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Electrochemical Reduction of Elemental Sulfur in Acetonitrile

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Electrochemical reduction of elemental sulfur (S_8) has been carried out in acetonitrile using a platinum electrode. The products were identified by means of spectrophotometry and ESR. Sulfur is reduced voltammetrically in two steps:

$$S_8 + 2e \longrightarrow S_8^{2-}, \qquad S_8^{2-} + 2e \longrightarrow 2S_4^{2-}$$

These products turns into more stable species by the succeeding chemical reactions in a bulk solution as follows:

$$S_8^{2-} \overset{K}{\rightleftharpoons} S_6^{2-} + 1/4S_8 \qquad (K = 1.6\times10^{-2})$$

$$S_6^{2-} \overset{K_d}{\rightleftharpoons} 2S_3^{\cdot-} \qquad (K_d = 1.2\times10^{-3})$$

The S_4^{2-} species was enough active to react with S_8 into S_8^{2-}, which was regarded as the cause of a current maximum on the current-time curve in a controlled potential coulometry of S_8 at a potential of the second reduction step.

The authors have reported in the previous paper[1] that sulfur monochloride (S_2Cl_2) is reduced electrochemically into chloride ion and elemental sulfur (S_8 form) in an aprotic solvent, acetonitrile (AN), and that the produced sulfur can be further reduced at the more negative potential. Elemental sulfur has been reduced[2-5] in dimethyl sulfoxide and *N*,*N*-dimethylformamide to produce blue colored species, which is attributed to $S_3^{\cdot-}$ (trisulfur anion radical). However, as the system is very complicated, the different values of the equilibrium constants for the present species in a solvent are reported between two groups[3,5] of investigators.

Moreover, the authors have showed that S_8 molecule exists stably in less basic solvents, such as acetonitrile or propylene carbonate (PC), but S_8 is activated by the basicity of the solvent, not only in *N*,*N*-dimethylformamide but also dimethyl sulfoxide according to the conductivity data.[1] In the present work, the electrochemical reduction of S_8 in acetonitrile has been studied, and the reaction mechanism in the solution is discussed.

Experimental

Commercial acetonitrile was purified, and Et_4NClO_4 used as the supporting electrolyte was prepared by the method described previously.[1] The electrode potential was measured against a silver electrode (Ag/0.1 M $AgClO_4$–AN). A rotating platinum electrode (geometric surface area of 0.13 cm^2) and a platinum-gauze electrode were used as the working electrode. The controlled potential coulometry was carried out using a Prinston Applied Research (PAR) Model 173 Potentiostat and Model 179 Didital Coulometer. Other apparatus and equipments were the same as those in the previous report.[1]

Elemental sulfur (S_8) was dissolved in acetonitrile, heating on a hot-plate. Absorption spectra of electrolyzed sulfur solution were measured in an optical flow-cell with 1 cm path length. As the electrolytic products were affected strikingly by oxygen gas, high-purity nitrogen gas was bubbled vigorously through the solution. ESR measurements were performed with a JEOL PE-3X following the method of Umemoto.[6]

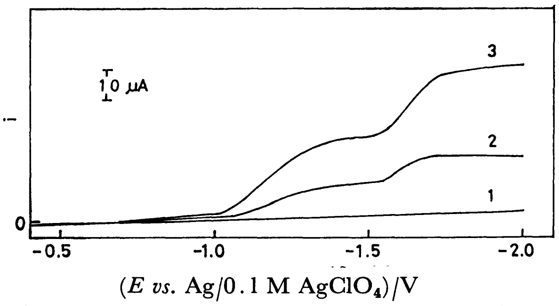

Fig. 1. Voltammograms of sulfur in 0.1 M Et_4NClO_4–AN on rotating platinum electrode.
Concn of S_8; 1: 0, 2: 0.5, 3: 1.25×10^{-4} M.

