POLAROGRAPHIC REDUCTION OF POLYSULPHIDES. I.
REDUCTION WAVE OF DISULPHIDE

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In basic medium the disulphide anion gives a polarographic cathodic wave in the region from —0·8 V (N.C.E.). The wave is two-electrone, irreversible and shows a characteristic anionic negative dip on the limiting current. Scheme of the electrode reaction has been found: $S_2^{2-} + 2e^- = 2S^{2-}$.

Polarographic study of polysulphides has been already performed by Werner and Konopik[1]. They found that in polarographic electrolysis on mercury dropping electrode Na_2S_2 gives with anodic and a cathodic curves a pronounced maximum. Therefore they payed attention to the investigation of the influence of different surfactants. In spite of the fact that these surfactants distort the whole wave, they endeavour after the highest possible suppresion of the maximum. The part of the wave after the current minimum (dip) was considered to be the cathodic wave of S_2^{2-} the $E_{1/2}$ of which equals to —1·4 V (S.C.E.) for $c = 2·5 . 10^{-3}$M-Na_2S_2 in 2M-NaOH (and which is independent of reaction conditions). A complete suppression of the maximum was not achieved.

Two waves were observed with $E_{1/2} = $ —0·8 V (S.C.E.) and $E_{1/2} = $ —0·58 V (S.C.E.) in the anodic part. On the basis of the similarity of the shape of the curve with the shape of S^{2-} wave the former was considered a wave of S^{2-} and the latter was thought to be a wave of S_2^{2-}. The facts that the authors have not differentiated between the maximum and the negative current dip typical for bivalent anions, that only the part of the curve after the minimum was considered a wave, and that the whole wave was distorted by an extreme ammount of surfactants (camphore, thymol blue) are the basic deffects of the paper by Werner and Konopik[1], which is otherwise carefully done.

Our interest in the polarographic behaviour of polysulphides is mainly given by our interest in the systematic polarographic study of anions contained linked sulphur.

EXPERIMENTAL

Na_2S_2 was prepared according to[2]. Purity of the obtained reagent was checked by gravimetric determination of sulphur content and by indirect argentometric determination of sodium[1,4]. The reagent was kept in vacuum desiccator with P_2O_5 at a lower temperature. Polarographic curves were registered by polarograph V 301 with mirror galvanometer having sensitivity 1·5 . 10^{-9} A/mm/m and by polarograph LP 60 with recorder EZ-2. Polarographic electrolysis was carried out in a Kalousek vessel with normal calomel electrode (N.C.E.) as anode. All potential values

are referred to its potential. A Smoler capillary was used with the drop-time $t_1 = 1\cdot85$ s and with the average flow rate $m = 2\cdot1$ mg/s. To control the time of drop an electromagnetic drop-timer was used in the measurements of the dependence of mean current on the time of the drop. pH was measured by a glass electrode using a pH meter Radiometer 28. Polarographic maxima were followed by the microscope Meopta G 21 P. Temperature dependence of Na_2S_2 reduction was carried out in ultrathermostat NBE. Kalousek's switch was used for the investigation of the polarographically active products. The controlled electrolysis on a stationary mercury macro-electrode with N.C.E. as a reference electrode was carried out in a special electrolytic vessel[5]. Iodine coulometer was used for the coulometric investigation of the electrolysis with a potentio-stat as voltage source[6]. Quantitative determination of the products of electrolysis was carried out by an iodometric procedure[3]. Curves of dependence of instantaneous current on time were registered by a special device[7,8] using a string galvanometer Stylogalvanometer Kipp Zonen with a period of $0\cdot05$ s. Electrolyses were made in the absence of oxygen which was displaced by bubbling of nitrogen. All other reagents used in this work were commercial preparations of the p.a. purity.

RESULTS

In the basic medium (citrate–phosphate buffer) the disulphide anion gives on the one hand an anodic wave and on the other hand a complicated cathodic wave with a pronounced maximum at its beginning. This cathodic wave is situated in the poten-tial range from $-0\cdot8$ V and is independent of acidity of the supporting electrolyte. Anodic wave has also a complicated pattern and shows a weak dependence on acidity. First the initial current maximum was investigated. By microscopical observation of the neighbourhood of the drop, after the addition of finely grinded active carbon into solution, it was found that the sharp part of maximum (up to $E = -0\cdot94$ V
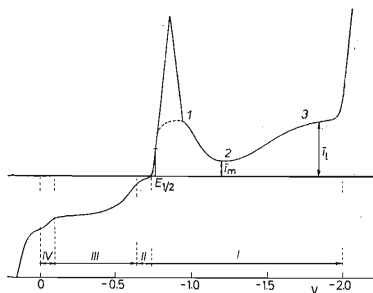

Fig. 1

Polarographic Curve of Na_2S_2

$0\cdot001$M-Na_2S_2, citrate–phosphate buffer pH $11\cdot4$, $[Na^+] = 0\cdot10$M; $\bar{i}_m$ limiting current in the minimum; $\bar{i}_l$ total limiting current.

