2Fk_A c_{\text{SO}_4^{2-}} \quad (1)$$

$$j_F = 2Fk_D c_{\text{HSO}_4^-} \quad (2)$$

The rate constants k_A and k_D are potential-dependent and may involve the constants of proportionality between the surface and volume concentrations of the discharging anions, which are unknown. The surface concentrations cannot be determined even from adsorption measurements with the use of radioisotopes^{47,48} since these do not

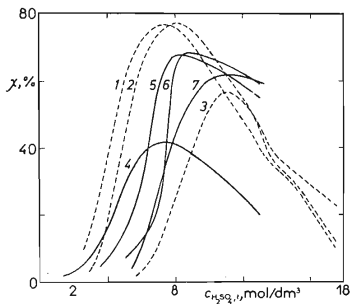


FIG. 5

Dependence of Current Yield of Peroxosulphates ($\text{S}_2\text{O}_8^{2-} + \text{SO}_3^{2-}$) on Analytical Concentration of H_2SO_4 at Different Current Densities

1 2 A/cm²; 2 0.75 A/cm²; 3 0.075 A/cm² (after ref.²³ at 7–10°C); 4 1 A/cm²; 5 0.5 A/cm²; 6 0.35 A/cm²; 7 0.1 A/cm² (present work at 25°C).

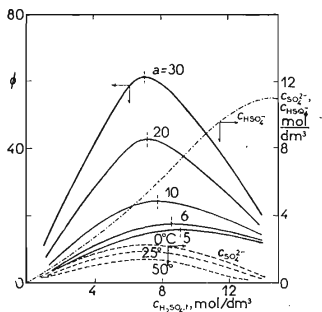


FIG. 6

Dependence of ϕ for Different Values of a at 25°C and Dependences of $c_{\text{SO}_4^{2-}}$ at 0, 25, and 50°C (ref.²⁹) and $c_{\text{HSO}_4^-}$ at 25°C (ref.^{29,45}) on Analytical Concentration of Sulphuric Acid $c_{\text{H}_2\text{SO}_4}$

distinguish the adsorbed reactants from the adsorbed products ($S_2O_8^{2-}$). The fraction of the total potential drop between the electrode and solution due to the oxide layer on the platinum anode and hence the potential difference influencing the anodic reaction rate is also not known. Nevertheless it is possible to discuss at least qualitatively the influence of the reaction conditions on the rate of the individual anodic processes.

Based on the concept about formation of $S_2O_8^{2-}$ by a simultaneous discharge of SO_4^{2-} and HSO_4^- ions the current yield of $S_2O_8^{2-}$ can be expressed as

$$\chi = (j_c + j_f)/j_a = 2F(k_A c_{SO_4^{2-}} + k_D c_{HSO_4^-})/j_a, \quad (3)$$

where j_a denotes total anodic current density which is considered constant, so that Eq. (3) can be rewritten as

$$\chi j_a / 2F = k_D (a c_{SO_4^{2-}} + c_{HSO_4^-}), \quad (4)$$

where

$$a = k_A / k_D. \quad (5)$$

The coefficient a depends probably on the value of j_a or on the anode potential E since the constants k_A and k_D are potential dependent, too. As they are unknown, Eq. (4) can be rewritten as

$$\chi j_a / 2F k_D = \phi = a c_{SO_4^{2-}} + c_{HSO_4^-} = f(a, c_{H_2SO_4}). \quad (6)$$

For chosen values of the coefficient a and known concentrations of the ions we thus obtain the dependence of ϕ on the analytical concentration of the acid $c_{H_2SO_4}$ (Fig. 6). It is seen that for $a \geq 20$ this dependence resembles that for the SO_4^{2-} ions concentration (shown by the dashed line). At lower values of a there is a shift of the maximum of ϕ toward increasing concentration of sulphuric acid. This shows that at $a \geq 20$ the $S_2O_8^{2-}$ ions are formed only by discharge of SO_4^{2-} and with decreasing ratio of $k_A/k_D = a$ the discharge of HSO_4^- also begins to play a role. A comparison of Fig. 6 with experimental results (Fig. 5) shows that the value of a diminishes with increasing acid concentration and decreasing current density (*i.e.*, lower anodic potential E).

