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The Effect of Iron(III) on the Cadmium Ion-selective Electrode

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Iron(III) interferes with the operation of a cadmium, lead and copper ion-selective electrode. The cadmium ion-selective electrode (CdS/Ag_2S) showed a potential shift to the positive direction of more than 100 mV for a decade change of iron(III) concentration. However, the exact mechanism for this interference is not known, though it is expected to be the oxidation of sulfide ion by Fe(III). The mechanism of interference by iron(III) was studied by using the cadmium ion-selective electrode, flow-through cell, pH buffer solutions, potentiometric titrations, and atomic absorption spectrophotometry measurements. It was found that iron(III) promotes dissolution reaction of cadmium ions from the solid cadmium sulfide electrode and that flow conditions of samples have no effect on the iron(III) interference.

An important group of ion-selective electrodes is composed of metal sulfide membranes such as pure silver sulfide or silver sulfide mixed with other metal sulfides (*e.g.* CuS, PbS, CdS).[1] As a rule, these electrodes are interfered with by ions which can react with the membrane. For example, Ag^+ and Hg^{2+} interfere with the determination of Cu^{2+} with CuS/Ag_2S membrane electrode. Other interference is caused by the dissolution of the membrane to form a soluble complex with some ion in the membrane. For example, the cyanide ion interferes with all silver salt membranes. Actually, silver salt membranes can be used as cyanide ion selective electrode on the basis of this phenomenon. Another kind of interference is caused by oxidizers. For example, iron(III) oxidizes sulfide ions on the electrode membrane and thus affects the membrane potential.

The effect of oxidation by iron(III) on CdS/Ag_2S electrode has been noted by Brand *et al.*,[2] Mascini and Liberti,[3] and Kivalo *et al.*[4] In the case of PbS/Ag_2S electrode, the potential of PbS electrode changed about 59 mV by a decade change in the iron(III) concentration.[5] By the use of a reductant, iron(III) interference could be eliminated in low level analysis of copper(II) ion with CuS/Ag_2S electrode.[6] The effect of iron(III) on mixed sulfide electrode (CuS/Ag_2S) was used for quantitative determination of iron(III) in the range of $(10^{-5}—10^{-2})$ M (1 M=1 mol dm^{-3}) iron(III).[7] Kivalo *et al.* measured the interference of iron(III) on PbS/Ag_2S electrode,[8] and Bixler *et al.* found a large interference of iron(III) on Ag_2S electrode.[9]

Under different oxidizing conditions without iron(III), Johansson and Edström discussed corrosion of CuS/Ag_2S electrode.[10]

The purpose of this work is to study the mechanism of oxidation by iron(III) on the CdS/Ag_2S membrane, by measuring the rate of oxidation reaction by iron(III), the effect of pH buffer solution, the concentration of iron(III), and the amount of Cd(II) which was dissolved from CdS-membrane.

Experimental

Equipment. The electrodes used were Orion cadmium electrode 94-48A (CdS/Ag_2S) and Orion double junction reference electrode 90-02. Potentials were measured with an Orion 801A digital pH/mV-meter and recorded with a Goerz Servogor RE 511 strip chart recorder. The stabilization of electrode potential was followed with the aid of the chart recorder. Potential measurements were made either in a dip cell or in a thermostated flow-through cell (Fig. 1), both at 298 K.

Measurements in the Dip Cell: The dip cell was a polyethylene vessel with volume of 2000 cm^3. The solution was stirred at constant speed with a teflon propellor.

Measurements in the Flow-through Cell: The reference electrode was dipped in the outlet of the sample solution about 10 cm from the cadmium ion-selective electrode. Flow rate was from 0 $cm^3\ min^{-1}$ to 45.1 $cm^3\ min^{-1}$. Possible streaming potential was checked by using two calomel electrodes, one in the place of the indicator electrode and the other in the place of the reference electrode. No streaming potential developed in the flow-through cell, at any flow rate, in the solutions at pH 2, 3, or 5, either in the presence or in the absence of iron(III).