in Fig. 1) is brought about by streaming of electrolyte from the top to the neck of the drop. However, even after the disappearance of eddying the limiting current further decreases and a current dip is formed with a minimum in the potential range around $-1\cdot2$ V. Maximum caused by eddying may be suppressed, as usual, by addition of surfactants, but these reagents influence the total course of the wave therefore the dependence of the shape of the wave on pH was investigated without any addition of surfactants. It was found that along with *an increase* of pH *a shift of the cathodic wave* to more negative potentials occurred Fig. 2. The potential location of the wave was determined approximately only, but in a standard way with help of the half-wave potential corresponding to the half height of the non-eddy maximum which was read on the increasing part of the curve. Furthermore it was found that the magnitude of the wave decreases slowly with an increase of pH (pH > 9); this magnitude is given by the height i_1 at the potential $E = -1\cdot84$ V. Following these dependence the concentration of cations in the supporting electrolyte was kept always constant ($[Na^+] = 0\cdot1$ mol/l). *The effect of depolarizer concentration on the height of the*

Fig. 2

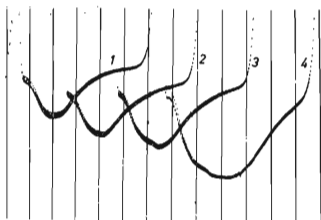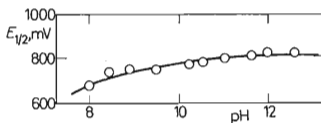Dependence of Potential Location of Cathodic Wave on pH ($0\cdot003$M-Na$_2$S$_2$)

Fig. 3

Effect of Potassium Ions on the Disulphide Wave

$0\cdot005$M-Na$_2$S$_2$, citrate–phosphate buffer pH 11·4, 198 mV/absc. Concentration of K$^+$: *1* 0·9M, *2* 0·5M, *3* 0·2M, *4* 0·0M.
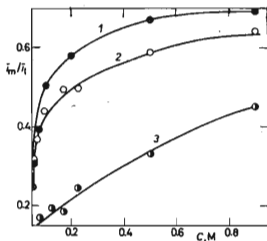
Fig. 4

Concentration Effect and Effect of Nature of Cations of Supporting Electrolyte

1 Cs$^+$; *2* K$^+$; *3* Na$^+$.

wave was followed in three media with different acidity: 8·00, 10·00 and 12·00 pH. The values of limiting current were measured at three potentials: just behind the streaming maximum, in the current minimum and in the developed rear part of the wave. In all three cases, in all media the dependence of limiting current on the concentration of the depolarizer was linear; with the *increase of concentration of depolarizer* (up to 6 . 10^{-3} mol/l) the wave is slightly shifted to more negative potentials.

From the *dependence of the wave on the height of reservoir*, which was investigated at pH 10, $[Na^+] = 0·1$ mol/l values of exponents of *i-t* relations obtained are 0·7, 0·2 and 0·47 in the potential regions marked *1, 2, 3* on the curve in Fig. 1.

Similarly from the *dependence on the drop-time at the constant height of reservoir* in the medium of pH 10 the calculated values of corresponding exponents for locations *1, 2, 3* in Fig. 1 were 0·24, 0·63 and 0·34, respectively. The most precise information for the determination of the character of limiting current in the individual potential ranges was obtained from the analysis of curves of the dependence of instantaneous current on time. This dependence was studied also in the regions of noneddy maximum, of minimum of limiting current and of developed limiting current. As a supporting electrolyte the Britton–Robinson buffer of pH 11·26 was used. Monotonic increasing exponential curves were obtained. By an analysis of their courses the values of corresponding exponents of *i–t* curves were determined as fol-
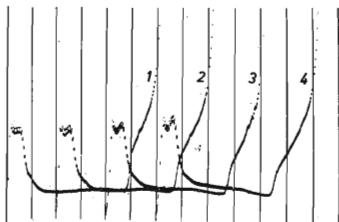

FIG 5

Effect of $(C_4H_9)_4N^+$ Ions on the Disulphide Wave

0·005M-Na_2S_2, citrate–phosphate buffer pH 11·4, 198 mV/absc. Concentration of $[N(C_4H_9)_4]^+$: *1* 0·045M, *2* 0·002M; *3* 0·001M, *4* 0·0005M.
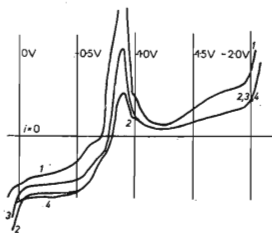

Fig. 6

Polarographic Curves Obtained Using a Commutator of Polarising Voltage

0·005M-Na_2S_2, citrate–phosphate buffer of pH 11·40, 0·10M-KCl. *1* curve without commutator, *2* commutator switched on, E_{aux} —1·00 V; frequency of commutator 1·56 Hz, *3* commutator switched on, E_{aux} —1·30 V, frequency 1·56 Hz, *4* commutator switched on, E_{aux} = —1·80 V, frequency 1·56 Hz.

lows: 0·3, 0·42, 0·27 at working potentials −1·00 V, −1·25 V, and −1·75 V, respectively.