This phenomenon can be elucidated by analysis of the dependence of the parameter a on the reaction conditions. From Eq. (5) and general equations of the electrode kinetics we obtain

$$\begin{aligned} a &= \langle k'_A \exp [2\alpha_A F(E - E_{r,c})/RT] \rangle / \langle k'_D \exp [2\alpha_D F(E - E_{r,f})/RT] \rangle = \\ &= a' \exp \langle 2F[\alpha_A(E - E_{r,c}) - \alpha_D(E - E_{r,f})]/RT \rangle, \end{aligned} \quad (7)$$

where

$$a' = k'_A/k'_D. \quad (8)$$

The rate constants k'_A and k'_D of the corresponding reactions are referred to their equilibrium potentials $E_{r,C}$ and $E_{r,F}$, respectively, α_A and α_D are the corresponding transfer coefficients. Generally two cases are possible. For $\alpha_A = \alpha_D = \alpha$ we obtain from Eq. (7):

$$(2.3RT/2F\alpha) \log(a/a') = E_{r,F} - E_{r,C}. \quad (9)$$

Accordingly, the coefficient a would depend only on the difference between the equilibrium potentials of reactions (F) and (C), *i.e.*, independent of the overall current density or anodic potential, which would be at variance with the experiments. For the coefficient a to increase with increasing current density or potential (at constant composition of the solution) it is necessary that $\alpha_A > \alpha_D$. The necessary difference between these quantities for a given variation of the coefficient a follows from Eq. (7) and is for a given change of the anodic potential from E_1 to E_2 corresponding to a change of the anodic overall current density from $j_{a,1}$ to $j_{a,2}$ (at a given solution composition) expressed as

$$\alpha_A - \alpha_D = [2.3RT \log(a_1/a_2)]/2F(E_1 - E_2). \quad (10)$$

For example, to change the anodic potential by 0.1 V (corresponding to a 2–3 fold change of the current density) and the coefficient a by the factor of 3 (*e.g.*, from 20 to 6.6 leading to a marked shift of the maximum of the parameter ϕ proportional to the current yield χ toward higher concentrations of the acid as in Fig. 6) it is necessary that $\alpha_A - \alpha_D = 0.14$, a plausible value.

The above conclusions derived from the simplified mathematical treatment of the concept about formation of $S_2O_8^{2-}$ ions by a simultaneous discharge of SO_4^{2-} and HSO_4^- ions with rates depending on the reaction conditions are in a qualitative accord with the experimental facts. A more detailed experimental proof is lacking mainly because of the much complicated influence of high anodic potentials on the reaction conditions of the electrode process and hence an inferior reproducibility of results.*

The correlation of the current yield of $S_2O_8^{2-}$ ions with the actual concentration of the discharging SO_4^{2-} and HSO_4^- ions in solutions of sulphuric acid leads to an

* The proposed mechanism of $S_2O_8^{2-}$ formation is supported also by the most recent work^{4,9}, which appeared after submitting our work for publication, where the formation of $S_2O_8^{2-}$ ions on a Ti-RuO₂ anode in the anodic oxidation of a mixture of (NH₄)₂SO₄ and H₂SO₄ is attributed to the discharge of SO_4^{2-} or HSO_4^- ions, hence a possible simultaneous discharge of both anions.

interesting conclusion about the influence of temperature on the current yield. The negative influence of temperature on the current yield of $S_2O_8^{2-}$ ions was usually attributed to an acceleration of the decomposition reactions of the primarily formed $S_2O_8^{2-}$ ions and to an acceleration of the parallel evolution of oxygen^{1-3,12}. From Raman spectroscopic measurements it follows²⁹, however, that the actual concentration of SO_4^{2-} ions decreases markedly with increasing temperature at constant concentration of the acid (Fig. 6). Hence it is obvious that the negative influence of temperature on the current yield of $S_2O_8^{2-}$ ions is partly due to a drop in the concentration of SO_4^{2-} ions, which are discharged much more rapidly. The maximum of the current yield is, however, at 25°C (our measurements) at the same concentration, about 8M- H_2SO_4 , as at 7–10°C (ref.^{23,30}), although the concentration of HSO_4^- ions increases with the temperature. This is in support of the mentioned assumption that — especially in the optimum concentration region — the discharge rate of SO_4^{2-} ions is many times higher than that of HSO_4^- , i.e., $k'_A \gg k'_D$.

Our thanks are due to Dr I. Paseka for stimulating comments.

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