Cadmium ions dissolved from CdS was determined by an Hitachi model 518 atomic absorption spectrophotometer equipped with a cadmium hollow cathode lamp (229.0 nm).

Solutions. Chemicals used were of analytical purity. The ionic strength of solutions was adjusted to 0.1 M. The pH was adjusted with buffers (pH 2; potassium chloride

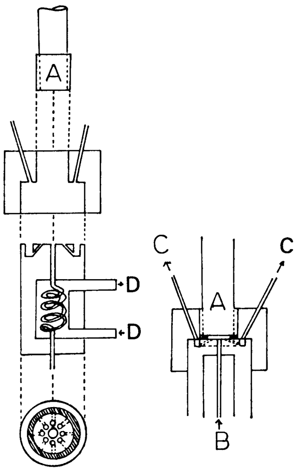

Fig. 1. The flow-through cell.
A: Cadmium ion-selective electrode, B: inlet of the solution, C: reference electrode and outlet of the solution, D: water to control the temperature (298 K).

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and hydrochloric acid, pH 3 and 5; potassium phthalate) or by nitric acid and potassium hydroxide (unbuffered solutions). The cadmium and iron(III) salts used were nitrates. Powder cadmium sulfide was the guaranteed reagent by Nakarai Co. Ltd.

Results

Figure 2 showed the results of the effect of iron(III) in the dip cell at buffered pH 2. The very severe effect of iron(III) is noticeable from the slope (115 mV for a decade change of iron(III) concentration). The selectivity coefficient for iron(III) of the cadmium electrode ($K=[\mathrm{Cd^{2+}}]/[\mathrm{Fe^{3+}}]^{2/3}$) was determined with the mixed solution method with constant activity of Cd^{2+} and varying activity of Fe^{3+} similar to the method recommended by IUPAC.[11] At pH 2, the value of K was 46 $\mathrm{mol^{1/3}\,dm^{-1}}$. And iron(III) began to interfere at concentrations of about 10^{-6} M. Table 1 shows the numerical values of the dip cell measurements at pH 2, 3, and 5 (all were buffered solutions). As the pH decreased, the effect of iron(III) became more severe. This pH effect is attributed to the increase of the activity of free iron(III) ion with decreasing pH.

The interference of iron(III) still remained at pH 5 ($K=7.8\ \mathrm{mol^{1/3}\,dm^{-1}}$), although a large decrease in interference could be expected on the ground of pH change. At pH 5 the ratio of free iron(III) to the hydroxide complex is only $10^{-3.7}$ in the absence of other ligands except OH^-.[12]

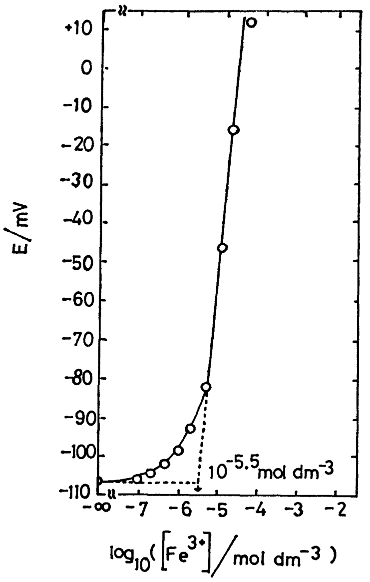

Fig. 2. The effect of iron (III) on the cadmium electrode in the dip cell in pH 2 buffered solution. Concentration of Cd^{2+} was 10^{-2} M.

Table 1. The effect of pH on the interference of iron(III) on the cadmium electrode potential in the dip cell (10^{-2} M Cd^{2+})

pH	Slope mV	$[\mathrm{Fe^{3+}}]$[a)] mol dm^{-3}	K[b)] $\mathrm{mol^{1/3}\,dm^{-1}}$
5.0	37.5	4.57×10^{-5}	7.8
3.0	125.0	1.59×10^{-5}	16
2.0	115.0	3.16×10^{-6}	46

a) Concentration at the break point.[11] b) Selectivity coefficient, $K=[\mathrm{Cd^{2+}}]/[\mathrm{Fe^{3+}}]^{2/3}$.