Results and Discussion

Figure 1 shows the voltammograms of S_8 in acetonitrile solution with a rotating platinum electrode. S_8 was reduced through two steps. The half-wave potential ($E_{1/2}$) of the first and second wave was -1.20—-1.16 V and -1.60 V, respectively. The first wave was irreversible (log-plot slope of 100—200 mV), whereas the second seemed to be less irreversible (the slope of *ca.* 60 mV). The wave height of both the first and second wave were proportional to the concentration of S_8. The number of electrons involved in each step was found to be both about 2 electrons by controlled potential coulometry measurements at -1.4 V and -1.8 V. Therefore, S_8 may be reduced voltammetrically through the following process;

$$\text{at the first wave,} \quad S_8 + 2e \longrightarrow S_8^{2-} \qquad (1)$$

$$\text{at the second wave,} \quad S_8^{2-} + 2e \longrightarrow 2S_4^{2-} \qquad (2)$$

Figure 2 shows the current-time curves during coulometry. The current decreases exponentially when the potential is setted at -1.4 V, which corresponds to the first wave in voltammetry. The current reached to almost zero when about 2 electrons was consumed, but it still continued to flow very slowly until about 2.7 electrons. The solution turned purple in color gradually during the electrolysis and it changed into blue after Z^{**}=*ca.* 2.0. At -1.8 V (at the second wave), a

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** *Z* indicates the number of electrons added to for S_8.

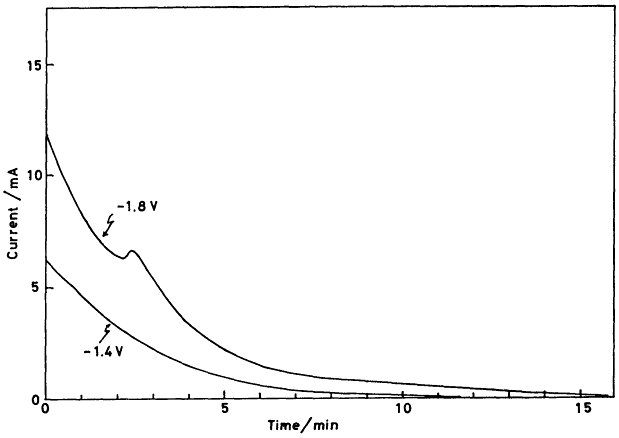

Fig. 2. Current-time relationship for the controlled potential coulometry of sulfur on Pt-gauze, $[S_8]=0.50\times10^{-4}$ M.

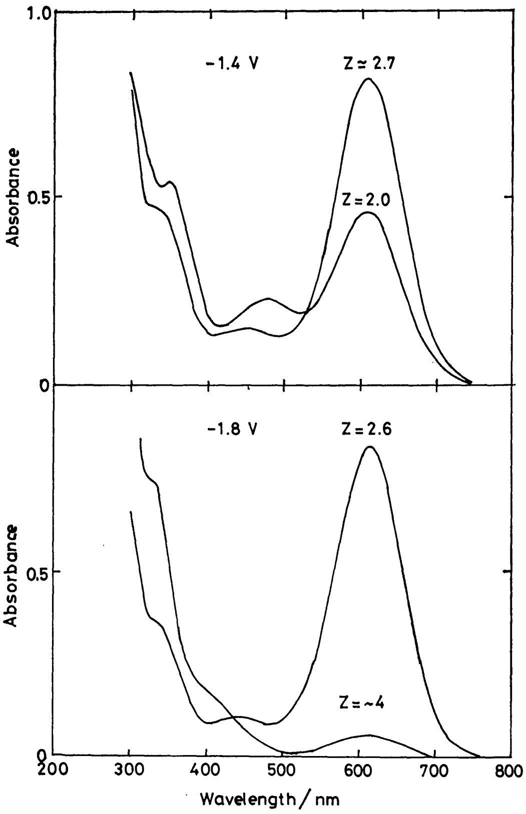

Fig. 3. Absorption spectra of sulfur solution after electrolysis at −1.4 and −1.8 V, $[S_8]=1.0\times10^{-4}$ M.

maximum of current was observed after a few minutes from the beginning of the electrolysis. The maximum and the minimum appeared each time at the constant number of electrons of 2.4—2.6 and 2.2—2.3, respectively, even if the position where they appear were shifted, changing the area of electrode or the concentration of the depolarizer ($[S_8]=0.1$—4.0×10^{-4} M***).

The relation between log *i* and *t* was linear for the both regions from the beginning of the electrolysis to the minimum and after the maximum. The slope of log *i*—*t* for the region after the maximum was larger than that to the minimum by the factor of 1.3—1.5. The color of the solution changed suddenly from purple to blue in the region where the current increased. These results may suggest that the electrode reaction in the region from the beginning of the electrolysis to the minimum is different from that after the maximum. The number of electrons reached 4 for S_8 after about ten minutes from the beginning of the electrolysis, but small current still continued to flow, the relation of log *i*—*t* deviating from the linearity.

