

THE EFFECT OF HALIDES, PSEUDOHALIDES, AND SOME ORGANIC SUBSTANCES ON THE INITIAL RATE OF PEROXODISULPHATE FORMATION

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The effects of various additions of halides, pseudohalides and selected organic substances on the overall anodic polarization curves and the polarization curves of oxygen evolution and peroxodisulphate formation were examined under conditions of low degree of sulphate-to-peroxodisulphate conversion. Of the tested substances, SCN^- and CN^- ions, thiourea, urea and acetonitrile have proved to cause the greatest increase in the current yields of peroxodisulphate. However, the current yield varies as a function of the concentration of additive and the total current density, and goes through a maximum in both cases. The observed phenomena are discussed in terms of potential-dependent adsorption of additives or their oxidation products or intermediates on the oxidized surface of platinum anode.

It is well-known¹⁻³ that the current yield of electrolytic preparation of peroxodisulphuric acid or peroxodisulphates by anodic oxidation of concentrated solutions of sulphuric acid or its mixtures with appropriate sulphates may be increased appreciably by small additions of various compounds, among which are above all halides (especially fluorides and chlorides), pseudohalides (simple and complex cyanides and thiocyanates), urea and thiourea. A variety of other surfactants of various types have been tested¹⁻¹⁴. In spite of the fact that these compounds mostly undergo oxidation under the reaction conditions (anodic potential around 3.0 V, the presence of strong oxidizing agents), the effect they produce upon the electrolysis is a long-term one, persisting as long as several hours after their presence in the anolyte can no longer be proved analytically⁴⁻⁵. This has recently been explained in terms of strong adsorption of the original additives or their effective oxidation products or intermediates on the oxide-covered surface of platinum anode, causing the blockage of the active centres for the simultaneously occurring anodic oxygen evolution. Some authors^{9,10} have concluded that additives have either no or very small effect on the kinetics of anodic formation of peroxodisulphates. In a recent work⁵, in contrast, the rate of peroxodisulphate formation was found to vary with additions of SCN^- at constant anodic potential. In an earlier paper¹³, the effect of SCN^- ions was ascribed to stabilization of peroxodisulphate ions which was not discussed in any further detail.

There are some differences in the quantitative data on the concentration dependence of the resulting effect of the tested compounds. In some cases, such data are completely lacking. In a recent paper¹² the effect of additives has been expressed in terms of the so-called efficiency coefficient, $K = (\Delta I/I_0)_{E_a}$, defined as the ratio of the decrease in the total anodic current on addition of the compound under test to a basic 6M- H_2SO_4 solution to the original current without the additive at a constant anodic potential $E_a = 2.7$ V. However, this paper does not say whether

or not there is a definite relationship between the coefficient K and the current yield of peroxodisulphate. In spite of the variety of so far tested compounds, thiocyanates, sometimes in combination with chlorides, are the ones almost exclusively used in the industrial practice.

The quantitative comparison of the effects of so far tested additives on the process under study is hampered by the fact that the available data were mostly obtained under more or less different experimental conditions. Therefore we have reinvestigated the effects of selected substances under comparable conditions. The results obtained are reported in the present communication.

EXPERIMENTAL

Procedure: The experiments were performed with the use of the same all-glass apparatus that had been used in previous investigation of the influence of sulphuric acid concentration¹⁵ and some cations¹⁶ on the initial rate of anodic formation of peroxodisulphate. The working procedure and the pretreatment of the platinum anode was also essentially the same as previously described. The measurements were carried out on a 5 mol dm^{-3} - H_2SO_4 solution made up from distilled water and concentrated acid of analytical grade, to which tested substances of the same grade or recrystallized in addition were added in required amounts. In order to keep the degree of conversion of the sulphate to peroxodisulphate ions as low as possible ($\alpha < 0.05$), the solution in the cell was replaced periodically by a fresh one without interrupting the electric current. The potential of the current-loaded anode, maintained potentiostatically at a required value with respect to the reference electrode, was corrected for the IR voltage drop between the electrode surface and the tip of the Luggin capillary, which was determined by the interruption technique at the end of the measurement. The reference electrode was a $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode placed in the same $5\text{M}-\text{H}_2\text{SO}_4$ solution without additives. The electrode potentials quoted in this paper are referred to the equilibrium potential of hydrogen electrode in the same solution. Simultaneously with the potentiostatic measurement of the steady-state overall polarization curves, the current yields of anodic evolution of oxygen were determined gasometrically. The current yields of peroxodisulphate were calculated from the simplified relation $\chi_{\text{S}_2\text{O}_8^{2-}} = 100 - \chi_{\text{O}_2}$ (%). The ozone content of the anodic gas had been found negligible under the applied experimental conditions¹⁷. In some cases, the current yields of peroxodisulphate were determined also by chemical analysis of the anolyte. There was very good agreement, under steady-state conditions, between results of both methods. The current densities are related to the true surface area of the platinum anode determined by measuring the charging curves in the double-layer region; the roughness factor of the platinum anode treated by a previously described procedure¹⁵ was $f_r = 1.5 \pm 0.07$. All the measurements were performed at $25 \pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