In the dip cell measurement, if the electrode was dipped in the iron(III) solution for a short time, the response time[11] (the time until the change of potential is less than 1 $\mathrm{mV\,min^{-1}}$) was short (about 1 or 2 s), although the change of the potential to the positive direction was large.

When the electrode was kept in 10^{-6} M iron(III) solution for a few seconds then rinsed by water, and the potential was measured in 10^{-2} M cadmium(II) solution, the potential was 10 mV lower than expected. When the electrode was polished with three successively finer grades of aluminium oxide (The German earth clay Nos. 1, 2, and 3, Jean Wirtz, Düsseldorf), it recovered.

If the electrode was kept some minutes in iron(III) solution (10^{-6} to 10^{-4} M), its potential in 10^{-2} M Cd^{2+} solution was found to have risen considerably, sometimes over 200 mV. And the response time[11] was very long (10 to 20 min). Slight polishing did not restore the potential to its original level. It was only after repeated polishing that the anomaly was removed. This result suggests that iron(II) has an interference effect on the deep interior of the CdS electrode membrane.

Measurements in the Flow-through Cell. The flow-through cell was used to study the effect of the flow conditions of the sample solution. Flow conditions are more easily and reproducibly effected in a flow-through cell than in the dip cell. The flow rate had no effect on the potential in the presence and absence of iron(III), either at buffered or unbuffered pH solution. The response time was as long as 120—150 min in the case of unbuffered pH 2 with 10^{-4} M iron(III). The response time at buffered pH 5 with 10^{-4} M iron(III) was also long (30—60 min). These results suggest that the oxidation of CdS is not controlled by the flow conditions in the solution, but by the reaction in the inside of solid CdS electrode.

The effect of iron(III) on the cadmium electrode was tested in buffered and unbuffered solutions at different pH at a fixed flow rate (5 $\mathrm{cm^3/min}$). The concentration of Cd^{2+} was 10^{-3} M. Figure 3 shows that at pH 2, the effect of iron(III) on the potential was very pronounced both in buffered and unbuffered solutions, though in buffered solution the effect started at about 10 times lower concentration. At pH 5 there was no interference in unbuffered solution, but in buffered solution interference began at 10^{-5} M iron(III). The behaviour is the same as in the dip-cell experiments, *i.e.* buffering of solution preserves the attack by iron(III) on the membrane even at higher pH-values. It seems that by complex formation of phthalate ion with iron(III), iron(III) is still kept in solution even at pH 5 and the penetration of iron(III) into CdS electrode is easy. In fact, in unbuffered solution at pH 5 incipient precipitation of $Fe(OH)_3$ could be seen and no interference of iron(III) was observed.