The absorption spectra of the sulfur solution electrolyzed at −1.4 V are shown in Fig. 3. The spectrum had peaks of 613, 480, and 350 nm at $Z=2.0$. At about $Z=2.7$, the spectrum had peaks of 613, 450, and 270 nm and a shoulder of 340 nm. When the solution was electrolyzed at −1.8 V, it gave a spectrum similar to that of −1.4 V up to $Z=$*ca.* 2.7. When the solution is completely electrolyzed at −1.8 V, however, the peak of 613 nm almost disappeared, and a peak of 330 nm and a shoulder of 400 nm appeared instead.

The change of absorbance at 613 and 480 nm during the electrolysis at −1.4 V is shown in Fig. 4. The absorbance at 613 nm increased with the increase of the number of electrons, and the increase of the absorbance was accelerated after $Z=2.0$. On the other hand, the absorbance at 480 nm reached the maximum at $Z=2$ and disappeared when the electrolysis was completed. The change of absorbance for the electrolysis at −1.8 V is also shown in Fig, 4. The same results were obtained as the case of the electrolyses at −1.4 V up to $Z=8/3$, although the speed of electrolysis at −1.4 V was much slower than that at −1.8 V, especially after $Z=2.0$. The peak intensity at 613 nm began to decrease after $Z=8/3$ and almost disappeared when the electrolysis was completed. The peak at 330 nm appeared instead of the peak of 340 nm after $Z=8/3$.

These results show that the same products are obtained regardless of the potential of electrolysis so long as the same number of electrons. Considering the number of electrons, the peak at 480 nm is due to S_8^{2-}, that at 613 nm to S_6^{2-} (or a species derived from S_6^{2-}), and that at 330 nm may be to S_4^{2-}.

The color of the solution turned blue when unelectrolyzed S_8 solution was added to the solution completely electrolyzed at −1.8 V which looks yellow. Figure 5 (upper) shows the absorbance of the solution of various mixing ratio. The change of absorbance at 613, 480, and 330 nm of the mixed solution is similar to that of the solution electrolyzed at −1.8 V (see Fig. 4). This experiment shows that the following reaction occurs easily.

$$S_8 + 2S_4^{2-} \longrightarrow 2S_8^{2-} \qquad (3)$$

Similary, the solution electrolyzed up to $Z=8/3$ at −1.8 V was mixed with unelectrolyzed S_8 solution (see the lower in Fig. 5). (At $Z=8/3$, all sulfur is formally S_6^{2-} state, as described in next paragraph). In this case, the resulting change of absorbance was the same as the case of the solution electrolyzed at −1.4 V. The appearence of the peak at 480 nm shows the formation of S_8^{2-} species.

*** Throughout this paper 1 M = 1 mol dm^{-3}.

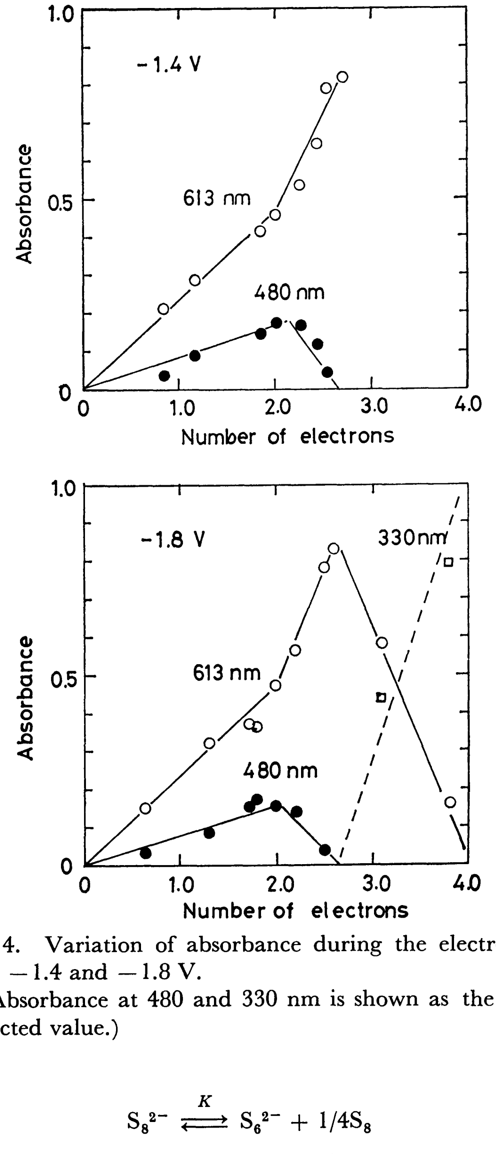

Fig. 4. Variation of absorbance during the electrolysis at −1.4 and −1.8 V.
(Absorbance at 480 and 330 nm is shown as the corrected value.)

