REDUCTION WAVE OF THE TETRASULPHIDE ANION*

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The polarographic reduction of the tetrasulphide anion S_4^{2-} exhibits features analogous to those of the disulphide anion S_2^{2-}. The reduction wave is irreversible, of a similar shape, occurs in the same potential region, but is a 6-electron wave. The characteristics of both waves were also compared theoretically, the appropriate values of the kinetic constants were determined, and mechanisms of the electrode reactions were proposed.

In our previous paper[1] we studied the polarographic behaviour of Na_2S_2. On the polarography of Na_2S_4 two papers[2,3] were published; in both a distinct similarity in shape and potential region of the polarographic waves of S_2^{2-} and S_4^{2-} was found. Using 2·0M-NaOH as supporting electrolyte as with S_2^{2+}, Werner and Konopik[2] found two anodic waves with $E_{1/2} = -0·80$ V and $-0·58$ V, as well as a cathodic wave with a distinct maximum at the beginning, of an apparent $E_{1/2} = -1·4$ V (s.c.e.). They found that the ratio of the limiting cathodic currents for equimolar solutions of Na_2S_2 and Na_2S_4 in the presence of surfactants is 12 : 15. From this fact they concluded that the same electrode process takes place in both cases, namely the reduction of sulphur released by the disproportionation of polysulphide anion to sulphide anion in the solution:

$$S_x^{2-} \rightarrow S_{x-1}^{2-} + S; \quad S + 2e \rightarrow S^{2-}.$$
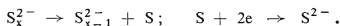
They use the assumption of an approximately equally slow dissociation of polysulphide anions to explain the approximate equality of the S_2^{2-} and S_4^{2-} wave heights.

Budnikov and coworkers[3] found that both S_2^{2-} and S_4^{2-} exhibit a cathodic and anodic wave in 3M-KOH and 2M-KNO₃. The $E_{1/2}$ of the S_2^{2-} cathodic wave slightly decreases with increasing concentration of the depolarizer in 3M-KOH from $-0·85$ V to $-0·89$ V, in 2M-KNO₃ from $-0·75$ V to $-0·87$ V. For S_4^{2-} the same values of $E_{1/2}$ were measured in the $-0·70$ V to $-0·84$ V range, dependent on the depolarizer concentration (both for 3M-KOH and for 2M-KNO₃). The authors further state that the sum of the heights of anodic and cathodic waves of Na_2S_2 is about half that of Na_2S_4. From analogies in the polarographic behaviour of S_2^{2-} and S_4^{2-} they assume that the cathodic process is due in both cases to reduction of the same particles of the depolarizer, —S—Hg—S—, which form could be formed on the electrode surface as the result of a fast chemical reaction:

$$-S-S- + Hg \rightarrow -S-Hg-S-$$

and which are subsequently reduced according to the final mechanism:

$$-S-Hg-S- + 2e \rightarrow Hg + 2S^{2-};$$

$$(-S-Hg-S-)_2 + 4e \rightarrow 2Hg + 3S^{2-} + S.$$
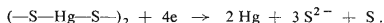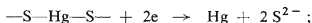
A not very detailed paper dealing with the polarographic behaviour of the pentasulphide appeared[10] as well. The pentasulphide was prepared, however, only *in situ*, by the action of iodine on the sulphide solution, which is not very suitable for these investigations.

The documentation of the papers quoted above is not sufficiently ample and the interpretation of the results is open to doubt, which has proved to be justified in the case of reduction of disulphides. In this paper we have studied the polarographic behaviour of S_4^{2-} as an example of a higher polysulphide in order to determine the validity of the quoted results and their interpretation.

EXPERIMENTAL

Na_2S_4 was prepared according to[4]. Quantitative analysis was used as a purity control: sodium was determined indirectly by argentometry, the content of so-called sulphidic sulphur by iodometry and the total sulphur content by gravimetric determination of barium sulphate[5]. The reserve reagent was stored in a vacuum dessicator over P_2O_5 at low temperature ($-30°C$).

All chemicals used were commercial products of analytical grade purity, except KCl which was used to study the effect of concentration of the indifferent electrolyte. In this case, twice recrystallized KCl was used.