Fig. 1 shows the overall polarization curves for the platinum anode and the partial polarization curves for the formation of peroxodisulphate in the $5\text{M}-\text{H}_2\text{SO}_4$ solution with 0.01M additions of halide and pseudohalide ions. The partial polarization curves of anodic evolution of oxygen, which can be constructed on the basis of the above given relation, have not been drawn in the figure for the sake of its clarity. The corresponding dependences of the current yield of peroxodisulphate on the total anodic current density, j_a , are represented in Fig. 2.

It is evident from Fig. 1 that additions of halide or pseudohalide ions do not alter the shape of the overall polarization curves and the partial polarization curves for peroxodisulphate formation. Within the measured potential range from 2.1 to 3.3 V (R.H.E.), both the overall polarization curves and the partial polarization curves for oxygen evolution show a characteristic S-shape for which the Tafel equation does not hold. As opposed to this, the partial polarization curves for peroxodisulphate formation satisfy the Tafel relationship over almost the whole potential range, and their slopes, $b = 0.15 - 0.16$, are in good agreement with previously published results^{15,16}. Only in the region of the highest potentials applied (around 3.3 V) do they show a slight deflection.

As a result of halide and pseudohalide additions, however, the overall polarization curves shift to lower current densities. The magnitude of the shift decreases in the order $\text{CN}^- > \text{SCN}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$, with the last anion in the series having already no effect on the position of the overall polarization curve of the basic

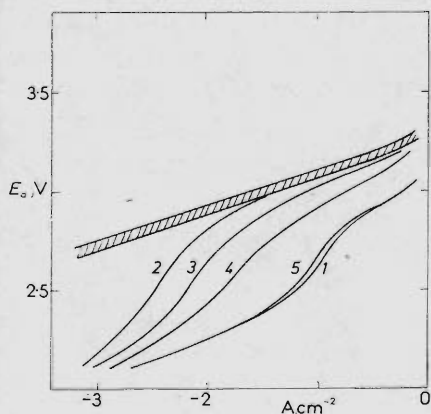


FIG. 1

Effect of additions of halide and pseudohalide ions (0.01 mol/dm^3) to $5\text{M-H}_2\text{SO}_4$ solution on the character of overall anodic polarization curves and partial polarization curves of peroxodisulphate formation (E vs. $\log j_a$). 1 basic solution; 2 SCN^- ; 3 F^- ; 4 Cl^- ; 5 Br^- . The hatched band denotes partial polarization curves of peroxodisulphate formation corresponding to the overall polarization curves 1 to 5

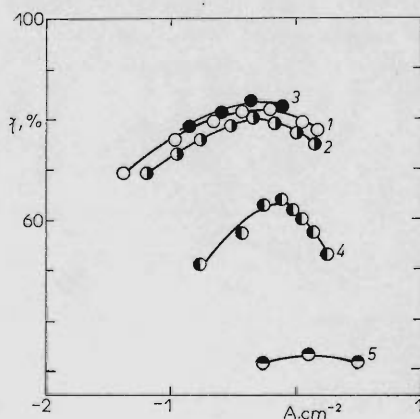


FIG. 2

Current yield of peroxodisulphate vs logarithm of total anodic current density at additions of halides and pseudohalides (0.01 mol/dm^3) to $5\text{M-H}_2\text{SO}_4$ solution: 1 SCN^- ; 2 F^- ; 3 CN^- ; 4 Cl^- ; 5 Br^- (the same as for the basic solution alone)

solution. On the other hand, the above additives have almost no effect on the partial polarization curves for peroxodisulphate formation since, owing to some scatter in the experimental data, the measured curves lie within a narrow band comparable with the limits of experimental accuracy. This finding is in agreement with previous observations^{9,10}. Hence it follows that halides and pseudohalides affect primarily the rate of the simultaneously occurring anodic evolution of oxygen.