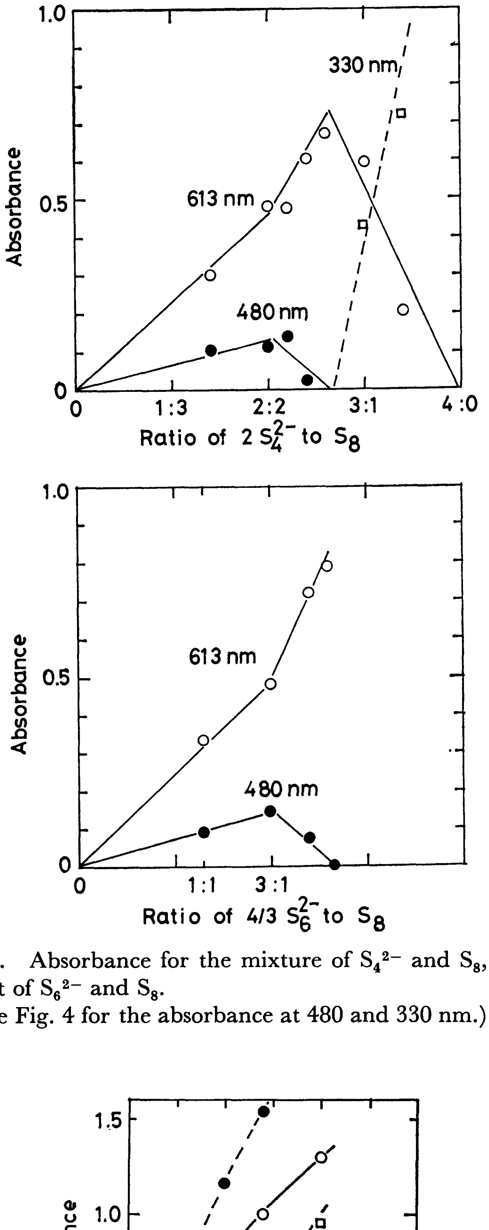

Fig. 5. Absorbance for the mixture of S_4^{2-} and S_8, and that of S_6^{2-} and S_8.
(See Fig. 4 for the absorbance at 480 and 330 nm.)

$$S_8^{2-} \underset{}{\overset{K}{\rightleftarrows}} S_6^{2-} + 1/4S_8 \qquad (4)$$

The absorbance at Z=8/3 is plotted against the S_8 concentration without electrolysis in Fig. 6. At this point of the number of the electrons, all sulfur species must be formally "S_6^{2-}" state. The peak at 613 nm showed negative deviation (absorptivity falls off with increasing concentration). On the other hand, the peaks at 450 and 340 nm showed positive deviation. The spectra at Z=8/3 of various concentrations of S_8 showed an isosbestic point at 510 nm as shown in Fig. 7. These results suggest that S_6^{2-} dissociates into $S_3^{\cdot -}$, and the peak at 613 nm can be assigned to $S_3^{\cdot -}$ and those at 450 and 340 nm to S_6^{2-}. The presence of a radical with the g-value of *ca.* 2.03 was proved by the ESR measurement for the sulfur solution of 4×10^{-4} M at Z=*ca.* 8/3. This g-value agrees well with that of $S_3^{\cdot -}$ species reported in the litareture.[7] Consequently, the blue species which shows the peak at 613 nm in acetonitrile is concluded to be $S_3^{\cdot -}$.

$$S_6^{2-} \overset{K_d}{\rightleftarrows} 2S_3^{\cdot -} \qquad (5)$$

The molar absorptivity of $S_3^{\cdot -}$ at 613 nm was obtained as $\varepsilon=3.9\times10^3$ and the dissociation constant for Eq. 5 as $K_d=1.2\times10^{-3}$ by the method of trial and error. The molar absorptivity of S_6^{2-} is 3.1×10^3 at 450 nm, 1.1×10^4 at 340 nm. The peak of 270 nm may be due to $S_3^{\cdot -}$ judging from the behavior of the calibration curve.