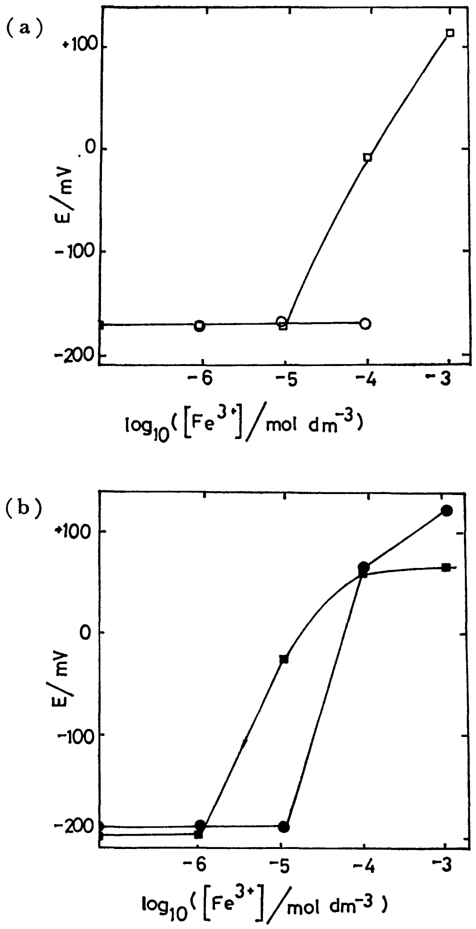

Fig. 3. The effect of iron(III) on the cadmium electrode in the flow-through cell, at pH 2 and pH 5. Concentration of Cd^{2+} was 10^{-3} M. Flow rate: 5 cm^3/min. (a): In unbuffered solution. □: pH 2, ○: pH 5. (b): In buffered solution. ■: pH 2, ●: pH 5.

Potentiometric Titrations and Atomic Absorption Spectrometry (AAS) Measurements. To determine whether the oxidation of CdS by iron(III) takes place, a suspension of CdS powder (guaranteed CdS was commercially obtained or wet CdS was obtained by freshly precipitation from equivalent $Cd(NO_3)_2$ and Na_2S) was titrated by iron(III) using platinum electrode. Titrations were performed in a nitrogen atomosphere. No noticeable oxidation of CdS took place, regardless of whether the CdS powder was dried or freshly precipitated. Obviously the oxidation of CdS by iron(III) is slow. On the other hand, the same titration curve of S^{2-} by iron(III) was obtained as was given in Ref. 13. Oxidation of S^{2-} by iron(III) takes place rapidly and quantitatively.

To measure the dissolution of Cd^{2+} from CdS, CdS powder was mixed with a deaerated solution; after one day the solution was filtered, and the concentration of cadmium in the filtrate was measured. If iron(III) was involved, fairly large amounts of Cd^{2+} were found in pH 2 solution (both for buffered and unbuffered solutions). Even in buffered pH 5 solution, a considerable amount of Cd^{2+} was found in the filtrate, though in unbuffered pH 5 solution, the dissolved Cd^{2+} in the presence of iron(III) was found to be just the same as in the absence of iron(III). The fact that a considerable amount of Cd^{2+} from CdS was found in buffered pH 5 solution in the presence of iron(III) supports the assertion that iron(III) and phthalate ion form stable complexes which remain in the solution.

Discussion

If oxidation of cadmium sulfide by iron(III) takes place according to the following reaction:

$$2Fe^{3+} + CdS \longrightarrow Cd^{2+} + S + 2Fe^{2+} \qquad (1)$$

the equilibrium constant is obtained to be 2.1×10^{14}, by calculating from various standard potentials.[14] The reaction proceeds completely to the right. The equilibrium constants for the oxidation of different sulfides, calculated by reactions analogous to (1), are as follows: PbS, 5.5×10^{13}; CuS, 18; and Ag_2S, 7.1×10^{-9}. Ignoring kinetic aspects, one may thus deduce that interference of iron(III) is most pronounced at a CdS/Ag_2S electrode and least pronounced at a pure Ag_2S electrode.

From Table 1, the change of the potential for a decade change of iron(III) concentration at pH 2 was 115 mV in the case of cadmium electrode. The value of this slope is remarkably larger than those in the cases of lead or copper electrodes (59 mV for the lead electrode[5]) and 25 mV for the copper electrode[7]).

In the case of a copper ion-selective electrode, it is reported that the potential drifts in the negative direction after prolonged use in high concentrations of iron(III).[7]) When the cadmium electrode was dipped in lower concentrations of iron(III) for a short time, the potential drifted in the negative direction like a copper electrode. When the cadmium electrode was kept in high concentrations of iron(III) for a few minutes, the potential drifted in the positive direction; extended polishing was needed to remove the anomaly. These facts support the conclusions that reaction(1) takes place and suggest that the iron(III) exerts an influence on the deep interior of the electrode membrane, according to the dipping time and concentration of iron(III).

This oxidation reaction(1) was not controlled by the flow conditions of iron(III); the reaction rate was very slow and the reaction proceeded even with the complexed iron(III).

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