Temperature dependence of limiting current shows a linear increase up to 45°C. Then a decrease occurs probably due to temperature decomposition of the substance in water solution which was even visually observable during further temperature increase. The dependence was determined for $5 . 10^{-3}$M-Na_2S_2 in the medium of pH 11·45 and $[Na^+] = 0·1$ mol/l. The value of the temperature coefficient for the current in the region of non-eddy maximum and for the developed wave equals 0·6%.

An important part of the investigation was the study of the *influence of supporting electrolyte*, the study of its nature and concentration. As supporting electrolyte a citrate–phosphate buffer of pH 11·40 was used to which solutions of NaCl, KCl, CsCl, $(C_2H_5)_4NBr$, $(C_4H_9)_4NI$ were successively added in increasing concentrations. The influence of cations of the first three mentioned salts on the shape of wave was investigated.

An evident effect of inorganic cations was found (Fig. 3). In their presence a gradual elimination of current minimum occurs. Effectiveness of individual cations increases in the following series: $Na^+ < K^+ < Cs^+$ (Fig. 4). However, the effect of quaternary ammonium salts substantially differs from the effect of inorganic cations. The region of negative current dip broadens, but the current in the minimum has nearly the same value (Fig. 5). In order to determine the probable products of electrode reaction the investigation of polarographic disulphide wave was performed using a commutator of polarization voltage. The results (Fig. 6) show an increase of anodic wave, if the auxiliary polarization voltage corresponds to the potentials of the cathodic part of the wave. The increase of anodic wave changes according to the chosen value of the auxiliary potential, *i.e.* a higher increase can be observed if the auxiliary potential is in the region of maximum or rear part of the polarographic curve, smaller increase occurs, if the potential is in the region of current dip.

Overall scheme of the electrode reaction was determined with the help of electrolysis on a stationary mercury macroelectrode with a controlled potential combined with a quantitative iodometry of the products of the electrode reaction and with a coulometric determination of the charge by iodine coulometer. All determinations as well as the coulometry were repeated approximately at the same conditions; the electrolysis was carried out 3 hours and 1·26 mmol S_2^{2-} was used. Iodometric titration was carried out before and after electrolysis. The following average values were calculated from the obtained results: ammount of reduced S_2^{2-} 1·19 mmol, ammount of produced S^{2-} 2·37 mmol, consumed charge 2·30 mF.

DISCUSSION

The examination of the maximum shows that it is necessary to differentiate the part which is brough about by eddying of electrolyte and the part in which no eddying

occurs but the current is still decreasing. This latter part cannot be considered as a maximum, but it is a current dip, which is typical for bivalent anions in the region of potentials more negative than electrocapillary zero. On the other hand the characteristic of the eddy-maximum in which the direction of eddying is from the top to the neck of the drop, indicates the so called negative maximum, which occurs in the region of potentials more negative than electrocapillary zero. The same conclusion is evident also from other studied dependences which were followed in potentials closely before the beginning of the current dip, in the minimum, $(E = -1\cdot2\ \text{V})$ and in the potentials of developed limiting current on the rear part of the wave after the minimum: The study of the dependence of average current on the height of reservoir on the time of drop and the dependence of instantaneous current on time or the values of exponents of corresponding dependences indicate that the irreversibility of electrode reaction in the region of the minimum is significantly higher than in the other regions of limiting current. In the potential region before minimum and in the region of limiting current of the rear part of wave the values of exponents show that the electrode process is diffusion controlled or, at least, that irreversibility of the process is certainly lower than in the region of minimum. This is supported by the values of temperature coefficients of current in the mentioned regions. For anionic dip the influence of cations of supporting electrolyte is characristic. In our case the comparison of effects of cations Na^+, K^+, Cs^+ shows a typical effect in increase of the rate of electrode process. The increasing effectiveness of elimination of current in the series $Na^+ < K^+ < Cs^+$ is in full agreement with the valid theory of anionic irreversible reductions[9]. Hence it is necessary to consider the whole curve, including the eddy-maximum as the disulphide wave and not only the most negative part of the curve, as it was erroneously presumed by Werner and Konopik[1]. Thus also the values of half-wave potentials determined by them have lost the validity.

The experiments with the commutator and electrolysis showed that the most probable scheme of the electrode reaction is $S_2^{2-} + 2\ e^- = 2\ S^{2-}$. The results with the commutator, *i.e.* the increase of anodic wave if the auxiliary polarization voltage corresponded to the potential of developed rear part of wave, favoured the mentioned scheme. Substantially more confirmative evidence was given by results of controlled electrolysis combined with iodometric analysis of the electrolysed solution and with coulometric determination of the consumed charge. It was found that the number of electrons which were consumed for reduction of S_2^{2-} anion equals two, and that during the reduction two anions of S^{2-} originate from one anion of S_2^{2-}. Hence the presumed working hypothesis has been sufficiently proved. The assumption that the wave is due to polarographic reduction of electroneutral elementar sulphur, which should have originated according to $S_2^{2-} = S^{2-} + S$ does not agree with the "anionic character" of the reduction wave.

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