As can be seen from Fig. 2, the plot of the current yield of peroxodisulphate against the total anodic current density goes through a maximum whose position depends on the nature and concentration of the additive. With increasing concentration of the halide and pseudohalide ions, the maximum shifts to lower current densities. The dependences of the current yield on the total current density for most of additives other than halides and pseudohalides have been found to follow an analogous pattern. The concentration of additives ranged from 10^{-3} to 10^{-1} mol/dm³, with the exception of cyanide solutions where concentrations below 10^{-2} mol/dm³ could only be used owing to desorption of gaseous hydrogen cyanide from the strongly acidic solutions.

Fig. 3 shows the variation of the maximum current yield with the concentration of halides and pseudohalides, derived from the dependence of the current yield on the total anodic current density. As seen from the figure, cyanides are the most effective additives in the concentration range below 10^{-2} mol/dm³. Slightly less effective

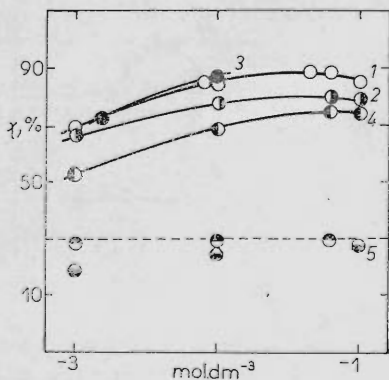


Fig. 3

Current yield of peroxodisulphate at the corresponding optimum current density as a function of logarithm of concentration of halides and pseudohalides in 5M-H₂SO₄ solution. The curves are assigned as listed in Fig. 2

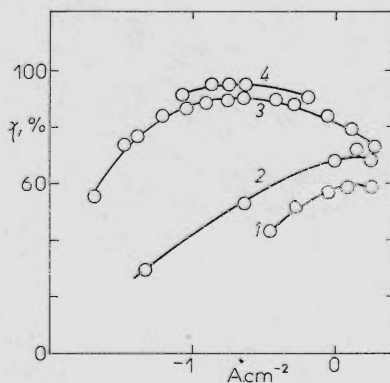


Fig. 4

Current yield of peroxodisulphate *vs* logarithm of total anodic current density at various additions of thiourea to 5M-H₂SO₄ solution: 1 $5 \cdot 10^{-4}$; 2 $1 \cdot 10^{-3}$; 3 $1 \cdot 10^{-2}$; 4 $5 \cdot 10^{-2}$ mol/dm³

are the SCN^- ions which give rise to a very flat maximum at a concentration of about $6 \cdot 10^{-2} \text{ mol/dm}^3$ under the reaction conditions applied. The efficiency of the halide ions decreases in the order $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$, which is in accord with their effects on the shift of the overall anodic polarization curve (see above). However, only the first two ions cause an appreciable increase in the current yield of peroxodisulphate as compared to results obtained with the $5\text{M-H}_2\text{SO}_4$ solution (broken line in Fig. 3). Similarly as the SCN^- ions, the halide ions produced fairly flat maxima in the concentration *vs* current yield plot at about $6 \cdot 10^{-2} \text{ mol/dm}^3$.

Table I gives data on the effects of selected organic substances. Here, optimum amounts of additives in the basic solution and the corresponding maximum current yields of peroxodisulphate and current densities have only been listed for clarity. The tests included various simple organic compounds containing nitrogen and sulphur, which had been known from earlier works¹⁻¹⁴ to increase appreciably the current yields of peroxodisulphate. Among these compounds were various aliphatic and aromatic amines, nitriles and isonitriles, cyanamide, amidoacetic acid, urea, and thiourea. Additional tests on the effects of siloxanes failed because these compounds proved to have little stability in the strongly acidic medium.