Polarographic electrolysis was carried out on a Radiometer polarograph of the Polariter PO 4 type. As mercury dropping electrode a straight capillary was used, of drop time $t_1 = 2.1$ s (at $E = 0$ V), mercury flow rate $m = 1.93$ mg/s, with reservoir height $h = 25$ cm. Saturated calomel electrode (s.c.e) was used as reference electrode and all potentials are referred to it. pH was measured on a precise compensation pH-meter Metrohm E 388 with a combined glass electrode EA 107. $i-t$ curves were registered on a device consisting of a potentiostat Tacussel of the PRT-20-2 type in a circuit for compensation of the ohmic drop on the measuring resistor; the current was recorded on a BAK 4 T (Aritma) recorder, of maximum rise-time 650 mm/s.

Electrolysis with controlled potential on a stationary mercury macroelectrode was carried out in a three-chamber electrolyser with three electrodes, using the potentiostat mentioned above. The amount of charge passing was determined by the usual iodine coulometer. Each electrolysis was carried out in absence of oxygen, in a nitrogen atmosphere. The Na_2S_4 solutions were freshly prepared for each experiment. Either a borate buffer with a constant concentration of $Na^+ = 0.1M$(pH 8.0 to 12.5) or a NaOH solution was used as indifferent electrolyte.

RESULTS

The S_4^{2-} anion in basic aqueous medium forms a complicated polarographic wave which in shape is very similar to the polarographic wave of S_2^{2-} and lies in the same potential region. The cathodic wave appears in the potential region more negative than -0.8 V, the anodic wave at potentials more positive than -0.8 V (Fig. 1).

The cathodic wave starts with a sharp maximum which ends at $E = -0.95$ to -1.0 V. This maximum is caused by streaming and is impossible to suppress without deforming the rest of the polarographic curve at the same time. We therefore had to use an approximate interpolation to determine $E_{1/2}$, assuming that the mean current following immediately after the maximum $(\bar{\imath}_1)$ is approximately equal to the mean limiting current (this assumption, though not very precise, is sufficient for relative comparisons). When the maximum disappears the current again decreases slightly, as with S_2^{2-}, as far as -1.3 V, when the minimum $(\bar{\imath}_2)$ current is reached. Then the current increases again until near the potential of decomposition of the supporting electrolyte $(-1.80$ V$)$ it reaches the value of the limiting current $(\bar{\imath}_3 = \bar{\imath}_{\lim})$.

The mean current $(\bar{\imath}_1, \bar{\imath}_2, \bar{\imath}_3)$ *depends* linearly on the concentration of S_4^{2-}. Compared with S_2^{2-}, however, its values are approximately three times greater (for equimolar solutions measured under equal conditions). The half-wave potential, similarly to S_2^{2-}, shifts slightly with increasing concentration of the depolarizer, from -0.85 V for 0.3 mM to more negative values, down to -0.95 V for 3.0 mM-Na$_2$S$_4$. The $E_{1/2}$ value of S_4^{2-} is more negative than of S_2^{2-} by about 40 mV, for equimolar solutions. Depending on pH of the medium, at pH > 9 current $\bar{\imath}_3$ changes very slightly, while $\bar{\imath}_1$ decreases slowly and $\bar{\imath}_2$ sharply, especially at pH 9–10. At pH < 9 the current decreases sharply in all potential regions (Fig. 2). The half-wave potential barely
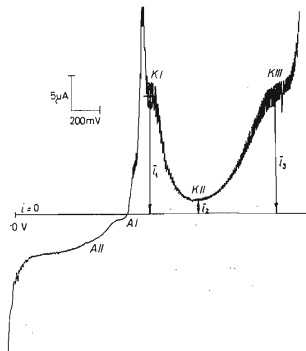

Fig. 1

The Polarographic Curve of Na$_2$S$_4$

1.0 mM-Na$_2$S$_4$, borate buffer pH 10.8;
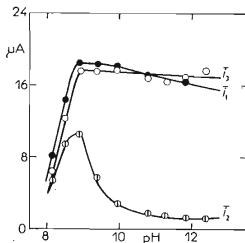$t_1 = 1.2$ s; $m = 1.93$ mg/s.

Fig. 2

The pH Dependence of the Mean Currents
1.0 mM-Na$_2$S$_4$, borate buffer.

shifts with increasing pH of the medium, to more negative values. The following values of the y exponent were found from measurements of the dependence of current on the reservoir height: 0·49 for $\bar{i}_1$, 0·38 for $\bar{i}_2$, 0·51 for i_3. The i–t curves were recorded for $c_{Na_2S_4} = 1\cdot0$ mM; at $E = -1\cdot2$ V they form monotonous exponential curves. The values of the γ exponent (instantaneous current) at $E = -1\cdot30$ V and $E = -1\cdot80$ V are 0·43 and 0·27.

