Standard Potential for the System S₂O₄²⁻/HSO₃⁻ 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 S₂O₄²⁻/HSO₃⁻ using the acidity equilibrium constant for HSO₃⁻ 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

$$S_2O_4^{2-} + 2H_2O ⇌ 2HSO_3^- + 2H^+ + 2e^-$$

The standard potentials found at various temperatures and ionic strengths are given in Table 1. (The redox reaction can formally be expressed in other ions by using the ionic product of water and the acidity constant for the reaction HSO₃⁻⇌SO₄²⁻+H⁺ determined at the corresponding conditions.⁶)

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 HSO₃⁻ 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 S₂O₄²⁻ and HSO₃⁻ but not one between S₂O₄²⁻ and SO₄²⁻. Another explanation for the phenomenon would be a mixed potential in-

<table>
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<th>[Na⁺] M</th>
<th>25°C</th>
<th>40°C</th>
<th>60°C</th>
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<tr>
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<tr>
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<td>26</td>
<td>8</td>
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<tr>
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<td>35</td>
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<td>54</td>
<td>44</td>
<td>38</td>
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</table>

Table 1. The standard potential in mV for the system S₂O₄²⁻/HSO₃⁻ at different temperatures and ionic strengths.

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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. Unlike the corresponding diethylidithiocarbamate complex, it was only very slowly converted to the Te(II) dithiocarbamate and the corresponding disulphide, when heated in solution.

Crystals of tetrakis (4-morpholinecarbodithioato)tellurium(IV) including three benzene molecules of crystallization, [Te(OC₇H₈NCS₂)₄][OC₇H₈], 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 = 15.455 (4) Å, b = 13.565 (4) Å, c = 26.591 (10) Å, β = 122.23 (4)° and Z = 4. The observed and calculated densities are 1.45 and 1.43 g/cm³, respectively, and the space group is P2₁/c.

Based on 2721 reflections above background obtained with a Siemens pater-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 $D_{4d}$ 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 TeS₄ group has a structure similar to that found for the corresponding group in tetrakis(diethylidithiocarbamato) tellurium(IV). 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

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