TABLE I

Maximum current yields of peroxodisulphate attained at optimum concentrations of tested additives in $5\text{M-H}_2\text{SO}_4$ solution, and the corresponding current densities, $j_{a,\text{max}}$, at 25°C

Additive	Formula	Concentration mol dm^{-3}	Max. current yield %	Current density $j_{a,\text{max}}$ A cm^{-2}
Urea	$\text{CO}(\text{NH}_2)_2$	0.02	92	0.15
Thiourea	$\text{CS}(\text{NH}_2)_2$	0.05	94	0.20
Propylamine	$\text{C}_3\text{H}_7\text{NH}_2$	0.01	66	0.5
Allylamine	$\text{C}_3\text{H}_5\text{NH}_2$	0.01	68	0.4
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	0.01	59	0.25
Tribenzylamine	$(\text{C}_7\text{H}_7)_3\text{N}$	0.01	28	0.2
Triaminotriazine	$(\text{CH}_2\text{NH})_3$	0.1	70	0.8
Cyanamide	CH_2N_2	0.01	73	0.8
Acetonitrile	CH_3CN	0.05	89	0.9
Propionitrile	$\text{C}_2\text{H}_5\text{CN}$	0.01	77	0.5
Butyronitrile	$\text{C}_3\text{H}_7\text{CN}$	0.01	62	0.5
Acrylonitrile	$\text{C}_2\text{H}_3\text{CN}$	0.01	77	0.6
Amidoacetic acid	$\text{NH}_2\text{CH}_2\text{COOH}$	0.01	87	0.9

Table I and Figs 4 to 7 clearly show thiourea, urea, acetonitrile and amidoacetic acid to be the most effective among the tested organic additives, thus confirming earlier observations on the effectiveness of these compounds. The less effective aliphatic and aromatic amines showed a trend toward decreasing effectiveness with increasing number of carbon atoms in the molecule. An addition of tribenzylamine produced current yields even lower than those observed in the basic solution. Nitriles proved to be more effective than amines, but showed an analogous dependence

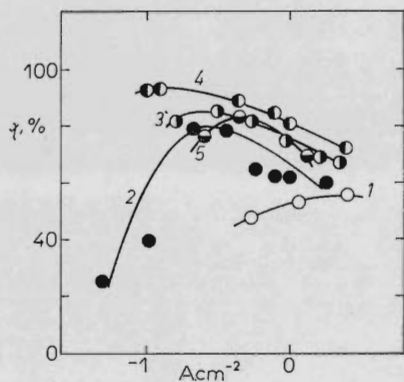


FIG. 5

Current yield of peroxodisulphate vs logarithm of total anodic current density at various additions of urea to $5\text{M-H}_2\text{SO}_4$ solution: 1 $5 \cdot 10^{-4}$; 2 $1 \cdot 10^{-3}$; 3 $1 \cdot 10^{-2}$; 4 $2 \cdot 10^{-2}$; 5 $5 \cdot 10^{-2} \text{ mol/dm}^3$

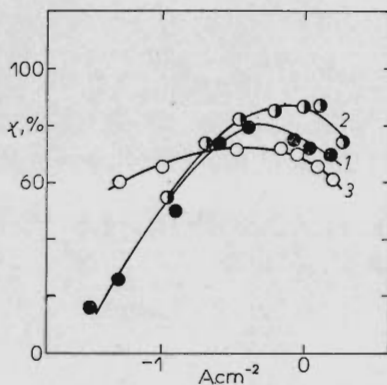


FIG. 6

Current yield of peroxodisulphate vs logarithm of total anodic current density at various additions of acetonitrile to $5\text{M-H}_2\text{SO}_4$ solution: 1 $1 \cdot 10^{-2}$; 2 $5 \cdot 10^{-2}$; 3 $1 \cdot 10^{-1} \text{ mol/dm}^3$

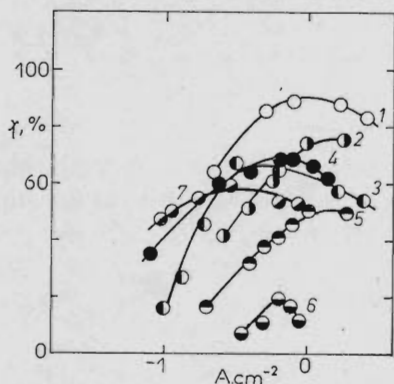


FIG. 7

Current yield of peroxodisulphate vs logarithm of total anodic current density at additions of some organic compounds in 0.01M concentration to $5\text{M-H}_2\text{SO}_4$ solution: 1 amidoacetic acid; 2 propionitrile; 3 butyronitrile; 4 triamine; 5 allylamine; 6 tribenzylamine; 7 aniline

of the current yield on the number of C-atoms in the molecule. Isonitriles were found to have the same effectiveness as n-nitriles.

