

Short Communications

Standard Potential for the System $S_2O_4^{2-}/HSO_3^-$ in Aqueous Solution

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Aqueous dithionite is extensively used in the pulping industry as a reducing bleaching agent for pulp. No direct measurements of the redox potential of dithionite solutions are, however, reported in the literature.¹ The values available for the standard potential dithionite/sulfite are obtained indirectly *via* thermodynamic calculations in which it is assumed that all components are in equilibrium with each other.² These data are limited to 25°C and the effect of ionic strength of the solutions has not been taken into consideration.

In the present investigation the redox potential of aqueous solutions containing dithionite, sulfite, and thiosulfate of different temperatures and ionic strengths was measured and transformed into the standard potential for the system $S_2O_4^{2-}/HSO_3^-$ using the acidity equilibrium constant for HSO_3^- previously reported.³ NaCl was used as the inert ionic medium.

In the experiments a smooth Pt-electrode, an Ag,AgCl reference electrode (Metrohm EA 420 + EA 698), a glass electrode (Metrohm EA 109 U or EA 109 H), and a millivoltmeter (ORION 801) were used. The reference electrode was calibrated against a hydrogen electrode in solutions of low and known hydrogen ion concentrations. The glass electrode was calibrated with solutions of known concentrations of H^+ or OH^- ions at the same ionic strength as the dithionite solution to be studied. The solutions were prepared from *p.a.* chemicals and analyzed according to previously described methods.^{4,5}

Thiosulfate ions do not seem to have any significant effect on the redox potential of dithionite solutions. The redox potential of neutral and slightly alkaline dithionite solutions can be described with a redox equilibrium between dithionite and hydrogen sulfite ions



The standard potentials found at various temperatures and ionic strengths are given in Table 1. (The redox reaction can for-

Table 1. The standard potential in mV for the system $S_2O_4^{2-}/HSO_3^-$ at different temperatures and ionic strengths.

[Na ⁺] M	25°C	40°C	60°C
0.05	17	7	-7
0.1	35	26	8
0.5	35	16	10
3.0	54	44	38

mally be expressed in other ions by using the ionic product of water and the acidity constant for the reaction $HSO_3^- \rightleftharpoons SO_3^{2-} + H^+$ determined at the corresponding conditions.³)

Above a certain level of alkalinity of the dithionite solutions, the redox potential was, however, higher than that expected from the standard potentials determined (Fig. 1). This level was found to be correlated with too low a concentration of HSO_3^- ions (which was found to be about 1 mM irrespective of sulfite concentration, temperature and ionic strength). This unexpectedly indicates a rapid redox equilibrium between $S_2O_4^{2-}$ and HSO_3^- but not one between $S_2O_4^{2-}$ and SO_3^{2-} . Another explanation for the phenomenon would be a mixed potential in-

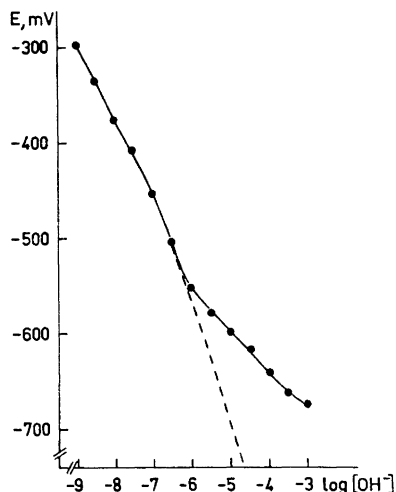


Fig. 1. An example of the deviation of the measured redox potential of dithionite-sulfite solutions from the theoretical one (broken line), calculated using the corresponding standard potential in Table 1. $[S_2O_4^{2-}] = 0.01$ M; $[HSO_3^-] + [SO_3^{2-}] = 0.01$ M. Temperature = 60°C .

volving also the H_2/H^+ potential. This is, however, improbable as the redox potential was dependent on the sulfite concentration also in the alkaline region.

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The Crystal Structure of an Eight-Coordinated Tellurium(IV) Complex

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During the study of compounds of divalent selenium and tellurium with bidentate dithio- and related ligands, it was found that the ligand 4-morpholinecarbodithioate (previously termed, morpholyl dithiocarbamate) upon reaction with Te(IV) gave a remarkably stable complex.¹ Unlike the corresponding diethyldithiocarbamate complex, it was only very slowly converted to the Te(II) dithiocarbamate and the corresponding disulphide, when heated in solution.^{2,3}

Crystals of tetrakis (4-morpholinecarbodithioato)tellurium(IV) including three benzene molecules of crystallization, $[Te(OC_4H_8NCS_2)_4] \cdot 3C_6H_6$, were prepared by adding an aqueous solution of sodium 4-morpholinecarbodithioate to a solution of tellurium dioxide dissolved in dilute hydrochloric acid, in the molar ratio 4:1. The resulting precipitate was then recrystallized from a mixture of benzene and ethanol. The following unit cell data were found: $a = 15.445$ (4) Å, $b = 13.565$ (4) Å, $c = 26.591$ (10) Å, $\beta = 122.23$ (4) $^\circ$ and $Z = 4$. The observed and calculated densities are 1.45 and 1.43 g/cm³, respectively, and the space group is $P2_1/c$.

Based on 2721 reflections above background obtained with a Siemens paper-tape controlled AED-1 diffractometer, the structure was solved by Patterson and Fourier syntheses and refined by a full-matrix least-squares program to an R -value of 0.094.

The dodecahedral D_{2d} coordination found around the central tellurium atom is shown on Fig. 1, while some bond lengths and angles are listed in Table 1. The dodecahedral TeS_8 group has a structure similar to that found for the corresponding group in tetrakis(diethyldithiocarbamato)tellurium(IV).^{3,4} Thus the lone pair of electrons in the valency shell of the central tellurium atom is essentially stereochemically inert. Each ligand spans an edge m between one corner of type A and one of