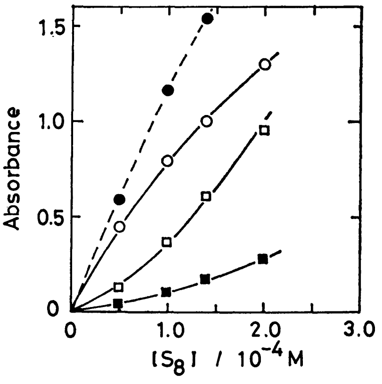

Fig. 6. Calibration curves of S_8 electrolyzed to Z=8/3 at −1.8 V.
●: 270, ○: 613, □: 340, ■: 450 nm.

In Fig. 8, the absorbance of electrolyzed solution at Z=2.0 is plotted against the initial S_8 concentration. At this point, sulfur must be electrolyzed to S_8^{2-} state.

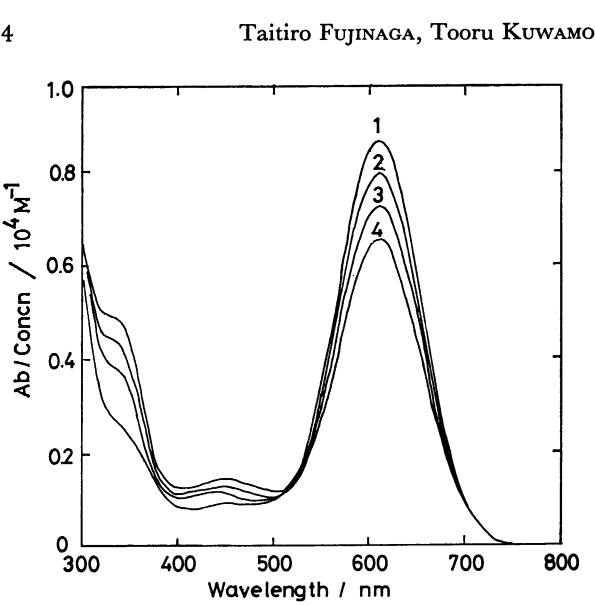

Fig. 7. Absorption spectra of S_8 electrolyzed to $Z=8/3$ at -1.8 V. Initial concn of S_8; 1: 0.5, 2: 1.0, 3: 1.4, 4: 2.0×10^{-4} M.

However, the S_8^{2-} produces more stable species, S_6^{2-} following the equilibrium of Eq. 4, so S_8^{2-}, S_6^{2-}, $S_3^{\cdot -}$, and S_8 exist together in the solution. The absorbance of $S_3^{\cdot -}$ at 613 nm deviated much more downwards from the linearity than the case of $Z=8/3$. The absorbance of 613 nm at $Z=2.0$, the molar absorptivity of $S_3^{\cdot -}$ ($\varepsilon=3.9\times10^3$) and the dissociation constant ($K_d=1.2\times10^{-3}$) enable the authors to calculate the equilibrium constant, K for Eq. 4 to be 1.6×10^{-2}. The peaks at 350 and 480 nm, due to S_8^{2-} showed positive deviation. The absorbances at 350 and 480 nm are enhanced by the additional absorption of the close peaks at 340 and 450 nm (both due to S_6^{2-}), respectively. From the corrected values of absorbance and the evaluated concentration of S_8^{2-}, the molar absorptivity of S_8^{2-} at 350 and 480 nm was obtained as 1.0×10^4 and 4.4×10^3, respectively.

As for the solution electrolyzed completely at the second wave, the absorbances at 330 and 400 nm, which may be due to S_4^{2-}, showed the linear dependence on the initial concentration of S_8. The molar absorptivity of S_4^{2-} at 330 and 400 is *ca.* 4.2×10^3 and 1.0×10^3, respectively. Sawyer *et al.*[3] reported the dissociation constant K_d to be 9×10^{-3}, and K in Eq. 4 to be 1.68×10^{-2} ($K^4=8\times10^{-8}$) in DMSO. However, the values obtained be Bonnaterre *at al.*[5] are much different from those by the present authors or Sawyer *et al.*[3]

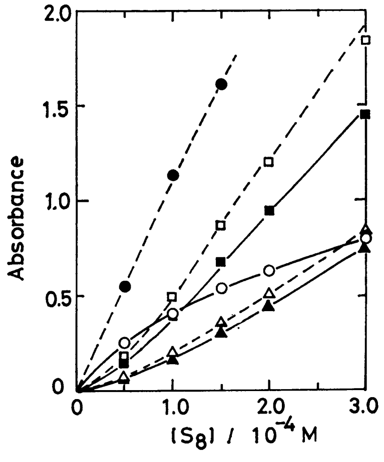

Fig. 8. Calibration curves of S_8 electrolyzed to $Z=2.0$ at -1.8 V.
●: 270, □: 350, ■: 350 corrected, ○: 613, △: 480, ▲: 480 nm corrected.