Potentiostatic electrolysis on a stationary mercury macroelectrode was chosen as the method of proving and quantitatively determining reaction products. At the same time we performed an iodometric and polarographic analysis of the electrolysed solution, both before and after electrolysis. Coulometric determination of the total charge was performed by iodine coulometer. The so-called sulphidic sulphur content was determined iodometrically, the concentration of polysulphide polarographically. The voltage conditions for electrolysis were chosen on analogy with polarography, *i.e.* the potential of the working electrode was usually $-1\cdot75$ V. The concentration of S_4^{2-} was decreased by electrolysis, while the concentration of S_2^{2-} increased. The average value of the ratio of the charge passed during electrolysis and the loss of polysulphide was 5·97 F/mol.

Lastly, we studied the effect of concentration of the indifferent electrolyte on the polarographic curves of S_4^{2-} and S_2^{2-}. As indifferent electrolyte a solution of KCl was used, to which a small amount of KOH of constant concentration $c = 0\cdot01$M was added, to ensure well defined and sufficient basicity of the solution so that all polysulphide anions exist in the divalent form. The KCl concentration was varied as follows: 0·10, 0·25, 0·50, 1·00M. Measurements were performed at constant depolarizer concentration of 1·0 mM and constant capillary conditions (drop time 2·0 s, flow rate 2·3 mg/s) (Fig. 3).

In view of analogies with the polarographic behaviour of S_2^{2-}, we did not determine the character and effect of the cation of the indifferent electrolyte, as studied in[1].

DISCUSSION

Comparisons of polarographic curves of S_4^{2-} and S_2^{2-} together with the results of basic measurements indicate important similarities in their behaviour. All classical examinations of the character of the reduction wave we performed, unambiguously show that the wave is an irreversible one, *i.e.* a wave limited by the rate of the electrode process. In the case of S_4^{2-}, the wave starts with a high, sharp negative maximum of the first kind, after which a "non-streaming" maximum follows — a dip on the limiting current, a feature typical of many divalent anions, a fact that was not discerned by the first authors[2]. The sharp increase in the current dip at pH > 9 can most probably be explained by a shift in the dissociation equillibrium of HS_4^- and S_4^{2-} ions in the solution and by a rise of the effective negative charge of the reducing anions.

The sharp decrease in current at all potentials at pH < 8 would then be caused by the decomposition of tetrasulphide into sulphide and sulphur.

The results of electrolysis allow us to assume that the electrode process also includes the reduction of the divalent tetrasulphide anion to a monosulphide anion, as given by the overall equation: $S_4^{2-} + 6e \rightarrow 4\,S^{2-}$.

For further comparisons we determined, from the dependence of the polarographic curves on the concentration of the supporting electrolyte, the values of rate constants, of the coefficient of charge transfer and of the stoichiometric numbers for both anions, S_4^{2-} and S_2^{2-}.

The calculations were carried out according to the "corrected" Tafel equation:

$$\log i + \frac{zf}{2 \cdot 3}\,\phi_2 = \log i_0 - \frac{\alpha n f}{2 \cdot 3 \nu}\,[(E - E^0) - \phi_2],$$
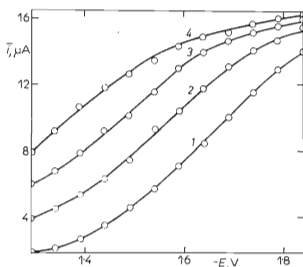

Fig. 3

The Effect of K^+ Concentration on the Shape of the Cathodic Wave of 1.10^{-3}M--Na$_2$S$_4$

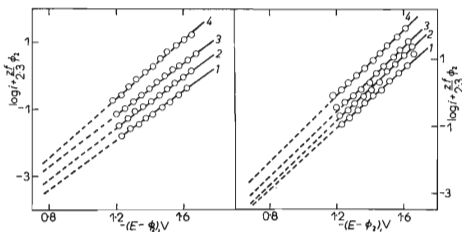K^+ concentration: *1* 0·1M; *2* 0·25M; *3* 0·5M; *4* 1·0M.