Inspection of Figs 4 to 7 reveals that the current densities at which maximum current yields are attained for a given concentration of additive cover a range from 0.1 to 1.0 A cm⁻². With the most effective additives (urea, thiourea), the maxima in the initial current yields shift toward lower values of total anodic current density with increasing concentration of the additives, in analogy with the effect of halides and pseudohalides. However, urea and thiourea allow maximum current yields to be attained at current densities around 0.1 A cm⁻², in contrast to 0.4–0.5 A cm⁻² necessary when thiocyanates and cyanides are used. With acetonitrile (Fig. 6) maxima of current yields did not show any systematic dependence on the concentration of the additive; the optimum current densities ranged from 0.4 to 1.0 A cm⁻², increasing – unlike the above described cases – with increasing concentration of acetonitrile.

The results obtained allow several conclusions to be drawn. In the first place, it is evident that the conditions of electrolysis under which the individual additives produce maximum increase in the current yield differ to some extent in both the anodic potential and the total anodic current density. Consequently, comparative measurements at only one value of anodic potential or current density – as was the case in most of the earlier studies – do not permit definite conclusions to be made about the effect of the additive under test. Such measurements must be carried out over wide ranges of variables.

As has been shown, the current yield of peroxodisulphate goes through a maximum with increasing current density at a fixed concentration of additive, the maximum being most frequently relatively flat. This behaviour may be due to the fact that the amount of additive or its effective oxidation product or intermediate adsorbed on the platinum anode is dependent on the anodic potential. An increase of the potential (and hence also of the current density) above a certain value results in desorption of the species from the anode surface, thus enhancing the rate of the energetically more favourable anodic evolution of oxygen. It is also possible that, as a result of the increase in the anodic potential, the sorbed species undergo the anodic oxidation more rapidly, giving products that are subsequently desorbed from the anode surface, which leads to the same result. Moreover, both these possible processes would be enhanced by an increase in the actual temperature of the anode surface with increasing anodic potential, even though the temperature of the bulk of the anolyte is kept constant.

However, the plausibility of the suggested alternative explanations cannot be decided at the present time since detailed information on the composition of the species sorbed on the platinum anode surface at high anodic potentials is still lacking. Recent radioisotopic research¹⁸ on the adsorption of thiourea on platinum anode led to the conclusion that the adsorbed species is most probably the =C(NH₂)₂

radical, which is also formed when urea is involved. Analogous research of adsorption of Cl^- on platinum¹⁹ at high anodic potentials has indicated that at potentials above 2.2 V the amount of chlorine-containing adsorbed species is potential independent. The ratio of chlorine to oxygen chemisorbed under these conditions suggests that oxygen-containing compounds of chlorine are probably involved. This is on the whole consistent with earlier views regarding the formation of platinum oxyhalides on the surface of platinum anode²⁰.

The observed pattern of variation in the current yield with the concentration of active additive, involving a steep increase in the current yield followed by a flat maximum and subsequent very slow decline, may be explained in terms of gradual increase in the degree of surface coverage of the anode up to a limiting value which remains constant as the concentration of additive is further increased. The subsequent slower decline in the current yield has been explained as the result of chemical reaction between the additive and the peroxocompounds present^{21,22}, or of direct anodic oxidation of the additive^{23,24} which begin to predominate under the conditions.

The presented results do not permit conclusions to be made about details of the mechanism by which the additives under study affect the kinetics and mechanism of anodic processes occurring in peroxodisulphate electrosynthesis, which, in fact, was outside the intended scope of this work. However, the obtained data on the effects of the additives over wide ranges of anodic potentials and current densities under the conditions of peroxodisulphate electrosynthesis have provided a sufficient basis for identification of the most effective additives. Of inorganic ionic-type substances, these are thiocyanates, cyanides, fluorides and chlorides, while thiourea, urea, and acetonitrile have proved to be the most effective among the organic additives.

As a further step, these additives were tested in a laboratory-scale flow-through electrolyzer with the aim of determining their optimum amounts under various operating conditions. The results will be the subject of next communications.

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