The detail conditions were examined about the maximum of current in course of the coulometry at the potential of the second wave. First, the sulfur solution was electrolyzed to a certain number of electrons at -1.4 V. Then the potential was stepped to -1.8 V quickly, and the electrolysis current was recorded as shown in Fig. 9. The solution which was electrolyzed up to $Z=2.0$ at -1.4 V showed the maximum after the current decreased once. The solution electrolyzed to $Z=2.2$ showed a maximum just after the potential was stepped at -1.8 V. While, for the solution of $Z=2.5$ or more, the current decreased without the maximum.

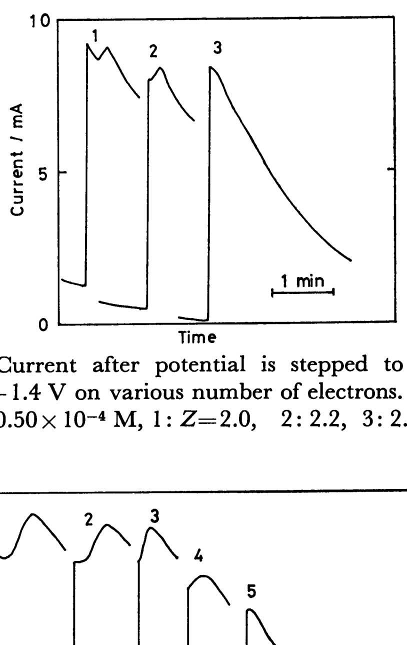

Fig. 9. Current after potential is stepped to -1.8 V from -1.4 V on various number of electrons. $[S_8]=0.50\times10^{-4}$ M, 1: $Z=2.0$, 2: 2.2, 3: 2.5.

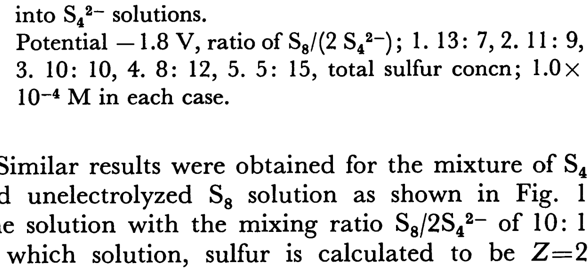

Fig. 10. Current change after addition of S_8 solutions into S_4^{2-} solutions.
Potential -1.8 V, ratio of $S_8/(2\ S_4^{2-})$; 1. 13: 7, 2. 11: 9, 3. 10: 10, 4. 8: 12, 5. 5: 15, total sulfur concn; 1.0×10^{-4} M in each case.

Similar results were obtained for the mixture of S_4^{2-} and unelectrolyzed S_8 solution as shown in Fig. 10. The solution with the mixing ratio $S_8/2S_4^{2-}$ of 10: 10, in which solution, sulfur is calculated to be $Z=2.0$ state, showed the maximum when electrolyzed at -1.8 V. The solution of the ratio of 5: 15 ($Z=3.0$ state), however, did not show the maximum any more. These results clarify again that the appearence of the maximum in the coulometry is related to only the number of electrons up to which the sulfur is electrolyzed. As shown above, the products are same, that is, S_8, S_8^{2-}, S_6^{2-}, and $S_3^{\cdot-}$ are present each other at the same ratio of concentration when electrolyzed at -1.4 V or -1.8 V, only if the solution is in a same "electron state." The difference between the solutions electrolyzed at -1.4 and -1.8 V is whether the species of S_4^{2-} exists or not, which is observed apparently only after $Z=8/3$ at -1.8 V. It seems that the maximum current in coulometry at the second wave potential is caused by attacking of S_4^{2-} to S_8.

Lingane and Niedrach[8] observed similar i—t behavior during the electrochemical reduction of selenium (IV) in an aqueous buffer. They attributed the cause of the maximum of current to the formation of easily reduced polyselenide Se_x^{2-} by attacking of the final product Se^{2-} to elemental selenium.

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