Fig. 4

The Corrected "Tafel Plots" of *a* 1.10^{-3}M-Na$_2$S$_2$ at K^+ Concentrations *1* 1·0M; *2* 0·5M; *3* 0·25M; *4* 0·1M and *b* 1.10^{-3}M-Na$_2$S$_4$ at K^+ Concentrations *1* 1·0M; *2* 0·5M; *3* 0·25M; *4* 0·1M

where i is the current density corrected for concentration polarization; $f = F/RT$; $i_0 = n/v\,F\,k^0 c$; n is the number of electrons participating in the electrode reaction, k^0 the rate constant of the electrode reaction at the standard redox potential of the system, c the concentration of depolarizer in the bulk of the solution, v the stoichiometric number[6], *i.e.* the number of repetitions of the rate determining step of charge transfer; α is the coefficient of charge transfer, z the charge of particles reducing on the electrode and ϕ_2 the potential of the outer plane of the Helmholtz double layer (measured against the potential within the bulk of the solution). As the potential region studied is very negative, we assumed the ϕ_2 potentials in KCl solutions to be approximately equal to potentials in NaF solutions of corresponding concentrations[7,8].

Graphic analysis of the plotted Tafel equations (Fig. 4ab) gave the following values of k^0: 0·2 to 1·9 . 10^{-2} cm/s for S_2^{2-}; 0·1 to 0·7 . 10^{-2} cm/s for S_4^{2-}, both inversely dependent on the concentration of indifferent electrolyte. The average values of α were: $\alpha_{S_2^{2-}} = 0·116$; $\alpha_{S_4^{2-}} = 0·045$. The value of k^0 was determined by extrapolating the Tafel plot to values of the corresponding standard potentials of the corresponding redox-systems, which have been tabelled in[9]. (These values are: $E^0 = -0·702$ V for the S_4^{2-}/S^{2-}-system and $-0·766$ V for the S_2^{2-}/S^{2-}-system.) The differences in k^0 values for different concentrations of the supporting electrolyte are reproducible and cannot be explained by experimental errors. Rather, they indicate that the equation used has only limited validity. Reasons of this phenomenon are now being investigated. The value of the α coefficient for $v = 1$ in the case of S_4^{2-} is unusually low, which suggests that for determination of k^0 and α a stoichiometric factor $v = 3$ has to be used. Then the values of k^0 and especially α become acceptable: $k^0 = 0·3$ to 2·1 . 10^{-2} cm/s (inversely proportional to the concentration of indiffrent electrolyte) and the average value of $\alpha = 0·141$.

The overall equation:

$$S_4^{2-} + 6e \rightarrow 4\,S_2^{2-}$$
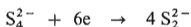
can thus be written as a series of fast consecutive reactions:

$$S_4^{2-} \rightarrow S_3^{2-} + S\,; \quad S + 2e \rightarrow S^{2-}$$

$$S_3^{2-} \rightarrow S_2^{2-} + S\,; \quad S + 2e \rightarrow S^{2-}.$$
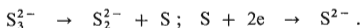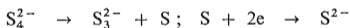
This theoretical analysis indicates that the electrode process of reduction of poly-sulphides on a mercury electrode proceeds probably through gradual dispropor-tionation of S_n^{2-} to a lower polysulphide and elementary sulphur, by its further reduction, to the final S^{2-} anion. In this sense we have to correct the conclusions on the reduction of the disulphide anion published in our previous paper[1]. The overall electrode reaction:

$$S_2^{2-} + 2e \rightarrow 2\,S^{2-}$$
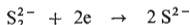
can be, in this case, divided into two steps:

$$S_2^{2-} \;\rightarrow\; S^{2-} + S\,; \quad S + 2e \;\rightarrow\; S^{2-}\,.$$
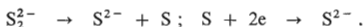
The value of v remains here of course 1. In our opinion, however, elementary sulphur originates in both cases in the mercury–water electrode interface as a part of the electrode process itself, and not within the solution as other authors have assumed[2,10], as the polarographic wave is of a clearly "anionic character". The spontaneous formation of elementary sulphur in water medium in the absence of air is not likely, either.

The theory of Budnikov and coworkers[3], that complexes of mercury with S_n^{2-} anions are formed, does not seem to us to be sufficiently founded: the formation of a $[HgS_2]^{2-}$ complex by the interaction of metal mercury with a polysulphide anion would mean that the mercury acts as a reducing agent; neither did we find elementary sulphur forming at cathodic polarization of the working electrode during prolonged electrolysis of Na_2S_4 with the mercury macroelectrode, which the authors expect for S_4^{2-}.

A complete evaluation of the electrode process requires a further study and discussion of anodic waves, which will form the subject of our next paper.

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